PART I

SYNTHESIS AND CHARACTERISATION
CHAPTER 1
INTRODUCTION

Coordination chemistry, the chemistry of metal complexes, is one of the most active research areas in inorganic chemistry. The study of coordination chemistry in the modern day context began with two notable scientists Alfred Werner and Sorphus Mads Jorgenson. The pioneering contribution of Werner to the study of coordination chemistry fetched him the Nobel Prize in Chemistry in 1913. Werner’s basic ideas on the stereochemistry of metal complexes, mechanism of isomerisation etc. remain unchallenged even today despite all the advanced technical developments which have taken place since his days. However the advent of sophisticated physicochemical techniques of high precision and capability has considerably enriched our understanding of the nature of the metal-ligand bond, the structure and stereochemistry of metal complexes, their stability and other properties. Research has come long way from the time of Werner and Jorgenson, in terms of the growth that the coordination chemistry has experienced over the last few decades. Their work was a stepping stone for the development of modern inorganic chemistry which is truly a multidisciplinary one in the present day context.

Coordination chemistry encompasses such diverse fields as dyes, colour photography, mineral extraction, nuclear fuels, toxicology,
bioinorganic chemistry, medicine, catalysis, material science, ceramics, microelectronics, photonics etc. Industries dealing with organic chemicals, pharmaceuticals, petrochemicals and plastics owe a lot to the findings in the field of coordination chemistry. Nature makes extensive use of coordination compounds and their study is becoming increasingly important in biology as well as in chemistry. Many of the biologically active compounds are complexes and even the simpler types of complexes have served as model compounds in investigating bodily process. The living system is partially supported by coordination compounds. Hemoglobin, an iron complex, carries oxygen to animal cells. Myoglobin, chlorophyll and cytochromes are some of the other important complex compounds in living systems. Inorganic compounds particularly metallic ions and complexes are essential cofactors in a variety of enzymes and proteins.

The elegance and the variety of the coordination compounds and the intriguing range of concepts that are required to interpret their behaviour have attracted many researchers to the study of their synthesis and to seek an understanding of their chemical reactions. The study of complexes has enabled the inorganic chemists to make significant progress in refining the concept of chemical bonding and to explain the influence that bonding has, on the various properties of the compounds.
Schiff base ligands

Schiff bases, named after Hugo Schiff (1834-1915), and their transition metal complexes continue to be of interest even after over hundred years of study. The condensation products of primary amines with carbonyl compounds were first reported by Schiff in 1864 and the products are often referred to as Schiff bases\textsuperscript{1-4}. Schiff bases are compounds containing azomethine group (\(>\text{C}=\text{N}\)) and have the general structure \(R-\text{N}=\text{C}-R'\) where \(R\) and \(R'\) are aryl, alkyl, cycloalkyl or heterocyclic groups which may be variously substituted. Often they are referred to as anils, imines or azomethines. The synthesis and properties of Schiff bases have been widely reviewed\textsuperscript{5-11}. The availability of different types of amines and carbonyl compounds enabled the synthesis of Schiff bases with diverse structural features. Nevertheless, most of the studies are on metal complexes derived from salicylaldehyde\textsuperscript{12}. The presence of phenolic \(-\text{OH}\) group sufficiently near to the azomethine group of salicylaldimines makes them versatile multidendate ligands complexing with almost all metal ions. In order to understand the chemistry of metal chelates, awareness about the formation and stability of complexes is of great help.

The bonding ability of the ligands depends on the nature of atoms that act as coordination site, their electro negativity and steric factors. By virtue of the presence of lone pair of electrons on the nitrogen atom, electron donating character of the double bond and low electro negativity of nitrogen,
N of the azomethine group (>C=N) act as good donor site and Schiff base as active ligands. The formation of chelates gives extra stability to the complexes especially when the ring is five or six membered. Hence the presence of a functional group with replaceable hydrogen atom near to >C=N will be additional factor of stability.

**Applications of Schiff bases and transition Metal Complexes**

The transition metal complexes find extensive application in technology, industry and medicine. There has been an upsurge of research in the area of catalysis by transition metal complexes since 1940’s. The demand for cheaper and more efficient process in the industry resulted in the rapid development of newer process technologies relevant to industrial scale reactions for the production of organic compounds using transition metal complexes as catalysts. A great number of soluble metal complexes are now being employed in industry as catalyst for preparation of variety of useful compounds. Platinum complexes containing diphosphine and other chelating agent containing asymmetric carbon atoms have found a place in the chemical industry as stereo specific catalysts. Some of them give products with high degree of specificity. This is important in the manufacture of some drugs. For example, laevodihydroxy phenyl alanine is used in the treatment of Parkinson’s disease. It is known that the Zeigler catalyst, a complex
aluminium and titanium is used for the low pressure polymerization of ethylene, which makes thousands of polythene articles.

The chelate metal complexes are a strong candidate as organic electroluminescent materials. The chelate metal complexes such as tris (8-hydroxy quinolinate) aluminium have excellent electroluminescent properties and used in the fabrication of electroluminescent devices\textsuperscript{13}. Transition metal complexes with low lying excited states are finding increasing use as photosensitizers. Major work horse is those derived from poly pyridine complexes and metallo porphyrins. With help of suitable molecular engineering, the metal complexes readily attached to the surface of mesoporous membranes type films. These films with anchored complexes are finding increasing use in energy conversion devices such as dye sensitized photo electrochemical solar cells, intercalation batteries, optical display and optical sensors\textsuperscript{14}.

Recently much interest has been paid to the rapid thermal decomposition of metal complexes based molecular precursors to create metals and metal oxides\textsuperscript{15}. Metal complexes with pyruvic acid oxime were studied as precursors to variety of nano metal oxides\textsuperscript{16-18}. Saravanan et al. had synthesised nano crystal of ZnO and ZnS by the thermal decomposition of cupferon complex\textsuperscript{19}.

Acid solutions are extensively used in the industries for manufacturing processes and other applications like acid pickling, acid cleaning, acid de-scaling and oil well acidifying. The use of acids leads the industrial pipe
lines and metal vessels to corrode and there by reducing the production and causing economical loss. Compounds containing functional groups with hetero atoms, which can donate lone pair of electrons, are found to be very efficient as inhibitors against metal corrosion in many environments. Many N-heterocyclic compounds with polar groups and or π electrons also act as efficient corrosion inhibitor in acidic solutions. Schiff base, an organic compound which has both these features combined in one molecule, will be potential inhibitor. Several Schiff bases have been previously reported as effective corrosion inhibitors for steel, copper and aluminum in acid mediums like hydrochloric acid, sulphuric acid, acetic acid, formic acid etc.\textsuperscript{20-31}

Epoxy resins are of considerable technological importance, as they form continuous phase that binds together many light weight, tough composite materials. In order to convert epoxy resins from liquid or semi-solid monomers into hard, infusible thermoset networks it is necessary to use cross-linking agents. Epoxy resins once cured, are thermoset polymers and tend to be both stiff and brittle and require some degree of modification to achieve acceptable physical properties in the processed resins. Use of metal containing epoxy polymers allow the possibility of producing epoxy polymers with good mechanical properties and high thermal stability as well as achieving low processing temperatures. Extensive work has been carried out, over the last thirty years, into the use of metals and their salts in the formulation of epoxy resin systems. Organo–transition metal complexes have
also been added to improve physical properties such as adhesion, flexural strength, fracture toughness, water adsorption and heat resistance. Hamerton in his review publication demonstrates the use of transition metal complexes for improving physical properties such as viscosity or fracture toughness and electrical, thermal and chemical properties of epoxy resins\textsuperscript{32}. Transition metal complexes containing acetyl acetonate ligands have been extensively used for the modification of different type of epoxy resins\textsuperscript{33-35}. Several reports have been published in which coordination compounds containing acrylate\textsuperscript{36}, imidazole\textsuperscript{37,38} and thalocyanine ligands\textsuperscript{39} were extensively used as catalysts or epoxy modifiers for resins to improve their final properties. Coordination compounds containing Schiff base ligands were also used for the curing of the epoxy resins. Chantarasiri and co-workers have developed tetradendate and hexadendate Schiff base having bisphenol structure and used their metal complexes as cross linking agents for BADGE-type epoxy resins. It was observed that the introduction of the Schiff base metal complexes into the BADGE network gave good thermal stability\textsuperscript{40,41}.

