Chapter 1

Introduction

Today coordination chemistry comprises a large body of inorganic chemistry research. It is mainly the chemistry of metal complexes and has fascinated and inspired the chemists all over the world. There is an ever increasing academic, commercial and biochemical interest on the metal complexes of organic chelating ligands. This has resulted in the emergence of allied fields like organometallic chemistry, homogeneous catalysis and bioinorganic chemistry. Among the chelating ligands, Schiff bases have attracted the attention of chemists due to the ease of preparation and complexation. Schiff bases contain the azomethine group (–RC=N–) and are usually formed by the condensation of a primary amine with an active carbonyl compound. They are stable and can tune the ligational aspects by varying denticity and basicity. Metal Schiff base complexes have been known since the mid nineteenth century [1] and even before the report of general preparation of the Schiff base ligands [2]. Intensive research on the physicochemical properties and molecular structure of complexes with Schiff bases has provided interesting new results, which need to be surveyed and compared with earlier literature on these types of compounds.

1.1 CHEMISTRY OF SCHIFF BASES

In 1864, German chemist Hugo Schiff developed a new class of organic compounds [2, 3]. This group of compounds, imines, are often referred to as Schiff bases in his honour. The preparations of these compounds are simple and smart. They are prepared by condensing a carbonyl compound with an amine, generally in refluxing alcohol. The active and well-designed Schiff base ligands are considered as ''privileged ligands'' by Cozzi [4]. In fact, Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations. Several studies [5-8] showed that the presence of a lone pair of electrons in a sp^2 hybridised orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Ligands containing sp^2 hybridized nitrogen atoms, particularly those in which the N-atom is a part of the aromatic system, show very extensive coordination chemistry [9-11]. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are considered as excellent chelating agents, [12, 13] especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered chelate ring with the metal ion. Details regarding the preparation of Schiff bases and their metal complexes are spread out in the literature. The general scheme of formation of a Schiff base is given in Figure 1.1.
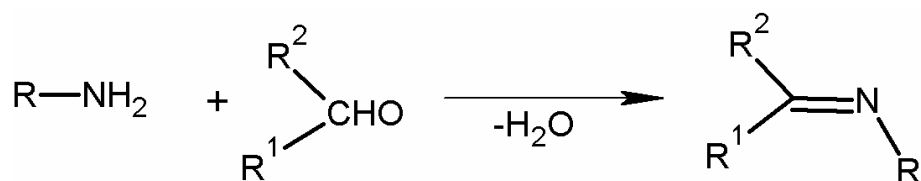

Figure 1.1: *Formation of Schiff base by condensation reaction (R groups may be variously substituted)*

Like aldehydes, the ketones are also able to form Schiff base ligands. However, Schiff base ligands with ketones are formed less readily than those with aldehydes. Schiff bases of aliphatic aldehydes are relatively unstable and readily

polymerizable [14]. In 1931, Dubsky and Sokol [15] isolated N-N'-bis (salicylidine ethylenediamino)copper(II) and nickel(II) complexes, which led to the formation of a new group of ligands called salen. The salen ligands are often the ligands of choice for several reasons. They are multidentate with four binding sites which form complexes with or without vacant sites for potential catalytic and enzymatic activity. Furthermore, substitution at the aromatic ring can modify the electronic and steric properties of the resulting complexes. In the review on metal complexes of Schiff bases by Holm *et al.*, more than half of the referred complexes are derived from salicylaldehyde [7].

1.1.1 Formation of Schiff bases

Condensation between aldehydes and amines are carried out in different reaction conditions, and in different solvents. The common solvents used for the preparation of the Schiff base are methanol or ethanol. Schiff base formation occurs either at room temperature or in refluxing conditions. The presence of dehydrating agents like magnesium sulphate normally favours the formation of Schiff bases. The water produced in the reaction can also be removed from the equilibrium mixture using a Dean Stark apparatus, if the syntheses are carried out in toluene or benzene. Degradation of the Schiff bases may occur during the purification step. Chromatography of Schiff bases on silica gel can cause some degree of decomposition of the Schiff bases through hydrolysis. In such cases, it is better to purify the Schiff bases by crystallization. In general, Schiff bases are stable solids and can be stored without precautions. A large series of Schiff bases could be easily prepared as there is enough scope for variying the amines and the aldehydes. The mono-, di-, tri- and multi- dentate chelating Schiff base ligands are designed according to the binding environments of metal ions. The preparation of Schiff bases and their complexes can be carried out by the following methods:

Transition metal complexes of quinoxaline based Schiff base ligands: Synthesis, characterization and catalytic activity study

3

a. Direct ligand synthesis followed by complexation:

In this method, the isolation and purification of Schiff bases are carried out before complexation. The complexes are then prepared by treating the metal ion and Schiff bases. One of the advantages of this method is that it is possible to perform the spectral characterization of complexes by comparing with the spectral data of the ligands.

b. Template synthesis:

In this method, the syntheses of complexes are carried out without the isolation of Schiff bases by interacting aldehyde, amine and the metal compound in a one step reaction [16-20]. The template reaction is illustrated in Figure 1.2. The metal ions catalyze the reaction by acting as a reaction template. Busch has defined template as the chemical species, which "*organizes an assembly of atoms, with respect to one or more geometric loci, in order to achieve a particular linking of atoms*" [21]. Template synthesis has been used to prepare assemblies that have unusual topologies, such as rotaxanes, helicates, macrocycles and catenanes [22]. Therefore, a templating agent can be said to contain the required information to organize a collection of building blocks so that they can be linked together in a specific manner. There are two types of templated processes: thermodynamic and kinetic. In the former, the template binds to one of the reactant and shifts the equilibrium towards the formation of the product. In the case of kinetic processes the templates operate under irreversible conditions stabilizing all the transition states leading to the formation of the wanted product. In many of the kinetically controlled reactions, the template is strongly bound to the final species. In these cases it acts not only as a kinetic template, but also as a thermodynamic one. In practice, it is often very difficult to unambiguously determine whether a template reaction is kinetically or thermodynamically controlled. Gimeno *et al.* in their review considered a template as any species that organizes an assembly of

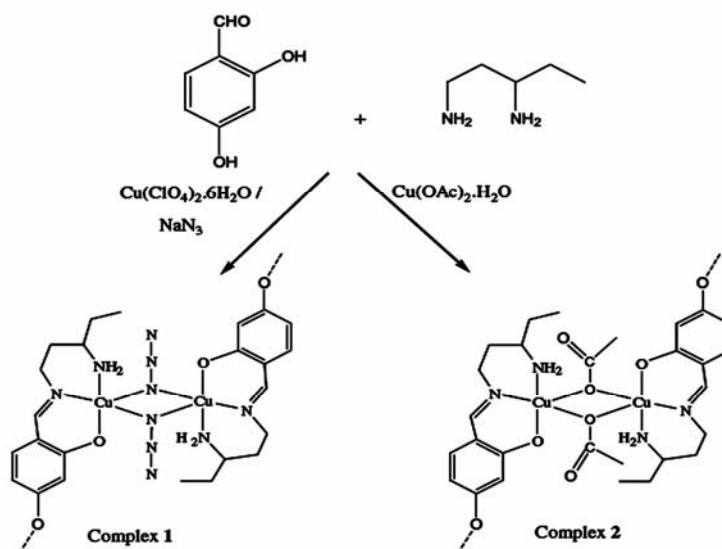molecular building blocks by non-covalent interactions favoring the formation of a specific product [23].

