

Introduction

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Schiff bases have been playing an important part in the development of coordination chemistry. Schiff base metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas. These types of complexes have been vigorously explored in recent years and such studies have been the subject of many papers and reviews. Many of them are centered on the catalytic activity of Schiff base complexes in a large number of homogeneous and heterogeneous reactions. It is difficult to cover in this chapter the literature on Schiff base metal complexes, which embraces very wide and diversified subjects comprising vast areas of organometallic compounds and various aspects of bioinorganic chemistry. Therefore, the introduction part is limited to a brief discussion on the Schiff bases, their metal complexes and general applications of Schiff base complexes with an emphasis on catalytic applications.

1. Schiff base ligands

Schiff base was first reported by Hugo Schiff in 1864 [1]. Schiff bases can be prepared by condensing carbonyl compounds and amines in different conditions and in different solvents with the elimination of water molecules. The presence of a dehydrating agent normally favours the formation of Schiff bases. Though the

Schiff bases are stable solids, care should be taken in the purification steps as it undergoes degradation. Chromatographic purification of Schiff bases on silica gel is not recommended as they undergo hydrolysis. The common structural feature of these compounds is the azomethine group with a general formula $\text{RHC}=\text{N}-\text{R}'$, where R and R' are alkyl, aryl, cyclo alkyl or heterocyclic groups which may be variously substituted. Presence of a lone pair of electrons in an sp^2 hybridised orbital of nitrogen atom of the azomethine group is of considerable chemical importance and impart excellent chelating ability especially when used in combination with one or more donor atoms close to the azomethine group. Examples of a few compounds are given in Figure 1. This chelating ability of the Schiff bases combined with the ease of preparation and flexibility in varying the chemical environment about the C=N group makes it an interesting ligand in coordination chemistry.

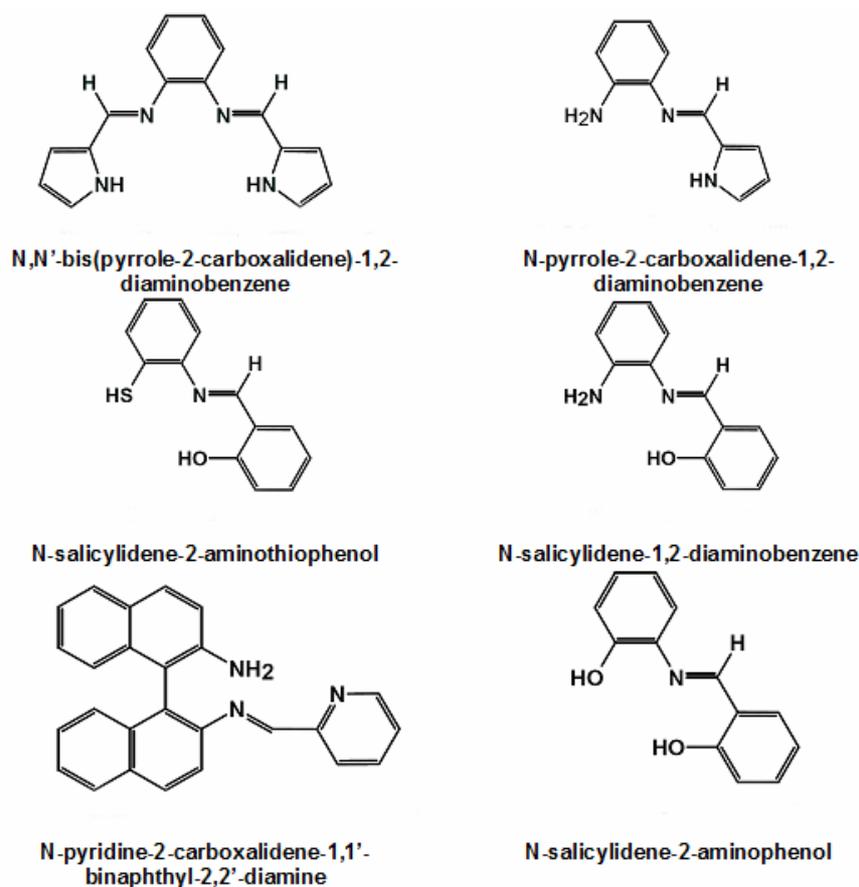


Figure 1: Some examples of Schiff bases

When aldehyde is a salicylaldehyde derivative and amine is a diamine derivative, the condensation produces interesting N_2O_2 Schiff base compounds (Figure 2). The so called salen ligands are very much like porphyrins and, unlike the latter, can be easily prepared. Although the term salen was originally used only to describe the tetradentate Schiff bases derived from salicylaldehyde and ethylenediamine, the term salen-type is now used in the literature to describe the class of (O, N, N, O) tetradentate bis-Schiff ligands. Stereogenic centers or other elements of chirality (planes, axes) can be introduced in the synthetic design of Schiff bases (Figure 2).

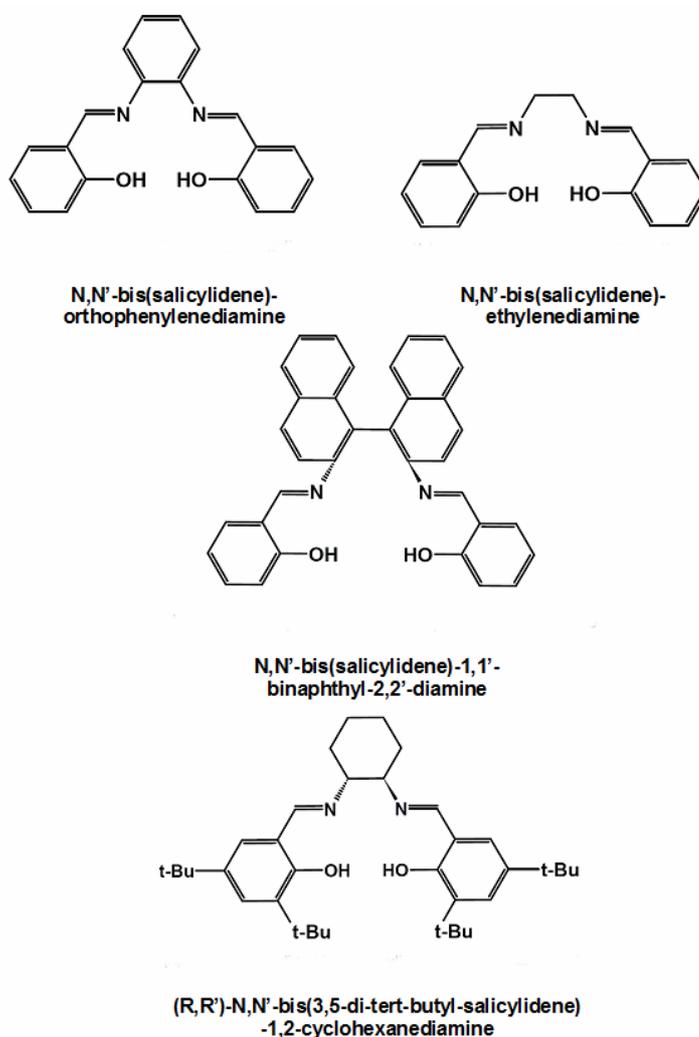


Figure 2: N_2O_2 Schiff base compounds

In addition to these, Schiff base macrocycles (Figure 3) have been prepared by well known self condensation reaction of appropriate formyl- or keto- and primary amine precursors and find wide applications in macrocyclic and supramolecular chemistry [2,3]. Schiff bases easily form stable complexes with most transition metal ions and stabilize them in various oxidation states.

