Details of the studies on the synthesis, spectral characterization and catalytic applications of some new transition metal complexes of the Schiff bases derived from 3-hydroxyquinoxaline-2-carboxaldehyde are presented in this thesis. The thesis is divided into eight chapters. Contents of the various chapters are briefly described as follows:

Chapter 1

This chapter involves a general introduction to Schiff bases and a brief discussion of their applications in various catalytic processes. The synthetic methodologies and various applications of quinoxalines are also discussed in this chapter for the reason that we employed 3-hydroxyquinoxaline-2-carboxaldehyde, for the preparation of the Schiff base ligands. The scope of the present work and the possible application of these complexes in various fields are also discussed in this chapter.

Chapter 2

Chapter 2 deals with the details on various experimental and characterization techniques employed in the present study. Information about the synthesis and spectral characterization of the five new Schiff bases, N,N’-bis(3-hydroxyquinoxaline-2-carboxalidene)1,8-diaminonaphthalene (hqcdan-H₂), N,N’-bis(3-hydroxyquinoxaline-2-carboxalidene)2,3-diaminomaleonitrile (hqcdmn-H₂), N,N’-bis(3-hydroxyquinoxaline-2-carboxalidene)trans-(R,R’)-1,2-
diaminocyclohexane (hqcdac-H₂), 3-hydroxyquinoxaline-2-carboxalidene-2-aminophenol (hqcap-H₂) and 3-hydroxyquinoxaline-2-carboxalidene-4-aminoantipyrine (hqcaap-H), are also included in this chapter. These Schiff bases formed via the condensation of 3-hydroxyquinoxaline-2-carboxaldehyde with the amines 1,8-diaminonaphthalene, 2,3-diaminomaleonitrile, trans-(R,R’)1,2-diaminocyclohexane, 2-aminophenol and 4-aminoantipyrine have been characterised with the aid of spectroscopic techniques such as FT-IR, UV-visible, NMR. These Schiff bases, like the other 2-hydroxyquinoxaline analogues, exhibit prototropic tautomerism.

Chapter 3

Oxovanadium(IV) complexes, [(VO)₂(hqcdan)SO₄].H₂O, [(VO)₂(hqcdmn)SO₄].H₂O, [(VO)₂(hqcdac)SO₄].H₂O, [(VO)₂(hqcap)₂].H₂O and [(VO)₂(hqcaap)₂SO₄].2H₂O, were synthesised and characterised by elemental analysis, FT-IR, UV-visible, TG-DTA-DTG, EPR, AAS, cyclic voltammetry, conductance and magnetic susceptibility measurements. The cyclic voltammograms for all the complexes in DMSO consist of an irreversible reduction wave due to reduction of V⁴⁺ to V³⁺ and an irreversible oxidation wave due to the oxidation of V⁴⁺ to V⁵⁺. The V=O stretching frequencies of these complexes are comparatively lower than that of other penta-coordinated oxovanadium(IV) complexes indicating that the V=O bond is weakened by strong σ and π electron donation by the electron rich Schiff base ligands to the antibonding orbital of the V=O group. Also these lower values for V=O stretching frequencies suggest the absence of −V=O—V=O− chain structure in these complexes. The presence of chelating bidentate coordination of the SO₄²⁻ group in each complex is evidenced by the presence of a triply degenerate ν₃ and single ν₁ bands in the IR spectra. The electronic spectra of all the complexes in methanol exhibit only a single d-d band and are dominated by ligand centered bands. However, the solid state diffuse reflectance spectra of these
complexes exhibit d-d bands corresponding to the electronic transitions of the square pyramidal oxovanadium complex ($^2B_2 \rightarrow ^2A_1$, $^2B_2 \rightarrow ^2B_1$, and the split $^2B_2 \rightarrow ^2E$ transitions). The ESR spectra of all the complexes in DMF at LNT display well resolved axial anisotropy with typical eight-line pattern characteristic of square pyramidal oxovanadium(IV) complexes. The presence of lattice water molecules in these complexes is confirmed by the TG weight loss below 130 °C. Thus, all these complexes have a binuclear structure with square-pyramidal geometry around each vanadium centre.

