CHAPTER 1
General

GENERAL

Transition metal complexes are being increasingly used as homogeneous catalysts for bulk production of various organic chemicals and oxygenated compounds [1]. For example, epoxides, alcohols, ketones, carboxylic acids and polymerized hydrocarbons like polyethylenes, polypropylenes etc. are being commercially prepared using various homogeneously catalyzed routes. Understanding of the chemical nature of transition metal complexes has played a critical role in the development of such systems [2]. Further, such studies have helped in understanding the role of transition metals in enzymatic catalysts in life sustaining biological reactions involving electron transfer, oxidation and oxygenation processes [3].

Oxygenases

Oxygenases are natural enzymes that insert O atom in substrates. They are of two types : monooxygenases and dioxygenases. Monooxygenases insert one O atom of dioxygen into substrate and the other O atom is reduced to water; e.g., in oxidation reaction involving cytochrome P-450 (cyt P-450), tyrosinase and dopamine 8-hydroxylase. Dioxygenases insert both the O atoms of dioxygen to substrate, e.g. tryptophan-2,3-dioxygenases and protocatecholate-3,4-dioxygenases

Cyt P-450 is an important class of monooxygenase enzymes. Recent advancements in their study concern three dimensional structure of some cyt P-450's [4] and the cloning of various P-450 genes [5] This family of enzymes show a great diversity of reactions, viz, isomerizations, dehydrations and reductions, aldoxime dehydration and nitric oxide synthesis [6], making use of the same ferriprotoporphyrin prosthetic group.

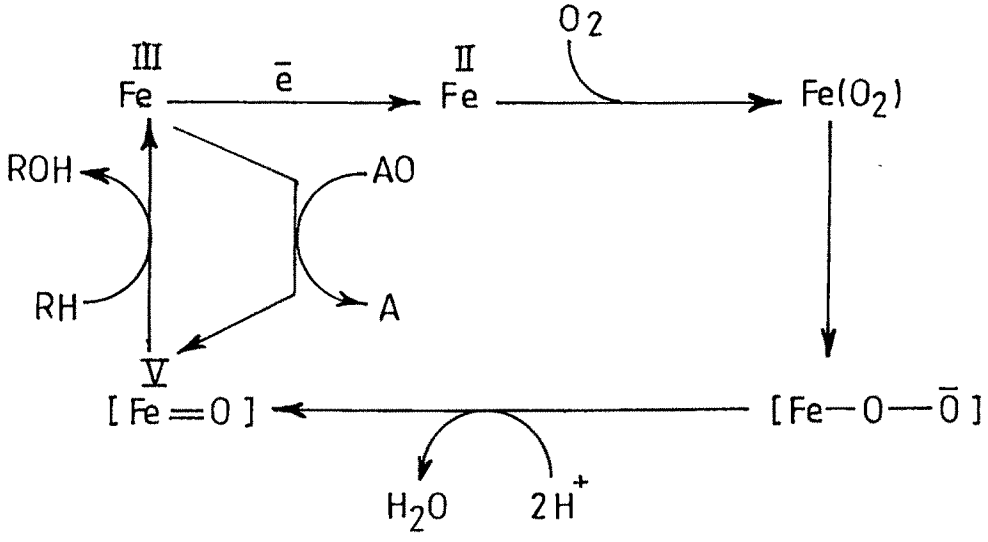


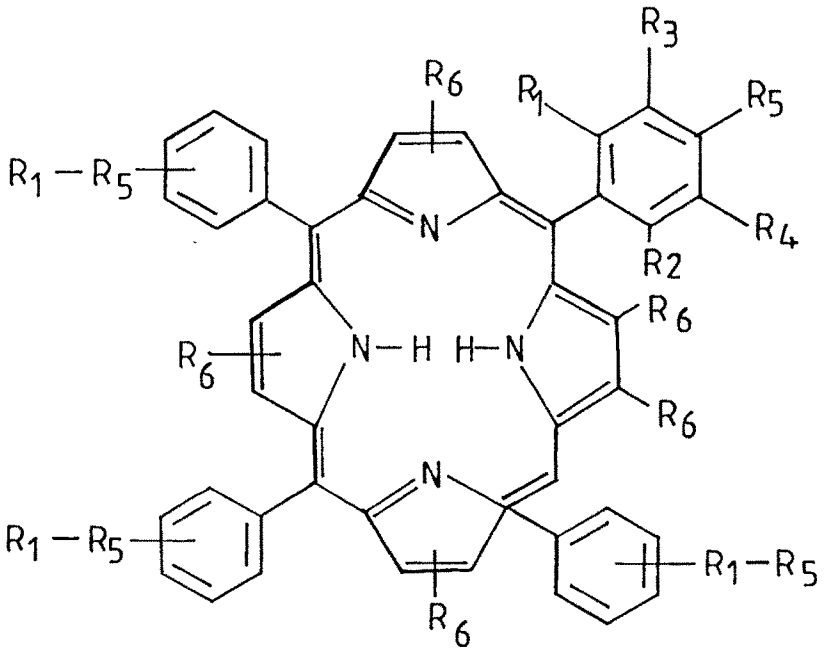
Figure 1.

In the monooxygenase activity of cyt P-450, high-valent metal-oxo is formed as active intermediate (Figure 1). As only one oxygen atom is used for oxidation, one molecule of NADPH is required to reduce the other O atom of dioxygen to water.

Model Studies

High selectivities and stereospecificities under mild conditions, as achieved by these enzymatic systems, led the researchers to pursue model catalytic systems capable of mimicking oxidations mediated by the enzymes The major goal in this area is to transform the biomimetic catalytic systems into practical ones, without sacrificing the selectivity. Metalloporphyrins were, obviously, the first choice, since they are analogous to the prosthetic group of heme containing enzymes. Thus, Groves et al [7] published the first article on the use of iodosylbenzene (PhIO) - a single O atom donor - in olefin epoxidation and alkene hydroxylation catalyzed by Fe(TPP)Cl (Figure 2 for TPP). PhIO was chosen to avoid use of stoichiometric amount of reductant required, when dioxygen is the oxidant. Later, Cr(TPP)Cl and Mn(TPP)Cl were also shown to function in similar manner. An "Oxygen Rebound" mechanism was suggested by Groves (The AO cycle or the Shunt Pathway in Figure 1) for such catalytic reactions.

These first generation of metalloporphyrins, comprising of different metal derivatives of H_2TPP, were more reactive towards meso cleavage via the formation of meso-hydroxyporphyrin derivatives [8]. Also, these were plagued with inactive μ-oxo formation and deactivation by N-alkylation [9,10]. These problems were overcome by second generation of tetraarylporphyrins having substitution at meso positions of aryl or halogen substituted aryl groups, viz., meso-tetramesitylprophyrin, H_2TMP etc. (Figure 2). These substituents provided



H_2TPP	$R_1—R_5 = H$, $R_6 = H$
H_2TMP	$R_1 = R_2 = R_5 = Me$, $R_3 = R_4 = H$, $R_6 = H$
H_2TPFPP	$R_1—R_5 = F$, $R_6 = H$
H_2TDCPP	$R_1 = R_2 = Cl$, $R_3—R_5 = H$, $R_6 = H$
H_2Br_8TDCPP	$R_1 = R_2 = Cl$, $R_3—R_5 = H$, $R_6 = Br$
H_2Cl_8TDCPP	$R_1 = R_2$ Cl , $R_3— R_5 = H$, $R_6 = Cl$
$H_2Cl_{12}TMP$	$R_1 = R_2 = R_5 = Me$, $R_3 = R_6 = Cl$, $R_4 = H$
H_2F_8TPFPP	$R_1— R_5 = F$, $R_6 = F$

Figure 2

steric effects, i.e., a cage effect or an open well effect to avoid formation of catalytically inactive μ-oxo complex and/or to enhance the electrophilicity of the metal-oxo entity by lowering electron density on the phenyl rings. The third generation is an extension of the previous idea of having bromine, chlorine or fluorine atom at the β-position of pyrroles, such as meso-tetrakis(2,6-di-chlorophenyl)-β-octabromoporphyrin, H_2Br_8TDCPP etc. (Figure 2) These give very robust metal complexes with very good catalyst stabilization and efficiency.

Nonporphyrinic metal complexes have also been demonstrated to exhibit selectivities and product distributions matching with those in natural systems. Thus, a host of schiff-base [11-15], amide [16-19], polypyridyl [20, 21], aminocarboxylate [22,23] and macrocyclic ligand complexes [24-26] have been used as oxidation catalysts with a veriety of oxidants, under very mild to rigorous reaction conditions. Choice of all possible different metal ions and ligands, convenient variations in structure, relatively easy synthesis and characterization are the advantages in such model systems, apart from the ease with which they can be studied mechanistically.