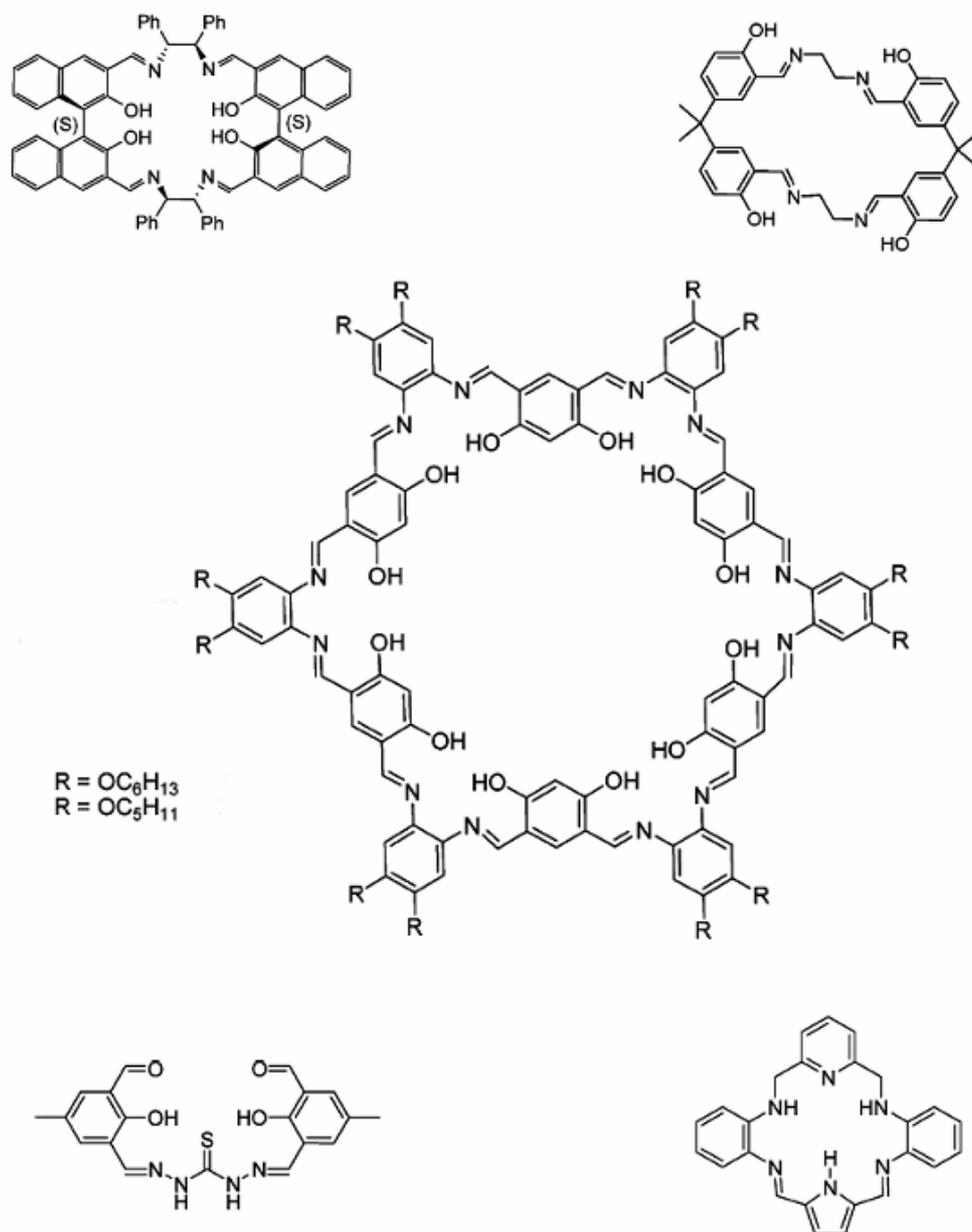
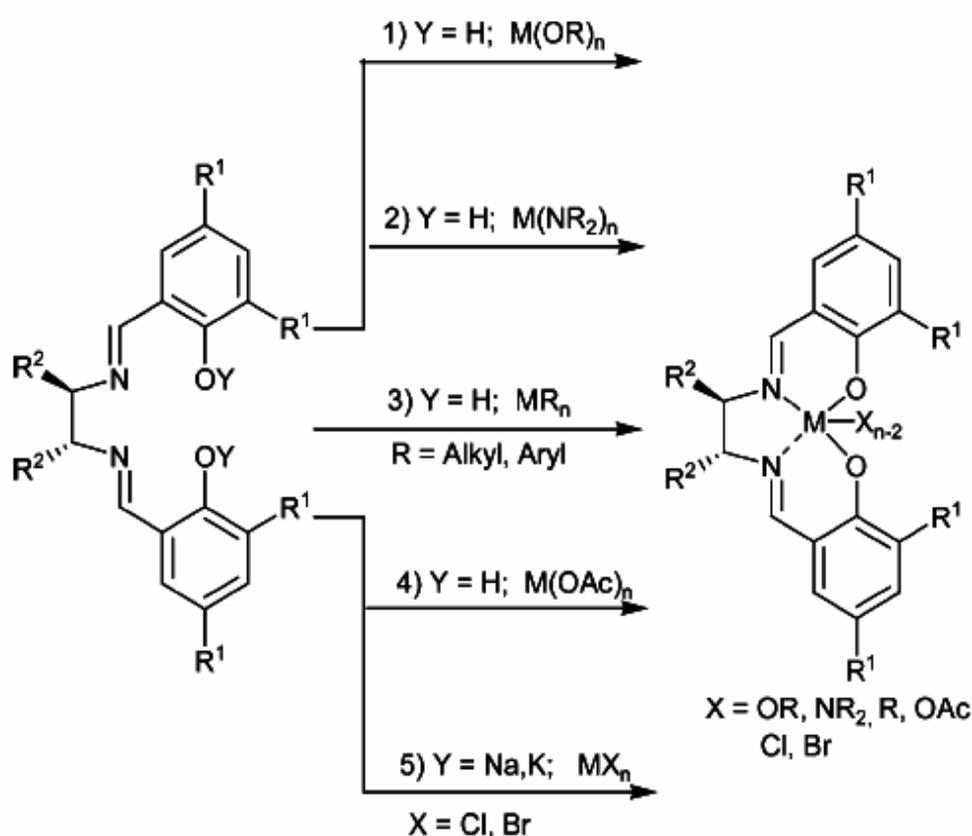


Figure 3: Macroyclic Schiff base compounds

2. Schiff base transition metal complexes

Metal complexes of the Schiff bases are generally prepared by treating metal salts with Schiff base ligands under suitable experimental conditions. However, for some catalytic application the Schiff base metal complexes are prepared in situ in the reaction system. Cozzi in his review has outlined five synthetic routes that are commonly employed for the preparation of Schiff base metal complexes and these are depicted in Scheme 1 [4].

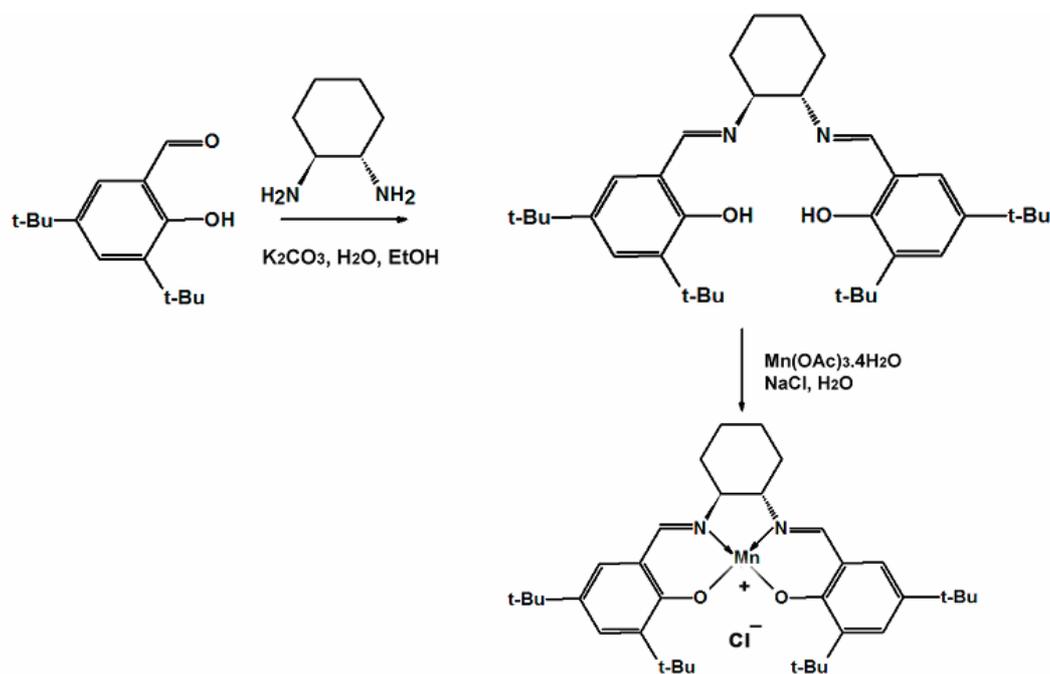


Scheme 1: Preparation of Schiff base complexes

Route 1 involves the use of metal alkoxides ($M(OR)_n$). Alkoxides of early transition metals ($M = Ti, Zr$), are commercially available and easy to handle. The use of other alkoxide derivatives is not easy, particularly in the case of highly moisture-sensitive derivatives of lanthanides. Metal amides $M(NMe_2)_4$ ($M = Ti, Zr$)

are also employed as the precursors in the preparation of Schiff base metal complexes (Route 2). The reaction occurs via the elimination of the acidic phenolic proton of the Schiff bases through the formation of volatile NHMe_2 . Other synthetic routes include treatment of metal alkyl complexes with Schiff bases (Route 3) or treatment of the Schiff base with the corresponding metal acetate under reflux conditions (Route 4). The synthetic scheme presented in route 5 which is quite effective in obtaining salen-type metal complexes consists of a two-step reaction involving the deprotonation of the Schiff bases followed by reaction with metal halides. Deprotonation of the acidic phenolic hydrogen can be effectively done by using NaH or KH in coordinating solvents and the excess sodium or potassium hydride can be eliminated by filtration. The deprotonation step is normally rapid at room temperature, but heating the reaction mixture to reflux does not cause decomposition.

An elaborate discussion on synthesis and characterisation of Schiff base metal complexes is not attempted here, as there are numerous literature reviews on these aspects [2,5-7]. The synthesis of the well known Schiff base complex, $\text{N,N}'$ -bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminomanganese (III)chloride, is presented in Scheme 2. This manganese complex is known as Jacobsen's catalyst. The Schiff base can be successfully prepared by the condensation between *trans*-1,2-diaminocyclohexane and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and finally Jacobsen's catalyst can be prepared from the ligand by treatment with manganese(II) acetate followed by oxidation with air.



Scheme 2: Synthesis of Jacobsen's catalyst

3. Applications of Schiff base transition metal complexes

The major applications of the Schiff base complexes are in catalysis and will be discussed in detail in [Section 4](#). The Schiff base complexes do have a number of other applications which are discussed briefly in this section.

3.1 As electroluminescent materials

Organic electroluminescent (EL) devices are useful in novel-type flat-panel displays since Tang and Van Styke first reported on high-performance organic EL devices [8]. Their discovery was based on employing a multilayer device structure containing an emitting layer and a carrier transport layer of suitable organic materials. Organic dyes, chelate metal complexes and polymers are three major categories of materials used in the fabrication of organic EL devices. Out of the three, chelate metal complexes having high-luminance blue emitting nature find use as materials for RGB (red, green, and blue) emission.

Schiff base complexes, especially those of Zn(II), are now a days used as electroluminescent materials [9,10]. Zinc complex of the Schiff base, N,N'-bis(2-hydroxy-1-naphthylidene)-3,6-dioxo-1,8-diaminooctane, emits blue light with an emission peak at 455 nm having maximum brightness of 650 cd m^{-2} , when it is used as the emitting layer in an electroluminescence device. Fabrication of EL devices employing this kind of zinc complexes as blue electroluminescent material was carried out by thermal vacuum-deposition. Wei et al. prepared blue luminescent zinc and beryllium complexes of the Schiff bases derived from calixarene [11]. These Schiff bases complexes have good solubility in normal solvents and can easily form thin films. Xie et al. reported the crystal structure, thermal stability and optoelectronic properties of bis[salicylidene(4-dimethylamino)aniline]zinc(II) [12]. This complex exhibits very good light emission and charge transporting performance in organic light emitting diodes (OLEDs). These experimental reports point to the possible application of Schiff base complexes as emitting materials in full colour flat-panel displays.

