Chapter 1
Introduction and literature survey

Transition metal complexes with N,O donor ligands show variable bonding and stereo-chemical possibilities depending on the nature of metal ions, structure of the ligands and metal-ligand interactions. A number of acylhydrazone Schiff base ligands and their coordination compounds have been found to be biologically important and exhibit antibacterial, antitumour and antitubercular activities. These compounds have been used as analytical reagents, catalysts, corrosion inhibitors and fluorescent sensing materials. Acylhydrazone ligands show a flexidentate behavior giving rise to different geometrical arrangement around metal ions. These Schiff bases can bond to the metal ions either in keto form or in enol form depending upon the nature of metal ion and pH of the medium. The aim of this work is to explore the ligational behaviour of some Schiff bases derived from acylhydrazine system towards some transition metal ions and to arrive at the probable structures of the complexes on the basis of spectroscopic studies and X-ray crystallography. Expecting some new compounds of interest and their potential use as DNA/BSA binding agents and corrosion inhibitors, we have synthesized a number of bivalent transition metal complexes with a variety of acylhydrazone ligands and characterized them by various physico-chemical and spectral techniques (electronic, IR, NMR, ESR). Molecular structure of some of the compounds has also been determined by single crystal X-ray diffraction techniques. A series of synthesized metal complexes show efficient DNA/BSA binding activity via intercalation mode and ability to cleave the DNA. Whereas, the compounds of other series exhibit appreciable corrosion inhibition property of mild steel in acid medium.

After giving a brief introduction to the formation of acylhydrazone Schiff bases, pertinent literatures on the acylhydrazones and other Schiff bases, and their respective metal complexes have been presented. The applications of these compounds in various fields viz. as biological probes, DNA binding & cleaving
agents, protein binding agents, as catalyst, as sensing materials, as electroluminescent materials and as corrosion inhibitors, etc. have been described in this chapter. An attempt has been made to make an up-to-date survey of the literature related with this study.

Chapter 2
Experimental

This chapter deals with the specifications of the commercially available starting materials, analytical procedures and technical details of the instruments used for physico-chemical studies. The experimental details pertaining to the preparation of the ligands under the present study viz. anthranilic acid hydrazide (ah), salicylic acid hydrazide (sh), N’-(phenyl-pyridin-2-yl-methylene)-thiophene-2-carboxylic acid hydrazide (Hpmtc), 2-hydroxy-benzoic acid [1-(2-hydroxy-phenyl)-propyldiene]-hydrazide (H₂hbpp), 2-amino-benzoic acid [1-(2-hydroxy-phenyl)-propyldiene]-hydrazide (H₂abph), 2-hydroxy-benzoic acid (1-phenyl-propyldiene)-hydrazide (Hhbh), 2-amino-benzoic acid (1-phenyl-propyldiene)-hydrazide (Habh) have been described.

A brief description about the method of analyses and the instruments used in various physico-chemical techniques viz. molar conductance, magnetic moment measurements, electronic spectra, IR spectra, NMR spectra and single crystal X-ray diffraction studies are given. The techniques for evaluation of DNA/BSA binding studies with metal complexes and corrosion inhibition properties of the ligands and the complexes for mild steel in acid medium are also described in this chapter.

Chapter 3
Synthesis, structural investigation, DNA and protein binding study of some 3d-metal complexes with N’-(phenyl-pyridin-2-yl-methylene)-thiophene-2-carboxylic acid hydrazide