Figure 1.2: *Formation of bridged dinuclear copper(II) Schiff base complexes by template method (Adopted from Ref. 19)*

c.   Rearrangement of heterocycles (oxazoles, thiazoles etc.):

The direct approach in synthesizing a Schiff base from the condensation of an o-hydroxy-, o-amino- or o-mercaptoamine with a carbonyl compound often results in the undesirable side reaction involving ring closure with the formation of a heterocyclic compound [24, 25]. The solution to avoid this problem, which was first used by Schiff in 1869, is to prepare the Schiff base in the form of its metal chelate by reacting the metal complex of one of the starting materials (aldehyde or amine) with the other one [26]. Benzothiazoline and benzoxazole ring are reported to open in specific environments in presence of metal ions, and rearrangement of the ring leads to the formation of corresponding metal chelates of the Schiff bases. Figure 1.3 illustrates such a ring opening complexation reaction reported by Duatti *et al.* [25]
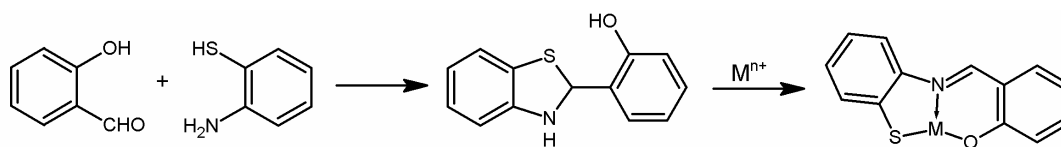
Transition metal complexes of quinoxaline based Schiff base ligands: Synthesis, characterization and catalytic activity study

5

Figure 1.3: *2-(2-Hydroxyphenyl)benzothiazoline: (a) synthesis; (b) interaction with metal ion (Adopted from Ref.25)*

1.1.2 Denticity and basicity of Schiff bases

Ligands are classified according to the number of donor atoms contained and are known as uni, di, tri, or quadridentate ligands. When donor sites of a ligand occupy two or more coordination positions on the same central metal ion, a complex possessing a closed ring is formed. The phenomenon of ring formation is called chelation and ring formed is called chelate ring. The term 'chelate' was first introduced in 1920 by Morgan and Drew. Schiff bases primarily possess nitrogen donor atoms, though many can act as bi-, tri-, tetra- or polydentate mixed donor capabilities as shown in Figure 1.4. In general, the donor nature of the ligands depends both on the type of aldehyde/ketone used and the nature of primary amine/diamine.
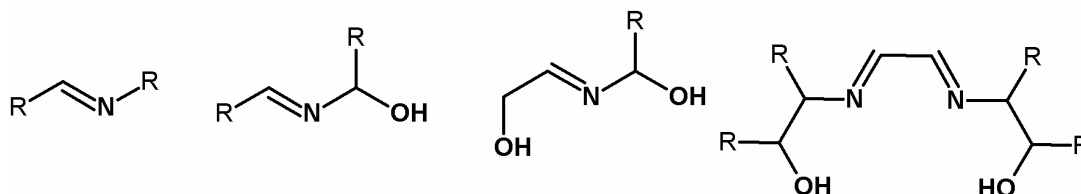

Figure 1.4: *Schiff bases of variying denticity; monodentate to tetradentate, R groups may be variously substituted*

A large number of tetradentate Schiff base ligands are reported in literature. Majority of them are derived from salicylaldehyde and 1,2-diamines (Figure 1.5). The ONNO donor Schiff bases form a family of compounds, salen or salophen, which possess a wide variety of applications [4]. Similarly there are a good number of reports on tridentate Schiff bases [27-30]. They may be of ONN, ONS, ONO, NNS or NNN donors. The tridentate ligands can tune the formation of complexes and these Schiff base complexes have found various applications in medicines such

as antibacterial agents, local anaesthetics, antiviral agents and antispasmodics [31, 32].
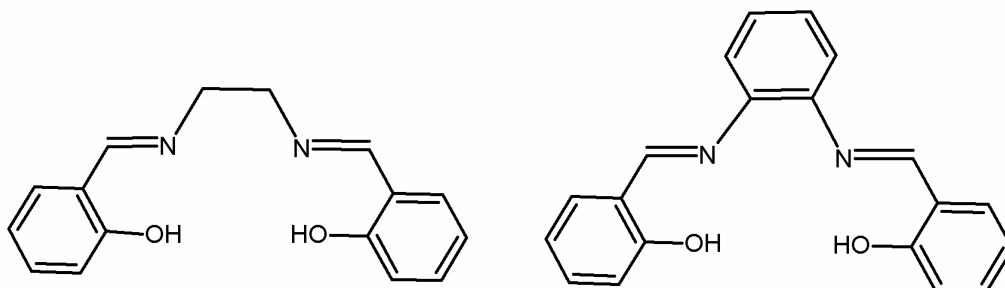

Figure 1.5: *Tetradentate Schiff base family salen and salophen*

For several reasons, Schiff bases have been found to be the most convenient and attractive ligands for forming complexes. First, steric and electronic effects around the metal core can be finely tuned by an appropriate selection of bulky and/or electron withdrawing or donating substituents incorporated into the Schiff bases. Secondly, the two donor atoms, N and O, of the chelated Schiff base exert two opposite electronic effects: the phenolate oxygen is a hard donor and stabilizes the higher oxidation state of the metal atom; whereas the imine nitrogen is a boarderline donor and stabilizes the lower oxidation state of the metal ion [33]. Thirdly, Schiff bases are currently prepared in high yield through one-step procedures via condensation of common aldehydes with amines, in practically quantitative yields. While sulphur donor ligands, being soft bases, prefer to combine with late transition elements and with metal ions in lower oxidation state, the ONS donor Schiff bases can show symbiosis [34]. The presence of soft sulphur atom softens the hardness of the oxygen atom, and this enables such ligands to form a large number of complexes with structural diversity.

The basicity of the Schiff bases also plays a key role in the formation and stabilisation of the complexes. The –OH or –SH groups present in the Schiff bases can induce tautomerism in the compound, which leads to complexes with different structures. A large number of salen complexes shows keto-enol tautomerism. Also

Transition metal complexes of quinoxaline based Schiff base ligands: Synthesis, characterization and catalytic activity study

7

the deprotonation of thiolic, alcoholic and phenolic groups are favoured due to the stabilisation of various oxidation states of the central metal ion.