Chapter 4

In this chapter, a discussion on the synthesis and characterization of copper(II) complexes, [Cu$_2$(hqcdan)Cl$_2$].H$_2$O, [Cu$_2$(hqcdmm)Cl$_2$], [Cu$_2$(hqcdac)Cl$_2$].H$_2$O, [Cu$_2$(hqcapi)$_2$] and [Cu(hqcapi)Cl(H$_2$O)$_2$], has been presented. The presence of coordinated and lattice water in these complexes are evidenced from the FT-IR and TG data. The complex, [Cu(hqcapi)Cl(H$_2$O)$_2$], exhibits a magnetic moment value of 1.76 BM as expected for a mononuclear copper(II) octahedral complex, where as in all other cases, subnormal magnetic moment values were observed suggesting binuclear nature of the complexes. A two-stepped cyclic voltammogram were observed for all the complexes. The first redox peak appearing in the positive potential range corresponds to Cu$^{II,II}$/Cu$^{II,I}$ redox couple, whereas the second peak appearing in the negative potential range is attributable to the Cu$^{II,II}$/Cu$^{II,I}$ redox processes. Cyclic voltammogram of the mononuclear copper(II) complex also exhibits two irreversible one-electron waves due to the Cu$^{III}$/Cu$^{II}$ couple and Cu$^{II}$/Cu$^{I}$ couple. FT-IR spectra reveal that the azomethine stretching frequency increases for all the complexes suggesting complex formation. The diffuse reflectance spectra of the binuclear complexes exhibit the three spin allowed transitions, viz., $^2B_{1g} \rightarrow ^2A_{1g}$ ($d_{x^2-y^2} \rightarrow d_{xy}$), $^2B_{1g} \rightarrow ^2B_{2g}$ ($d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$) and $^2B_{1g} \rightarrow ^2E_{g}$ ($d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$), expected for square-planar complexes.
Summary and conclusion

However in solution spectra (in methanol) only one broad band was observed. The electronic spectral data for the complex, \([\text{Cu(hqcaap)Cl(H}_2\text{O)}_2]\), suggest an octahedral geometry. EPR spectra of all the complexes were recorded in polycrystalline state and in DMF solution at 77 K. The presence of half-field signals in the spectra of \([\text{Cu}_2(\text{hqcdmn})\text{Cl}_2]\) and \([\text{Cu}_2(\text{hqcdac})\text{Cl}_2]\).\text{H}_2\text{O}\) supports the binuclear structure for these complexes.

Chapter 5

Chapter 5 deals with the synthesis and characterization of the ruthenium(II) complexes, \([\text{Ru}_2(\text{hqcdan})\text{Cl}_2].\text{H}_2\text{O}\), \([\text{Ru}_2(\text{hqcdmn})\text{Cl}_2].\text{H}_2\text{O}\), \([\text{Ru}_2(\text{hqcdac})\text{Cl}_2]\).\text{H}_2\text{O}\), \([\text{Ru}_2(\text{hqcap})\text{Cl}_2(\text{H}_2\text{O})].\text{H}_2\text{O}\) and \([\text{Ru(hqcaap)Cl(H}_2\text{O})_2]\).\text{H}_2\text{O}\). The presence of coordinated and lattice water molecules in the complexes could be confirmed from the TG and IR studies. All the complexes are diamagnetic and EPR silent suggesting that the ruthenium is in the +2 oxidation state. A two-stepped cyclic voltammogram was observed for all the ruthenium(II) complexes. The first redox peak appearing in the positive potential range for the binuclear complexes corresponds to \([\text{Ru}_2^{\text{III,III}}/\text{Ru}_2^{\text{III,II}}]\) redox couple, where as the second redox couple appearing in the negative potential range is attributable to the \([\text{Ru}_2^{\text{III,II}}/\text{Ru}_2^{\text{II,II}}]\) redox processes. Cyclic voltammogram of the mononuclear ruthenium(II) complex also exhibits two irreversible one-electron waves due to the \([\text{Ru}^{\text{IV}}/\text{Ru}^{\text{III}}]\) couple and \([\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}]\) couple. An increase in azomethine stretching frequency was observed in the IR spectra of all the complexes. Presence of the three bands corresponding to the electronic transitions, \(1^A_{1g} \rightarrow 1^E_g\), \(1^A_{1g} \rightarrow 1^B_{1g}\) and \(1^A_{1g} \rightarrow 1^A_{2g}\) in the diffuse reflectance spectra of the binuclear complexes suggests a square planar geometry. The electronic spectrum of \([\text{Ru(hqcaap)Cl(H}_2\text{O)}_2]\).\text{H}_2\text{O}\) suggests an octahedral structure.
Chapter 6