Considerable interest has been shown in the synthesis and study of molecular complexes which may behave like semiconducting materials. Intense work has been done to prepare and develop new inorganic complexes which show semiconducting properties. Several reports published in which the electrical conductivities of the metal complexes and ligands and their
temperature dependence were studied. It was found that many of the complexes shown typical semiconductor property\textsuperscript{42-46}.

A number of cobalt complexes are used as driers for the conversion of liquids to solids and in inks, paints, varnishes and other surface coatings. The most important among them are cobalt soaps, which are complexes of carboxylate anions such as oleate, stearate, naphthenate, octanoate etc. Cobalt octanoates and naphthenates have been investigated as driers for linseed oil on paper\textsuperscript{47}. Both bis(acetylacetonato)cobalt(II) and tris(acetylacetonato)cobalt(III) have been found to possess fungicidal activity\textsuperscript{48}. Besides, bis(salicylaldehyde)diimine complexes of cobalt take up and release molecular oxygen and are used in the purification of oxygen\textsuperscript{49}. Cobalt complexes find various applications as additives for polymers. Thus cobalt phthalocyanines act as smoke retardants for styrene polymers. Bis(acetylacetonato)cobalt(II) in the presence of triphenyl phosphate has been found to act as an antioxidant for polyenes. Azides of cobaltamines have been suggested as detonators.

Nickel complexes are used in heterogeneous catalysis, electroplating, and in making pigments and ceramics. The Ni(II) complex of benzoic acid derivative acts as a stabilizer against oxidation of polybutadiene\textsuperscript{50}. A number of nickel complexes of Schiff bases have been seen to possess fungicidal and bacterial activity. Nickel complex of N-benzoyl-N’-(2-amino phenyl)thiocarbamide has been shown to exhibit antifungal activity. The organisms ‘Pyricularia oryzae’ which cause rice blast and ‘Helmithosporium oryzae’
which cause brown leaf spot can be controlled with Ni(II) complexes of 1-phenyl-3-methyl-4-nitroso-2-pyrazolin-5-one and 3-methyl-4-nitroso-2-pyrazo-lin-5-one\textsuperscript{51}.

The applications of copper complexes are extremely varied and of great importance. Copper complexes are widely used as polymer additives, fungicides and crop protectors. They are also used in antifouling paints and as fungicides for textiles\textsuperscript{52}. Bis(acetylacetonato)copper(II) has been used as a source of copper in copper–vapour\textsuperscript{53} lasers and it has also been investigated as a substitute for silver iodide as an ice–nucleating agent for the initiation of rainfall\textsuperscript{54}. Copper phthalocyanine is more effective as smoke retardant for polystyrene than such complexes of other first row transition metals. Bis(acetylacetonato)copper(II) is employed in the protection of fabrics against fungicidal attack. Copper complexes of ligand N-benzoyl-N’-(2-aminophenyl)thiocarbamide are found to be effective fungicides for \textit{Aspergillus niger}, \textit{Fusarium oxysporium} and \textit{Helminthosporium oryzae}\textsuperscript{51}. Copper complexes are reported to be more active fungicides than similar iron, cobalt and nickel complexes. The complexes were found to be more effective than the free ligands\textsuperscript{55}.

Coordination compounds are widely used for the estimation and separation of metal ions. Dimethylglyoxime, 8-hydroxyl quinoline, oxidation-reduction indicators such as ferroin, volumetric reagent EDTA etc. are examples for such compounds. The role of coordination compounds in
colorimetric, spectrophotometric and polarographic analysis is also significant.

Complexes of alkali, alkaline earth and noble metals have found use in the treatment of diseases. For example, gold compounds are used in the treatment of arthritis and platinum compounds for some cancer. Complexes of alkali and alkaline earth metals with crown ethers and other cyclic ligands play important biological roles. Chelating agents in connection with cation exchange resin and solvent extraction have been particularly useful in the separation of radioactive metal. One of the general methods used for water softening is the effective removal of ions from solution by the formation of soluble complexes. Chemotherapy and chelation therapy using metals have now drawn attention as additional outlet for coordination chemistry. The classical example is the use of D-Pencillamine to treat Wilson’s disease, which is caused by the inability of body to metabolize copper in the normal way. Another example is the use of desferrioxamine for the iron overload in Cooley’s anemia, which is caused by the fault in hemoglobin synthesis. Heavy metal poisons can be removed from the body by the use of complexing, chelating or sequestering agents. In various imaging techniques, coordination complexes are used so that they transport metal to specific sites in the body. For example technetium complexes are used in radio imaging. In nmr imaging, paramagnetic complexes are used so that they go to specific sites in the body and improve the contrast\textsuperscript{56,57}. Biological significance of the
azomethine group has never been doubt. Major biochemical interest in Schiff base compounds stems from their ability in designing metal containing model systems, which mimic biologically active systems\textsuperscript{58}.

Metal chelates of Schiff bases hold exciting possibilities for the future, particularly in designing novel corrosion inhibitors, epoxy curing agents, semi conducting materials, catalytic systems, in formulating new synthetic routes and in developing new analytical, antifungal and antibacterial agents. Hopefully results of this investigation would attract increased interest in these fields.

**Review of metal complexes of Schiff bases derived from 2-amino phenol**

Schiff bases are an important class of ligands in coordination chemistry and find extensive applications in different spheres\textsuperscript{59,60}. Synthesis and characterisation of number of metal complexes of Schiff bases derived from aminophenols have been reported\textsuperscript{61,62}. Syamal et al.\textsuperscript{63} have characterised Fe(III) complexes of tridentate Schiff bases derived from simple or substituted salicylaldehyde and 2-aminophenol. Tez Can\textsuperscript{64} has prepared and characterised the complexes of transition metals, rare earth metals and main group metals with Schiff base salicylidene-2-aminophenol and salicylidene-2-hydroxy-1-naphthyl amine. Salam\textsuperscript{65} have synthesised Cu(II) and Ni(II) complexes of some dibasic tridentate Schiff bases prepared by condensation
of 2-aminophenol with 5-X-salicylaldehyde and 2-hydroxyl-1-naphthaldehyde. Syamal and Singh have carried out the synthesis and characterisation of Cu(II), Ni(II), Fe(III), Zn(II) and Cd(II) complexes of polystyrene supported resin containing Schiff base derived from 3-formyl salicylic acid and 2-aminophenol. Complexes of some metal ions with Schiff base ligands derived from isatin and 2-amino-phenol were synthesised and characterised via elemental analysis, IR, electronic spectral data, \(^1\)H NMR spectra, conductance and magnetic measurements.

Zelentsov reported the synthesis of new high spin Co(II) chelates with tetradendate Schiff base ligand obtained by condensing 2-aminophenol or 4-nitro-2-aminophenol with glyoxal or glutaricaldehyde. The complexes were characterised by spectral and other techniques. The synthesis and characterisation of Schiff bases from 2-aminophenol and crocetindialdehyde, 2, 7-dimethylocatatrienedial or terephthaldehyde were carried out by Fehn et al. Mayadevi synthesised and characterised new transition metal complexes of Schiff base quinoxaline-2-carboxalidene-2-aminophenol. A tetrahedral structure was assigned for the Mn(II), Co(II), Ni(II) and Cu(II) complexes. For the Fe(III) complex, an octahedral dimeric structure was suggested.

Schiff bases derived from salicylaldehyde and 2-aminophenol were synthesised and characterised by Naik and co-workers. Magnetic electronic spectral studies provide the evidence of the existence of octahedral geometry.
for the complexes. Chae et al.\textsuperscript{72} have prepared Schiff base ligands by the reaction of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with 2-amino phenol and 2-amino-p-cresol respectively. The structures and properties of ligands and their Co(II) complexes were studied by elemental analysis, \textsuperscript{1}H NMR, IR, UV-Visible spectra and TGA. The molar ratio of Schiff base to the metal of complexes is 1:1. Co(II) complexes have a hexacoordinated octahedral configuration. The redox process of ligands and complexes in DMSO solution were studied by cyclic voltammetry.