1.1.3 Applications of Schiff bases and their metal complexes

Versatility of Schiff base ligands and the biological, analytical and industrial applications of their complexes make further investigations in this area highly desirable. The applications of the Schiff bases and their complexes are discussed here briefly:

1.1.3.1 Catalytic applications

In Schiff base metal complexes, the environment at the coordination center can be modified by attaching different substituents to the ligand and a useful range of steric and electronic properties essential for the fine-tuning of structure and reactivity can thus be provided [35-37]. The Schiff bases form metal complexes with p-block and d-block metals and these complexes have been known to act as highly efficient catalysts in various syntheses and other useful reactions [38-42]. Many Schiff base complexes of ruthenium and palladium are used as catalyst in the syntheses of quality polymers. Unique asymmetric catalysis of metal complexes of salen and the related Schiff-base ligands has been reviewed by Katsuki [43]. The review summarises the generation of *cis* metallo-salen and its related complexes, their structural features, and their application to asymmetric syntheses. Wang *et al.* in 1999 reported the effective oxidation of olefins using Mn(II) amino acid Schiff base complexes [44]. Gupta and Sutar reviewed the catalytic activities of transition metal complexes-both simple and polymer anchored. They have highlighted the potential of Schiff base complex as catalyst towards oxidations, hydrogenations, polymerizations, various coupling reactions and ring closures [45, 46]. Heterogenization of homogeneous catalysts has recently attracted the attention of chemists due to better selectivity and recyclability of the catalysts. In recent years there is an exponential increase in the number of publications in catalysis by supported Schiff base complexes. However, homogeneous catalysis is more

relevant as the mechanism of the reaction can be arrived. BINAP ligands (BINAP is the abbreviation for the organophosphorus compound 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) are famous for their stereoselective transformations. Che and Huang [47] have reviewed the catalytic activity of chiral BINAP Schiff base complexes in stereoselective organic transformations. Their studies reveal that these types of chiral metal complexes are active catalysts for stereoselective organic transformations including hydroxylation of styrene, aldol reactions, alkene epoxidation, trimethylsilyl cyanation of aldehydes, desymmetrization of *meso-N*-sulfonylaziridine, Baeyer-Villiger oxidation of aryl cyclobutanone, Diels-Alder reactions of 1,2-dihydropyridine, and ring-opening polymerization of lactide. A discussion on the catalytic reactions carried out in the present investigation is given in section 1.3.

1.1.3.2 Biological and medicinal applications

Many ligands have been designed to mimic the function of natural carriers in recognizing and transporting specific metal ions, anions or neutral molecules and in understanding and reproducing the catalytic activity of metallo-enzymes and proteins [29]. Schiff bases are known to be important intermediates in many enzymatic reactions involving interaction of an enzyme with an amine or carbonyl group of the substrate [48]. One of the most prevalent types of catalytic mechanism in enzyme is usually that of a lysine residue with a carbonyl group of the substrate to form an imine or Schiff base. Similarly the biosynthesis of porphyrin, for which glycine is a precursor, which involves the intermediate formation of a Schiff base, is another important pathway. Synthetic chemists are interested in studiying the efficiency of the biosynthetic machinery by designing biomimetic reactions that approximate natural reaction pathways. Probably the most astonishing biomimetic reactions are the ones, which combine several transformations in sequence and produce complicated structures from comparably simple starting materials, in a simple laboratory operation. In such a simple method, Matsumoto *et al.* [49] used Co(II), Mn(II) and Fe(II) complexes of salen as catalyst for the synthesis of

carpanone in good yield by the oxidation of trans-2-(1-propenyl)-4,5-methylenedioxyphenol with molecular oxygen. The Schiff bases derived from pyridoxal and amino acids are extensively studied and are considered as very important ligands from the biological point of view [50-54]. Transition metal complexes of such ligands might work as important enzyme models.

Schiff bases can accommodate different metal centres involving various coordination modes allowing successful synthesis of homo- and heterometallic complexes with varied stereochemistry. This feature is employed for modelling active sites in biological systems [55]. Morrow and Kolasa reported the cleavage of plasmid DNA by square planar nickel-salen in the presence of either magnesium monoperoxypthalic acid (MPPA) or iodosylbenzene [56]. According to cell biologists deoxyribonucleic acid (DNA) is the primary target molecule for most anticancer and antiviral therapies. Investigations on the interaction of DNA with small molecules are important in the design of new types of pharmaceutical molecules. In the 1980s the chemical nuclease activity of transition metal complexes was discovered and is recently used extensively in bioengineering. Literature search reveals that a large number of Schiff base complexes are excellent DNA cleavagers [57-61]. The metal DNA interaction is described in detail by Hadjiliadis and Sletten in their book: 'Metal complexes-DNA interaction' [62]. A number of research groups are actively engaged in developing new therapeutic reagents and DNA probes from transition metal Schiff base complexes. Silveria *et al.* used oxindazole Schiff base complexes of copper(II) for the cleavage of double stranded DNA and the potency of the complex as anti tumour agent was also explored [63].

Almost all transition metal complexes of Schiff bases show good antibacterial, antiviral, antimalarial and antitubercular activity [64-67]. The potent biological activity can be related to the presence of nitrogen atom with a lone pair of electron in it so that the nitrogen can participate in hydrogen bonding with NH or OH groups present in biomolecules like amino acids, proteins, DNA or RNA.

1.1.3.3 Applications as fluorescent and electronic materials

Zinc(II) Schiff base complexes have been shown to be effective emitters. Recently Zhou *et al.* [68] reported the Schiff base 2-(hydroxymethyl)-4-methyl-6-((quinolinyl-8-imino)methyl)phenol and its zinc(II) complex (Figure 1.6). The complex acts as a visual and fluorescent sensor. The electron transfer from the nitrogen atom of the heterocycle to the metal ion enhances the internal charge transfer (ICT) process. As a result, a red-shift in emission wavelength can be observed which is also favoured by the strong binding of the zinc. Nowadays there is an increasing interest in the development of fluorescent sensors for the enantioselective recognition of chiral organic compounds and drug molecules [69, 70].
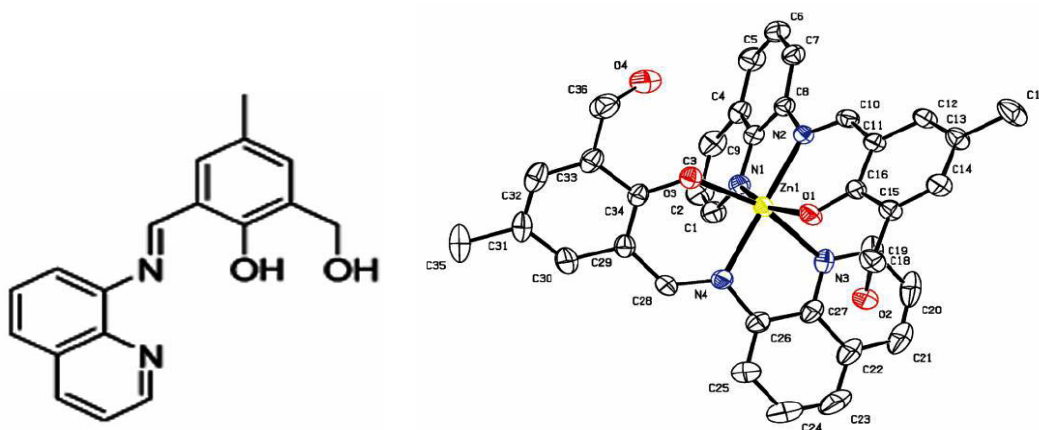

Figure 1.6: *Structure of the Schiff base, 2-(hydroxymethyl)-4-methyl-6-((quinolinyl-8-imino)methyl)phenol, and its zinc(II) complex (Adopted from ref. 68)*

Banerjee *et al.* [71] developed a highly enantioselective fluorescent sensor from the chiral Schiff base, 4-methyl-2,6-bis-[(2-hydroxy-1-phenylethylimino) methyl] phenol. It acts as highly enantioselective fluorescent agent for α-hydroxycarboxylic acid, e.g., mandelic acid. They observed that, within a certain concentration range, one enantiomer of the chiral acid increases the fluorescence intensity of the Schiff-base compound by 122-fold, while the other enantiomer

enhances the intensity only by 42-fold. Such highly enantioselective responses towards the chiral acid make the Schiff-base compound attractive as a fluorescent sensor for determining the enantiomeric composition of α-hydroxycarboxylic acids. Similarly there are a number of reports in which Schiff base complexes find application as active fluorescent sensors [72-75].