The Reaction Pathway

A high-valent metal-oxo is proposed as reactive intermediate in the oxidation studies Formation of diverse oxidation products, with the use of metal-oxo as active site in model systems, lead to suggestion of different pathways, leading to products. Thus, metallooxetane (**I**) [27], carbon radical (**II**) [28-31], carbocation (**III**) [32], carbocation radical (**IV**) [33-35] or charge-transfer complex (**V**) [36,37] have been shown to be involved in the epoxidation reactions, depending on the catalyst-oxidant-substrate systems (Figure 3).

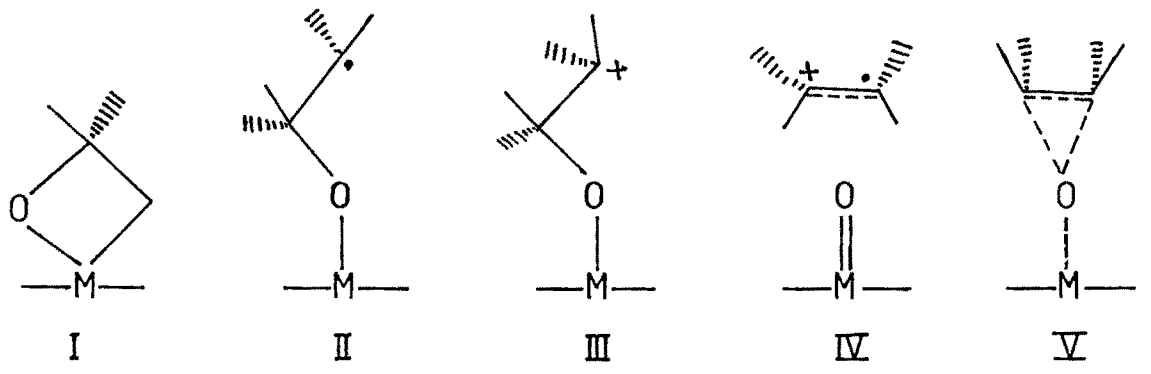


Figure. 3

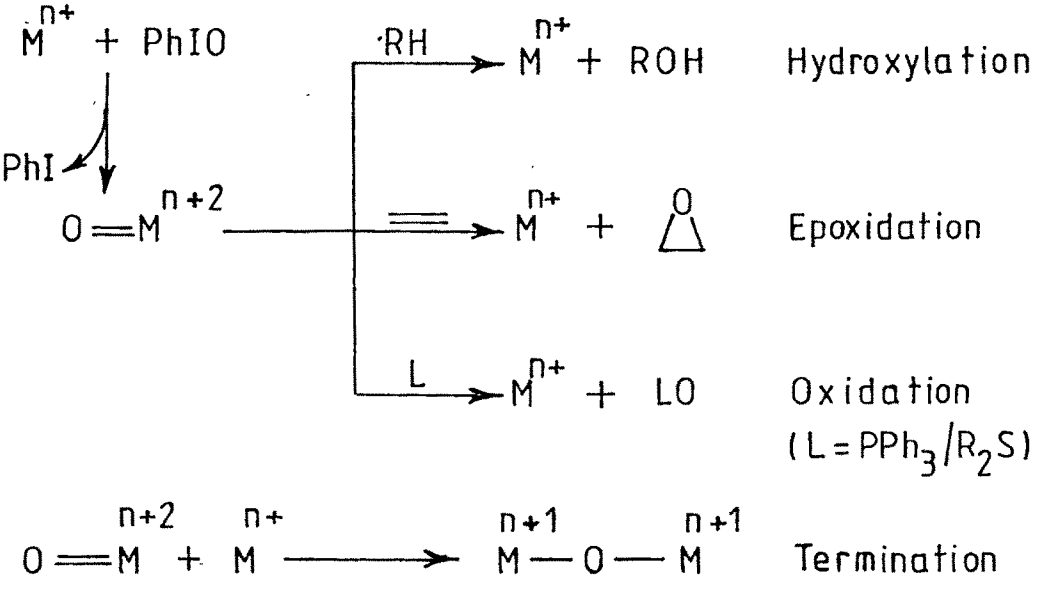


Figure.4

The high-valent metal-oxo M^{V}=O intermediate has been characterized in-situ or by isolation for many systems [38-40]. Single crystal structure for an isolated (salen)$Cr^{V}(O)^{I}$ complex has also been reported [41] and its catalytic efficiency for epoxidation studied [42]. Similarly, metal-oxo has been shown to be the active species in epoxidation reactions for various Fe(III), Cr(III), Mn(II), Mn(III) and Ru(III) complexes [16,43,44] using electrochemical and spectroscopic techniques Iodosylbenzene was used as oxidant in these studies.

The metal-oxo intermediates are capable of affecting various types of oxidative transformations (Figure 4).

Termination

Transfer of O atom from metal-oxo to the substrate brings the catalyst back to original state and the cycle continues Alternatively, the metal-oxo may react with another metal complex molecule to form μ-oxo species (Figure 4) which are poorly active or inactive as catalysts [9,45]. This leads to termination of the catalytic process. Another reason for the termination of the catalytic cycle is oxidative degradation of the ligand part of the complex catalyst [46,47].

Factors Responsible

That a particular reactive intermediate (**I** to **V**, Figure 3) is formed in the catalytic cycle will depend on various parameters, viz., type of metal centre, type of ligand(s), substituents on the ligand(s), nature of substrate, nature of oxidant, solvent and additive, if any These effects often work in conjunction with each other and implication of a single factor

is difficult to suggest in many cases. However, substantial information can be obtained by varying a particular factor while keeping the rest of them constant. The following sections try to review the important and conclusive studies pertaining to the above said factors.

Metal Centre : Efficiency of a metal complex to form high-valent metal-oxo complex and to act as an epoxidation catalyst depends on the ability of the metal centre to acquire various oxidation states. The redox potential of the metal centre determines the ease of a complex to go from one oxidation state to another In a catalytic oxidation reaction, this means how easily the formation of the active catalytic species, the metal-oxo, takes place. Hence, redox potential of a metal ion in the complex should be moderate, so that the oxo species formed is neither unstable nor rigid. This will enable the metal-oxo to remain stable till it comes in contact with a substrate and transfer the oxygen easily to it, affecting its oxidation. When the intermediate metal-oxo formed is very stable, its utility as catalyst is limited to electron rich olefins only. In the case where metal-oxo is less stable, an oxide free radical M^{n+1}-O° is generated, leading to formation of additional oxidation products.

The catalytic ability of oxo compounds of titanium(IV), molebdenum(VI) and tungsten(VI) in epoxidation reactions is attributed to their strong Lewis acid character in their highest oxidation states, with d^0 configuration [48,2], which facilitates the heterolysis of O atom sources such as alkylperoxides and H_2O_2. Chromium(VI), being a strong lewis acid, is expected to be a good catalyst for epoxidation reactions. However, its poor efficiency may be due to the fact that it is a strong oxidant and hence promotes the decomposition of O atom from sources like TBHP [49].

Lewis-acid oxidation catalysis using iron, copper, zinc and aluminium metal salts and complexes has also been reported [50-54]. Such reactions generally yield a mixture of products which include, apart from epoxide, various allylic oxidation products.

However, in case of complexes of transition metal ions in low oxidation states as catalysts, the oxidation reaction proceeds through the formation of intermediate oxo cation. Among the chromium, manganese and iron oxo-species, tendency to give radical chain products increases as one goes from Fe^{V}=O to Mn^{V}=O for same ligand system. *cis*-Stilbene has been used as mechanistic probe in manganese porphyrin catalyzed epoxidations with different O atom sources (viz., NaOCl, O_2 and electron, $KHSO_5$) to evidence radical character of high-valent Mn-oxo species in these catalytic oxidations [32]. The degree of free radical character in Mn-prophyrin catalyzed oxidations compared to that for iron reactions has been attributed to the relative stability of Mn^{IV}-OH(Porphyrin)X compared to that of Fe^{IV}-OH(Porphyrin)X [55, 56] Thus, it has been noted that under same reaction conditions, manganese and chromium prophyrins give better yields for hydroxylation of alkanes compared to epoxidation of alkenes. With chromium prophyrins, a large amount of allylic oxidation is observed with cyclic olefins. PhIO/Cr(TPP)Cl is, in fact, a good catalyst system for oxidation of alcohol to aldehyde or ketone [57].