Mehta\textsuperscript{73} have synthesised Schiff bases derived from condensation of 2-hydroxy-1-naphthaldehyde and 2-amino phenol. The copper complex was characterised by elemental analysis, molar conductance, electronic absorption spectra, IR and ESR spectral data and magnetic susceptibility data. The application of ligands and copper complexes as antibacterial agents were carried out.

The synthesis of new coordination compounds of Cu(II), Ni(II), Co(II), Sn(II), Hg(II) etc. with Schiff bases derived from 7-formyl-8-hydroxy quinoline(oxine) and 2-aminophenol have been reported by Sonbati and Bindary\textsuperscript{74}. The ligands and the complexes were characterised by elemental analysis, IR, UV, EPR and NMR spectra together with magnetic susceptibility measurements. Infrared and NMR studies show that Schiff bases behave as monobasic and tridentate ligand, coordinating through the oxygen atom of
the deprotonated phenolic group, the nitrogen atom of the azomethine group and pyridine.

Saidul Islam\(^75\) reported the synthesis of mixed ligand transition metal complexes of Cu, Ni and Co ions with Schiff base ligands derived from the condensation of o-hydroxy benzaldehyde with amino phenols and nitrogen donor amine bases, like ethylenediamine, 2-aminopyridine, and o-phenylene diamine or thiocyanate. These complexes were characterised and their antibacterial, anti-fungal and toxicological activity have been evaluated.

Neutral complexes of Cu(II), Ni(II), Co(II), Mn(II), VO(IV) and Zn(II) have been synthesised from the Schiff bases derived from salicylidene-4-aminoantipyrine\(^76\) and 2-aminophenol and acetoacetanilido-4-amino antipyrine\(^77\) and 2-aminophenol. Complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn (II) and VO(II) have been prepared in ethanol using Schiff bases derived from acetoacetanilido-4-aminoantipyrine and 2-amino phenol.

Minu and co-workers reported the synthesis of ruthenium and lanthanide complexes of Schiff base N-(2-pyrrolymethylene)-2-amino-phenol\(^78\). All complexes were characterised by analytical and spectroscopic method. Three new Schiff base complexes \([\text{Ni(HL)}(L)](\text{ClO}_4)\cdot 0.16(\text{H}_2\text{O})\text{(1)}, [\text{ZnLZn(OOCCH}_3)_4\text{ZnL}]\text{ (2) and [Cd}_2\text{(L)}_2(\text{OCH}_3\text{CO})_2(\text{H}_2\text{O})_2]\text{ (3)}\) have been synthesised using the Schiff base ligand and the corresponding metal ions\(^79\). The Schiff base has been prepared by mixing pyridine-2-carboxaldehyde and 2-aminophenol and was isolated prior to the reaction with metal ions.
Complex 1 is mononuclear, 2 is trinuclear and 3 is diphenoxo-bridged dimer. 3 forms infinite 1D chains through hydrogen bonding interactions. Only 2 and 3 exhibit strong fluorescence emission bands at 635 and 630 nm, respectively.

**Review of metal complexes of Schiff bases derived from 2-aminothiophenol**

The NS donor systems incorporating into the Schiff base skeleton have attracted the interest of the researchers due to their pharmacological and physicochemical activities and have been widely studied. Schiff bases derived from o-aminothiophenol and various aldehydes, ketones, and their complexes have been extensively reviewed\(^ {61,62}\). Characterisation of transition metal complexes of Schiff base derived from 2-aminothiophenol and pyridine-2 aldehyde have been reported by Mehta et al\(^ {80}\). The spectral data and magnetic measurements suggest that these complexes have planar configuration. Cu(II), Ni(II), Cu(II) and Zn(II) complexes of the Schiff bases derived from 2-formyl cyclohexanone and 2-aminothiophenol were reported\(^ {81}\). IR and \(^1\)H NMR data show that while the free ligands exist in the ketamine form, in the complexes, they exist in the enamine form. The subnormal magnetic moments of Cu(II) complexes were ascribed to antiferromagnetic interaction arising from dimerization. Metal complexes of heterocyclic Schiff bases derived from 2-acetyl thiophene and 2-aminothiophenol were prepared
by Varsheny and Ambwani\textsuperscript{82}. Serial dilution method was used to evaluate antimicrobial activity against two bacteria, \textit{staphylococcus aureus} and \textit{E. Coli} and two fungi, \textit{Aspergillus niger} and \textit{Candida albicans}.

Synthesis, characterisation and antimicrobial activities of some Pd(II) complexes of ethylidene aminothiophenol having NS donor sets are reported by Nighet and Singh\textsuperscript{83}. Ruthenium(II) and oxovanadium(IV) complexes of highly conjugated Schiff base derived from diketones and 2-aminothiophenol were reported\textsuperscript{84}. The subnormal magnetic moments and hyperfine splitting of these complexes were ascribed to an antiferromagnetic exchange interaction arising from dimerization.

Bouwman et al.\textsuperscript{85} synthesised and characterised nickel complexes of 2-aminothiophenol and 2-tert-butyl thiobenzaldehyde. The benzathiozolidine ring opens upon reaction with nickel acetate in ethanol to form a mononuclear complex. Soliman\textsuperscript{86} synthesised new transition metal chelate of 3-methoxy salicylidene-2-aminothiophenol Schiff base and found that Schiff base coordinated as a tridentate ligand with ONS donors derived from the phenolic O, azomethine N and thiophenolic S. The thermal decomposition of the complexes was found to follow first order kinetics. The preparation and characterisation of complexes of Schiff base salicylidene-2-amino thiophenol and some neutral ligand with manganese, cobalt and zinc(II) have been reported\textsuperscript{87}. All the complexes except the complexes of Zn(II) are paramagnetic.
Neutral complexes of Cu(II), Ni(II), Co(II), Mn(II), VO(IV) and Zn(II) have been synthesised from the Schiff bases derived from salicylidene-4-aminoantipyrine and 2-aminothiophenol\(^{76}\). All of the complexes exhibit square-planar geometry except the Mn(II) and VO(IV) complexes. The Mn(II) chelates show an octahedral environment and the VO(IV) chelates exist in a square-pyramidal geometry. The reactivity studies of \([\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)(\text{phen})_2-(\text{CH}_3\text{CN})_2][\text{PF}_6]_2\) with the model ligand 2-aminothiophenol were reported\(^{88}\). The main finding of this study is that \([\text{Rh}_2(\mu\text{O}_2\text{CCH}_3)(\text{phen})_2]^{2+}\) reacts with 2-aminothiophenol to form a stable Rh(III) compound in the presence of O\(_2\). The ligand 2-aminothiophenol was used as a model for the chemistry of reactive thiol groups such as those found in amino acids and glutathione. Eikey\(^{89}\) have been carried out a detailed review of the synthesis and reactivities of Groups 6, 7, and 8 metal complexes of 2-aminothiophenol until August 2002. In this report general description of the bonding and reactivity of transition metal nitrido and imido complexes followed by a discussion of the common synthetic routes were done.

Complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and VO(II) have been prepared in ethanol using Schiff bases derived from acetoacetanilido-4-aminoantipyrine and 2-aminothiophenol\(^{77}\). Micro analytical data, magnetic susceptibility, spectral techniques were used to confirm the structures of the chelates. The \textit{in vitro} antimicrobial activity of the investigated compounds was tested against the microorganisms. A bis(phenol-armed) acyclic Schiff
base ligand H$_2$L has been synthesised from 3,6-diformylpyridazine and two equivalents of o-aminothiophenol. The ligand H$_2$L has been structurally characterised and is shown to be close to planar with both intramolecular and intermolecular hydrogen bonding interactions present. Three complexes of Co, Ni, and Cu with the ligand have been prepared and characterised$^{90}$.