3.2 In non-linear optical devices

Nonlinear optics (NLO) deals with the interactions of applied electromagnetic fields with various materials to generate new electromagnetic fields, altered in frequency, phase, or other physical properties. Such materials that are able to manipulate photonic signals efficiently are of importance in optical communication, optical computing, and dynamic image processing [13-17]. In this connection transition metal complexes have emerged as potential building blocks for nonlinear optical materials due to the various excited states present in these systems as well as due to their ability to tailor metal-organic-ligand interactions [18-23]. Compared to the more common organic molecules, the metal complexes offer a large variety of novel structures, the possibility of enhanced thermal stability, and a diversity of tunable electronic behaviours by virtue of the coordinated metal center and hence they may find use as NLO materials with unique magnetic and electrochemical properties [24-26]. The investigations on NLO properties of metal

complexes are being pursued by several research groups [19,20,27-33]. It has been reported by Di Bella and co-workers that bis(salicylaldiminato) metal Schiff base complexes exhibit good second order NLO properties [34-40].

3.3 In electrochemical sensors

Schiff bases have been used as carriers in the preparation of potentiometric sensors for determining cations and anions [41-50]. A ruthenium(III) Schiff base complex was used in the fabrication of chloride PVC-based membrane sensor [51]. The sensor with a composition of 30% PVC, 62% benzyl acetate, 5% ruthenium(III) Schiff base complex and 3% hexadecyltrimethyl ammonium bromide displays near-Nernstian behavior over a wide concentration range. It shows high selectivity toward chloride ions over several organic and inorganic anions and was successfully applied for the determination of chloride in serum samples. It could also be used as an indicator electrode in the potentiometric titration of chloride ions with silver nitrate solution. Gupta et al. recently reported a potentiometric aluminium sensor based on the use N,N'-bis(salicylidene)-1,2-cyclohexanediamine as a neutral carrier in poly(vinyl chloride) matrix [52]. It was successfully applied for direct determination of aluminium(III) in biological, industrial and environmental samples. The electrode could be used in the pH range of 2.0–9.0 and mixtures containing up to 20% (v/v) non-aqueous content. It has been used as an indicator electrode in potentiometric titration of aluminium ion with EDTA. The Schiff base, N,N',N'',N'''-1,5,8,12-tetraazadodecane-bis(salicylaldiminato), has been used as ionophore for preparing Mn^{2+} selective sensor [53]. The sensor was found to be sufficiently selective for Mn^{2+} over a number of alkali, alkaline and heavy metal ions and could therefore be used for the determination of manganese in various samples by direct potentiometry.

3.4 In medicinal chemistry

Many Schiff bases are known to be medicinally important and used to design medicinal compounds [54-57]. It was seen that the biological activity of Schiff bases either increase or decrease upon chelation with metal ions [58-60].

Cobalt(II), nickel(II) and copper(II) complexes of Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and 8-formyl-7-hydroxy-4-methylcoumarin show potent antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, *Streptococcus pyogenes*, *Pseudomonas aeruginosa* and *Salmonella typhi* and antifungal activities against *Aspergillus niger*, *Aspergillus flavus* and *Cladosporium* [61].

Ru(II)-PPh₃/AsPh₃ complexes, containing hydrazone oxime ligands, show considerable activity against selected bacterial species and are capable of binding to Herring sperm DNA in mixed modes [62]. The Cr(III), Fe(III) and Co(III) complexes formed from tetradentate (ONNO) Schiff base ligands, 1,4-bis[3-(2-hydroxy-1-naphthaldimine)propyl]piperazine and 1,8-bis[3-(2-hydroxy-1-naphthaldimine)-*p*-menthane, show moderate antimicrobial activity [63] compared to standard antibiotics [64]. The antibacterial activity of the tridentate Schiff base, formed by condensation of 2-amino-3-carboxyethyl-4,5-dimethylthiophene with salicylaldehyde, was found to increase on chelation with transition metal ions [65]. Co(II), Ni(II), Cu(II) and Zn(II) complexes of the Schiff base derived from vanillin and DL- α -aminobutyric acid were also found to exhibit higher antibacterial activity compared to the free Schiff bases [66]. Several mono and binuclear transition metal complexes of the Schiff base derived from phenylaminoacetohydrazide and dibenzoylmethane, are more potent bactericides and fungicides than the ligand [67]. Sharma and Piwnica-Worms reported Schiff base complexes that target hemozoin aggregation like the antimalarial drug, chloroquine [68-70].

Investigations on the interactions of DNA with transition metal complexes provide leads for rational drug design, as well as means for the development of

sensitive chemical probes for DNA [71-83]. These interactions would be either covalent or non-covalent. In covalent binding the labile part of the complexes is replaced by a nitrogen base of DNA. On the other hand, the non-covalent DNA interactions include intercalative, electrostatic and groove binding of cationic metal complexes along periphery of the DNA helix, the major or minor groove. Intercalation involves the partial insertion of aromatic heterocyclic rings between the DNA base pairs.

Gupta and co-workers reported DNA binding properties of a series of transition metal complexes having potential NNO-tridentate donor Schiff bases derived from the condensation of 2,6-dibenzoyl 4-methylphenol with diamines [84-90]. DNA binding studies of the cationic Ni^{II} complex of the 5-triethyl ammonium methyl salicylideneortho-phenylendiimine ligand, shows that the metal complex strongly interacts with DNA [91]. Zn(II) and Cu(II) complexes of this Schiff base interact with native calf thymus DNA by groove or intercalating binding mode [92]. The cobalt(II) and nickel(II) complexes of salicylaldehyde-2-phenylquinoline-4-carboylhydrazone interact with calf-thymus DNA via a groove binding mode [93]

The interaction of chromium(III) Schiff base complexes, [Cr(salen)(H₂O)₂]⁺ where salen = N,N'-ethylenebis(salicylideneimine) and [Cr(salprn)(H₂O)₂]⁺ where salprn = N,N'-propylenebis(salicylideneimine) with calf thymus DNA (CT-DNA), has been reported [94]. Chromium(III) complexes derived from chiral binaphthyl Schiff base ligands (R- and S-2,2'-bis(salicylideneamino)1,10-binaphthyl) are also found to interact with CT-DNA through groove binding [95]. Binuclear copper(II) complexes having the Schiff base ligand, N,N'-bis(3,5-tert-butylsalicylidene-2-hydroxy)-1,3-propanediamine, are found to be effective in the cleavage of plasmid DNA without the addition of any external agents and in the presence of hydrogen peroxide at pH = 7.2 and 37 °C. DNA cleavage mechanism studies show that complexes examined here may be capable of promoting DNA cleavage through an oxidative DNA damage pathway [96].

Silvestri et al. showed that the interaction between native calf thymus deoxyribonucleic acid (DNA) and Fe^{III}-N,N'-ethylene-bis (salicylideneiminato)-chloride, Fe(Salen)Cl, take place through an electrostatic binding between the Fe(Salen)⁺ cation and the phosphate groups of DNA [97]. The Mn(II) complex, MnL (L = sodium (E)-3-(1-carboxyethylimino)methyl)-4-hydroxybenzenesulfonate), is capable of intercalating into the double-stranded salmon sperm DNA [98]. Chaviara et al. reported a series of Cu(II) complexes of the Schiff bases derived by the condensation of diethylenetriamine with 2-thiophene-carboxaldehyde/2-furaldehyde/2-pyrrole-2-carboxaldehyde [81]. The DNA electrophoretic mobility studies show that these compounds interact with DNA either by a simple mode of coordination, leading to the formation of a DNA complex cationic adduct or by acting as chemical nucleases able to promote its degradation.

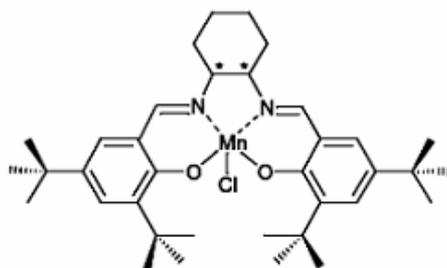
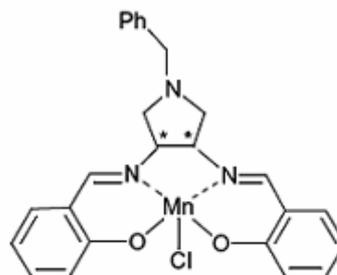
4. Schiff base transition metal complexes in catalysis

Schiff base complexes play a central role in various homogeneous catalytic reactions and the activity of these complexes varies with the type of ligands, coordination sites and metal ions. Literature reports reveal that a large number of Schiff base metal complexes exhibit catalytic activities. Chiral Schiff base complexes are more selective in various reactions such as oxidation, hydroxylation, aldol condensation and epoxidation. A discussion on the catalytic activity of Schiff base metal complexes in various reactions are outlined in this section.