Among the platinum group metals, ruthenium complexes have got more attention recently [58] due to availability of a wide range of oxidation states of the metal ion. Oxidation states VI, VII and VIII are readily available in ruthenium oxo complexes [59]. An important aspect of Ru epoxidation activity is the interesting catalyst system of Ru(II)/O_2 [60] which

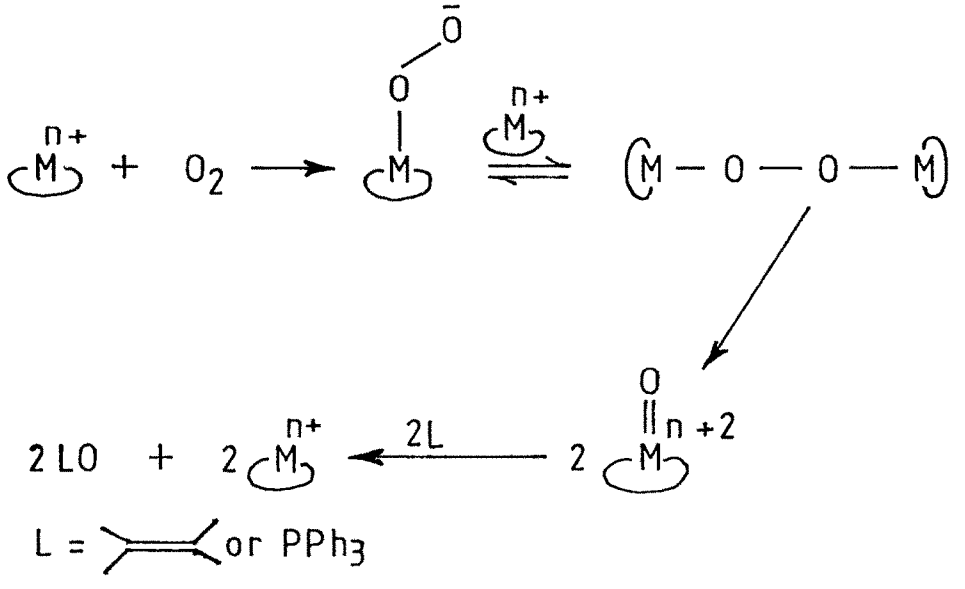


Figure 5

yields two Ru^{IV}=O intermediates, without use of any reductant, via binuclear Ru^{III}-μ-peroxo species (Figure 5).

Such a mechanism was suggested earlier for Fe(II)porphyrin system by A L Balch for oxidation of PPh_3 at low temperature [61,62]. A similar observation was made by Taquikhan et al in the case of Ru(III)-EDTA complex as catalyst [22] The catalyst combines with O_2 to form two equivalents of active species [Ru(V)(O)(EDTA)], which causes epoxidation of two alkene molecules. Such a formation has also been suggested for a [mixed ligand Ru(III)]/O_2 system [63].

Ligand : Besides the metal centre, ligand is the most important factor in deciding the efficiency of a metal complex to act as catalyst. Ligand not only affects redox potential of the metal centre, but also decides the overall stability of the catalyst. This, then decides the number of catalytic cycles the complex will undergo before succumbing to the rigorous reaction conditions. Further, the ligand type decides the ultimate stereochemistry of the product(s)

The remarkable effectiveness of natural metallo-porphyrins as oxygenase enzymes is attributed to their planar porphyrin ring with extensive conjugation system and the prosthetic protein environment which creates a cavity around the active site, controlling regio- and stereoselectivity of products and stability of the active systems. General features that a model ligand, used for epoxidation catalyst complex, should bear, can be outlined as below :

- it should stabilize the metal centre at rest (the native state) such that appropriate alteration in environment can activate the centre for reaction.

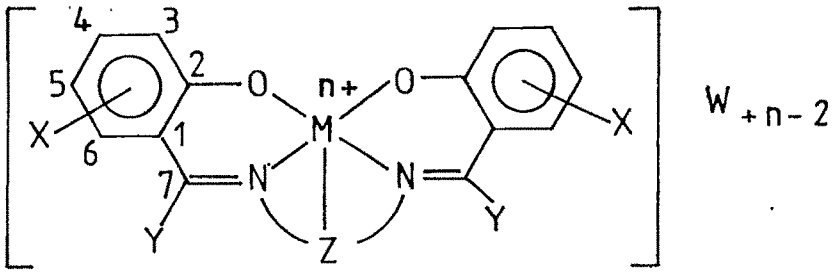
- should stabilize the active intermediates with varying oxidation states of metal centre on time scale sufficient for the reaction to occur.

- should facilitate variation of substituents over it for fine tuning.

- should withstand the rigorous reaction conditions.

Ligand nature affects catalytic activity of metal complexes by affecting redox potential of the metal centre and hence that of the active intermediate formed. Fine tuning of catalytic activity of metal complexes,by systematically changing ligand and varying substituents over ligands,has been well documented in literature.

Taylor et al [64-70] studied thoroughly the effect of various substituents on the salen type of ligands on the O_2 binding properties of their Mn(II) and Mn(III) complexes (Figure 6) The correlation of electron donating/withdrawing properties of substituents with O_2 binding capacities of the metal complexes was confirmed by electrochemical studies. It was shown for various tri-, tetra-, penta- and hexa- dentate substituted salen type of schiff-base ligand complexes that electron withdrawing substituents like $-NO_2$ or -X on sal moiety shift the redox potential of metal to more positive value compared to the unsubstituted one, whereas electron donating groups shift it to more negative value. In other words, electron withdrawing groups make the Mn(III)/Mn(II) reduction more favorable while electron donating groups



X = 5-NO_2, 3-NO_2, 5Cl, 5Br, H, 3-MeO, 5MeO, 5Me

Y = H, CH_3, C_6H_5

Z = NH, NCH_3, NC_6H_5, $(CH_2)_2$, O

Figure 6.

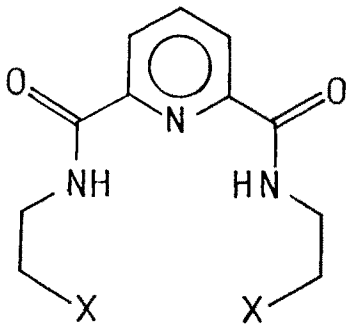
require more negative potential before reduction of Mn(III) is possible. Further, it was clearly shown that a substituent on phenyl ring of salen at position 5 is more effective than the same substituent at 3rd position (Figure 6). Nitro substituents on aromatic part of ligand in the Mn(II) complex were shown to inhibit ligand oxidation in the reaction with O_2. This was attributed to the electron withdrawing nature of the -NO_2 group. Comparison of electrochemistry of pentadentate Mn(III) complexes of schiff-bases derived from salicylaldehyde and DPT, [Mn(saldpt)] or methyl DPT, [Mn(salmdpt)] showed that due to electron donating Me group, Mn(III) to Mn(II) reduction was less favourable in Mn(salmdpt) and was cathodic to that in Mn(saldpt) complex. Also, replacement of NR group of DPT by a less basic donor such as an ether O atom leads to shifting of the Mn(III) to Mn(II) reduction in anodic direction compared to the Mn(saldpt) complex. Replacement of phenyl moiety in the schiff-base complexes by pyridine (yielding complexes derived from pyridine-2-carboxaldehyde and aliphatic diamine ligands) makes the complexes oxygen insensitive and electrochemically inactive. This was due to strong π-acceptor properties of pyridine N compared to the strong σ–donor capability of phenyl O donor atom

A comparison of catalytic activity of Mn(III)(TPP), Mn(III)(saloph) and Mn(III)(saldpt) complexes for styrene epoxidation using NaOCl oxidant under phase-transfer conditions showed that Mn(III)TPP complex was superior catalyst with respect to better epoxidation yields Also it was found to be more resistant towards oxidative degradation [71]

Traylor et al [72] studied various substituted Fe(III), Mn(III) and Cr(III) porphyrin complexes for epoxidation of olefins They noted that in case of halogen substituted pyrroles in Fe(III)TPP, extent of N-alkylation decreases while the resistance of the porphyrin towards oxidative destruction increases Putting electron withdrawing substituents on porphyrins resulted in enhanced epoxide yields and allylic products decrease The life of the catalyst also increased.