The ternary complexes of Cu(II) with salicylidene-2-amino thiophenol and glycine, alanine, valine and histidine amino acids have been studied in solution and in solid state by Soliman$^{91}$. The complexes were found to have the formula [M(L)(AA)] and five coordinated square bi-pyramidal distorted trigonal bipyramidal geometry. The thermal stability of the complexes was studied and the weight losses were correlated with the mass fragmentation pattern.

Ruthenium complexes of Schiff base salicylideneimine-2-thiophenol were reported by Khalill and co-workers$^{92}$. UV-VIS spectra of the two complexes in different solvents exhibited visible bands due to metal-to-ligand charge transfer. Electrochemical investigation of the free ligand and complexes showed some cathodic and anodic irreversible peaks due to interconversions through electron transfer. Oxovanadium(IV) complexes with Schiff base ligand, salicylidene-o–aminothiophenol, have been synthesised and characterised by Pragnesh et al.$^{93}$ Spectral studies indicate that the oxovanadium(IV) complexes assume a six-coordinate octahedral geometry. The antibacterial activities of the complexes against *Salmonella typhi*,
*Escherichia coli* and *Serratia mercescens* are higher as compared to the free ligands.

Spectroscopic and electrochemical studies of transition metal complexes of Schiff base derived from 1,7-bis(2-formylphenyl)-1,4,7-tri oxaheptane and 2-aminothiophenol were reported\(^9^4\). It was found that the ligand can effectively be used in solvent extraction of Cu(II) and Ni(II) from the aqueous phase to the organic phase.

**Review of metal complexes of Schiff bases of semicarbazone**

The chemistry of transition metal complexes of semicarbazones has been receiving considerable attention largely because of their special properties. According to the IUPAC recommendations\(^9^5\) for the nomenclature of organic compounds, derivatives of semicarbazide of the types R-CH=N-NH-CO-NH\(_2\) and R\(^1\)R\(^2\)C=N-NH-CO-NH\(_2\), which are usually obtained by condensation of semicarbazide with suitable aldehydes and ketones, may be named by adding the class name ‘semicarbazone’ after the name of the condensed aldehydes RCHO or ketone RR'C=O. It is usual also to include in this class derivatives with substituents on the amide or thio amide nitrogen, R\(^1\)R\(^2\)C=N-NH-CX-NR\(^3\)R\(^4\) on the X atom, R\(^1\)R\(^2\)C=N-N=CX R\(^3\)-NH\(_2\) or on the ‘hydrazinic’ nitrogen R\(^1\)R\(^2\)C=N-NR\(^3\)-CX-NH\(_2\).

These classes of compounds usually react with metallic cations giving complexes in which semicarbazones behave as chelating ligands. Research
on the coordination chemistry\textsuperscript{96}, analytical applications\textsuperscript{97} and biological activities\textsuperscript{98} of these complexes has increased steadily for many years. Cambridge structural database reveals that a thousand papers related to semicarbazones were published in the last decade\textsuperscript{99}.

Casas\textsuperscript{100} have conducted a detailed review of the structural aspects of the complexes formed by semicarbazones with metallic elements of group 12, 13, 14 and 15 up to year 1998. This paper elaborately explains about the nature of the metal-to-ligand bonds and the coordination behaviour of the ligand.

Potent cytotoxic Cu(II) complexes of furannic semicarbazones like 2-furfuralsemicarbazone, 5-methyl-2-furfuralsemicarbazone, 2-furfural-4-phenyl semicarbazone and 3-(2-furyl)prop-2-enalsemicarbazone were prepared by Ibrahim et al\textsuperscript{101}. The stability constants were calculated and a relation between stability and molecular weight of the ligands were proposed. Kasuga\textsuperscript{102} synthesised and structurally characterised 4-and 6-coordinate Ni(II) complexes of three semicarbazone ligands. Their antimicrobial activities were evaluated by the MIC against four bacteria (\textit{B. subtilis}, \textit{S. aureus}, \textit{E. coli} and \textit{P. aeruginosa}), two yeasts (\textit{C. albicans} and \textit{S. cerevisiae}) and two molds (\textit{A. niger} and \textit{P. citrinum}). The structure–activity correlation in this series of Ni(II) complexes was discussed based on their ligand-replacement abilities. The Cu(II) complexes of the Schiff base salicylaldehyde semicarbazone have been prepared and structurally characterised by Patole\textsuperscript{103}. They proposed that
compound shows a distorted square planar geometry where the metal atom lies slightly below the ligand donor atom plane and exhibits a longer Cu–Cl bond distance (2.226 Å). It was observed that the superoxide dismutase activity of the compound can be synergistically enhanced by the addition of heterocyclic bases. Complexes of semicarbazone of starch dialdehyde with Ca(II), Cd(II), Co(II), Cu(II), Fe(II), Mg(II), Mn(II), Ni(II), Pb(II) and Zn(II) were reported. The spectral characterisation showed that the carbonyl oxygen atoms and the C=N nitrogen atoms of the semicarbazone are involved in chelation of the metal atoms.

Lee investigated Cu(II) complexes containing a series of salicylaldehyde semicarbazone ligands using physicochemical techniques. The X-ray structure of copper complex of salicylaldehyde-N,N-dibenzyl semicarbazone shows that the complex is monomeric and the copper atom is four coordinated in a distorted square planar geometry. Twelve Zn(II) complexes with semicarbazone ligands were reported. Seven three-dimensional structures of Zn(II) complexes were determined by single-crystal X-ray analysis. Their antimicrobial activities were evaluated by MIC against four bacteria, two yeasts and two molds.

Cu(II) and Ni(II) complexes of new Schiff base ligand 2-acetyl-2-thiazoline semicarbazone were synthesised and characterised by physical measurements and crystal structures determined with help of X-ray technique. The geometry around the metallic atoms is described as a
distorted square-pyramid for the copper complex and as a distorted octahedron for the nickel complex. 2-benzoylpyridine semicarbazone and its Cu(II) and Zn(II) complexes were reported by Rebolledo$^{108}$. In both cases, the neutral semicarbazone acts as a tridentate ligand which coordinates the metal through the pyridine and imine nitrogen atoms and the carbonyl oxygen.

Leovac$^{109}$ carried out the synthesis and physicochemical characterisation of Ni(II) complexes of pyridoxal semicarbazone. Spectral studies on Co(II), Ni(II) and Cu(II) high-spin type complexes with semicarbazone derived from 2-acetylfuran were conducted by Chandra et al.$^{110}$ and different geometries were assigned to each complex. Cu(II) complexes of 2-hydroxyacetophenone-N(4)-phenyl semicarbazone were studied by Kala$^{111}$.

**Review of metal complexes of Schiff bases of thiosemicarbazone**

Thiosemicarbazones which comprise a well known group of NS donors have been extensively used for complex formation in the recent past and are widely employed in medical science$^{112}$. A number of reviews on various aspects of the thiosemicarbazones have been published$^{100,113-115}$. In this section, emphasis is given for the synthetic, physicochemical and structural aspects of the metal complexes of thiosemicarbazones.
Thiosemicarbazone are prepared through the condensation, between aliphatic, aromatic or heterocyclic carbonyl compounds and thiosemicarbazide. Neutral cationic or anionic complexes can be formed from thiosemicarbazones because of its existence in two tautomeric forms such as thione (I) and thiol (II) forms.

![Thiosemicarbazone](image)

When the thiosemicarbazone exist in cis-configuration, it forms stable five membered rings with metal ion during the complex formation, by coordinating through the azomethine nitrogen and thioketosulfur atoms. Some times they exist in trans configuration and the bonding is through sulphur atom alone i.e. it acts as a monodendate.

Ferrari reported synthesis and characterisation of several new transition metal complexes with novel ligands like pyridoxal thiosemicarbazone, 5-formyluracil thiosemicarbazone, p-fluorobenzaldehyde thiosemicarbazones, methyl pyruvate thiosemicarbazone, α-keto glutaricacid thiosemicarbazone and 1-methylisatin-3-thiosemicarbazone.