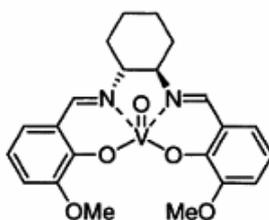
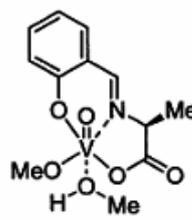
4.1 Oxidation reactions

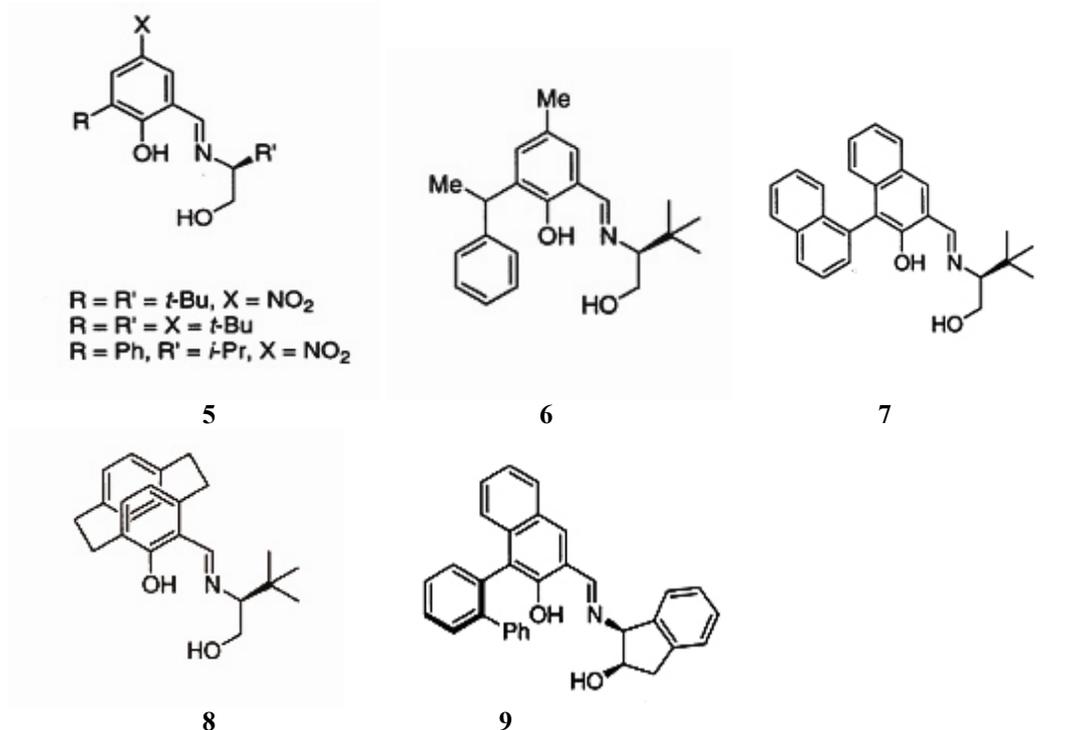
Uchida and Katsuki reported the activity of cationic cobalt(III)salen complexes in Baeyer–Villiger oxidation of 3-phenyl cyclobutanone with H₂O₂ or urea hydrogen peroxide adduct [99]. The analogous [Zr(salen)] catalysts are also active in Baeyer–Villiger oxidation of cyclobutanone derivatives to produce lactones in 75–99% yields and 69–78% ee in the presence of H₂O₂ as an oxidant [100]. Reddy and Thornon reported that complexes **1** and **2** catalyse the oxidation of a range of ketone silyl enol ethers to give α -hydroxyketones using iodossylbenzene as

oxidant in acetonitrile at room temperature [101]. Later, Waldemar et al. showed that **1** also catalyses the asymmetric oxidation of silyl ketene acetals in high enantioselectivity [102].

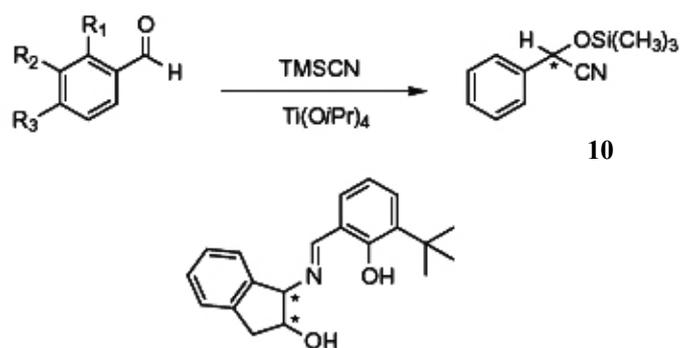
**1****2**

In 1986 Nakajima et al. studied the application of chiral Schiff base complexes in enantioselective sulfide oxidations [103]. Using tetradentate Schiff base-oxovanadium(IV) complex, **3**, as catalyst, they could achieve an enantioselectivity of 42% ee in the oxidation of methylphenyl sulfide to the corresponding sulfoxide. The oxovanadium(V) complex, **4**, having an amino acid-derived tridentate –O-N-O-type Schiff base as ligand was reported to catalyse the asymmetric oxidation of sulphoxide [104]. The catalytic behaviour of the complexes formed in-situ from Schiff base derivatives of salicylaldehyde and aminophenol, **5**, and vanadyl acetylacetonate is remarkable for the oxidation of sulphides [105]. Vetter and Berkessel reported the enantioselectivities associated with the sulfoxidations of vanadium catalysts derived from Schiff-base ligands **6-8** [106]. Katsuki and coworkers extended this study using **9** as ligand and vanadium as the metal [107].

**3****4**

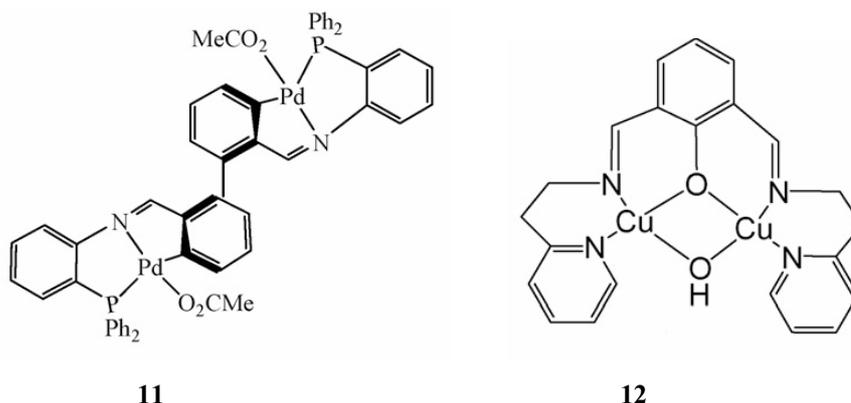


Titanium(IV), vanadium(IV), copper(II) or zinc(II) complexes of chiral Schiff base ligands of –O-N-O- type were used in various asymmetric chemical transformations. The addition of trimethylsilylcyanide (TMSCN) to benzaldehyde in the presence of titanium(IV) ions resulted in trimethylsilyl cyanohydrins **10** in 40–85% enantioselectivity (Scheme 3) [108,109].



Scheme 3: Schiff base catalysed synthesis of trimethylsilyl cyanohydrins

The binuclear palladium Schiff base complex, **11**, was found to be effective catalysts in direct oxygenation of unfunctionalized hydrocarbons and phenols [110-114]. Dinuclear Schiff base complexes of copper(II) ions **12** were used successfully in hydroxylation of phenol [115].



Co(salen) and its analogues, **13-17**, have been used for catalysing the oxidation of phenols and alcohols with dioxygen as oxidant [116]. Reports on oxidation of alkenes also exist [117,118]. In order to efficiently bind dioxygen and to be catalytically active, Co(salen) needs an axial ligand (Figure 4). The dioxygen is coordinated orthogonally to the square planar coordination sphere of Co(salen). The axial ligand is needed to fill the sixth coordination site, opposite to dioxygen. Pyridine is the most common axial ligand used in the Co(salen) catalysed oxidation reactions [116]. Other bases, for example, imidazole and pyrimidine have also been used [119]. An alternative way to provide an axial ligand is to use modified salen structure, which has extra nitrogen, for intramolecular axial coordination in the ligand frame (Figure 4).

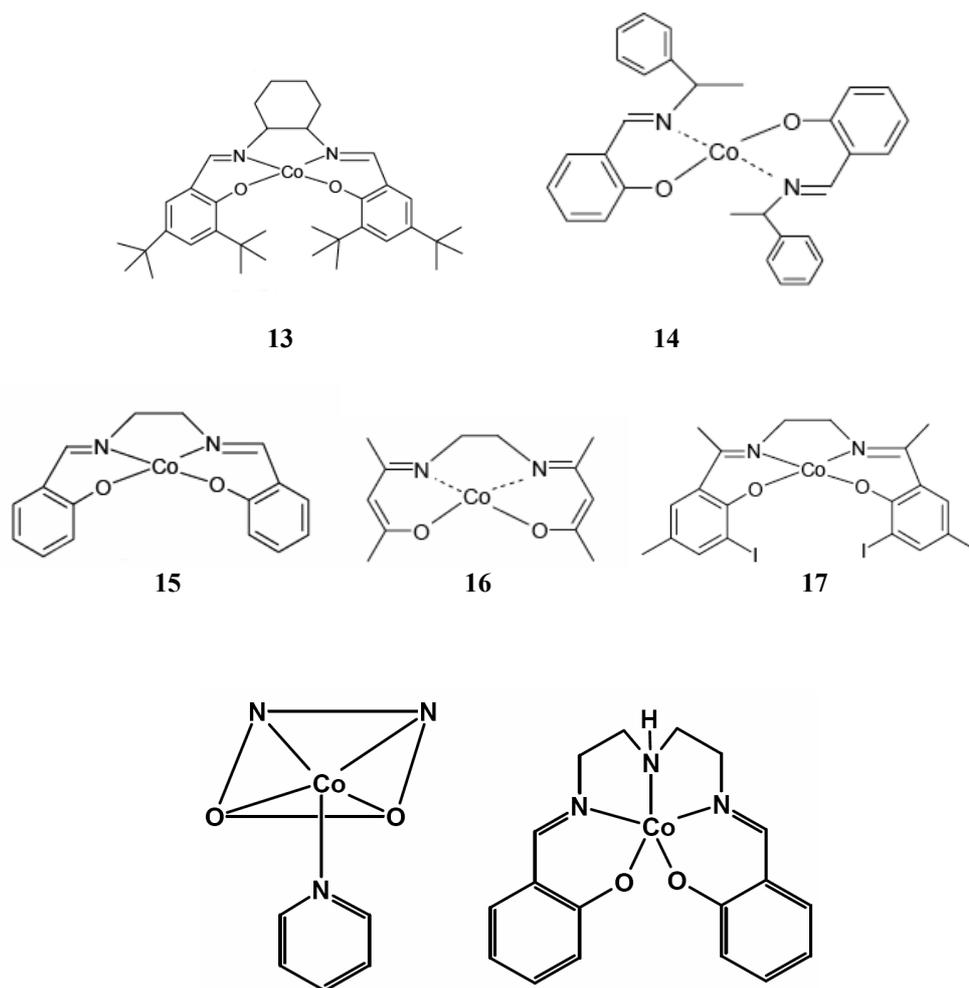


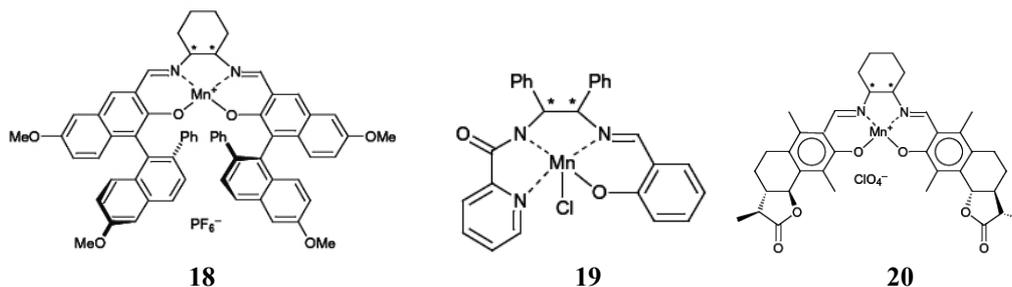
Figure 4: Axial ligand in cobalt Schiff base complexes

Reports on the studies with ruthenium complexes containing salen-type Schiff base ligands in the catalysis of hydrocarbon oxidation are noticeably few in literature [120].