Cozzi *et al.* reviewed the photophysical properties of the Schiff base complexes with several metal ions [76]. They evaluated the photophysical properties of salen complexes for possible use in the luminescent probes. Mixed valence Schiff base complexes are considered as functional materials for optoelectronics and molecular magnets. The salicylidene Schiff base derivative, *N*-salicylidene-(*S*)-α-naphthylethylamine, has been used for making multistate/ multifunctional switches by Zhao *et al.* [77]. Wei *et al.* [78] prepared blue luminescent zinc and beryllium complexes of Schiff bases derived from calixarene. These Schiff bases complexes have good solubility in normal solvents and can easily form thin films. Some of the Schiff base complexes may find application in the development of new molecular switches. In NLO studies, transition metal complexes are of more importance than conventional organic compounds due to the intense charge transfer transition and the possible donor acceptor capabilities.

1.1.3.4 Other applications

Many Schiff base compounds are found to be good corrosion inhibitors. Emregül and Atakol [79] studied the corrosion behavior of iron in 2 M HCl solution at 298 K with three Schiff base compounds and found that these compounds have the perfect inhibition efficiency. Literature survey reveals an increased attention to Schiff base compounds as corrosion inhibitors especially in acidic environments for various metals like steel, aluminum and copper [80-85]. Organocobalt complexes with tridentate Schiff base act as inhibitor of emulsion polymerization and copolymerization of dienyl and vinyl monomers.

Chromium [86] and cobalt Schiff base complexes [87] have been used as dyes which give fast colour to leather, food packages and wools. Cobalt complexes of a salen type Schiff base have excellent light resistance and storage ability and resist degradation even in acidic gases like CO_2. Tetradentate Schiff bases like salens and salophens act as chromogenic reagent for determination of nickel in some natural food samples [88].

1.2 QUINOXALINE SCHIFF BASES

Quinoxalines, also called benzopyrazines, are heterocyclic compounds containing a fused ring made up of a benzene ring and a pyrazine ring. They along with the isomers cinnolenes, phthalazines and quinazolines belong to a class of heterocyclic compounds known as diazanaphthalenes with two heteroatoms in the same or different rings. The fusion of a benzene ring, however, causes decrease in the aromaticity due to the bond alternation (Figure 1.7). Quinoxalines have 10-π electrons that are located in five bonding molecular orbitals. There are also two non-bonding orbitals that lie in the molecular plane and are confined to the nitrogen atoms. Each of these orbitals contains an electron pair and these electrons are responsible for the basic properties of quinoxalines [89]. Quinoxaline can act as Lewis base, form metal complexes, and can participate in hydrogen bonding with hydrogen atoms present in electronegative atoms.
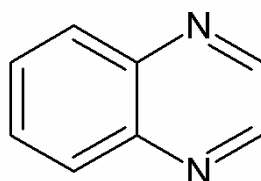
Figure 1.7: *Structure of quinoxaline*

Quinoxaline derivatives have been widely used in dyes, pharmaceuticals, and in electrical/photochemical materials. Quinoxaline ring moiety is a part of the chemical structures of various antibiotics such as echinomycin, levomycin and actinoleutin, which are known to inhibit growth of gram positive bacteria and are

active against various transplantable tumors. A number of synthetic strategies have been developed for the preparation of substituted quinoxalines. Quinoxalines are readily made from 1,2-dicarbonyl compounds and aromatic 1,2-diamines. A well-known route to quinoxalines is the reaction of o-phenylenediamine with a 1,2 – dicarbonyl compound [89]. Heravi *et al.* used Suzuki–Miyaura coupling (Figure 1.8) reaction for the synthesis of 2,3-disubstituted quinoxalines [90].
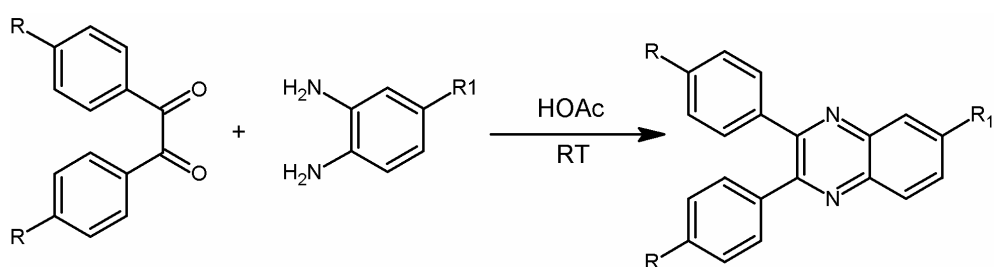

Figure 1.8: *Synthesis of quinoxaline by condensation of 1,2-dicarbonyl compound and orthophenylenediamines (Adopted from Ref. 90)*

Quinoxaline compounds show tautomerism if they have a hydroxy, thiolic or amino group at the ortho position. 2-Hydroxy- and 2-mercaptoquinoxalines exist in the quinoxalin-2-one and quinoxaline-2-thione forms, whereas 2-aminoquinoxaline exists as such rather than as an imine (Figure 1.9) in the solid state [89].

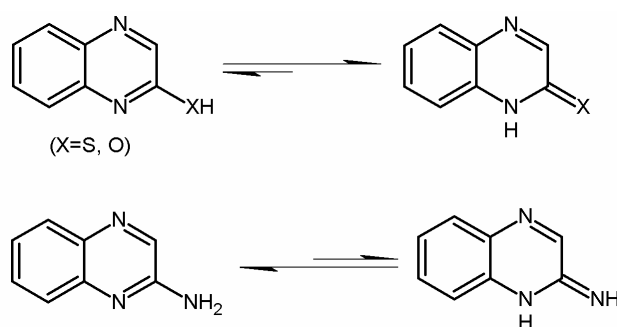**Figure 1.9:** *Tautomerism in quinoxaline derivatives (Adopted from Ref. 89)*

Ovchinnikov and Muèller (1974) reported the possibility of linking of metal ions to heterocycles to form stable complexes, which permits the utilization of heterocyclic systems with pendant arms for modelling cation receptors in proteins [91, 92]. During the past several years, quinoxalines have been used effectively as building

blocks for metal-containing two dimensional networks [93]. Metal halides coordinate readily with quinoxalines to form interesting coordination polymers. Substituted quinoxalines, which have the potential to form novel three-dimensional structures upon coordination, have been synthesized. Quinoxaline heterocycles have attracted much attention owing to their natural occurrences [94] and biological activities [95]. Many quinoxaline derivatives display unusual solid-tumor selectivity against multi drug-resistant cancer cells. The synthetic utility and pharmacological importance of these compounds have prompted many scientists to synthesize and characterize novel quinoxaline derivatives [96, 97].