In this chapter, the ligand, N’-(phenyl-pyridin-2-yl-methylene)-thiophene-2-carboxylic acid hydrazide (Hpmtc) derived from thiophene-2-carboxylic acid hydrazide and 2-benzoyl pyridine, and its metal complexes with Co(II), Ni(II), Cu(II)
and Zn(II) have been synthesized. These compounds are characterized by elemental analyses, magnetic susceptibility measurements, IR, NMR and UV-Vis spectral studies. The molecular structures of Hpmtc and its Co(II), Ni(II), Cu(II) and Zn(II) complexes are finally determined by X-ray crystallography. Various spectral and single-crystal X-ray diffraction studies suggest that Hpmtc coordinates with metal ions as a monobasic tridentate ligand forming mononuclear distorted octahedral complexes of the type \([M(pmtc)_{2}]\). The molecular structures of the complexes are stabilized by C–H···N, C–H···O intermolecular H-bonding, and C–H···π and π···π interactions. The DNA binding experiment of the Co(II), Cu(II) and Zn(II) complexes by UV-Vis absorption, and EB-DNA displacement by fluorescence spectroscopy, reveal an intercalative mode of binding between CT-DNA (calf-thymus DNA) and the metal complexes. These complexes exhibit a moderate ability to cleave pBR322 plasmid DNA. A comparative bovine serum albumin (BSA) protein binding activity of the Co(II), Cu(II) and Zn(II) complexes has also been determined by UV-Vis absorption and fluorescence spectroscopy. The DNA binding and protein binding studies suggest that the complex Cu(II) exhibits more effective binding activity (\(K_b = 5.54 \times 10^5\) and \(K_q = 1.26 \times 10^6\) M\(^{-1}\), respectively) than complexes Co(II) and Zn(II). However, the Co(II) complex shows better hydrolytic DNA cleavage activity compared to Cu(II) and Zn(II) complexes.

**Chapter 4**

**Synthesis, structural and corrosion inhibition studies on Mn(II), Cu(II) and Zn(II) complexes with a Schiff base derived from 2-hydroxypropiophenone**

In this chapter, a Schiff base, 2-hydroxy-benzoic acid \([1-(2-hydroxy-phenyl)-propylidene]-hydrazide (H\(_2\)hbpp)\) and its Mn(II), Cu(II) and Zn(II) complexes have been synthesized. These compounds have been characterized by different physico-chemical and spectroscopic techniques (UV-Vis, IR, NMR and ESI-Mass). The molecular structure of H\(_2\)hbpp and its Mn(II) and Zn(II) complexes are determined by single crystal X-ray diffraction technique. In Mn(II) and Cu(II) complexes, the ligand coordinates through azomethine-N, carbonyl-O and phenolate-O (2-hydroxypropiophenone) forming a mono-nuclear 6-coordinate distorted octahedral
geometry around metal. However, Zn(II) complex forms a phenoxy-bridged centrosymmetric dimer with 5-coordinate distorted square pyramid geometry around each metal ion. In this complex, the ligand bonds through azomethine-N, carbonylate-O and two phenolate-O, and a DMSO molecule occupies one of the vacant site of each metal. The structure of Cu(II) complex has been satisfactorily modeled by density functional theory (DFT) and time dependent-DFT (TD-DFT) calculations. The corrosion inhibition study of the synthesized compounds for mild steel in 1 M HCl medium has also been performed and the activity is found in the order: H₂hbpp < Cu(II) complex < Mn(II) complex < Zn(II) complex.

Chapter 5
Versatile coordination behaviour of a multi-dentate Schiff base with manganese(II), copper(II) and zinc(II) ions and their corrosion inhibition study

In this chapter, a Schiff base, 2-amino-benzoic acid [1-(2-hydroxy-phenyl)propylidene]-hydrazide (H₂abph) and its mononuclear complex [Mn(Habph)₂] and one-dimensional coordination polymers [Cu(abph)_n·DMSO] and [Zn₂(abph)₂·2DMSO]n have been synthesized and characterized by various physico-chemical and spectroscopic techniques. The molecular structures of the compounds are also determined by single crystal X-ray crystallography. The reaction of ligand with Cu(II) and Zn(II) in methanol gives polymeric complex, while the similar reaction with Mn(II) results in the formation of a cyclised quinazoline derivative 2,2-dimethyl-3-(1-phenyl-propylideneamino)-2,3-dihydro-1H-quinazolin-4-one. However, the reaction of ligand with Mn(II) in ethanol gives a mononuclear Mn(II) complex. In Mn(II) complex, the ligand coordinates through azomethine-N, carbonyl-O and phenolate-O forming a 6-coordinate distorted octahedral geometry around metal ion. In Cu(II) and Zn(II) complexes, the ligand bonds through azomethine-N, carbonylate-O and phenolate-O. The Cu(II) complex forms a distorted square planar geometry, which polymerizes via anthranilate–NH₂ group of second unit. The Zn(II) complex exhibits a phenoxy-bridged dimer, which polymerizes through anthranilate–NH₂ group forming a 5-coordinate distorted square pyramid geometry around each metal ion. The synthesized compounds show an appreciable corrosion inhibition
property for mild steel in 1M HCl medium which varies in the order: $\text{H}_2\text{abph} < \text{Mn(II)}$ complex $< \text{Cu(II)}$ complex $< \text{Zn(II)}$ complex.