Duran and co-workers electrochemically synthesised and structurally characterised the binuclear complex bis(1-phenylglyoxalbis(3-...
piperidyl thiosemicarbazone)zinc(II). Diaz et al.\textsuperscript{126} carried out EPR characterisation of Cu(II) complexes of acetaldehyde thiosemicarbazone, pyruvic acid thiosemicarbazone and ribose bis-thiosemicarbazone at room temperature and low temperature. Computer simulation of the EPR spectra has revealed differences in the magnetic parameters of the compound. Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with a new Schiff base vitamin K\textsubscript{3}-thiosemicarbazone was synthesised, characterised and antibacterial activity determined by Li\textsuperscript{127}. In all the complexes, the ligand coordinates through sulfur and oxygen atoms, and the geometry around metal atom is best described as octahedral.

West and his co-workers have been reported numerous new ligands and their transition metal complexes. The newly synthesised ligands were 2-pyridineformamide-N(4)-methylthiosemicarbazone\textsuperscript{128}, 2-pyridineformamide-3-piperidyl thiosemicarbazone\textsuperscript{129}, acetone-3-hexamethyleneiminyl thiosemicarbazone\textsuperscript{130}, pyrazineformamide-N(4)-methyl thiosemicarbazone\textsuperscript{131} and 5-methyl-2-hydroxyacetophenone N(4)-substituted thiosemicarbazones\textsuperscript{132}. The ligands and complexes were characterised by molar conductivities, magnetic susceptibilities and spectroscopic and X-ray techniques.

The synthesis of three bis(thiosemicarbazone) compounds formed by the reaction of benzil with either thiosemicarbazide, 4-methyl-3-thiosemicarbazide or 4-phenyl-3-thiosemicarbazide were reported by Alsop et al\textsuperscript{133}. Sharma prepared novel complexes of Cu(II) derived from 5-
nitrofuran-2-carboxaldehyde thiosemicarbazones and characterised using spectroscopic techniques. These copper complexes are bidentate and possess octahedral geometry around Cu(II) ion. Ni(II) complexes of ortho-naphthaquinone thiosemicarbazone were synthesised and spectroscopically characterised by Afrasiabi. The X-ray crystal structure and in vitro anticancer studies were also carried out.

A variety of thiosemicarbazones 2-benzoylpyridine N(4), N(4)-(butane-1,4-diyl)thiosemicarbazone, di-2-pyridylketone N(4), N(4)-(butane-1,4-diyl)thiosemicarbazone, 2-benzoylpyridineN(4)-phenylthiosemicarbazone, N(4)-phenylthiosemicarbazone and salicylaldehyde N(4)-cyclohexyl thiosemicarbazone were synthesised and their transition metal complexes were reported by Kurup et al. The metal complexes were characterised using conventional techniques. The antibacterial properties of some of them were investigated.

Zn(II) complexes derived from pyridine-2-carbaldehyde thiosemicarbazone and (1E)-1-pyridin-2-ylethan-1-onethiosemicarbazone were synthesised and characterised using spectral and XRD techniques by Demertz. The antiproliferative activity of Zn(II) complexes were also studied. Leovac describes the synthesis of Ni(II) complexes with Schiff base pyridoxal semicarbazone and proposed that Schiff bases are coordinated as tridentate ligands with an ONX set of donor atoms. Ni(II) complexes of picolinaldehyde N-oxide thiosemicarbazone were synthesised and
characterised by single crystal X-ray diffraction, IR, and thermal analysis by Yu-Qing\textsuperscript{142}. The antimicrobial activities of complex were also evaluated. Ni(II) complexes of 5-methyl-2-furfuraldehyde thiosemicarbazone were prepared and structural and biological activities were determined by Jouad\textsuperscript{143}.

Chandra reported Co(II), Mn(II), Co(II) and Ni(II) complexes with new ligands like indoxyl thiosemicarbazone\textsuperscript{144,145}, 2-methylcyclohexanone thiosemicarbazone and 2-methylcyclohexanone-4N-methyl-3-thiosemicarbazone\textsuperscript{146}. A new macrocyclic Schiff base (1,2,5,6,8,11-hexaazacyclododeca-7,12-dithione-2,4,8,10-tetraene) containing thiosemicarbazone moiety was also synthesised and its Cu(II) and Ni(II) complexes were reported\textsuperscript{147}. The complexes were characterised on the basis of elemental analysis, molar conductance, magnetic susceptibility, IR, electronic, \textsuperscript{1}H NMR, mass and EPR spectral studies. The geometry of the complexes was also described.

Very few reports are available for the metal complexes of furoin based ligands. Mehta\textsuperscript{148} has reported the synthesis and characterisation of transition metal complexes of 2-furoinoxime. A new Schiff base formed by the condensation of the S-benzyldithiocarbazate and furoin was reported by Mahmoud\textsuperscript{149}. Cu, Ni, Cd, Co and Pd complexes of the above Schiff base were prepared and characterised by conventional methods. Daoud\textsuperscript{150} prepared silicon and organosilicon derivatives of furoin, benzoin and pyridine. They have proposed a chelating structures for the resulting derivatives in which ligands acted as bidendate.
Scope of present investigation

It becomes evident from the above review that much systematic investigation has already been on metal complexes of Schiff bases derived from 2-aminophenol, 2-aminothiophenol, semicarbazone and thiosemicarbazone on various aldehydes and ketones. However no work has been reported on metal complexes of furoin-2-aminothiophenol, furoin-2-aminophenol, and furoin thiosemicarbazone and furoin semicarbazone. The observation is that many such ligands and their metal complexes have ample applications and demand detailed investigation. In the present investigation, the focus is mainly on the metal complexes of Schiff bases mentioned above. The metal complexes of these Schiff bases with transition metal ions like Co(II), Ni(II), Cu(II) and Zn(II) have been synthesised and characterised by various physicochemical methods. The thermal decomposition of the representative complexes have been studied by thermogravimetric technique so as to understand the thermal stabilities and their decomposition pattern. Crystalline states of selected complexes were established by indexing its X-ray powder diffraction pattern. To find out some potential application of the new ligands and complexes, the corrosion inhibition efficiency of the four new Schiff base ligands as well as the solid state electrical conductivity were also envisaged.
CHAPTER 2
MATERIALS, METHODS AND INSTRUMENTS

In this chapter, a brief description of the general reagents employed for the present study and purification procedures adopted wherever necessary are described. It also gives details of the analytical and physical methods used for the characterisation of ligands and complexes synthesised.

Materials

Analar grade metal acetates were used as source of metal for synthesis of the complexes. For preparation of ligands, analar grade samples of furnoin from Sigma Aldrich and other chemicals 2-aminothiophenol, 2-aminophenol, and thiosemicarbazide and semicarbazide hydrochloride from E-Merck were used. The solvents were purified by standard procedures. All the reagents such as perchloric acid, nitric acid, hydrochloric acid, sulphuric acid, ammonia and sodium acetate used in the present investigation were of analar grade. The procedure for the preparation of ligands and complexes are given in the following chapters of part I of this thesis.
Analytical methods

C H N S analysis

Carbon, hydrogen nitrogen and sulphur content of the ligands and their metal complexes were determined by microanalysis using Elementar make Vario EL III model CHNS analyzer.

Estimation of metals

The standard methods\textsuperscript{152} were adopted for the estimation of metal content in the complexes. The metal content of the complex was estimated volumetrically after decomposing the complexes with a mixture of nitric, hydrochloric and perchloric acids. For this a known amount of complex (0.2-0.3g) was digested with concentrated nitric acid perchloric acid mixture followed by concentrated HCl. The digestion process was repeated three times by adding fresh amounts of hydrochloric acid. The resultant solution was then quantitatively made up to 100 ml. The metal content in the complex was estimated using a definite volume of this solution.

Amount of copper was determined iodometrically by the addition of KI and subsequent titration of liberated iodine by standard sodium thiosulphate. Cobalt and Zinc was estimated volumetrically by complexometric titration using standard EDTA with Erichromeblack–T as indicator. Gravimetrically, nickel was estimated by precipitating as dimethyl glyoxymate.
Metal content in the metal complexes were also estimated by pyrolysis method. About 0.2g complex was weighed out in a silica crucible and heated strongly. During heating, all the organic particles in the chelate were burnt off and the metal oxide left behind was weighed. From the weight of the metal oxide, the metal percentage was calculated.