1.2.1 Transition metal complexes of quinoxaline Schiff bases

Complexes derived from quinoxalines have been reported in the literature [98-100]. The presence of quinoxaline ring helps in the formation of one dimensional structures and may provide potential supramolecular recognition sites for π–π aromatic stacking interactions to form high-dimensional supramolecular networks [101]. Schiff bases with an electron withdrawing heterocyclic ring system derived from quinoxaline-2-carboxaldehyde would be interesting as their ligand field strengths are expected to be weaker than the Schiff bases containing only aromatic rings, like naphthaldehyde [102-104]. Dong *et al.* in 2005 synthesized a silver(I) complex of quinoxaline diazine Schiff base and are found to form one dimensional and two dimensional network structure depending upon the counter ion [105]. Two series of transition metal complexes of Schiff bases formed by the condensation of quinoxaline-2-carboxaldehyde with semicarbazide, 2-aminophenol or furfurylamine were synthesised and characterised by Mayadevi *et al.* [104, 106] Sreekala *et al.* synthesized transition metal complexes of quinoxaline-2-carboxalidineglycene by adopting template method [107]. There are a couple of reports of formation of Schiff base complexes of diamines which contain quinoxaline moiety [104, 105, 108 and 109].

1.2.2 Applications of complexes of quinoxaline backbone

Quinoxaline is abundant in chemical and biological systems. Its derivatives appear in proteins and are extensively employed for modelling in biological applications, to electronic devices and materials. Quinoxaline derivatives are also used as analytical reagents in the determination of metal ions [110].

The quinoxaline-type ligands can act as either neutral or anionic chelators and, in addition, could possibly act as bridging ligands. This leads one to expect that these ligands will exhibit various coordination modes in metal complexes and it is even possible that they can function as controlling ligands in catalytic reaction.

The quinoxaline metal complexes are found to be more active than the free ligand and some side effects may decrease upon complexation. Numerous quinoxaline derivatives are important as biocidal agents, as these compounds have the ability to bind and cleave double stranded DNA under physiological conditions. They are used for genomic research and as diagnostic agents in medicinal applications [111-114].

Numerous quinoxalinoporphyrins have been electrochemically examined in recent years as models for the development of porphyrin-based molecular wires and devices [115]. Organic light-emitting devices (OLEDs) have received much attention because of their potential applications in flat-panel displays. Doping of a suitable dye into a host layer can improve both the efficiency and the stability significantly. Thus, there is great interest in the synthesis of dyes with desired properties, such as high emission quantum yield, high thermal and photochemical stability and good colour purity. Fluorescent molecules having quinoxaline building blocks usually display high electron affinities and good thermal stabilities, and also act as electron-transporting materials [116]. Quinoxalines have been successfully incorporated in polymers for use as electron-transport materials in multilayer OLEDs [117-120].

1.3 APPLICATIONS OF TRANSITION METAL SCHIFF BASE COMPLEXES AS CATALYST FOR ORGANIC TRANSFORMATIONS

Catalysis is an area of research which still continues to be a premier frontier area of chemistry. It plays a key role in modern chemical technology; in fact, it is the backbone of chemical industry. During the last decades, chemists shift their phenomenological approaches towards the structural and mechanistic investigation at the molecular level by a combination of instrumentation, quantum mechanical calculation and computational methods. This renovation has improved the understanding of catalysis.

There are a large number of important organic transformations such as oxidation, hydrogenation, hydroformylation, carbonylation, polymerization and various coupling reactions. The possibility of multiple oxidation states, accessibility of vacant coordination sites, tuning of the redox potentials by the ligand and the facility to undergo substitutions at the ligands, are one or more of the characteristics of transition metal complexes to behave as catalysts. But the major problems of homogeneous catalysis are the separation of the catalysts from the reaction medium. The procedure for separation of catalysts from reaction mixture generates large volumes of waste eluent and devours a lot of energy. However homogeneous catalysts are still attractive due to the very good activity and selectivity. The chemical and mechanical aspects of the homogeneous reaction can be studied. The catalyst can be easily modified for optimizing selectivity. Furthermore, these reactions need low temperatures and pressures.

There is a continuing interest in studies on the catalytic transformations by transition metal complexes. Information regarding their structure, environment of the metal atom, the number of ligands attached and the coordination changes during a reaction can be obtained proficiently. Thus design of catalysts, which lead to better selectivity, is possible. The generation of chirality on complexation is found to be worthwhile in asymmetric catalysis. Many Schiff base complexes show

Transition metal complexes of quinoxaline based Schiff base ligands: Synthesis, characterization and catalytic activity study

17

excellent catalytic activity at reasonable temperatures *ie.* below 100 ºC. Similarly the activities of the complexes are varied by the changing the nature of the ligand.

Over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis. Schiff bases are able to transmit chiral information to produce non racemic products through catalytic processes. For the preparation of such Schiff bases, either chiral aldehydes or chiral amines can be used. They are extensively used as oxidation catalysts. The oxidation of organic compounds has been considered as a reaction of academic and industrial interest to analyze the catalytic activity of various metal complexes.

The high atom efficiency of peroxides makes them an efficient oxidant for industrial applications. Hydrogen peroxide and TBHP are the main peroxides used as reagents for oxidation reactions. As this oxidant is often partially destroyed by catalase type activity of the complexes, the development of novel synthetic methodologies employing H_2O_2 is a major challenge. It should be noted that, unselective side reactions might occur after the homolytic cleavage of H_2O_2 leading to hydroxyl radicals. Several attempts have been successfully made to suppress the unselective side reactions by fine tuning the catalyst or optimising the reaction conditions.

1.3.1 General reactions catalyzed by Schiff base complexes

Schiff base complexes are found to catalyse a large number of organic transformations such as polymerization reaction, epoxidation, ring opening of epoxides, reductions, oxidations, alkylation, Michael addition, Heck reaction, annulation, carbonylation, benzoylation, cyclopropanation, Diels Alder reaction, aldol condensation etc.

Schiff base complexes have been used as catalysts in reduction of ketones to alcohols [121] and in the alkylation of allylic substrates [122]. Jacobsen *et al.* found that the enantioselective ring opening of large cycloalkanes are catalysed by

chiral Schiff base complexes of cobalt(II) [123] and chromium(III) [124]. The reaction is found to be difficult to take place with routine reagents. Binaphthyl ligands are considered as versatile frameworks for chiral ligands in coordination and metallosupramolecular chemistry [125]. BINAP Schiff base complexes are found to catalyse many reactions [126]. Michael addition was easily carried out in presence of chiral salen Schiff base complexes and complexes of BINAP Schiff bases. Some of the chiral binaphthyl Schiff bases used by Zhou *et al.* are given in Figure 1.10.
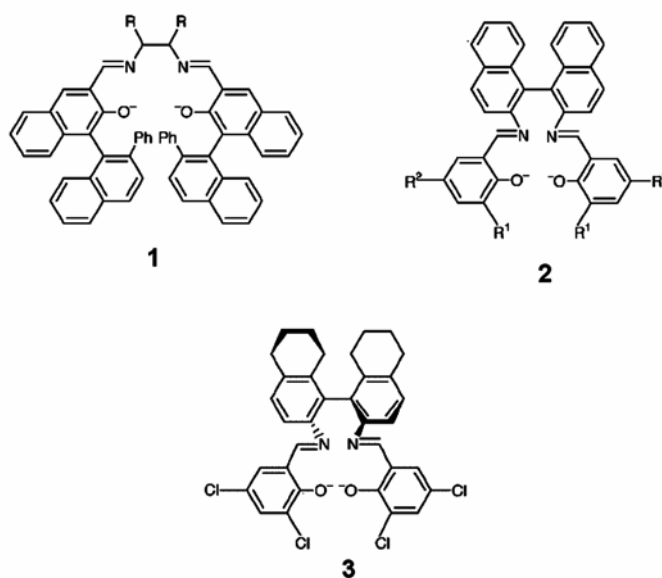