**Chapter 6**

**Synthesis, characterization and corrosion inhibition property of nickel(II) and copper(II) complexes with some acylhydrazine Schiff bases**

In this chapter, Ni(II) and Cu(II) complexes with 2-amino-benzoic acid (1-phenyl-propyldene)-hydrazide (Habh) and 2-hydroxy-benzoic acid (1-phenyl-propyldene)-hydrazide (Hhbh) have been synthesized and characterized by different physico-chemical and spectroscopic techniques (UV-Vis, IR & NMR). The molecular structures of the ligands and their complexes $[\text{Ni(abh)}_2\text{(DMSO)}_2]$, $[\text{Ni(hbh)}_2\text{(DMSO)}_2]$ and $[\text{Cu(abh)}_2]$ have also been determined by single crystal X-ray diffraction technique. In all the complexes, each ligand coordinates to metal through azomethine-N and carbonylate-O resulting a 4-coordinate distorted square planar geometry for Cu(II) complexes and 6-coordinate distorted octahedral geometry for Ni(II) complexes in which two DMSO molecules occupy the axial positions. The structure of $[\text{Cu(hbh)}_2]$ complex has been satisfactorily modeled by density functional theory (DFT) and time dependent-DFT (TD-DFT) calculations. The corrosion inhibition study of the synthesized compounds has also been performed for mild steel in 0.5 M $\text{H}_2\text{SO}_4$ medium. The activity is found in the order: Ni(II) complexes $> \text{ligands} > \text{Cu(II)}$ complexes. The DFT study on ligands also supports the experimental observation that Habh is better corrosion inhibitor than Hhbh.

**Chapter 7**

**Structural investigations on bis-(semicarbazido)dihydrazine nickel(II) complex synthesized by using uracil and hydrazine hydrate**

In this chapter, a mixed-ligand bis-(semicarbazido)dihydrazine nickel(II) complex, $[\text{Ni(sem)}_2\text{(hz)}_2]$ ($\text{Hsem} = \text{semicarbazide}, \text{hz} = \text{hydrazine}$) has been synthesized by unusual ring opening of uracil reacting with hydrazine hydrate in the presence of nickel(II) chloride. The complex was characterized by elemental analyses, IR, UV-Vis spectral studies and magnetic susceptibility measurement. The molecular
structure of the complex was finally determined by single crystal X-ray diffraction study. The complex acquires a six coordinate distorted octahedral geometry in which semicarbazide ligand binds through hydrazinic–NH$_2$ and a deprotoneted C-O$^-$ group whereas, hydrazine coordinates through one of the –NH$_2$ group to nickel(II) centre. The structure was stabilized by the presence of strong inter-molecular hydrogen bonding interactions N-H…N and N-H…O forming a huge supramolecular network. Further, the structure was satisfactorily modeled by density functional theory calculations (DFT). UV–Vis and IR spectra are analyzed in depth with the help of time dependent-DFT. The theoretical analyses of electronic structure and molecular orbitals have suggested that the high-energy absorption bands in UV–Vis spectrum are mainly $\pi \rightarrow \pi^*$ ligand-to-ligand charge transfer transitions (LLCT) and lower energy absorption bands are $\pi \rightarrow$ (d$_z^2$ or d$_{x^2-y^2}$, d$_{yz}$) ligand-to-metal charge transfer transitions (LMCT) in nature.