4.2 Epoxidation reactions

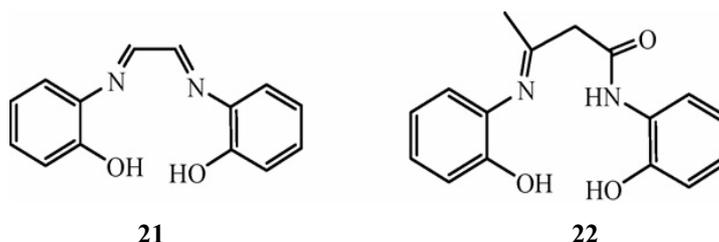
McGarrigle and Gilheany have given a detailed discussion on the achiral and asymmetric epoxidations of alkenes catalysed by chromium and manganese-salen complexes [121]. They mainly focussed on the mechanism, catalytic cycle, intermediates, and mode of selectivity. Among these Mn-(salen)-type complexes,

Jacobsen's complex, **1**, has been demonstrated to be very effective for the enantioselective epoxidation of unfunctionalised olefins [122,123]. However, the second-generation Mn-(salen) catalysts introduced by Katsuki and co-workers, **18**, have surpassed Jacobsen's catalyst in terms of selectivity and activity, but they are not as synthetically accessible, and this has limited their application [124-126].

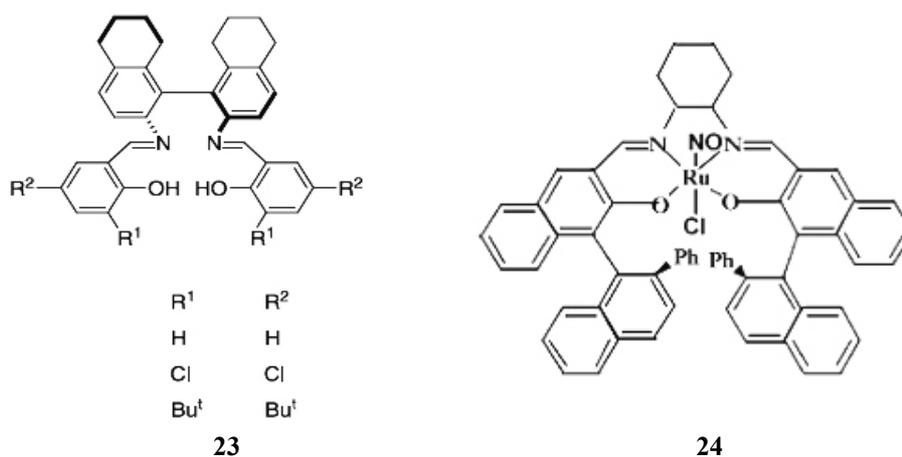


The manganese Schiff base chelate, **19**, synthesised by Zhao et al. exhibit moderate asymmetric induction (31–74% ee) in the epoxidation of dihydronaphthalene with higher turnover number [127]. Fernandez et al. epoxidised various unfunctionalised olefins with very high yield and poor asymmetric induction in presence of the manganese Schiff base complex, **20** [128].

Ruthenium complexes of $\text{trans-[RuCl}_2(\text{bpydip})]$ and $\text{trans-[Ru(OH)}_2(\text{bpydip})](\text{PF}_6)_2$ with tetradentate Schiff base ligand N,N' -bis(7-methyl-2-pyridylmethylene)-1,3-diiminopropane (bpydip) were used as remarkable catalysts in the epoxidation of cyclohexene in the presence of iodosobenzene [129]. Kureshy et al. have reported the catalytic activity of the nickel(II) Schiff base complexes of N,N' -bis(2-hydroxyphenyl)ethylenediimine, **21**, and N,N' -(2-hydroxyphenyl)acetylaldimine N -(2-hydroxyphenyl)acetamide, **22**, in the epoxidation of olefins such as cyclohexene, 1-hexene, *cis*- and *trans* stilbenes, indene with sodium hypochloride [130].

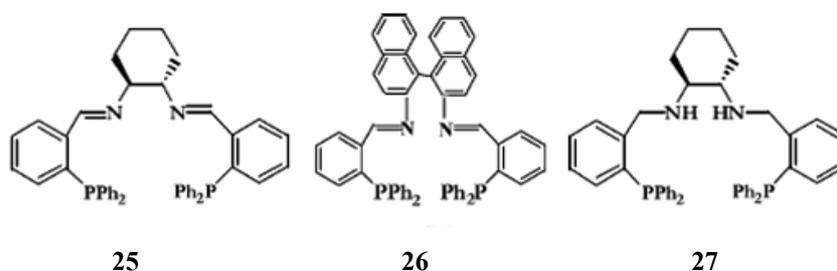


Potentially tetradentate binaphthyl N_2O_2 Schiff bases, **23**, were prepared by the condensations of aromatic aldehydes with amines like 2,2'-diamino-1,1'-binaphthyl or 2-amino-2'-hydroxy-1,1'-binaphthyl. Metal complexes of these Schiff bases have wide application in catalysis especially in asymmetric epoxidation of unfunctionalised olefins [131].

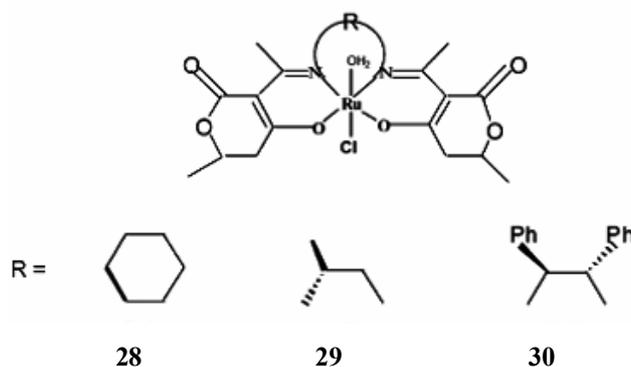


Katsuki and co-workers first reported the synthesis and catalytic application of ruthenium(II)-complex, **24**, containing chiral tetradentate (N_2O_2) Schiff base ligand in the asymmetric epoxidation of conjugated olefins in the presence of various terminal oxidants [132,133].

Mezzetti and co-workers have carried out the asymmetric epoxidation using ruthenium(II) complexes containing tetradentate chiral Schiff base ligands with N_2P_2 donors, **25–27**, with hydrogen peroxide as terminal oxidant [134,135].

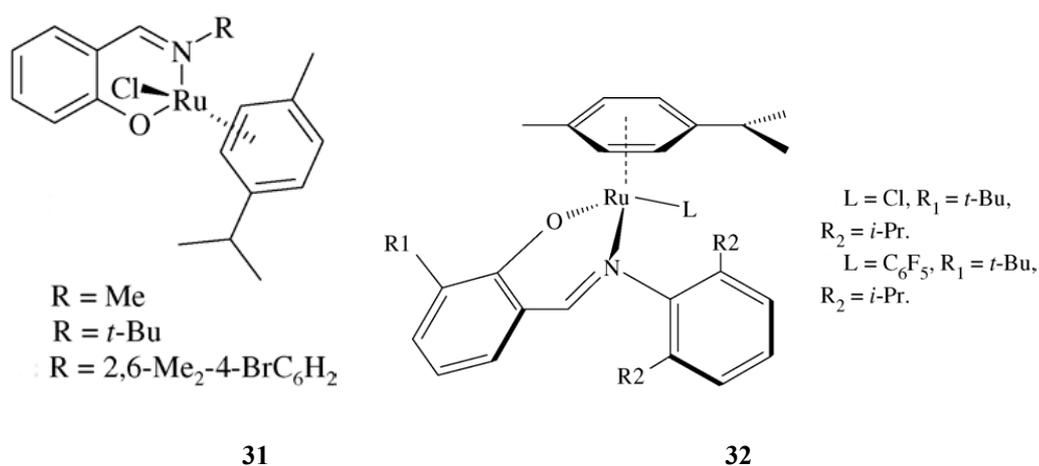


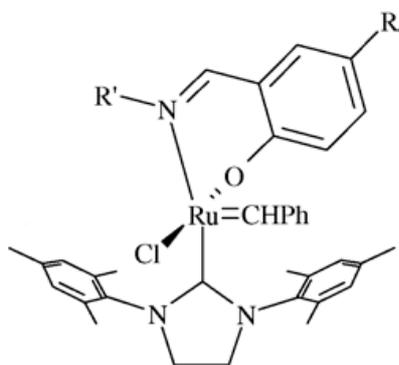
Ruthenium(III) complexes, **28-30**, of the tetradentate Schiff base ligands obtained by the condensation of 3-acetyl-6-methylpyran-2,4-dione with various diamines, exhibit catalytic activity in the asymmetric epoxidation of styrene and substituted styrenes [136].