Figure 1.10: *Some commonly used binaphthyl Schiff bases (Adopted from Ref. 126)*

Schiff base complexes showed catalytic activity in carbonylation of alcohols and alkenes at low pressure to produce arylpropionic acid and their esters [127], which are used as non-steroidal anti-inflammatory drugs. In addition to monometallic, the bimetallic Schiff base complexes also show catalytic activity in carbonylation reactions. The use of salen complexes as catalyst was first carried out in 1985 by Kochi and co-workers. Chiral manganese salen complexes were first developed by Jacobsen and Katsuki and are generally known as Jacobsen's Catalyst. Jacobsen's catalyst is (R,R)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamino manganese(III) chloride which is prepared by resolving 1,2-

diamino cyclohexane as the appropriate tartrate, and reacting with 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde in the usual method of preparing salen-type ligands. Reaction with manganese(II) acetate in the presence of air gives the manganese(III) complex, which may be isolated as the chloro complex by addition of lithium chloride. These complexes are efficient catalyst towards epoxidation of *cis* olefins. One such complex used by them and the scheme of one of the reaction carried out using this catalyst are shown in Figure 1.11 and Scheme 1.1. It is generally agreed that the Jacobsen's catalyst (Figure 1.11) is oxidised to a reactive oxo-Mn(V)salen complex. The latter has not been isolated and characterised but related species with other metal centres are known. The Mn(salen)Cl is almost certainly planar; the oxo species has been postulated as planar, bent and twisted (folded) by different researchers.
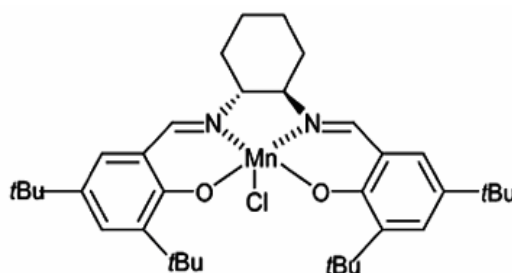

Figure 1.11: *Structure of the Jacobsen's catalyst, (R,R)-N,N'-bis(3,5-di-tert butylsalicylidene)-1,2-cyclohexanediamino manganese(III) chloride*
*(Adopted from **Ref. 4**)*
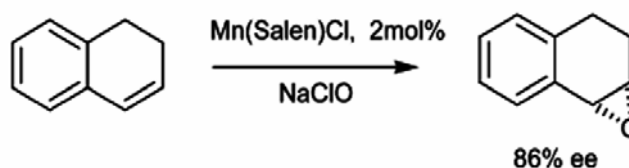
Scheme 1.1: *A stereoselective epoxidation catalysed by Jacobsen's catalyst*
(Adopted from Ref. 4)

Schiff base complexes are used as catalyst in Heck reaction [128]. Usually complexes of phosphene ligands are used to catalyse this reaction. But compared to phosphene, Schiff bases can easily be prepared. Palladium(II) complexes of salen

Schiff base ligands showed high catalytic activity in Heck reaction than the commercially used phosphene complexes [129]. Arellano *et al.* [130] used the palladium(II) Schiff base complex of 2-*tert*-butyl-4-methyl-6{(*E*)-[(2*S*)-1-(1-arylmethyl)pyrrolidinyl]imino}methylphenol as catalyst for Heck reaction. Legros and Bolm [131] reported the preparation of a tridentate Schiff base iron catalyst, prepared in situ from Fe(acac)₃, which is able to promote the enantioselective oxidation of sufide to sulfoxides.

The iron(III) and cobalt(II) complexes of pyridine Schiff base ligands showed significant activity in the polymerization of ethylene. These complexes were also used successfully for copolymerization of ethylene with 1-hexene [132]. They have observed that the iron(III) Schiff base complexes showed higher yield and activity than the cobalt(II) complexes.

Canali and Sherrington reviewed the utilisation of homogeneous and supported metal salen complexes in asymmetric catalysis [133]. They have focused on the chiral salen ligands, and in particular on the use of their optically pure metal complexes as asymmetric catalysts. The activity of the chiral metalloporphyrins in the enantiomeric synthesis of aziridines and amides was moderate [134, 135] but the activity was improved in the presence of manganese(III) complex of the chiral Schiff base, tetrabromo substituted salen [136]. The preparation of Schiff base ligands by condensation of readily available amines with aldehydes/ketones is much easier as compared to the lengthy steps involved in the synthesis of porphyrin ligands. The chiral complexes, *tert*-butyl glycinate-benzophenone nickel(II), diphenylmethylene imino palladium(II) and (1*R*,2*R* or 1*S*,2*S*)-[*N*,*N*′-bis(2′-hydroxybenzylidene)]-1,2-diaminocyclohexane copper(II), have increased enantioselectivity in alkylation of enolates [137-139]. The isomerization of norbornadiene to quadricyclane was significantly catalyzed using (9,10-phenanthrenequinone diimine) rhodium complexes [140, 141]. These interconversions are useful for the storage of solar energy. The asymmetric reduction of dialkyl ketones to alcohols [142, 143] is very difficult to achieve, but

salen Schiff base complexes of transition metals have been found to be efficient catalysts in these reductions [144]. The cobalt complexes with 3-oxobutylideneaminato ligands were efficient catalysts for the enantioselective borohydride reduction of ketones, imines, and α,β-unsaturated carbonyl compounds to afford the corresponding secondary alcohols [145]. Chiral Cr(salen)Cl complexes are used as catalyst in hetero-Diels-Alder reaction [146]. The product yield and enantioselectivity were influenced by the nature of catalysts. These studies reveal that Schiff base complexes are potential catalysts to influence the yield and selectivity in chemical transformations.

1.3.2 Hydroxylation of phenol

The oxidation of phenol by hydrogen peroxide (H_2O_2) is a widely applied process in the chemical industry for the preparation of the dihydroxylated derivatives. This oxidation process is frequently reported as taking place through the decomposition of H_2O_2 with formation of an unstable electrophilic intermediate, which attacks the phenol nucleus to give a phenoxy ion. This ion can be considered as the precursor of the products usually formed in this process: hydroquinone, catechol and benzoquinone. Phenol and its derivatives are found in wastewaters including those from the oil refining, petrochemical, coke and coal gasification industries. Removal of phenol from such wastewaters is an important challenge for chemists. Diphenols, *i.e.*, catechol and hydroquinone, are considered as important chemicals in industrial chemistry. Manufacture of diphenols through phenol hydroxylation with H_2O_2 as the oxidant has become one of the promising approaches in the 21st century, as the process demands for the simple techniques and produces little environmental pollution.