**Experimental Techniques**

Physicochemical techniques such as solution conductance, magnetic susceptibility measurements and spectral studies like UV-Visible and IR have been used to elucidate the structure and geometry of the complexes. Thermogravimetric and X-ray diffraction studies have also been carried out.

**Molar conductance measurements**

Molar conductance of the approximately $10^{-3}$M solutions of the complexes was carried out using a Philips conductivity bridge at $28 \pm 2^\circ$C.

**Magnetic measurements**

Magnetic susceptibilities of the complexes were determined at room temperature by Gouy method using Hg[Co(NCS)$_4$] as calibrant$^{153}$. Diamagnetic corrections were applied using Pascal constants taking into consideration the magnetic contribution of various atoms and structural units$^{154,155}$. The effective magnetic moments were calculated from the corrected susceptibilities using the equation.
\[ \mu_{\text{eff}} = 2.84\sqrt{\psi'_M . T} \quad (1) \]

where \( \psi'_M \) is the molar susceptibility corrected diamagnetism and \( T \) is the absolute temperature. The theoretical magnetic moments were calculated using the formula

\[ \mu_{\text{eff}} = g \sqrt{S(S+1)} \quad (2) \]

**Infrared Spectra**

The infrared spectra of the ligands and metal complexes were recorded using KBr disc technique in the range 4000-400\,cm\(^{-1}\) on a Thermonicolet Avatar make 370 DTGS model FT-IR Spectrophotometer. The importance of IR spectroscopy lies in the fact that characteristic infrared absorption of a group occurs at about the same frequency irrespective of the molecule in which the group is present.

**Electronic spectra**

The UV-Visible spectra of the ligands and complexes were recorded on a Carry UV-Visible Spectrophotometer using DMSO as solvent. Electronic spectral studies were carried out mainly in a structural diagnostic perspective so as to supplement any information obtained from magnetic studies.
Thermo gravimetric analysis

Thermograms of the complexes were recorded on a Perkin Elmer make Pyris diamond model thermal analyzer in air or oxygen atmosphere at a heating rate of 10 or 15°C/ m. Each mass loss consideration from the TG plot can be assigned to the decomposition or volatilization of a particular group.

Powder X-ray diffraction technique

The X-ray powder diffraction pattern of the complexes and ligands was recorded on AXS Bruker Germany make D 5005 model powder X-ray diffractometer with copper Kα radiation.

Instruments

The following instruments have been used for the present investigation

1. Elementar make Vario EL III model CHNS analyzer
2. Philips make conductivity bridge
3. Gouy Type magnetic balance
4. Thermonicolet Avatar make 370 DTGS model FT-IR Spectrophotometer
5. Carry make UV-VIS Spectrophotometer
6. Perkin Elmer make Pyris diamond model thermal analyzer
7. AXS Bruker make D 5005 model powder X-ray diffractometer.
CHAPTER 3
STUDIES ON Co(II), Ni(II), Cu(II) AND Zn(II) COMPLEXES OF FUROIN-2-AMINOTHIOPHENOL (FATP)

Furoin-2-aminothiophenol (FATP) a potential tridentate Schiff base ligand has been synthesised for the first time. This ligand forms a variety of complexes with various transition metals. Detailed investigation on synthetic and structural aspects of metal complexes derived from furoin and 2-aminothiophenol are rare. In this chapter, therefore, the results of a brief study of the coordination compounds of Schiff base derived from furoin and 2-aminothiophenol are discussed.

Preparation of furoin-2-aminothiophenol

An ethanolic solution of furoin (2.88g, 0.015mol) was mixed with a solution of 2-aminothiophenol (1.87g, 0.015 mol) in hot ethanol and refluxed for four hours on a water bath. The resulting solution was concentrated and cooled in an ice bath. The precipitate formed was collected through filtration using a vacuum pump and washed with ethanol and dried over anhydrous CaCl₂. The melting point of FATP was found to be 115°C.
Characterisation of the ligand

The ligand FATP was characterised on the basis of elemental analysis and spectral data. The analytical data obtained are shown in the table 1.3.1 and were found to be in agreement with the empirical formula for FATP. The UV and IR spectra of the ligand showed the characteristic bands. Based on the above results, the structure of the ligand FATP was confirmed and shown in the figure 1.3.1.

Table 1.3.1 Analytical data for the ligand FATP

<table>
<thead>
<tr>
<th></th>
<th>FATP</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
<th>S %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found</td>
<td></td>
<td>63.85</td>
<td>4.30</td>
<td>4.32</td>
<td>9.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>64.14</td>
<td>5.01</td>
<td>4.68</td>
<td>10.71</td>
</tr>
</tbody>
</table>

Figure 1.3.1 Structure of Schiff base furoin-2-aminothiophenol
Synthesis of complexes

Co(II), Ni(II), Cu(II) and Zn(II) complexes of FATP were prepared by mixing ethanolic solutions of metal acetate (0.005mol), 2-amino thiophenol (0.005mol) and furoin (0.005mol) in the presence of sodium acetate (1g). The resulting solution was refluxed for about 3-4 hours, concentrated and kept overnight in an ice bath. The complex formed was filtered using a vacuum pump and washed with ethanol, chloroform and ether, dried in a desiccator over anhydrous calcium chloride. In the preparation of Cu(II) complex, sodium acetate was not added.

Characterisation of the complexes

The complexes were characterised on the basis of elemental analysis, magnetic measurements, electronic and infrared spectral data, conductance measurements, thermal analysis and X-ray diffraction data.

Results and discussion

The complexes are coloured, non hygroscopic solids and are air and photo stable. They are insoluble in water but slightly soluble in organic solvents like ethanol, methanol and completely soluble in DMSO.

Elemental analysis

The complexes were analyzed for metal and sulphur content by standard methods. Percentage of carbon, hydrogen and nitrogen was
determined by microanalytical methods. The results are summerised in table 1.3.2.

**Molar conductance**

It is observed that the molar conductance values of the complexes in DMSO at a concentration of $10^{-3}$M at room temperature are in the range of 4-12 ohm$^{-1}$cm$^2$ mol$^{-1}$. The very low values indicate that these complexes behave as non electrolytes in DMSO and are neutral in nature.$^{156}$

**Magnetic measurements**

The values of the magnetic moments of the complexes are tabulated in table 1.3.2. The Co(II) complex possess magnetic moment of 4.90 BM. It is reported that an octahedral geometry can be assigned to Co(II) complexes, if the measured $\mu_{\text{eff}}$ value is in the range of 4.3-5.2 BM.$^{157}$ Ni(II) complex exhibited magnetic moment values of 3.20 BM which suggests an octahedral arrangement around the metal ion. The magnetic moment values of Cu(II) complex is 1.84 BM as expected for an octahedral geometry which corresponds to a d$^9$ configuration with one unpaired electron.$^{158,159}$ Zn(II) complex was found to be diamagnetic.
Table 1.3.2 Microanalytical, magnetic and conductance data of transition metal complexes of furoin-2-aminothiophenol

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>M%</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>S%</th>
<th>µ_{eff} (BM)</th>
<th>Ω^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(FATP) (H₂O)₃]</td>
<td>Purple</td>
<td>14.69</td>
<td>(14.36)</td>
<td>46.88</td>
<td>(46.80)</td>
<td>4.91</td>
<td>(5.12)</td>
<td>3.48</td>
</tr>
<tr>
<td>[Ni(FATP) (H₂O)₃]</td>
<td>Greenish yellow</td>
<td>13.95</td>
<td>(14.19)</td>
<td>45.90</td>
<td>(46.82)</td>
<td>3.77</td>
<td>(3.65)</td>
<td>3.85</td>
</tr>
<tr>
<td>[Cu(FATP) (H₂O)₃]</td>
<td>Black</td>
<td>16.25</td>
<td>(15.40)</td>
<td>47.75</td>
<td>(46.27)</td>
<td>4.75</td>
<td>(5.06)</td>
<td>3.41</td>
</tr>
<tr>
<td>[Zn(FATP) (H₂O)₃]</td>
<td>Greenish yellow</td>
<td>15.38</td>
<td>(15.75)</td>
<td>47.48</td>
<td>(46.07)</td>
<td>4.00</td>
<td>(4.56)</td>
<td>3.36</td>
</tr>
</tbody>
</table>