4.3 Polymerization reactions

Reports on various polymerisation reactions catalyzed by Schiff base metal complexes are found in the literature. Verpoort et al. reported a detailed discussion on catalytic activity in the atom transfer radical polymerization and ring opening metathesis polymerization of various substrates using Ru-catalysts having salicylaldiminato-type Schiff bases as one of the ligands, **31-36** [137].

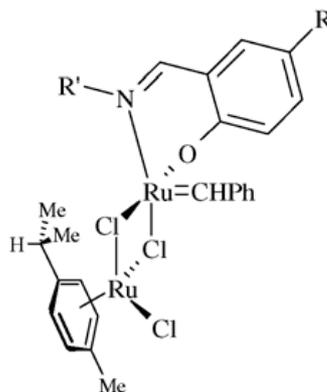




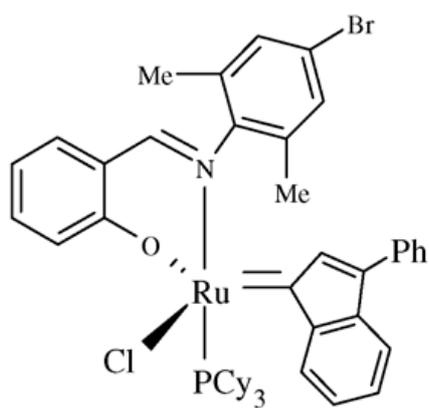
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 R = NO₂, R' = Me
 R = H, R' = 2,6-Me₂-4-BrC₆H₂
 R = NO₂, R' = 2,6-Me₂-4-BrC₆H₂
 R = H, R' = 2,6-*i*-Pr₂C₆H₃
 R = NO₂, R' = 2,6-*i*-Pr₂C₆H₃

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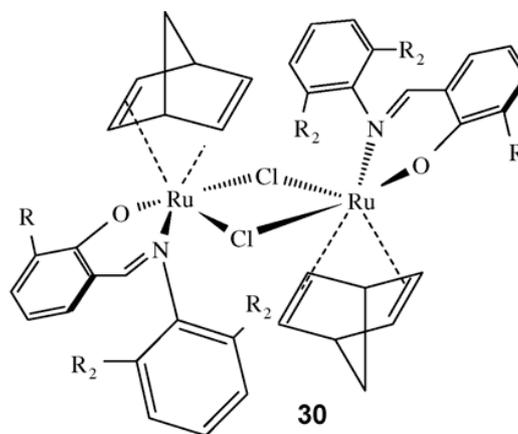
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 R = NO₂, R' = 2,6-*i*-Pr₂C₆H₃



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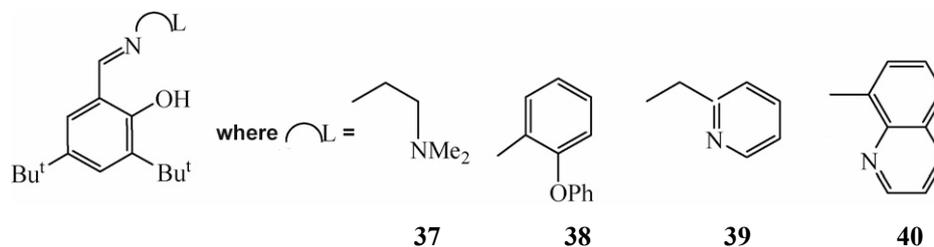
35



diolefine = norborane diene
 R₁ = *t*-Bu, R₂ = *i*-Pr

36

Aluminum complexes of a series of tridentate Schiff base ligands, **37-40**, were found to catalyse the polymerization of ethylene [138].



A number of pyridyl bis(imide) complexes and phenoxy imine complexes are used as catalysts in the polymerization of ethylene [139-142]. Pyridine bis(imine) complexes of iron(III) and cobalt(II) show significant activity in the polymerization of ethylene and copolymerization of ethylene with 1-hexene [143]. The salicylaldiminato complexes of zirconium were found to be effective catalysts in ethylene polymerization and promoted radical decomposition in certain cases [144]. Polymethylmethacrylate was prepared in presence of Cr(III) and Ni(II)salen complexes as catalysts for the controlled radical polymerization of the methylmethacrylate monomer [145].

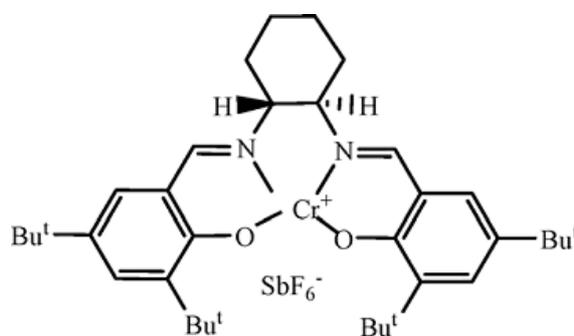
4.4 Hydrogenation reactions

Schiff base complexes of transition metals are efficient catalysts in carrying out asymmetric reduction of dialkyl ketones [146-149]. The catalytic activity in the transfer hydrogenation of aliphatic and aromatic ketones in the presence of isopropanol and KOH has been investigated with ruthenium(III) Schiff base complexes of general formula $[\text{RuX}(\text{EPh}_3)(\text{LL}')]]$ where $\text{X} = \text{Cl}$ or Br , $\text{E} = \text{P}$ or As and $\text{LL}' = [\text{ONNO}]$ donor of the heterocyclic Schiff base ligands, **41-43** [150]. Venkatachalam and Ramesh also reported the transfer hydrogenation of imines to amines mediated by ruthenium(III) bis-bidentate Schiff base complexes [151].

carried out under hydrogen pressure (30 bar) at room temperature in the presence of the chiral catalyst prepared in situ.

4.5 Miscellaneous reactions

In addition to the above mentioned three major types of catalytic reactions, some other reactions are also catalysed by the Schiff base complexes. Chiral Schiff base lanthanum(III) complexes displayed catalytic activity in the asymmetric Diels–Alder reaction of 3-(2-propenoyl)-2-oxazolidinone with cyclopentadiene [157]. Schiff base complex catalyzed acylation of 4-furyl-4- *N*-benzylaminobut-1-enes with maleic anhydride produced 4-oxo-3 aza-10-oxatricyclo[5.2.1.0]dec-8-ene-6-carboxylic acid via amide formation through intramolecular Diels–Alder reaction of furan [158,159]. The new family of enantiomerically enriched Schiff base chromium(III) complexes, **47**, were also used as catalysts in Diels–Alder reactions [159].

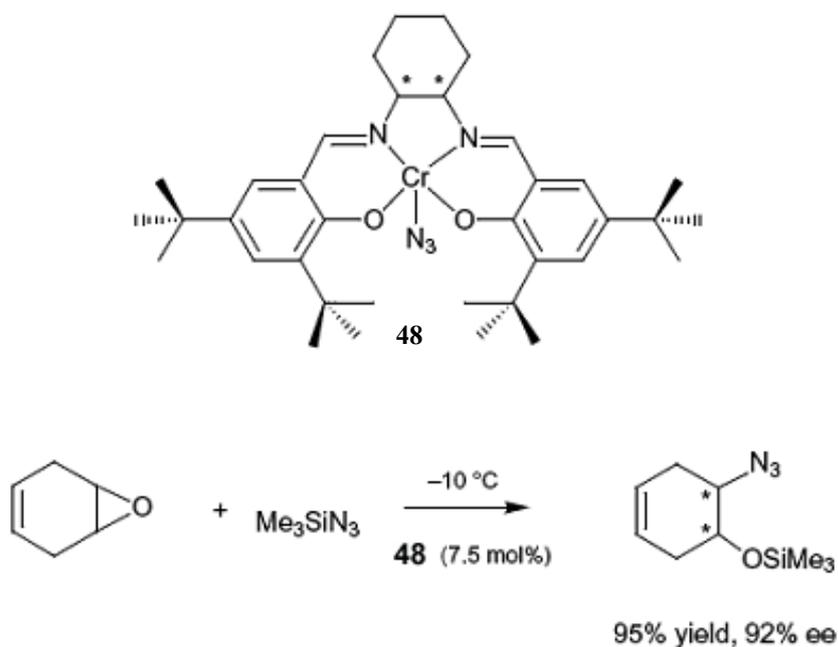


47

Jacobsen et al. have also achieved the asymmetric hetero-Diels–Alder reaction between [(2-chlorobenzoyl)oxy]-acetaldehyde and 1-methoxy-3-[(trimethylsilyl)oxy]buta-1,3-diene in the presence of 2 mol% Cr(salen) using a noncoordinating ethereal solvent at 230 °C in the presence of dried 4 Å molecular sieve [160]. Aluminum(III) chiral complexes of binaphthal Schiff base ligand are used as catalysts in the aldol addition/acyl transfer reactions between 5-methoxyoxazoles and aldehydes [161], which afforded corresponding (4*S*, 5*S*)-

oxazoline products with 98% ee and 60% turnover number. Schiff base complexes of aluminum(III) were active in the reaction between 5-methoxyoxazoles and benzaldehydes to produce optically active *cis*-oxazoline adducts with >99% ee [161].

The ring-opening of cyclohexa-1,4-diene monoepoxide was carried out by Jacobsen's group [162] under solvent free conditions in presence of 7.5 mol% of **48** and azidotrimethylsilanolate to produce the azido silyl ether in 92% enantiomeric excess (Scheme 4).



Scheme 4

Jacobsen also discovered [163] that the Co(salen) complex **49** was active in the hydrolytic kinetic resolution of racemic epoxides which enables access to terminal epoxides and diols in high enantiomeric purity (Scheme 5).

the Mizoroki–Heck reaction with Pd(II) complexes of dimethyl glyoxime, **51**, 8-hydroxyquinoline, salen and picolinic acid ligands.

In addition to the homogeneous catalytic reaction, supported transition metal Schiff base complexes also find wide application in catalysis [168-176]. Among these polymer supported [177-189] and zeolite encapsulated Schiff base complexes are the most widely used in heterogeneous catalysis [190-195].