Two factors should be taken into account in the hydroxylation of phenol. First, the introduction of a second hydroxyl substituent onto the aromatic nucleus tends to activate the molecule towards further reaction and this leads to the formation of a mixture of unwanted tarry by-products. Secondly, hydroquinone and catechol are generally used for different purposes. For example, hydroquinone is a

photographic developer and catechol is an intermediate in the production of industrial anti-oxidants. Consequently, one has to obtain hydroquinone or catechol selectively. A commercial catalytic process has been developed for hydroxylating phenol using hydrogen peroxide, which tends to produce mixtures containing a major fraction of catechol. A significant fraction of hydroquinone was also formed. The proportion of tarry by-products has been controlled by limiting the use of very low mole ratios of hydrogen peroxide to phenol; but, inevitably, this restricts the extent of conversion of the phenol and hence the space yield of the plant.

The catalysts reported to be used in phenol hydroxylation to date are molecular sieves, heteropoly compounds of the Dawson structural type: molybdovanadophosphate and tungstovanadophophosphate, copper–aluminum hydrotalcite-like compounds and metal complexes. The catalysts mentioned above have some catalytic activity for phenol hydroxylation, but the reaction lacks industrial value because of their relatively low yield. Therefore, catalysts with high activity and high selectivity have become an important target in this field.

Many Schiff base complexes are used for catalytic phenol hydroxylation reaction. Copper(II) salicylaldimine complexes have been successfully employed in hydroxylation of phenol [147]. Van Wyk *et al.* reported the catalytic hydroxylation of phenol in aqueous media using a cobalt(II) N-(aryl)salicylaldimine Schiff base complexes [148]. They reported catechol and hydroquinone as the products and at higher pHs benzoquinone was also obtained. In 2001, Musie *et al.* reported a new method for phenol hydroxylation. They used supercritical carbon dioxide as the medium for reaction which is inert towards oxidation [149]. Polymeric iron(III) Schiff base complexes catalyze hydroxylation of phenol. Due to the insolubility of the complex, the reaction is a heterogeneous catalytic reaction and catechol is obtained as the main product with good selectivity (78-85 %) [149]. The structure suggested for the polymeric iron(III) complex of the Schiff base, 4-(naphthalen-1-yliminomethyl)-phenol, is given in Figure 1.12.
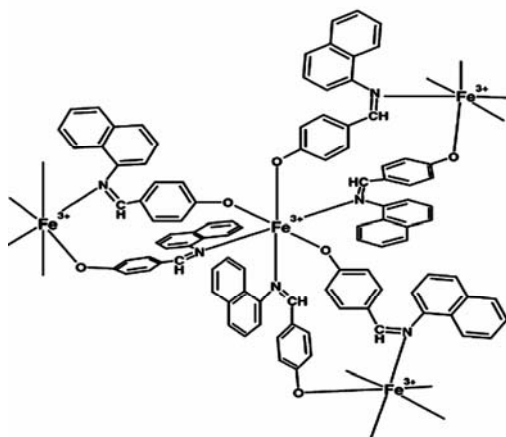
Figure 1.12: *Suggested structure of the polymeric iron(III) complex with 4-(naphthalen-1-yliminomethyl)-phenol Schiff base (Adopted from Ref. 149)*

Zhang *et al.* [150] studied the hydrogen peroxide oxidation of phenol using a manganese(II) Schiff base complex as mimetic peroxidase and the mechanism suggested by them is given in Figure 1.13. The mechanism of phenol hydroxylation may follow an ionic pathway or free radical pathway. The reaction proceeds through the formation of the active species from hydrogen peroxide, OOH^-, which initially forms an intermediate with metal ion. In the next step a new intermediate, phenol-metal-OOH, is formed. This intermediate facilitates the attack of OOH^- at the ortho and para position of the phenol to form catechol and hydroquinone.
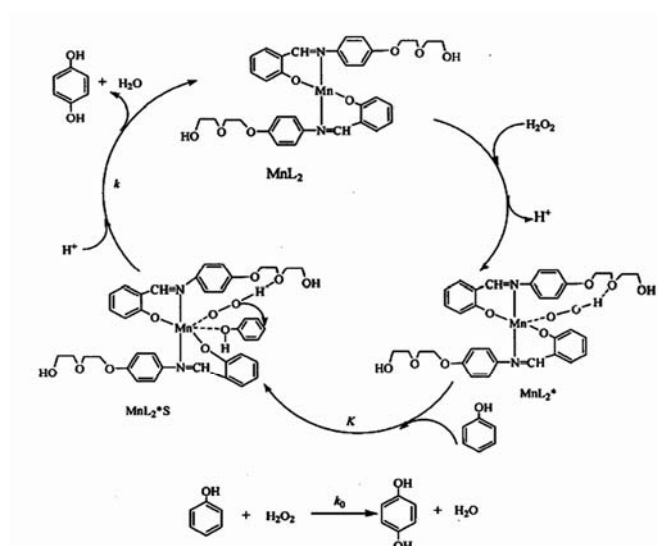

Figure 1.13: *The mechanism of the oxidation of phenol catalyzed by the Schiff base complexes (Adopted from Ref. 150)*

1.3.3 Oxidation of cyclohexane

The selective oxidation of saturated hydrocarbons is one of the most challenging and promising subjects in oxidation chemistry. Cycloalkanes are an important chemical class of hydrocarbons found in diesel, jet and gasoline fuels. The significant industrial production of cyclohexane derivatives—10^6 ton per year of cyclohexanone alone—has stimulated studies aiming to find milder, energy-saving conditions for the oxidation of cyclohexane [151]. The system currently used makes use of soluble salts of cobalt and manganese as catalysts for the oxidation of cyclohexane by oxygen to cyclohexanol and cyclohexanone. Cyclohexanol and cyclohexanone are oxidized by nitric acid to give adipic acid (Figure 1.14). The oxidation of cyclohexanone by nitric acid leads to the generation of nitrogen dioxide, nitric oxide, and nitrous oxide. The first two gases can be recycled for the synthesis of nitric acid. Nitrous oxide, however, is an ozone depleter and cannot be recycled. Indiscriminate nitrous oxide emission from this process is therefore the cause of considerable concern. Part of the cyclohexanone can also be converted to the corresponding oxime and then to caprolactam—the monomer for nylon 6. Phthalic acids are one of the monomers for the manufacture of polyesters.
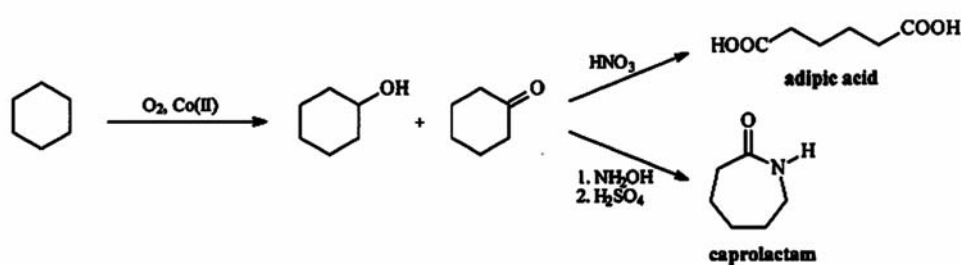

Figure 1.14: *Conversion of cyclohexane to adipic acid or ε-caprolactam.*

The functionalization of unactivated C-H bonds of cyclohexane requires high pressure and temperature, and a number of catalysts have been developed. In this reaction, various oxidizing agents having active oxygen such as hydrogen peroxide, iodosobenzene, t-butyl peroxide and ozone have been used. Solvents

(heptanol, 2-methylpropanal, acetaldehyde), and cocatalysts (such as acetic acid, chloroacetic acid, trifluoroacetic acid) have also been used for this reaction.