D- Diamagnetic, M- Metal, Ω^{-1}- Molar conductance in ohm^{-1} cm^{2} mol^{-1}. Calculated values are given in parenthesis.
Infrared spectral studies

The infrared spectroscopic results provide support for the molecular constitution of these complexes. The assignments are made on the basis of comparison with the spectra of similar type of compounds. A representative IR spectrum of the ligand FATP and its Cu(II) complex are given as figures 1.3.2 and 1.3.3 respectively. The selected infrared absorption frequencies of the ligand and complexes are given in the table 1.3.3

Figure 1.3.2 IR spectrum of the ligand FATP
On complex formation most of the bands in the IR spectrum of the ligand FATP undergo frequency shift and in many cases intensity changes. A strong intense band approximately at 1676 cm$^{-1}$ in the spectrum of the ligand may be assigned to $\nu$C=N stretch. This band shows a downward shift by about 25-35 cm$^{-1}$ in the spectra of all the metal complexes, indicating the participation of the azomethine nitrogen in coordination with metals$^{160}$. The depression in stretching frequency may tentatively attributed to a lowering of the C=N bond order as a result of the M-N bond formation in the complexes$^{161}$. The shifted band in many cases is coincident with the C=C band, which then shows greater intensity or broadening. Further evidence for

Figure 1.3.3 IR spectrum of Cu(II) complex of FATP
bonding by nitrogen and oxygen atoms is provided by far IR spectra of complexes. Due to interference of skeletal vibrations of ligands with M-N and M-O vibrations, definite assignments of bands are difficult. Therefore only tentative assignments are made on the basis of information available in literature. Spectra of all complexes showed bands at 586-579 cm\(^{-1}\) and 483-478 cm\(^{-1}\) which may be assigned to the \(\nu\) M-N and \(\nu\) M-O stretching vibrations\(^{162-164}\).

It was observed that the symmetric vibrations of C-S, which appeared as a band near 701 cm\(^{-1}\) in the ligand spectrum, has been shifted to lower frequencies after complexation. Similarly a weak band of S-H, which appeared at 2650 cm\(^{-1}\) in the case of ligand, has been disappeared in the spectrum of all complexes\(^{165}\). This suggests that the –SH group is involved in coordination. A broad band at 3450-3400 cm\(^{-1}\) in the spectra of several complexes is attributed to the hydroxyl stretching mode of water molecule \(^{166,167}\). In addition a medium band approximately at 870-950 cm\(^{-1}\) suggests that water molecules are coordinated.
Table 1.3.3 Characteristic Infrared absorption frequencies (cm$^{-1}$) of metal complexes of furon-2-aminothiophenol

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\nu$ H$_2$O</th>
<th>$\nu$ C=N</th>
<th>$\nu$ M-N</th>
<th>$\nu$ M-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand</td>
<td>FATP</td>
<td>_</td>
<td>1676</td>
<td>_</td>
</tr>
<tr>
<td>Co(FATP) (H$_2$O)$_3$</td>
<td>3405</td>
<td>1646</td>
<td>586</td>
<td>481</td>
</tr>
<tr>
<td>Ni(FATP) (H$_2$O)$_3$</td>
<td>3410</td>
<td>1646</td>
<td>586</td>
<td>481</td>
</tr>
<tr>
<td>Cu(FATP) (H$_2$O)$_3$</td>
<td>3443</td>
<td>1647</td>
<td>586</td>
<td>483</td>
</tr>
<tr>
<td>Zn(FATP) (H$_2$O)$_3$</td>
<td>3430</td>
<td>1645</td>
<td>579</td>
<td>478</td>
</tr>
</tbody>
</table>

**Electronic spectra**

The electronic spectrum depends on the energy of metal d orbital, their degeneracy and the number of electrons distributed. These features are in turn controlled by the oxidation state of the metal, number and kind of the ligand and the geometry of the complex.$^{168}$ The electronic spectral data obtained were found to agree with conclusions arrived from magnetic susceptibility measurements.

The expected octahedral transitions of Co(II) are $^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (F), $^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F) and $^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$ (P)$^{169,170}$. The middle band is due to a transition of two electron which is forbidden and give a weak band and $^4A_{2g}$ (F) and $^4T_{1g}$ (P) are very close in octahedral geometry. Due to these
factors detection of middle band is very difficult. The electronic spectrum of Co(II) gives two peaks at 1075nm and 442nm due to $^4T_{1g} (F) \rightarrow ^4T_{2g} (F)$ and $^4T_{1g} (F) \rightarrow ^4T_{1g}(P)$ transitions corresponding to octahedral geometry. The purple colour of Co(II) complex is also suggestive of octahedral geometry.

Ni(II) complex of FATP exhibit two d-d transitions in the electronic spectra at about 544nm and 978nm due to $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ transitions of octahedral geometry. The distorted octahedral geometry for Cu(II) complex is indicated by a peak at 666nm. The Zn(II) complexes do not show any characteristic d-d transition bands.

**Thermal analysis**

The prepared complexes were subjected to thermal analysis. Mass loss considerations of the decomposition indicate that the complexes have been converted to corresponding metal oxides. Detailed kinetic analysis of the TG traces of selected complexes is described in Part II.

**X-ray diffraction**

The powder X-ray diffraction pattern of the ligand and complexes are shown in the figure 1.3.4. The XRD patterns indicate that the ligand and its complexes are crystalline, with various degrees of crystallinity. Some of the extra peaks present in the complexes compared to ligand prove the coordination of metal ion. The residue obtained after the thermal treatment of metal complexes was subject to X-ray diffraction analysis and patterns
obtained are given in the figure 1.3.5. It was found that the diffraction patterns obtained matches with the corresponding metal oxide diffraction patterns. The detailed X-ray diffraction studies of the selected complexes are described in part III.

**Figure 1.3.4** X-ray diffraction patterns of the ligand FATP and its metal complexes

Based on these observations, the structure of the Co(II), Ni(II), Cu(II) and Zn(II) complexes of FATP can be confirmed to be octahedral. From all these studies, it is clear that the ligand acts as dianionic tridentate towards metal ion. Above discussion suggest the following structure (figure 1.3.6) for these complexes.
Figure 1.3.5 X-ray diffraction patterns of the residues of complexes of FATP

M= Co(II), Ni(II), Cu(II) and Zn(II)

Figure 1.3.6 Structure of metal complexes of ligand FATP
CHAPTER 4
STUDIES ON Co(II), Ni(II), Cu(II) AND Zn(II) COMPLEXES OF FUROIN-2-AMINOPHENOL (FAP)

Schiff bases are an important class of ligands in coordination chemistry and find extensive applications in different spheres. Much attention has been given to metal complexes of aminophenol. But Schiff base, furoin-2-aminophenol and its metal complexes were not reported yet. FAP a potential tridentate Schiff base ligand, has been synthesised for the first time. This ligand forms a variety of complexes with various transition metals. In this chapter, therefore, the results of a brief study of the coordination compounds of Schiff base derived from furoin and 2-amino phenol are discussed.

Preparation of the ligand furoin-2-aminophenol

Hot ethanolic solutions of furoin (2.88g, 0.015mol) and 2-amino phenol (1.64g, 0.015 mol) were mixed and refluxed for 3 hours on a water bath. The resulting solution was concentrated and cooled in an ice bath. The separated precipitate was collected through filtration using a vacuum pump and washed with ethanol, dried over anhydrous CaCl₂. The melting point of FAP was determined and found to be 173°C. The ligand was soluble in a mixture of ethanol and DMSO.
Characterisation of the ligand

Elemental analysis and spectral techniques were adopted for the characterisation of the ligand. The obtained analytical results are given in the table 1.4.1 and found to be in good agreement with the empirical formula.