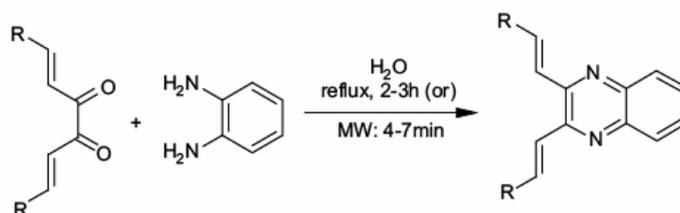
Most of the afore mentioned Schiff base complexes are derivatives of salicylaldehyde. It is clear from the above discussion that they have wide applications in various fields especially in that of catalysis. There are many reports to prove that the catalytic properties of the Schiff base complexes can be altered by changes in the Schiff base portion [196-198]. In the present investigation, we have employed an electron rich and bulky 3-hydroxyquinoxaline-2-carboxaldehyde for the preparation of Schiff bases to know whether their complexes have structures and catalytic activities different from that of the salen complexes. Metal complexes of the Schiff bases derived from quinoxaline-2-carboxaldehyde and 3-hydroxyquionxaline-2-carboxaldehyde are rare [199-203]. However there are many reports on the synthesis, biological and other applications of the compounds having quinoxaline rings. So a brief discussion on these types of compounds is included here.

5. Chemistry of quinoxaline compounds

The chemistry of quinoxaline (which are known as “benzopyrazine”) and its derivatives attracts continuous attention because of their wide applicability in various areas. A discussion on the synthesis of quinoxalines and their metal complexes and their optoelectronic and biological applications are included in this section.

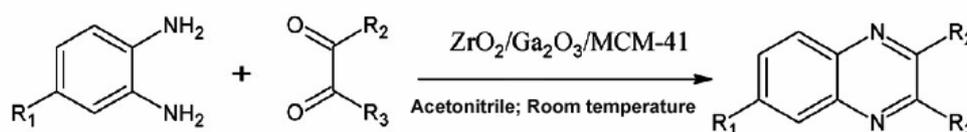
5.1 Synthesis of quinoxalines

A number of synthetic strategies have been developed for the synthesis of substituted quinoxalines and the most common method relies on the condensation of an aryl 1,2-diamine with 1,2 dicarbonyl compound in refluxing ethanol or acetic acid [204-209]. Thirumurugan et al. reported a simple and convenient method for the synthesis of quinoxaline derivatives from cinnamils in water under reflux/microwave irradiation conditions (Scheme 6) and these quinoxaline derivatives show good photophysical properties and stable fluorescence [210].



Scheme 6: Synthesis of quinoxalines

Binary metal oxides supported on Si-MCM-41 mesoporous molecular sieves were employed as catalysts in the synthesis of quinoxaline derivatives (Scheme 7) by the condensation of 1,2-diamine with 1,2 dicarbonyl compounds [211].



Scheme 7: Quinoxaline synthesis

Palladium-catalyzed Suzuki-Miyaura coupling of 2,3-dichloroquinoxaline with various boronic acids results in the formation of symmetrical and unsymmetrical 2,3-disubstituted quinoxalines [212]. Li et al. reported a novel approach for the synthesis of 6,7-disubstituted-1H-quinoxalin-2-ones starting from substituted phenylamines and chloroacetyl chloride through the efficient sequence of acylation, nitration, reduction, intramolecular alkylation, and oxidation [213]. Lewis acid-promoted addition of allyltri-n-butylstannane to o-quinonediimines afforded

tetrahydroquinoxaline derivatives or allylated amides depending on the nature of the substituent on imine nitrogen [214].

Mamedov et al. developed a new and effective procedure for the synthesis of 3-ethylquinoxalin-2(1H)-one from *o*-phenylenediamine and ethyl 2-oxobutanoate [215]. Gui et al. synthesized quinoxalines through the condensation reaction of *o*-phenylenediamine with aryl aldehydes or ketones [216]. Various biologically important quinoxaline derivatives were efficiently synthesized in excellent yields using molecular iodine as catalyst [217]. *o*-Phenylenediamines react with an array of vicinal-diols in diglyme in the presence of a catalytic amount of a ruthenium catalyst along with KOH to afford the corresponding quinoxalines in good yields [218,219]. A series of new quinoxalines has been obtained from a one pot, three-component reaction of (2-arylsulfanyl-3-aryl-2-oxiranyl)(aryl)methanones with *o*-phenylenediamine in the presence of a catalytic amount of acetic acid. This reaction presumably involves a tandem oxirane aminolysis-cyclisation-elimination-air oxidation-condensation sequence [220]. Hui et al. reported the synthesis of various pharmacologically active non-symmetrical 2,3-disubstituted quinoxalines [221]. Quinoxaline derivatives have been synthesized with excellent yields by the condensation of 1,2-diamines with aliphatic or aromatic 1,2-dicarbonyl compounds or benzilmonoxime with solid acid catalyst, silica sulphuric acid [222].

Wu and Gorden reported the synthesis of potentially bioactive 2-quinoxalinol salen ligands suitable for metal coordination [223]. Gris et al. employed biocatalysis or microwave irradiation for the synthesis of quinoxaline derivatives. Some of these quinoxalinone derivatives exhibited good inhibitor activity against some human tumoral cells and the lymphoma related to HIV-1 [224]. A cheap and efficient method for the synthesis of quinoxaline derivatives catalysed by *N,N,N*-trimethyl-*N*-propanesulfonic acid ammonium hydrogen sulphate was reported by Dong et al. [225].

5.2 Metal complexes of quinoxalines

The quinoxaline class of ligands meet the expectations of modern metallo-organic chemistry with their low-lying LUMOs, two nitrogen atoms in para-position, suitable for bridging and easy functionalization [226]. Xie et al. reported the crystal structure of tetraaquabis[2,3-bis(5-methyl-1,3,4-thiadiazol-2-ylsulfanylmethyl) quinoxaline]nickel(II) bis(perchlorate) acetone disolvate in which the Ni^{II} center adopts a slightly distorted octahedral coordination geometry, with two N atoms from two distinct ligands and four O atoms from water molecules [227]. Rotondo et al. reported the synthesis and ¹H and ¹³C NMR study of Pt^{II} complexes of [6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline] (DMeDPQ) and the crystal structure of [Pt(DMeDPQ)(bipy)](PF₆)₂ [228]. The rigid seven-membered chelate quinoxaline ligand holds the fused aromatic rings nearly perpendicular to the Pt^{II} coordination plane, generating the peculiar L-shaped structure.

The compound, [Cu(C₉H₅N₂O₃)₂(C₂H₆O₅)₂], consists of octahedrally coordinated Cu^{II} ions, with the 3-oxo-3,4-dihydroquinoxaline-2-carboxylate ligands acting in a bidentate manner [229]. Lee et al. reported the crystal structure of paddle wheel-type centrosymmetric dinuclear complex, [Cu₂(C₇H₅O₂)₄(C₈H₆N₂)₂], containing four bridging benzoate groups and two terminal quinoxaline ligands [230]. The reaction of 1,4-dihydro-2,3-quinoxalinedione (H₂L) with CuCl₂ in the presence of LiOH in DMF has led to a three dimensional coordination polymer [Cu₃L₂Cl₂(DMF)₄]_n where L²⁻ is 2,3-dioxyquinoxalinate [231]. Variable-temperature (2–300 K) magnetic susceptibility and variable-field (0–5 T) magnetization studies of this complex reveal that L²⁻ propagates weak antiferromagnetic exchange interactions through its “quinoxaline” moiety.

In [RuCl(C₁₀H₁₄)(C₂₀H₁₆N₄)]PF₆·CH₃CN, the coordination of one pyridyl ring and of one N atom of the quinoxaline unit to ruthenium imposes considerable distortion on the 6,7-dimethyl-2,3-dipyridin-2-ylquinoxaline ligand. Here the pyridyl ring and the quinoxaline unit are in almost coplanar [232]. The electrochemical and

photophysical properties of a series of luminescent ruthenium(II) amidodipyridoquinoxaline biotin complexes have been investigated [233]. Luminescent tricarbonylrhenium(I) dipyridoquinoxaline indole complexes are sensitive for indole-binding proteins [234].

In the crystal structure of dibromidobis(quinoxaline)zinc(II), the quinoxaline ligands are monocoordinated to the Zn^{II} atom and, with the bromide ions, form a distorted tetrahedral geometry [235]. The combination of π -stacking interactions between inversion-related quinoxaline ligands and the bridging Zn creates layers parallel to the *bc* plane. Novel mercury(II) complexes of 2,3-bis(1H-pyrrol-2-yl)quinoxaline-functionalized Schiff bases were prepared and characterized [236]. They were found to be fluorescent and highly selective for mercury(II) ion in aqueous solution. In the crystal structure of dichlorodiquinoxaline zinc(II), the two quinoxaline ligands are mono-coordinated to a Zn^{II} atom. With the two chloride ions, they form distorted tetrahedral coordination geometry and a combination of π stacking interactions between inversion-related quinoxaline ligands and the coordination to zinc creates layers parallel to the *bc* plane [237].

The use of dipyrido[3,2-d:2',3'-f]quinoxaline (Dpq) combined with three structurally related benzene dicarboxylic acid ligands [benzene-1,3-dicarboxylic acid (H_2L1), benzene-1,2-dicarboxylic acid (H_2L2), and biphenyl-4,4'-dicarboxylic acid (H_2L3)] has allowed the rational design of three novel Cd(II) coordination polymers, $[Cd_3(Dpq)_3(L1)_3] \cdot 4.5H_2O$ (1), $[Cd(Dpq)(L2)(H_2O)]$ (2), and $[Cd_2(Dpq)_2(L3)_2] \cdot 1.5H_2O$ (3), which were hydrothermally synthesized and structurally determined by X-ray analysis [238]. Compound 1 features a 1-D ribbonlike structure, compound 2 shows novel 2-D four-connected networks, and compound 3 possesses an interesting 6-connected 2-fold interpenetrated 3-D α -Po-related architecture. The Dpq ligand takes a chelating coordination mode while the other two nitrogen atoms did not coordinate to the Cd(II) ions. In these complexes, the three benzene-dicarboxylate ligands are able to link Cd(II) ions in various coordination modes, giving rise to 1-, 2-, and 3-dimensional Cd complexes,

respectively. In addition, complexes 1-3 exhibit blue/green emission in the solid state at room temperature.