The oxidation of cyclohexane under mild condition is a topic of great interest. The reaction proceeds through the formation of peroxy intermediate. The cyclohexyl hydroperoxide is formed initially when hydrogen peroxide is used, which is later oxidised to cyclohexanol and cyclohexanone. Imamoto et al. used porphyrin complexes as catalyst towards oxidation of cyclohexane [152]. Zhou *et al.* used transition metal complexes of deuteroporphyrins as catalyst. They proposed the reaction mechanism involving the intermediate formation of the μ–oxo dimer. In 2002, Rathnaswamy *et al.* used cobalt and manganese cluster compounds for the oxidation of cyclohexane [153]. Supported metal complexes are also largely used for cyclohexane oxidation. The Co(II) complex of the Schiff base derived from dialdehyde starch (obtained by the periodate oxidative cleavage of the C2-C3 bond in starch) and amino alcohol has been found to be an active and reusable catalyst for cyclohexane oxidation with oxygen. The reaction takes place in the absence of solvents or reducing agents and high turnover number of catalyst and high selectivity of the product could be obtained [154].

In 2009 Comba *et al.* [155] proposed a mechanism for the catalytic cyclohexane oxidation on the basis of labelling and computational studies. They have used high valent iron complexes and have proposed both aerobic and anaerobic mechanism (Figure 1.15) for the reaction.
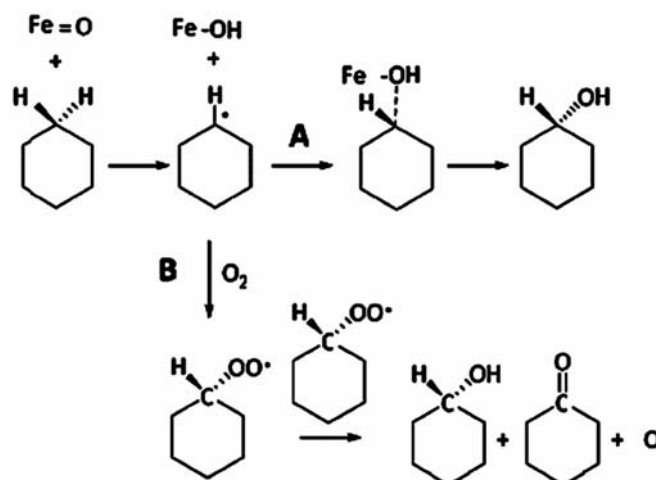
Figure 1.15: *Anaerobic (A) and Aerobic (B) Pathway for the Ferryl-Based Oxidation of Cyclohexane (Adopted from Ref. 155)*

1.3.4 Oxidation of benzyl alcohol

Traditionally, oxidation of benzyl alcohol to benzaldehyde is performed with stoichiometric amounts of chromium(VI) reagents. These oxidants are not only relatively expensive, but also they generate copious amounts of heavy-metal waste. Moreover, the reaction is often performed in environmentally undesirable solvents like chlorinated hydrocarbons. Hydrogen peroxide is a clean oxidant compared to other oxidants [156]. To reduce the harmness and cost of solvents, studies towards solvent free process have been carried out [157-160].

The copper(II) [161], manganese(II) [162] and ruthenium(II) [163] complexes are found to catalyze the selective oxidation of benzyl alcohol to benzaldehyde. Highly selective oxidation of benzylic alcohols to benzaldehydes using an active dinuclear manganese(IV) complex as catalyst and hydrogen peroxide or *tert*-butyl hydroperoxide as oxidant was reported by Feringa *et al.* [164]. From an economic and environmental perspective, catalytic aerobic alcohol oxidation represents a promising protocol. [165-167]. Wang *et al.* [168] in 2007, reported the selective oxidation of benzyl alcohol to benzaldehyde using a supported Cr(salen) complex. The supported complexes show good conversion and selectivity. Kang *et al.* [169] and Ali *et al.* [170] utilized the catalytic activity of

nanocubic zinc hexacyanoferrate for solvent-free oxidation of benzyl alcohol using H_2O_2 as oxidant. The reaction was carried under the optimum conditions of certain parameters such as benzyl alcohol to H_2O_2 molar ratio, the amount of catalyst, reaction time and temperature. Figiel *et al.* [171] reported the oxidation of benzyl alcohols to benzaldehydes by the TEMPO/O_2 system (TEMPO=*2,2,6,6-tetramethylpiperidine-1-oxyl*). They used copper(II)ethanolamine complexes and the reaction proceeds with a high efficiency (up to 99% yield of benzaldehyde with >99% selectivity) and without the need of any organic solvent, or of an ionic liquid. Thus this reaction has both environmental and economical benefits in comparison with previously reported systems for benzyl alcohol oxidation.

Scope of the present investigation

Study of the transition metal complexes with quinoxaline derivatives has gained much attention because of their potential diverse applications as catalysts, chemotherapeutic agents, insecticides, fungicides and organic light emitting diodes. Thus in the recent years there is an upsurge in synthesizing compounds suitable for such applications. Literature survey revealed that there are only scanty reports on Schiff base complexes derived from quinoxaline-2-carboxaldehyde and 3-hydroxyquinoxaline-2-carboxaldehyde. The ligational aspects of quinoxaline based Schiff bases are more attractive than those of Schiff bases derived from benzaldehyde due to the presence of two nitrogen atoms in the ring, which may affect the electronic properties of the complexes. These effects may modify the electron transfer properties involved in catalysis. Thus, it is worthwhile to carry out the structural and spectral studies of quinoxaline based Schiff bases and their metal complexes with different structural features. Hence, we have carried out detailed study on the quinoxaline based compounds with the following objectives in mind.

➤ To synthesize some novel Schiff bases derived from the heterocyclic aldehydes, quinoxaline-2-carboxaldehyde and 3-hydroxyquinoxaline-2-carboxaldehyde

➤ To tune the denticity of the Schiff bases as three by selecting amines which contain a hydroxyl/thiolic group in the ortho position.

- ➢ To synthesize and characterize the transition metal complexes of the above Schiff bases.

- ➢ To study the complexation by template reaction without isolating Schiff base.

- ➢ To study the catalytic activity of the synthesized complexes in some oxidation reactions.

The ligands chosen for the present study are the following:

1. Quinoxaline−2−carboxalidine−2−amino−5−methylphenol (qamp)

2. 3−Hydroxyquinoxaline−2−carboxalidine−2−aminothiophenol (hatp)

3. 3−Hydroxyquinoxaline−2−carboxalidine−2−amino−5−methylphenol (hamp)

Manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of these Schiff bases have been synthesized and characterized. The template synthesis of amino acid Schiff base complexes are successfully carried out using quinoxaline-2-carboxaldehyde, L-histidine and metal ion. The synthesized complexes were screened for their catalytic activity in the oxidation of phenol, cyclohexane and cbenzyl alcohol. The crystal structures of two of the complexes are studied through single crystal XRD.

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Transition metal complexes of quinoxaline based Schiff base ligands: Synthesis, characterization and catalytic activity study

31

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