

Conclusions and future prospects

The attempts to design new tridentate Schiff base complexes and their utilization as oxidation catalysts are the main goals of this work. Details regarding the synthesis, spectral characterization and catalytic applications of some new transition metal complexes of the Schiff bases derived from 3-hydroxyquinoxaline-2-carboxaldehyde or quinoxaline-2-carboxaldehyde are presented in this thesis.

Schiff bases play a key role in the development of coordination chemistry. Schiff bases have different denticity and basicity, which will influence the stability and properties of the complex. The Schiff base complexes may be synthesized by template method, rearrangement of heterocycles in the presence of metal ions or by direct ligand synthesis followed by complexation. They find application as catalysts, medicines, biocidal agents, fluorescent materials, dyes and corrosion inhibitors. They are found to catalyse a large number of organic transformations and play an important role in asymmetric catalysis, as chiral Schiff bases are able to transmit chiral information to produce non racemic products. Quinoxaline based Schiff bases are versatile chelating ligands due to the presence of two heterocyclic nitrogen atoms in the ring. This chapter presents an overview of the chemistry of Schiff bases and their complexes and the application of Schiff base complexes as catalysts especially with regard to phenol hydroxylation, cyclohexane oxidation and benzyl alcohol oxidation. The scope of the present work is also given in chapter 1. Details regarding the general reagents, experimental techniques employed and the synthesis of quinoxaline-2-carboxaldehyde and 3-hydroxyquinoxaline-2-carboxaldehyde are presented in chapter 2.

Chapter 3 deals with the synthesis and characterization of the Schiff base quinoxaline-2-carboxaldehyde-2-amino-5-methylphenol (qamp) and its manganese(II), iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) complexes. The complexes have the general empirical formula $[M(qamp)_2]$ for the cobalt(II),

nickel(II) and Zn(II) complexes, [Fe(qamp)Cl₂] for the iron complex, [Mn(qamp)(OAc)] for the manganese complex and [Cu(qamp)Cl] for the copper complex. All the complexes are stable and are non electrolytes in DMF. On comparing the infrared spectrum of the ligand with that of the complexes, a shift in stretching frequencies of azomethine (C=N), quinoxaline (C=N) and phenolic (C-O) is observed supporting the tridentate nature of the ligand. The electronic spectral and magnetic moment studies of the complexes reveal an octahedral geometry for the Co(II) and Ni(II) complex, a tetrahedral geometry for Mn(II) complex, square pyramidal geometry for Fe(III) complex and square planar geometry for Cu(II) complex. Crystal structure determination of the cobalt(II) and nickel(II) complexes are carried out. Crystal structures of [Co(qamp)₂].H₂O and [Ni(qamp)₂].H₂O confirm the octahedral geometry of the complexes. Each of the crystals is a racemic mixture of two crystallographically independent enantiomers of the complex. The molecules exhibit a two dimensional chain structure parallel to [010] plane, formed by O–H...N and O–H...O intermolecular hydrogen bonding and π – π stacking interaction.

The synthesis and characterization of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of the Schiff base, quinoxaline–2–carboxalidine–L–histidine (qlh) are presented in chapter 4. This Schiff base cannot be isolated and the syntheses of the complexes were carried out by template method in which aldehyde, amine and metal compound are refluxed in 1:1:1 molar ratio. The analytical data show that the complexes have the general empirical formula [M(qlh)(OAc)] for the manganese(II), cobalt(II) and zinc(II) complexes and [M(qlh)Cl] for the copper(II) complex, [M(qlh)(OAc)(H₂O)] for the nickel(II) complex and [M(qlh)Cl₂(H₂O)] for the iron(III) complex. All the complexes are found to be stable and conductivity studies show that the complexes are non electrolytes in DMF. FTIR spectra indicate that bands due to histidine and quinoxaline-2-carboxaldehyde are present in complexes, while C=O stretching was found to be absent, which indicates the formation of the Schiff base complex. The ¹H NMR spectrum of the zinc(II) complex also confirms the formation of the

Schiff base, in which the azomethine CH resonates at 9.45 ppm. All the results of our study clearly demonstrates that the ligand is monobasic tridentate ligand. The physicochemical and spectral data reveal an octahedral geometry for the Fe(III) and Ni(II) complexes. The manganese(II), cobalt(II) and zinc(II) complexes are found to be tetrahedral; while the copper(II) complex has a square planar geometry.

Chapter 5 is a discussion on the synthesis and characterization of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of the Schiff base 3-*{(E)-[(2-hydroxy-4-methylphenyl)imino]methyl}* quinoxalin-2(1*H*)-one (hamp). The ligand exhibits tautomerism in solution. The analytical data reveal that all the complexes are formed in the metal:ligand ratio 1:1. All the complexes are stable and non electrolytes in DMF. The proton NMR spectrum of hamp indicate that the ligand exists as the keto tautomer. NMR spectrum of the zinc(II) complex suggests the enolisation of hamp on complexation. IR spectral studies reveal that the ligand acts as a tridentate ONO donor and it can coordinate either in keto form or in enol form. In all the complexes, there is a shift in azomethine stretching frequency towards lower wavenumbers suggesting the coordination of imine nitrogen. FTIR spectra further reveal that the Schiff base in the cobalt(II) complex exists in the keto form while that in all other complexes exists in the enol form. The physicochemical and spectral data suggest a tetrahedral geometry for the Mn(II), Ni(II), Cu(II) and Zn(II) complexes. The iron(III) and cobalt(II) complexes are octahedral in geometry.