Details on the catalytic activity studies of the oxovanadium(IV) complexes, \([\text{VO}_2(\text{hqcdan})\text{SO}_4]\cdot\text{H}_2\text{O}, \quad [\text{VO}_2(\text{hqcdmn})\text{SO}_4]\cdot\text{H}_2\text{O}, \quad [\text{VO}_2(\text{hqcdac})\text{SO}_4]\cdot\text{H}_2\text{O}, \quad [\text{VO}_2(\text{hqcap})\cdot\text{H}_2\text{O} \quad \text{and} \quad [\text{VO}_2(\text{hqcaap})\cdot\text{SO}_4]\cdot\text{H}_2\text{O}, \quad \text{in the liquid phase oxidation of cyclohexene are presented in this chapter. All the complexes are found to catalyze liquid phase oxidation of cyclohexene using H}_2\text{O}_2 \quad \text{as oxidant. More selectivity was observed for allylic oxidation products rather than that for epoxidation product. The oxovanadium(IV) complex of the Schiff base, N,N’-bis(3-hydroxyquinoxaline-2-carboxalidene)2,3-diaminomaleonitrile, exhibits comparatively better catalytic activity and a detailed investigation was carried out with this complex. A low H}_2\text{O}_2 \quad \text{efficiency seen for this reaction might be due to the high activity of the complex towards the decomposition of hydrogen peroxide.}

Chapter 7

Studies on the catalytic activity of the copper(II) complexes (synthesis of which are presented in chapter 4) in the liquid-phase hydroxylation of phenol using H}_2\text{O}_2 \quad \text{as an oxidant are presented in this chapter. Catechol and hydroquinone are the sole products of the reaction. All the complexes were screened for their activity towards the hydroxylation of phenol. The complex, [Cu_2(\text{hqcdmn})\text{Cl}_2], gave maximum conversion in the screening studies and detailed investigations were carried out with this complex. The effect of amount of catalyst, reaction time, reaction temperature, amount of oxidant, and that of the amount of solvent on the reaction were studied. It was found that there exists an optimum value for the catalyst amount, temperature and time. Increase in the amount of H}_2\text{O}_2 \quad \text{has a positive effect on the reaction, while the quantity and nature of solvent have no significant effect.
Chapter 8

This chapter deals with the application of the ruthenium(II) complexes (synthesis of which are presented in chapter 5) in the hydrogenation of benzene and toluene. All the complexes were screened for their catalytic activity and were found to be effective catalysts in the reduction of benzene and toluene. Catalytic experiments were carried out in a 100 mL bench top mini-reactor. Both partial and complete reduction products were obtained during the hydrogenation. A detailed kinetic study was carried out with [Ru₂(hqcdmn)Cl₂].H₂O, as it exhibited maximum catalytic activity in the screening study. Influence of various parameters on the rate of reaction was investigated. Turnover frequencies of 7362 h⁻¹ and 5873 h⁻¹ have been found for the reduction of benzene (0.34 mol) and toluene (0.28 mol) respectively at 60 °C with 2.82 × 10⁻⁶ mol catalyst and at a hydrogen pressure of 30 bar. These values are much higher than that of some of the reported ruthenium catalysts for the homogeneous aromatic hydrogenation reactions. An intermediate hydride complex, believed to be the catalytically active species, has been isolated and identified by FT-IR spectroscopy. This active species is presumed to control the overall hydrogenation rate.
List of Publications


* Not related to the work presented in this thesis