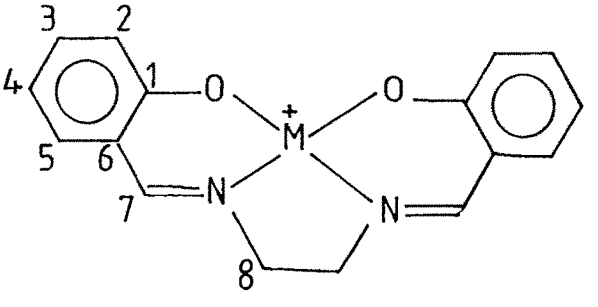
T. Hirao et al [19] report an interesting catalyst system for epoxidation of olefins with dioxygen without the use of coreductant $FeCl_2$ in DMF in presence of a podand ligand (Figure 7) effect epoxidation of olefins with dioxygen as oxidant The order of catalytic efficiency was in the order BIPA > 2BPEPA > BPHEPA Details regarding mechanism for the system, however, are not available A diiron-μ-oxo active species has been postulated.

Kochi and co-workers [42] exhaustively studied mechanistic aspects of epoxidation of alkenes catalyzed by $Cr^{V}(salen)O^{\cdot}$ analogues, generated from corresponding $Cr(salen)^{+}$ complexes (Figure 8) and PhIO Studies of substituent effects showed that tetra-methylated ethano bridge oxo-chromium(V)(salen) complexes were the most effective epoxidizing agents, whereas, unsubstituted salen complexes and complexes of substituted salen with chlorine or phenyl ring or Me/Ph on imine carbon 7, were less effective. Chloride substitution on phenyl



X = Im BIPA
= Py 2BPEPA
= C_6H_5 BPHEPA

Figure 7



M = Cr (III)
Mn (III)

Figure 8

ring increased yield of epoxide, compared to the unsubstituted one. Also, chloride on 5,5' position promotes C=C cleavage more than the unsubstituted metal-oxo.

For analogous Mn(III)salen complexes (Figure 8), the redox properties of the complexes were shown to depend on substituents on the ligands [44]. For instance, presence of electron withdrawing groups such as 5,5'-dinitro or 5,5'-dichloro substituents, which enhanced the catalytic activity of the Mn(III)(salen) catalysts, were correlated with the electron-deficient character of the resulting cationic metal-oxo complex, as evaluated by the standard reduction potentials. Thus, for epoxidation of 1-octene, electron releasing substituents like 5,5'-dimethoxy and 7,7'-diphenyl gave poor epoxide yields whereas with 5,5'-dichloro and 5,5'-dinitro substituents, much improved epoxide yields were observed.

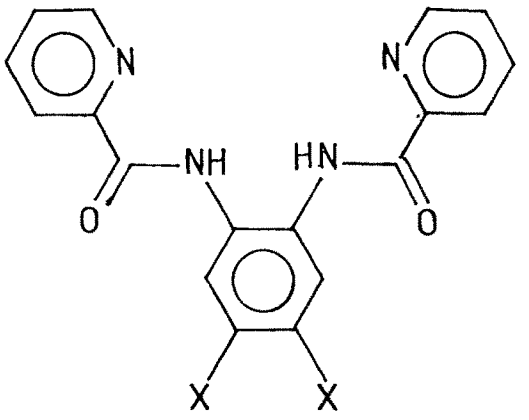
A similar observation was made for epoxidation of cyclohexene using Mn(III)(salen) type of complexes with PhIO as oxidant [73], where the 5,5'-dimethoxy Mn(III)(salen) gave lesser epoxide yields, compared to the unsubstitued ones, whereas the 5,5'-dinitro-Mn(III)(salen) complex was the best among the three.

Variously substituted iron(III) porphyrins (such as iron(III)tetrakis-2,6-dichlorophenyl)- (octabromo-porphyrin)) were used for hydroxylation of norbornane using PF_5IO [74] Percentage hemin loss, indicating stability of the catalyst (against oxidative degradation) for various Fe(III) porphyrin complexes, showed dependence on the nature of substitution. It is clearly demonstrated that there is increased catalytic stability with increase in electronegativity of substituents on porphyrin.

An analogous study has been conducted by D. Mansuy [75] who compared ability of various iron porphyrins with or without halogen substituents on the pyrrole ring to catalyze the hydroxylation of poorly reactive alkanes like heptane or pentane by PhIO. The presence of halogen substituents on the porphyrin ring not only dramatically increased the yield of hydroxylation of alkanes but also led to active species exhibiting different chemo- and regio-selectivities. Oxidation of a mixture of cyclooctene and heptane (molar ratio 1:100) with PhIO, using these catalysts, shows that the ratio of cyclooctene epoxide to heptanols + heptanones was a function of porphyrin structure. It decreased from 10 for most electron rich Fe(TMP)Cl catalyst (see Figure 2 for porphyrin structure) to 1.5 for most electron deficient Fe(TPFPP)Cl as catalyst. Increase in halogen substitution on porphyrin results in its increased tendency to abstract H, even though its addition to double bond remains predominant, i e., an iron-oxo species with more Fe-O° character is formed with highly halogenated porphyrins Thus, electron rich complexes may form $PFe^{\bullet+IV}=O$ (or $PFe^{V}=O^{+}$) whereas electron deficient may form PFe^{IV+}-O° intermediate [74] (P = Porphyrin).

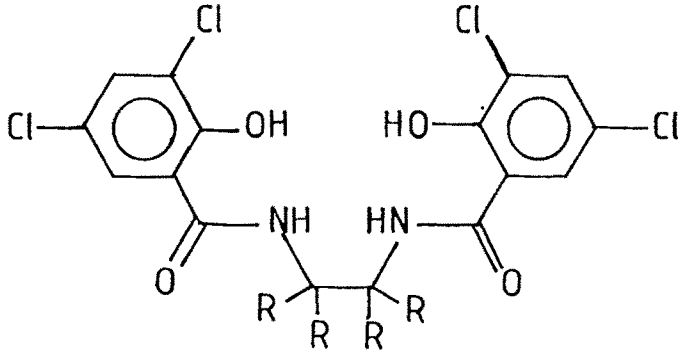
In fact, Tsuchiya [76] has prepared stable $(O)Fe^{IV}(porphyrin)^{+0}$ at 8 °C and characterized it in solution by UV-vis, ESR and NMR spectroscopic methods. It was prepared by the action of meta chloroperbenzoic acid on Fe(III) complex of a new porphyrin-5,10,15,20-tetrakis(2',6'-dichlorophenyl)-2,3,7,8,12,13,17,18 - octaphenylporphyrin in CH_2Cl_2 (see Figure 2 for porphyrin structure).

C M Che studied Mn(III) and Cr(III) complexes of amide ligands bpb and bpc (Figure 9) using PhIO as oxidant [17]. The chloro substituted bpc complexes were found to be more efficient as epoxidation catalysts and Mn(III) complexes were better catalysts compared to corresponding Cr(III) complexes



X = H bpb
= Cl bpc

Figure 9



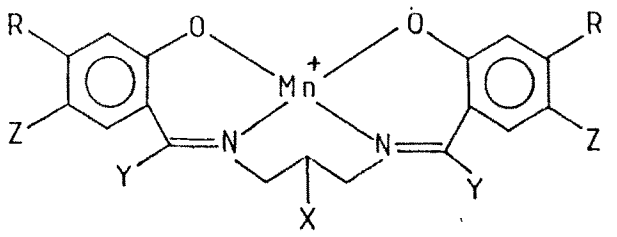
R = CH_3
= o-phen
= c-hexylidene
= 3,5-dichloro-o-phen
= H

Figure.10

Similar bis-amide complexes of Co(II) have been used for epoxidation of alkenes using PhIO or TBHP oxidant [77]. With PhIO, Co^{II}-(2,3-bis(3,5-dichloro-2-oxy-benzamido)-2,3-dimethylbutane) (Figure 10) gave 90% norbornene oxide in CH_2Cl_2. Replacing four methyls on ethano bridge by 1,2-trans-cyclohexylidene gave 75% epoxide yield. Substituting the ethano bridge with o-phenylene or 3,4-dichloro-o-phenylene gave 44% and 48% norbornene oxide, respectively. Co(salen) gave still lower yield of norbornene oxide (16%).

Various iron(III) schiff-base complexes used as catalysts with PhIO gave efficiencies in the order Fe (saloph) > Fe(salen) > Fe(acen) [78]. With Mn(III) schiff-base complexes [79] for cyclo-hexene epoxidation, bis(anthranilic acid/acetyl acetonate) complex gave better yield of epoxide compared to Mn(salen), but corresponding amounts of -ol and -one were high. In contrast, $Mn(acac)_2$ gave relatively poor yield, but epoxide was formed selectively.