A novel benzothiazolidine derivative, 3-(2,3-dihydro-1,3-benzothiazol-2-yl)quinoxalin-2(1*H*)-one (abbreviated as btq) and the Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of the Schiff base (abbreviated as hatp), which is formed by the rearrangement of btq, has been synthesized and characterized. The formation of ring closed benzothiazoline compound will get rearranged to form the form the tridentate ONS donor Schiff base in the presence of metal ions. All the complexes are stable and non electrolytes in DMF. The Schiff base may get coordinated either in the keto form or in the enol form. The ¹H NMR spectra of the compound btq and

that of [Zn(hatp)(OAc)] complex are taken in DMSO- d_6 . The thiazolidine CH of btq exhibits a doublet at 7.16 ppm which indicates the ring closure. In the NMR spectrum of the diamagnetic zinc(II) complex, the azomethine proton appears at 8.93 ppm as a singlet. The FTIR spectra of the hatp complexes suggest that the Schiff base exists in the enol form in the cobalt(II) and nickel(II) complexes, which is evidenced by the disappearance of band due to (C=O) stretching. But it exists in the keto form in the manganese(II) copper(II) and zinc(II) complexes, these complexes exhibit strong $\nu(\text{C}=\text{O})$ bands at 1650, 1676 and 1657 cm^{-1} respectively. On the basis of physicochemical and spectroscopic techniques, the copper(II) complex is found to be square planar and the zinc(II) complex is tetrahedral. The manganese(II), cobalt(II) and nickel(II) complexes are octahedral in geometry. The details of these results are presented in chapter 6.

Chapter 7 deals with the studies on the use of the Schiff base complexes as catalysts in some oxidation reactions and is divided into three sections. Section 7.1 deals with studies on the liquid phase hydroxylation of phenol. The section 7.2 presents the studies on the oxidation of cyclohexane and section 7.3 deals with the studies on catalytic activity of the copper(II) Schiff base complexes in the oxidation of benzyl alcohol.

Catalytic activity of the prepared complexes in the liquid-phase hydroxylation of phenol was studied using H_2O_2 as an oxidant. Catechol and hydroquinone are the sole products of the reaction. The copper(II), manganese(II), iron(III) and cobalt(II) complexes were screened for their activity towards the hydroxylation of phenol. The major product of the reaction was found to be catechol in all cases. The cobalt(II) complex of qamp is found to be inactive, which may be due to the coordinative saturation. In $[\text{Co}(\text{qamp})_2]\cdot\text{H}_2\text{O}$ two molecules of the Schiff bases are tightly bound the metal ion, so that it is unable to bind with the oxygen to form the intermediate. The complex, $[\text{Cu}(\text{qamp})\text{Cl}]$, was found to be the most active catalyst with ~16 % conversion. Detailed study of the catalytic activity of the complex, $[\text{Cu}(\text{qamp})\text{Cl}]$, that gave maximum conversion in the screening

studies, was carried out by changing the different parameters like the concentration of catalyst and oxidant, reaction time and reaction temperature. It was also found that there exists an optimum value for the amount of catalyst as well as temperature and time, after which conversion decreases or remains more or less the same. It is observed that the order of activity of the metal ions follows the order; copper(II)>manganese(II)~iron(III)>cobalt(II). The catalytic activity of the complexes of hatp is found to be lower compared to that of the other Schiff base complexes.

The catalytic activity of the prepared complexes was studied in the cyclohexane oxidation using H₂O₂ as an oxidant. Cyclohexanol, cyclohexanone and adipic acid are the products. The selectivity was found to be greater for cyclohexanol. The copper(II), manganese(II) and iron(III) complexes were screened for their activity towards the oxidation. Detailed study of the catalytic activity of the complex, [Cu(qamp)Cl], that gave maximum conversion in the screening studies, was carried out by changing the different parameters like the concentration of catalyst and oxidant, reaction time and reaction temperature.

The catalytic activity of the prepared complexes was studied in the benzyl alcohol oxidation using H₂O₂ as an oxidant. The products obtained are benzaldehyde and benzoic acid. The selectivity was found to be greater for benzaldehyde. The copper(II) complexes were screened for their activity towards the oxidation. Detailed study of the catalytic activity of the complex, [Cu(qlh)Cl]·2H₂O, that gave maximum conversion in the screening studies, was carried out by changing the different parameters like the concentration of catalyst and oxidant, reaction time and reaction temperature. Complexes of qlh and qamp, which are ONO donor ligands, show highest activity towards benzyl alcohol oxidation.

FUTURE PROSPECTS

Transition metal complexes derived from quinoxaline Schiff bases and their catalytic activity studies are the central topic of research described in this thesis.

The major goal of coordination chemists nowadays is to develop new complexes that have potential applications. The reports on transition metal complexes derived from quinoxalines are scanty. Since quinoxaline moiety contains two heterocyclic nitrogen atoms, it is possible to prepare coordination polymers. The ligand is easily modifiable in order to control the geometries and nuclearities of the complexes formed. The utilization of quinoxaline Schiff base complexes in medicine, catalysis, photonics and electronics are not fully explored.

This thesis also deals with the catalytic activity studies of transition metal complexes derived from quinoxalines towards some oxidation reactions. In the current study the exact nature of the catalytically active species is not studied. Detailed kinetic studies are necessary for the better understanding and future development of the efficient catalysts. Kinetic studies would expose several aspects of these reactions, such as rate constants and order of the reaction, pH and solvent dependency, and the active species responsible for catalytic activity. Furthermore, a broader range of substrates should be studied to investigate and correlate the selectivity and activity correctly to the structures of the catalysts. From the combined catalytic, mechanistic and kinetic studies of metal complexes using systematically varied structures of the ligands, certainly more powerful catalysts are likely to be developed.

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