The synthesis and spectroscopic properties of lanthanide nitrate complexes of 1,4-di(N,N-di-n-butyl-acetamido)-quinoxaline-2,3-dione (L), $[\text{Ln}(\text{NO}_3)_3\text{L}\cdot\text{H}_2\text{O}]$ (Ln = La, Nd, Eu, Gd, Tb, Er), have been studied by Song et al. [239]. The fluorescence property of the europium complex in solid state and in acetonitrile, acetone, ethylacetate and tetrahydrofuran was also evaluated.

A new solid-state pH sensor has been constructed based on a poly 3,4-dihydro-2-hydroxyquinoxaline (HOQ) thin film electrochemically deposited onto a Pt disc electrode whose surface had previously been modified with Pt nanoparticles by electrochemical depositing from $\text{HPtCl}_6\text{-H}_2\text{SO}_4$ solution at -0.2 V. The poly HOQ film was deposited from HAc-NaAc solution by cycling the potential between 0.4 V and 1.1 V [240].

5.3 Biological applications of quinoxalines

The quinoxaline moiety is widely distributed in nature. Also quinoxaline ring is part of a number of synthetic antibiotics such as echinomycin, leromycin, and actinomycin, which are known to inhibit the growth of gram-positive bacteria and are also active against various transplantable tumours [241-243]. The well known antibiotics echinomycin [244,245] and triostins [246] consist of two quinoxaline-2-carboxylic acid moieties attached to a cyclic octadepsipeptide containing a sulfur cross-linkage. Besides, quinoxaline structure is recognized in a great number of naturally occurring compounds such as riboflavin (vitamin B2), flavoenzymes, molybdopterines and antibiotics of streptomyces type that are implicated in considerable intra and interelectron transfer biochemical processes. The quinoxaline derivatives show antibacterial, antiviral, anticancer, antifungal, antihelminthic, insecticidal activity [247-264].

Mitsopoulou et al. reported the synthesis, characterization and DNA binding of mixed platinum(II) complexes containing quinoxaline and 1,2-dithiolate ligands [265]. Interactions of the metal complexes and free ligands with double stranded calf thymus DNA were studied. These studies suggest that both complexes form adducts with DNA and distort the double helix by changing the base stacking. A novel Ru(III) complex, mer-[RuCl₃(CH₃CN)(dpq)] (1), has been synthesized and characterized by X-ray diffraction, where dpq = dipyrido[3,2-d:2',3'-f]quinoxaline [266]. Interactions of this complex with DNA have been investigated by DNA melting experiments, DNA competitive binding with ethidium bromide, plasmid DNA cleavage experiments and viscosity measurements. The interaction with bovine serum albumin has also been studied using fluorescent quenching method. A series of acyclonucleosides 6,7-disubstituted 1-(pent-4-enyl)quinoxalin-2-one derivatives and the O-analogs were synthesized by a one-step condensation of the corresponding quinoxaline bases with 5-bromo-1-pentene are shown to inhibit HIV-1 and HIV-2 in MT-4 cells [267].

A large number of quinoxaline-N-oxides are also associated with a wide spectrum of biological activity ranging from antiinfective [268-270], anticancer [260], antimycobacterium tuberculosis [271] and angiotensin II receptor antagonists [272]. The quinoxaline 1,4-di-N-oxide derivative, 3-(4-bromophenyl)-2-(ethylsulfonyl)-6-methylquinoxaline 1,4-dioxide, exhibits high anti-cancer activity in hypoxia [273]. Quinoxaline 1,4-di-N-oxide derivative also induces DNA oxidative damage not attenuated by vitamin C and E treatment [274]. Potent antitumoral copper complexes of 3-aminoquinoxaline-2-carbonitrile N1,N4-dioxide derivatives were synthesized and characterized [266]. The hypoxic selective cytotoxicity towards V79 cells and the superoxide dismutase-like activity of the complexes were determined and related to physicochemical properties of the compounds.

The complexation of the quinoxaline-2-carbonitrile N1,N4-dioxide derivatives with vanadium improve their bioavailability [275]. The vanadyl

complex with the formula $\text{VO}(\text{L1})_2$, where $\text{L1} = 3\text{-amino-6(7)-chloroquinoxaline-2-carbonitrile}$ N1, N4-dioxide, is more potent cytotoxins than the free ligand, and showed excellent selective cytotoxicity in hypoxia. Torre et al reported Cu(II) quinoxaline N1,N4-dioxide complexes as selective hypoxic cytotoxins for the first time [276].

5.4 Optoelectronic applications of quinoxalines

Fluorescent heterocyclic compounds are of interest as functional materials in the emitters of electroluminescence devices. In particular, fluorescent dye materials whose fluorescence emission occurs at a longer wavelength in the red light region are expected to play a leading role in full colour electroluminescence displays. Quinoxaline is known to emit both the (n, π^*) fluorescence and the (π, π^*) phosphorescence in the vapor phase, for which the relative fluorescence and phosphorescence quantum yields depend on the pressure as well as on the excitation energy [277-280]. A large number of quinoxaline derivatives find application as dyes and as electroluminescent materials.

Karastatiris et al. synthesised and characterised soluble poly(p-phenylenevinylene) derivatives containing one or two quinoxaline moieties per repeat unit and has studied their use as emissive and electron transport materials in polymer light-emitting diodes [281]. These poly(p-phenylenevinylene) derivatives of quinoxaline emits greenish-yellow electroluminescence with a brightness of up to 450 cd/m^2 . The reaction of bis(1,2-diketone) chromophore monomer and a tetramine at room temperature resulted in the formation of second-order non-linear optical poly(phenylquinoxalines) with high glass transition temperatures [282]. Six new copolymers of 9,9'-dioctylfluorene and 2,3-bis(p-phenylene) quinoxaline were synthesized, characterized, and used as blue-emitting materials in light-emitting diodes [283]. Significant enhancements in LED brightness and external quantum efficiency by factors of up to 120 were observed in copolymers containing 15-50 mol % 2,3-bis(p-phenylene) quinoxaline when using bilayer LiF/Al cathodes.

The properties of the lowest excited triplet states of quinoxaline derivatives 2,3-dimethylquinoxaline and 2,3,6,7-tetramethylquinoxaline in acetonitrile have been investigated by using time-resolved laser flash photolysis at 266 nm [284]. New 6,7-bis-(3-methylbutoxyl)quinoxaline fluorescent dyes with groups of different electron-donating ability were synthesized by the condensation of [3-(diethoxyphosphoryl methyl)-6,7-bis-(3-methylbutoxy)-quinoxalin-2-ylmethyl]-phosphonic acid diethyl ester with arylaldehydes [285]. Three novel poly(aryl ether)s were synthesized from the reaction of three bisphenols with 2,3-bis(4-fluorophenyl)-quinoxaline via nucleophilic aromatic substitution [286]. In THF solutions the polymers showed absorption maxima at 349-354 nm and emission maxima at 417-454 nm, with quantum yields of 22-41%. Matsumura et al. reported the synthesis of 2,3-dimorpholino-6-aminoquinoxaline derivatives and their application as fluorescent probe [287].

Durmus et al. reported the synthesis of polymeric 3,4-ethylenedioxythiophene-bis-substituted quinoxalines and their potential use toward green polymeric materials [288]. Spectroelectrochemistry showed that both polymers reveal two distinct absorption bands as expected for a donor-acceptor polymer. The electrochromic properties of polymeric quinoxalines are employed in the manufacture of anode material for electrochromic devices [289]. Quinoxaline derivatives are used as photoinitiators in UV-cured coatings [290]. The iridium(III) complexes bearing 2,3-diphenylquinoxalines are shown to be highly efficient and pure-red emitting materials for electrophosphorescent organic light-emitting diodes and excellent quantum efficiencies for photoluminescence within the range of 50-79% were attained in dichloromethane solution at room temperature [291]. Hwang et al. synthesised and characterised four iridium complexes having substituted quinoxalines. One of the complexes was used to fabricate the red-emitting polymer light emitting diodes by blending it into a polymer mixture [292]. Porphyrins bearing quinoxaline derivatives were synthesized by the condensation reaction of 2,2'-(p-tolylmethylene)bis(1H-pyrrole) and a bisstyryl derivative containing 6,7-diisopentyloxyquinoxaline [293]. The chromophoric system of the fluorescent and

highly conjugated porphyrin macrocycles were studied from the viewpoint of protonation and deprotonation effects on their absorption and emission spectra in solution. The liquid crystalline properties and crystal structure of 5,6-didodecyloxyquinoxaline-2-(1H)-one oxime were studied using differential scanning calorimetry, optical polarizing microscopy and X-ray investigation [294]. The compound displayed a discotic mesophase over a large temperature interval. X-ray diffraction studies also revealed that this compound forms a discotic hexagonal ordered columnar mesophase and thus, has potential use as a colored liquid crystal.

6. Scope of the present work

A variety of Schiff base complexes derived from salicylaldehyde were found to have immense application in various fields. In the present investigation, we have used 3-hydroxyquinoxaline-2-carboxaldehyde in the place of salicylaldehyde and so what ever studies have been done in the case of Schiff base derivatives of salicylaldehyde, can be explored in the case of the Schiff base derivatives of 3-hydroxyquinoxaline-2-carboxaldehyde. Starting from this aldehyde one can prepare a large number of Schiff bases and their metal complexes and these compounds may find interesting applications in medicine, material science and catalysis. Indeed, to the best of our knowledge, not much work has been carried out to understand the catalytic behaviour of the Schiff base complexes derived from 3-hydroxyquinoxaline-2-carboxaldehyde. In this thesis, results of our studies on the synthesis and characterisation some new transition metal complexes derived from the above aldehyde and their catalytic activities in some oxidation and hydrogenation reactions are presented.

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