Substituted salpn type of schiff-base complexes of Mn(III) (Figure 11) were used to epoxidize norbornene with PhIO as oxidant [43]. With R=Z=Y=X=H, epoxide yield was lowest among all the complexes Replacement of X with OH and Z with Br, respectively, yielded more epoxide. Use of naphthaldehyde in place of salicylaldehyde in the complex also gave more epoxide yields However, it was observed that the complexes of schiff-bases derived from 2-hydroxyacetophenone show greater catalytic activity compared to those derived from salicylaldehyde. This was in contrast to the expectation, indicating that factors other than ligand basicity were in play in determinig the catalytic activity of the complexes The enhanced catalytic activity may be due to steric effect of the methyl groups inhibiting formation of terminating μ-oxo complex



R = H
X = H ,OH
Y = H, OH
Z = H, Br

Figure.11

S. Valentine [26] used different N-4 macrocyclic and amide complexes of iron(II) for epoxidation of alkenes using 30% aq H_2O_2 as oxidant. Iron(II)cyclam was found to be the best catalyst, whereas, Fe(II) complex of amide bpb (see Figure 9 for ligand structure) was found to be inactive, also N-Me substituted iron(II)cyclam complexes were inactive as epoxidation catalysts.

Lindsay Smith [80] studied chemical oxidation of some charged iron(III)tetrarylporphyrins in water and in methanol. The studies reveal that the aryl group on the porphyrin has a marked influence on the life-time of the oxo-iron(IV) species and on the stability of the porphyrin towards oxidative bleaching. Thus, most stable intermediates were formed by the dichlorosulphonatophenyl- and the two N-methylpyridyl-porphyrin complexes of iron.

Balavoine and co-workers [81] studied effect of various substituents on o-phenanthroline (o-phen) ligand used in conjunction with Fe(III) or Ru(III) salts for epoxidation of olefins using $NaIO_4$ as oxidant. They showed that electron rich ligands slow down rate of the reaction but improve selectivity in case of ruthenium complexes. Thus, with o-phen bearing electron donating groups, such as 3,4,7,8-tetramethylphen, the oxidative

cleavage of olefinic double bond was almost completely avoided and a very high selectivity for epoxidation was observed. With iron, however, lower rates and higher selectivities were observed compared to the corresponding ruthenium complexes. Electrophilicity and reactivity of an iron-oxo intermediate were enhanced by using diamine ligand bearing electron withdrawing substituents.

Oxidant : A large variety of oxidants have been used for oxidation studies viz., dioxygen [82,83], dioxygen-$NaBH_4$, dioxygen-Pt/H_2 [84-86] alkylhydroperxides [87,88], peroxycarboxylic acids [89], hydrogenperoxide [90,91], iodosylarenes [16,43,44,72,92,93], hypochlorites [94-96], ozone [97], monopersulphates [98,99], amine oxides [100,101], oxaziridines [102,103], perchlorates and periodates [104] etc.

Iodosylbenzene has achieved certain importance in the model studies due to its easy synthesis and handling and formation of PhI as the final oxidation product, which is easy to detect and determine. Its disadvantages are the high cost, relative instability and very poor solubility in most of the solvents

Axial ligand : Williams [105,106] has pointed out that the essential difference between the prosthetic group of an oxygen carrier (hemoglobin) and that of an oxygen activator (cyt P-450) is the presence in the latter of a second electron donor site. In cyt P-450, this is a cysteinyl mercaptide (RS) group, whereas the axial ligand in hemoglobin is a histidinyl imidazole group. The exact role of the mercaptide group is not clearly defined although the facile one electron change ($RS^{\circ-} \rightarrow RS^{\circ}+e^-$), is undoubtedly important in mediating electron transfer. Based on model studies, Hirobe [107] suggested, that reactivity of an

Fe(III)porphyrin complex, with side-arm thiolate ligand coordinating at 5th site, greatly enhances the reaction rates for hydroxylation, compared to corresponding Im complex or Fe(III)Cl complex.

In model studies, improvement of the rate, chemo and stereoselectivities has been observed in the catalytic epoxidation studies [71,90,91,108-110], by the use of an axial ligand. Kochi [42] showed weakening of the Cr^{V}=O bond due to the trans PyO coordination, as studied by the single crystal X-ray study of the isolated complex

Solvent : Solvent polarity is important not only to dissolve the complex, substrate and oxidant, but also in stabilizing or destabilizing reactive intermediates. Nature of the reactive intermediate may depend on the type of the solvent used for the reaction, resulting into different reaction products. Thus, studies by Groves [111] and Watanabe [30,112] with Fe(III)TMP and m-CPBA in two different solvents, CH_2Cl_2 and toluene, show formation of two different species in absence of olefin. (Figure 12)

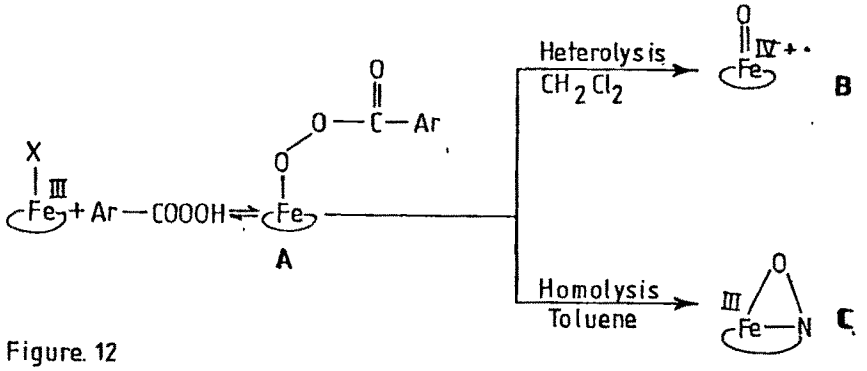


Figure. 12

The iron-peracid intermediate **A** is the intermediate generated on reaction of iron-porphyrin and m-CPBA in both the solvents. Heterolysis of **A** to ferryl iron porphyrin **B** is more favourable in CH_2Cl_2 whereas in toluene homolysis of **A**, leading to the formation of **C**

is more dominant. Competitive epoxidation of norbornene and α-methylstyrene (1:1) using substituted iron(III)prophyrins show shape-selectivity of the olefins. The intermediate **B** favours formation of norbornene oxide over α-methylstyrene oxide due to steric hindrance of α-methylstyrene with porphyrin. Thus, in CH_2Cl_2, competitive epoxidation yields 100·30 ratio of the epoxides of norbornene and α-methylstyrene whereas in toluene, **A**, the epoxidizing species, gives comparable yields of both the epoxides [112]

Chemical oxidation of metal complex catalysts has been studied using UV-vis, NMR and RR methods to see the effect of oxidant on their stability and to study intermediates formed. The complexes used were charged iron(III)-tetraarylporphyrins and the oxidations were carried out in water and in methanol [80]. The aryl substituents used were 4-N-methylpyridine, 4-Sulphonatophenyl, 2,6-di-chloro-3-sulphonatophenyl, 4-carboxyphenyl etc. In aqueous solution, the complexes were converted by TBHP or monopersulphate into their corresponding oxo-iron(IV)prophyrin, whereas, in methanol only the iron(III)-tetra(N-Methylpyridyl)porphyrin formed detectable ferryl-porphyrin at ambient temperature. Factors found to be responsible for such discrimination were H-bonding, steric effects and electron withdrawing substituents. Solvent oxidation is important in methanol.

Substrate Size, shape and electronic nature of the substrate being oxygenated is very important. Cyclohexene, with abstractable allylic H atom, on reaction with electron rich metal-oxo centre gives allylic hydroxylation - a side reaction in the epoxidation of cyclohexene Electron deficient alkenes, like acyclic ones, do not react with the metal-oxo species readily. Substituents on the substrate affect approach of the active centre in the

substrate to the metal-oxo, due to steric constraints, and may thus affect overall yield and stereochemistry of the product

An important achievement over the last decade was the highly stereoselective epoxidation of allylic alcohols by the Sharpless reaction discussed below. The stereospecificity is observed due to the coordination of OH of substrate to metal centre, thereby, orienting the C=C for further attack [113].

Asymmetric Epoxidation

As noted earlier, regio - and shape-selectivity of products in the epoxidation reactions is, in many cases, governed by the coordinated ligand in the complex. Such observations led to the use of the ligands with chiral centres, leading to enantiomeric products from prochiral substrates. Specific enantiomer synthesis is very important for the drug industry. An important breakthrough came in 1980 when Sharpless reported allylic epoxidation using Titanium alkoxides and chiral alkyl tartarate with TBHP [113-115]. The Sharpless epoxidation catalyst can be prepared from simple, relatively inexpensive sources and results in the enantiomeric excesses (ee's) more than 90%. The Sharpless chemistry is used commercially to produce (+) disparlure, a sex pheromone of the gypsy moth [116] and for the manufacture of both enantiomers of glycidol by ARCO [117] Optically pure glycidol is used for the manufacture of propranolol - a drug for heart disease and hypertension.

Later, Jacobsen [118-121] reported use of very simple salen-based metal complexes bearing chiral centres as epoxidation catalysts for unfunctionalized olefins, yielding enantiomerically pure epoxides

More recent developments in the area are use of chiral Cu-glycosides [122] and chiral Ru(II) schiff-base complexes [123] as epoxidation catalysts for olefins. A new concept has been introduced recently [124], namely, Ligand Accelerated Catalysis, wherein addition of a ligand increases the reaction rate of an already existing catalytic transformation. If the accelerating ligand has chiral centre(s), it leads to stereo-selectivity, e.g. in titanium catalyzed asymmetric epoxidation of allyic alcohols the chiral ligand diethyltartrate acts as the accelerating ligand (Figure 13).

Another such example is catalytic asymmetric di-hydroxylation of olefins using OsO_4 as catalyst (Figure 14). The accelerating ligands used are alkaloids such as bis-cinchona derivatives. The product stereochemistry is decided by chirality of the bis-cinchona substituents bearing asymmetric centres [125,126].

Binuclear Metal Complexes as Catalysts

It is well known that many metalloproteins contain more than one metal ion as active site and their biological activity can be attributed to presence of two or more metal centres [127]. Thus, the manganese containing enzymes, namely manganese catalase [128-131], ribonucleotide reductase [132] and the Oxygen Evolving Complex (OEC) [133-135] are known to contain active sites composed of two or more metals. Methane monooxygenase catalyzes the insertion of one atom of dioxygen into methane, thereby producing methanol The substrate oxidation occurs at the hydroxylase component of the enzyme which contain a diiron centre [136]. Also, non heme oxygen carrying hemerythrin proteins contain a diiron centre, which can coordinate dioxygen reversibly [137].

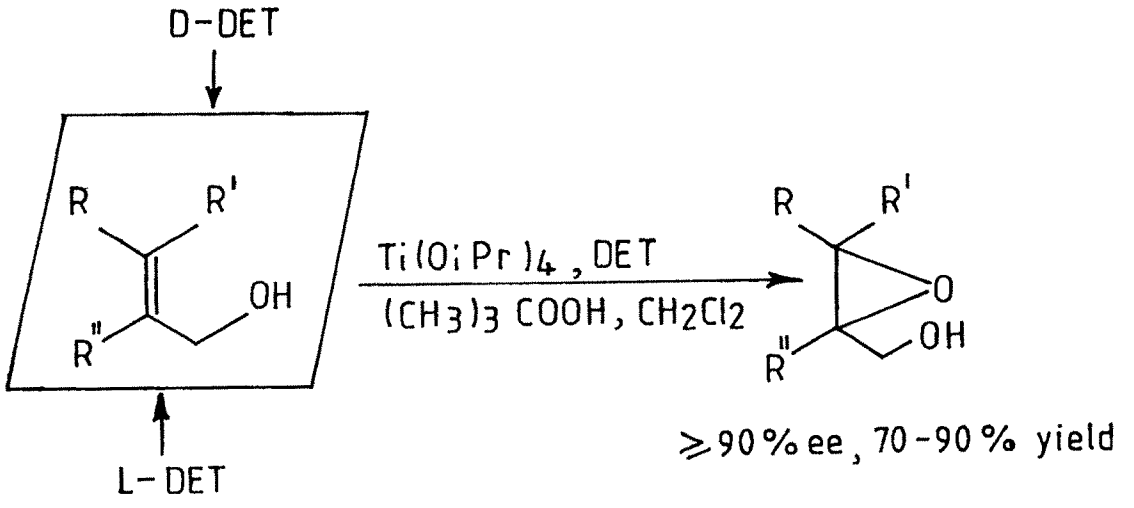


Figure 13

Top (β) attack

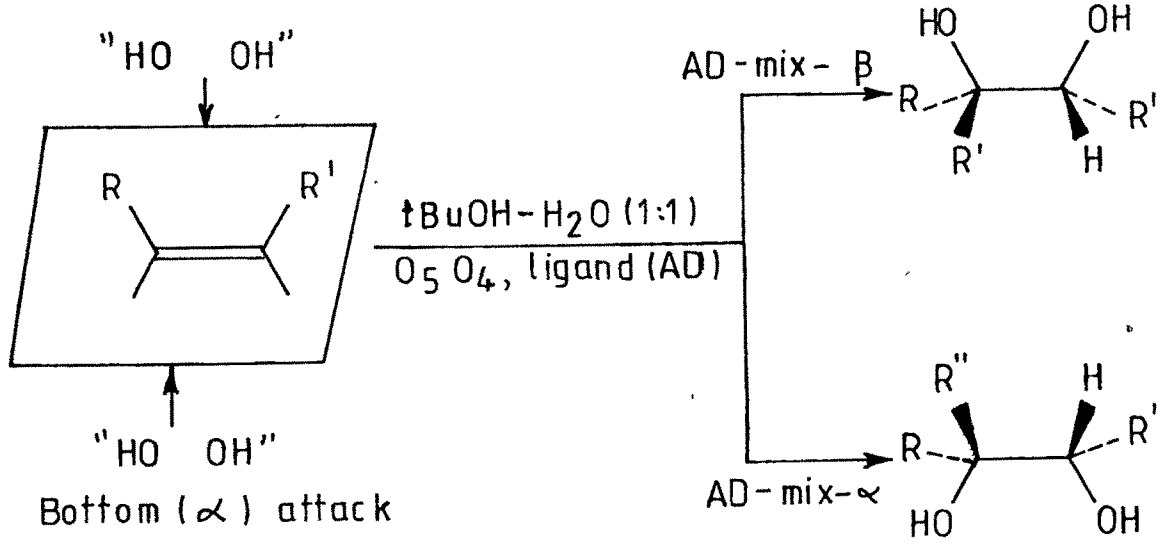


Figure 14

Studies with binuclear model complexes have helped to understand the role of multinuclear metal centres in such systems [138,139]. Binuclear non-heme iron complexes [140] have been shown to catalyze the oxidation of hydrocarbons by H_2O_2. Binuclear Mn(II), Fe(III) [11,12] and Ru(III) [93] complexes of schiff-bases derived from pyridyl-2-carboxaldehyde and aromatic diamine have been used in epoxidation catalysts. Also, Mn(II), Cr(III), Fe(III) and Ru(III) binuclear complex of schiff-base derived from pyridine-2-carboxaldehyde and 1,3-diaminopropanol were shown to epoxidize olefins efficiently [92,141]. Pyridine-2-carboxylic acid and aromatic diamines give bis-amides which yield binuclear complexes with Ru(III). These were used as epoxidation catalysts for olefins [16].

Present Work

Thus, it is seen that in a metal complex catalyst, ligand is an important and versatile factor to achieve the goals of better product yields, catalyst stabilities and catalytic efficiencies. This study tries to fill in some of the gaps present in the existing knowledge in the field with respect to studies with new types of ligands and their metal complexes. Hence there is focus on the effect of varying ligand nature on the catalytic activity of an epoxidation or isomerization catalyst. The chapters 2-5 deal with epoxidation studies. Metal complexes used for epoxidation studies are manganese(III), iron(III), and chromium(III), with a variety of ligands. The last chapter 6, explores mechanism of alkene isomerization for an important industrial reaction where different cobalt(II)schiff-base complexes have been used as catalysts in homogeneous reaction.

REFERENCES

1 R H Holm, *Chem Rev*, 1987, **87**, 1401

2 R A Sheldon, J K Kochi, *Metal Catalyzed Oxidations of Organic Compounds, Academic Press, New York*, 1981.

3 R W Hay, Ed.,*Bioinorganic Chemistry, Ellis Harwood Limited, Halsted Press*, 1984.

4 R Raag, T L Poulos, *Biochemistry*, 1989, **28**, 917.

5 K Kawajiri, Gotoh, KSogawa,Y Tagashira, M Muramatsu, Y F Kuriyama, *Proc Natl Acad Sci, USA*, 1984, **81**, 1649.

6 D Mansuy, *Pure Appl Chem*, 1994, **66**, 737.

7 J T Groves, T E Nemo, R S Myers, *J Am Chem Soc*, 1979, **101**, 1032

8 C K Chang, M S Kuo, *J Am Chem Soc*, 1979, **101**, 3413.

9 B C Shardt, F J Hollander, C L Hill, *J Am Chem Soc*, 1982, **104**, 3964.

10 T Mashiko, D Dolphin, T Nakano, T G Traylor, *J Am Chem Soc*, 1985, **107**, 3735.

11 M Jacob, P K Bhattacharya, P A Ganeshpure, S.Satish, S.Sivaram, *Bull Chem SocJpn*, 1989, **62**, 1325.

12 M Jacob, P K Bhattacharya, P A Ganeshpure, S Satish, S Sivaram, *J Mol Catal*, 1989, **54**, 131.

13 J D Koola, J K Kochi, *Inorg Chem*, 1987, **26**, 908.

14 A R Oki, D J Hodgson, *Inorg Chim Acta*, 1990, **170**,65.

15 M M Taquikhan, S A Mirza, A P Rao, C Sreelatha, *J Mol Catal*, 1988, **44**, 107.

16 M J Upadhyay, P K Bhattacharya, P A Ganehpure, S Satish, *J Mol Catal*, 1994, **88**, 287.

17 W H Leung, Ji X Ma, V W W Yam, C M Che, C K Poon, *J Chem Soc, Dalton Trans*, 1991, 1071.

18 T Hirao, S Mikami, Y Ohshiro, *Synlett*, 1990, 541.

19 T Hirao, T Moriuchi, S Mikami, I Ikeda, Y Ohshiro, *Tetrahedron Lett*, 1993, **34**, 1031.

20 M Fontecave, B Roy, C Lambeaux, *J Chem Soc, Chem Commun*, 1991, 939.

21 A S Goldstein, R S Drago, *J Chem Soc, Chem Commun*, 1991, 21.

22 M M Taquikhan, A P Rao, *J Mol Catal*, 1987, **39**, (185) 331.

23 M M Taquikhan, D Chatterjee, R R Merchant, A Bhatt, *J Mol Catal*, 1990, **63**, 147.

24 C M Che, T F Lai, K Y Wong, *Inorg Chem*, 1987, **26**, 2289.

25 C J Cairns, R A Heckman, A C Melnyk, W M Davis, D H Busch, *J Chem Soc, Dalton Trans*, 1987, 2505.

26 W Nam, R Ho, J S Valentine, *J Am Chem Soc*, 1991, **113**, 7052

27 K A Jorgensen, B Schiott, *Chem Rev*, 1990, **90**, 1483.

28 F P Guengerich, T L MacDonald, *Acc Chem Res*, 1984, **17**, 9.

29 J T Groves, W J Kruper Jr, R C Haushalter, *J Am Chem Soc*, 1980,**102**,6375.

30 J T Groves, Y Watanabe, *J Am Chem Soc*, 1986, **108**, 507.

31 M Fontecave, D Mansuy, *J Chem Soc, Chem Commun*, 1984, 879.

32 A J Castellino, T C Bruice, *J Am Chem Soc*, 1988, **110**, 158.

33 T G Traylor, A R Miksztal, *J Am Chem Soc*, 1987, **109**, 2770.

34 T G Traylor, T Nakano, B E Dunlap, P S Traylor, D Dolphin, *J Am Chem Soc*, 1986, **108**, 2782.

35 O Bartolini, B Meunier, *J Chem Soc, Perkin Trans 2*, 1984,1967.

36 G X He, H Y Mei, T C Bruice, *J Am Chem Soc*, 1991,**113**,5644.

37 G X He, R D Arasasingham, G H Zhang, T C Bruice, *J Am Chem Soc*, 1991, **113**, 9828.

38 A L Balch, C R Cornman, L L Grazynski, M W Renner, *J Am Chem Soc*, 1992, **114**, 2230.

39 T J Collins, R D Powell, C Slebodnick, E S Uffelman, *J Am Chem Soc*,1990,**112**,899.

40 S E Creager, R W Murray, *Inorg Chem*, 1985, **24**, 3824.

41 T L Siddal, N Miyaura, J C Huffman, J K Kochi, *J Chem Soc, Chem Commun*, 1983, 1185.

42 E G Samsel, K Srinivasan, J K Kochi, *J Am Chem Soc*, 1985, **104**, 7606.

43 B M Trivedi, P K Bhattacharya, P A Ganeshpure, S Satish, *J Mol Catal*, 1992, **75**,109.

44 K Srinivasan, P Michaud, J K Kochi, *J Am Chem Soc*, 1986, **108**, 2309.

45 M Bressan, A Morvillo, *Inorg Chem*, 1989, **28**, 950.

46 T J Collins, S Ozaki, T G Richmond, *J Chem Soc, Chem Commun*, 1987, 803.

47 F C Anson, J A Christie, T J Collins, R J Coots, T T Furutani, S L Gipson, J T Keech, T E Kraft, B D Santarsiero, G H Spies, *J Am Chem Soc*, 1984, **106**, 4460.

48 R A Sheldon, *Aspects of Homogeneous Catalysis*, R Ugo, Ed., *D Redial, Dordrecht*, 1981, Vol. 4, P3.

49 R A Sheldon, J A van Doom, *J Catal*, 1973, **31**, 427, 438.

50 A F Tai, L D Margerum, J S Valentine, *J Am Chem Soc*, 1986, **108**, 5006.

51 W Nam, J S Valentine, *J Am Chem Soc*, 1990, **112**, 4977.

52 W Nam, J S Valentine, *J Am Chem Soc*, 1991, **113**, 7449.

53 Y Yang, F Diederich, J S Valentine, *J Am Chem Soc*, 1990, **112**, 7826.

54 Y Yang, F Diederich, J S Valentine, *J Am Chem Soc*, 1991, **113**, 7195.

55 J A Smeagal, C L Hill, *J Am Chem Soc*, 1983, **105**, 3515.

56 J T Groves, T E Nemo, *J Am Chem Soc*, 1983, **105**, 6243.

57 J T Groves, W J Kruper, *Isr J Chim*, 1985, **25**, 148.

58 G A Barf, R A Sheldon, *J Mol Catal A.Chemical*,1995,**102**, 23, and references therein.

59 W P Griffith, S V Ley, *Aldrichim Acta*, 1990, **23**, 13.

60 B R James, S R Mikkelsen, T W Leung, G M Williams, R Wong, *Inorg Chim Acta*, 1984,**85**,209.

61 D H Chin, G N La Mar, A L Balch, *J Am Chem Soc*, 1980, **102**, 5945.

62 A L Balch, Y W Chan, R J Cheng, G N La Mar, L L Grazynski, M W Renner, *J Am Chem Soc*, 1984, **106**, 7779.

63 M J Upadhyay, P K Bhattacharya, P A Ganeshpure, S Satish, *J Mol Catal*, 1993, **80**,1.

64 W M Coleman, L T Taylor, *Inorg Chem*, 1977, **16**, 1114.

65 W M Coleman, L Taylor, *J Inorg Nucl Chem*, 1980, **42**, 683.

66 W M Coleman, L T Taylor, R K Boggess, J W Hughes, *Inorg Chim Acta*, 1980, **38**, 183.

67 W M Coleman, L T Taylor, R K Boggess, J W Hughes, *Inorg Chem*, 1981, **20**, 700.

68 F C Fredrick, W M Coleman, L T Taylor, *Inorg Chem*, 1983, **22**, 792.

69 W M Coleman, R K Boggess, J W Hughes, L T Taylor, *Inorg Chem*, 1981, **20**, 1253.

70 F C Fredrick, L T Taylor, *Polyhedron*, 1986, **5**, 887

71 B Meunier, E Guilmet, M E D Carvalho, R Poilblanc, *J Am Chem Soc*, 1984, **160**, 6668.

72 T G Traylor, A R Miksztal, *J Am Chem Soc*, 1989, **111**, 7447.

73 K Srinivasan, S Perrier, J K Kochi, *J Mol Catal*, 1986, **36**, 297.

74 T G Traylor, K W Hill, W P Fann, S Tsuchiya, B E Dunlap, *J Am Chem Soc*, 1992, **114**, 1308.

75 J F Bartoli, O Brigaud, P Battioni, D Mansuy, *J Chem Soc, Chem Commun*, 1991, 440.

76 S Tsuchiya, *J Chem Soc, Chem Commun*, 1991, 716.

77 J D Koola, J K Kochi, *J Org Chem*, 1987, **52**, 4545.

78 D D Agarwal, R P Bhatnagar, R Jain, S. Srivastava, *J Mol Catal*, 1990, **59**, 385.

79 D D Agarwal, R P Bhatnagar, R Jain, S Srivastava, *J Chem Soc, Perkin Trans 2*, 1990, 989.

80 S E J Bell, P R Cooke, P Inchley, D R Leonord, J R L Smith, A Robbins, *J Chem Soc, Perkin Trans 2*, 1991, 549.

81 C Eskenazi, G Balavoine, F Meunier, H Riviere, *J Chem Soc, Chem Commun*, 1985, 1111.

82 J T Groves, R Quinn, *Inorg Chem*, 1984, **23**, 3844.

83 M Baccouche, J Ernst, J H Fuhrhop, R Schlozer, H Arzoumanian, *J Chem Soc, Chem Commun*, 1977, 821.

84 T Santa, T Mori, M Hirobe, *Chem Pharm Bull*, 1985, **33**, 2175.

85 M P Fauvet, A Gaudemer, *J Chem Soc, Chem Commun*, 1981, 874.

86 I Tabushi, K Morimitsu, *J Am Chem Soc*, 1984, **106**, 6871.

87 C M Che, W T Tang, K Y Wong, W T Wong, T F Lai, *J Chem Res (S)*, 1991, 30.

88 S Menage, E C Wilkinson, L Que Jr, M Fontecave, *Angew Chem Int Ed Engl*, 1995, **34**, 203 and references therein.

89 J T Groves, Y Watanabe, *Inorg Chem*, 1987, **26**, 785.

90 A Thellend, P Battioni, D Mansuy, *J Chem Soc, Chem Commun*, 1994, 1035.

91 J P Renaud, P Battioni, J F Bartoli, D Mansuy, *J Chem Soc, Chem Commun*, 1985, 888.

92 P K Bhattacharya, M J Upadhyay, *J Indian Chem Soc*, 1993, **70**, 951.

93 M J Upadhyay, P K Bhattacharya, P A Ganeshpure, S Satish, *J Mol Catal*, 1992, **73**, 277.

94 N H Lee, E N Jacobsen, *Tetrahedron Lett*, 1991, **32**, 6533.

95 H Yoon, T R Wagler, K J O Connor, C J Burrows, *J Am Chem Soc*, 1990, **112**, 4568

96 R W Lee, P C Nakagaki, T C Bruice, *J Am Chem Soc*, 1989, **111**, 1368.

97 S Compestrini, A Robert, B Meunier, *J Org Chem*, 1991, **56**, 3725

98 B de Poorter, B Meunier, *J Chem Soc, Perkin Trans 2*, 1985, 1735.

99 C Querci, M Ricci, *J Chem Soc, Chem Commun*, 1989, 889.

100 M W Nee, T C Bruice, *J Am Chem Soc*, 1982, **104**, 6123.

101 T Higuchi, H Ohtake, M Hirobe, *Tetrahedron Lett*, 1991, **32**, 7435.

102 L C Yuan, T C Bruice, *J Chem Soc, Chem Commun*, 1985, 868

103 L C Yuan, T C Bruice, *J Am Chem Soc*, 1985, **107**, 512

104 K S Suslick, F V Acholla, B R Cook, *J Am Chem Soc*, 1987, **109**, 2818.

105 H A O Hill, A Roder, R J P Williams, *Struct Bonding (Berlin)*, 1970, **8**, 123.

106 R J P Williams, *Biochem J*, 1970, **117**, 14p.

107 M Hirobe, *Pure Appl Chem*, 1994, **66**, 729.

108 E Guilmet, B Meunier, *French Patent* No. 81 23665, 1981, CA 99 : P213027v

109 P Battioni, J P Renaud, J F Bartoli, M Reina-Artiles, M Fort, D Mansuy, *J Am Chem Soc*, 1988, **110**, 8462.

110 S Campestini, J O Edward, F D Furia, F Novello, *J Mol Catal, A*, 1995, **97**, 79.

111 J E P Hahn, KS Eble, T J McMurry, M Renner, A L Balch, J T Groves, J H Dawson, K O Hodgson, *J Am Chem Soc*, 1986, **108**, 7819.

112 Y Watanabe, K Yamaguchi, I Morishima, K Takchira, M Shimizu, T Hayakawa, H Orita, *Inorg Chem*, 1991, **30**, 2581

113 T Katsuki, K B Sharpless, *J Am Chem Soc*, 1980, **102**, 5974.

114 Y Gao, R M Hanson, J M Klunder, S Y Ko, H. Masamune, K B Sharpless, *J Am Chem Soc*, 1987, **109**, 5765.

115 M G Finn, K B Sharpless, *J Am Chem Soc*, 1991, **113**, 113

116 G W Parshall, W A Nugent, *Chem Tech*, 1988, 376.

117 J N Armor, *Appl Catal*, 1991, **78**, 141

118 W Zhang, J L Loeback, S R Wilson, E N Jacobsen, *J Am Chem Soc*, 1990, **112**, 2801.

119 W Zhang, E N Jacobsen, *J Org Chem*, 1991, **56**, 2296

120 E N Jacobsen, W Zhang, A R Muci, J R Ecker, L. Deng, *J Am Chem Soc*, 1991, **113**, 7063.

121 E N Jacobsen, W Zhang, M L Guler, *J Am Chem Soc*, 1991, **113**, 6703

122 T Tanase, K Mano, Y Yamamoto, *Inorg Chem*, 1993, **32**, 3995

123 R I Kureshy, N H Khan, S H R Abdi, *J Mol Catal, A*, 1995, **96**, 117

124 D J Berrisford, C Bolm, K B Sharpless, *Angew Chem Int Ed Engl*, 1995, **34**, 1059

125 K B Sharpless, W Amberg, Y L Bennani, G A Crispino, J Hartung, K S Jeong, H L Kwong, K Morikawa, Z M Wang, D Xu, X L Zhang, *J Org Chem*, 1992, **57**, 2768

126 G A Crispino, K S Jeong, H C Kolb, Z M Wang, D Xu, K B Sharpless, *J Org Chem*, 1993, **58**, 3785

127 D E Fenton, *Advances in Inorganic and Bioinorganic Mechanisms*, Ed A G Sykes, *Academic Press, London*, 1982.

128 W F Beyer Jr, I Fridovich, *Manganese in Metabolism and Enzyme Function, Academic Press, New York*, 1986, p 193

129 S V Khangulov, V V Barynin, V R M Adamyan, A I Grebenko, N V Voevodskaya, L A Blumenfeld, S N Dobryakov, V B Ilyasova, *Bioorg Khim*, 1986, **12**, 741

130 R M Fronko, J E P Hahn, C J Bender, *J Am Chem Soc*, 1988, **110**, 7554.

131 G S Allgood, J J Perry, *J Bacteriol*, 1986, **168**, 563, CA 106 : 15001g.

132 A Willing, H Follman, G Auling, *Eur J Biochem,J Biochem*, 1988, **175**, 167, CA 109 : 88727v.

133 V L Pecoraro, *Photochem Photobiol*, 1988, **48**, 249, CA 109 : 146277m.

134 J Amesz, *Biochim Biophys Acta*, 1983, **726**, 1, CA 98 : 176115d.

135 G C Dismukes, *Photochem Photobiol*, 1986, **43**, 99, CA 104 : 85357k.

136 B G Fox, W A Froland, J E Dege, J D Lipscomb, *J Biol Chem*, 1989, **264**, 10023.

137 P C Wilkins, R G Wilkins, *Coord Chem Rev*, 1987, 7, 195.

138 W H Armstrong, A Spool, G C Papaefthymiou, R B Frankel, S J Lippard, *J Am Chem Soc*, 1984, **106**, 3653.

139 S J Lippard, *Angew Chem Int Ed Engl*, 1988, **27**, 344.

140 R H Fish, M S Konings, K J Oberhausen, R H Fong, W M Yu, G Christou, J B Vincent, D A K Coggin, R M Buchanan, *Inorg Chem*,1991, **30**, 3002

141 M J Upadhyay, B M Trivedi, P K Bhattacharya, P A Ganeshpure, S Satish, *J Mol Catal*, 1992, **73**, 287