<table>
<thead>
<tr>
<th>FAP</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found</td>
<td>67.42</td>
<td>4.16</td>
<td>3.94</td>
</tr>
<tr>
<td>Calculated</td>
<td>67.77</td>
<td>4.58</td>
<td>3.38</td>
</tr>
</tbody>
</table>

The UV and IR spectra of the ligand showed characteristic bands. Based on the above results, the structure of the ligand was confirmed and is shown in the figure 1.4.1.

Figure 1.4.1 Structure of Schiff base furoin-2-aminophenol
Synthesis of complexes

The hot ethanolic solutions of corresponding metal acetate (0.005mol), 2-amino phenol (0.005mol) and fuorin (0.005mol) were mixed and refluxed for about 3-4 hours in the presence of sodium acetate (0.5-1.0g) to get the Co(II), Ni(II), Cu(II) and Zn(II) metal complexes of FAP. The refluxed solution was concentrated, cooled in an ice bath for overnight and filtered. The obtained metal complexes dried in a desiccator over anhydrous calcium chloride.

Characterisation of the complexes

The metal complexes were subjected to magnetic and conductance measurements, elemental, electronic, IR, thermal and X-ray diffraction analysis.

Results and discussion

The complexes are coloured and non hygroscopic in nature. They are insoluble in water but slightly soluble in organic solvents like ethanol, methanol and completely soluble in DMSO.

Elemental analysis

Percentage of carbon, hydrogen and nitrogen was determined by micro analytical methods. The complexes were analyzed for metal by standard
methods\textsuperscript{152}. The analytical data and physical appearance are summerised in table 1.4.2.

**Molar conductance**

The molar conductance values of the complexes in DMSO at a concentration of $10^{-3}\text{M}$ at room temperature were indicative of their non electrolytic nature\textsuperscript{156}.

**Magnetic measurements**

The values of the magnetic moments of the complexes are tabulated in table 1.4.2. The Co(II) complex has a magnetic moment value of 4.8 BM. An octahedral geometry is suggested around the metal ion\textsuperscript{157}. Ni(II) complex has a magnetic moment value of 3.3 BM which is suggestive of octahedral configuration. Cu(II) complex give a magnetic moment value of 1.74 BM, which is expected for one unpaired electron of the d\textsuperscript{9} configuration indicating the octahedral geometry\textsuperscript{158,159}. Zn(II) complex was diamagnetic as expected.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>M%</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
<th>$\Omega^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(FAP) (H$_2$O)$_3$]</td>
<td>Black</td>
<td>14.20</td>
<td>49.25</td>
<td>3.68</td>
<td>3.40</td>
<td>4.8</td>
<td>7.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(15.02)</td>
<td>(48.71)</td>
<td>(4.31)</td>
<td>(3.50)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(FAP) (H$_2$O)$_3$]</td>
<td>Greenish black</td>
<td>14.35</td>
<td>50.58</td>
<td>4.03</td>
<td>3.17</td>
<td>3.3</td>
<td>7.66</td>
</tr>
<tr>
<td>[Cu(FAP) (H$_2$O)$_3$]</td>
<td>Greenish black</td>
<td>15.92</td>
<td>50.99</td>
<td>4.20</td>
<td>3.99</td>
<td>1.74</td>
<td>7.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(16.01)</td>
<td>(48.26)</td>
<td>(4.27)</td>
<td>(3.52)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Zn(FAP) (H$_2$O)$_3$]</td>
<td>Greenish black</td>
<td>15.35</td>
<td>50.61</td>
<td>4.23</td>
<td>3.86</td>
<td>D</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(16.39)</td>
<td>(48.19)</td>
<td>(4.27)</td>
<td>(3.51)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

D- Diamagnetic M- Metal, $\Omega^{-1}$. Molar conductance in ohm$^{-1}$cm$^2$mol$^{-1}$. Calculated values are given in the parenthesis.
Infrared spectral studies

The characteristic IR absorption bands of the ligands and the complexes are summarised in table 1.4.3. The comparison of the infrared spectra of the chelates and the ligand reveal that the spectra of chelates differ from that of the ligand in some characteristic frequencies. A strong intense band appears at 1676 cm\(^{-1}\) in the spectrum of the ligand due to \(\nu_{C=N}\) vibrations, has undergone a frequency shift of about 25-35 cm\(^{-1}\) in all metal complexes. This shift indicates the coordination of nitrogen to metal ion\(^{160}\). The band at 1240 cm\(^{-1}\) is characteristic of the C-O in the free ligand\(^{86}\). The shifting of this band to lower frequencies in the complexes indicates O-H group is ionised and coordinated. The presence of the -OH group in the ligand is indicated by a broad band approximately at 3300 cm\(^{-1}\). In metal chelates this band is absent which suggests that, the -OH group is involved in the coordination\(^{165}\). The aromatic out of plane vibration is seen near 870 cm\(^{-1}\) and in plane vibration at 770 cm\(^{-1}\) and 725 cm\(^{-1}\).

Conclusive evidence of bonding of the ligand to the central metal ion is provided by the appearance of bands at \(~586\) cm\(^{-1}\) and \(~481\) cm\(^{-1}\), which can be assigned to M-N and M-O bands respectively\(^{161}\). The presence of coordinated water molecules in the complexes is confirmed by the appearance of band between \(3250-3415\) cm\(^{-1}\) and is followed by a sharp rocking mode of vibration between \(840-850\) cm\(^{-1}\)\(^{166}\).
### Table 1.4.3 Characteristic Infrared absorption frequencies (cm⁻¹) of metal complexes of furoin-2-aminophenol

<table>
<thead>
<tr>
<th>Substance</th>
<th>νH₂O</th>
<th>νC=N</th>
<th>νM-N</th>
<th>M-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand FAP</td>
<td>_</td>
<td>1676</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td>[Co(FAP) (H₂O)₃]</td>
<td>3382</td>
<td>1646</td>
<td>586</td>
<td>481</td>
</tr>
<tr>
<td>[Ni(FAP) (H₂O)₃]</td>
<td>3413</td>
<td>1647</td>
<td>586</td>
<td>481</td>
</tr>
<tr>
<td>[Cu(FAP) (H₂O)₃]</td>
<td>3398</td>
<td>1649</td>
<td>586</td>
<td>481</td>
</tr>
<tr>
<td>[Zn(FAP) (H₂O)₃]</td>
<td>3251</td>
<td>1647</td>
<td>579</td>
<td>470</td>
</tr>
</tbody>
</table>

### Electronic spectra

The electronic spectral data were found to be in agreement with the conclusions arrived from magnetic susceptibility measurements. The electronic spectra of Co(II) complexes are characterised by two peaks at 1080nm and 450nm due to \( ^4T_{1g} (F) \rightarrow ^4T_{2g} (F) \) and \( ^4T_{1g} (F) \rightarrow ^4T_{1g}(P) \) respectively\(^{169,170}\). Ni(II) complexes also exhibit two d-d transitions in the region at about 550nm and 370nm due to \( ^3A_{2g}(F) \rightarrow ^3T_{1g}(F) \) and \( ^3A_{2g}(F) \rightarrow ^3T_{1g}(P) \) transitions of octahedral geometry\(^{171}\). The electronic spectrum of Cu(II) complexes showed peak at 650nm which support a distorted octahedral geometry\(^{171}\).
Thermal analysis

The prepared complexes were subjected to thermal analysis. Mass loss considerations of the decomposition indicate that the complexes have been converted to corresponding metal oxides. Detailed kinetic analysis of the TG traces of the selected complexes is described in Part II.

X-ray diffraction

The powder X-ray diffraction pattern of the ligand and complexes are shown in the figure 1.4.2.

Figure 1.4.2  X-ray diffraction patterns of the FAP and its metal complexes
The well defined diffraction patterns were observed in the case of Ni(II) and Cu(II) of complexes of FAP. Very less number of peaks were observed in the case of Co(II) and Zn(II) complexes. The X-ray diffraction patterns of the residues obtained after thermal decomposition of metal complexes in air atmosphere confirms the presence of pure oxides of metal. The detailed X-ray diffraction studies of the selected complexes are described in part III.

Based on these observations, the structure of the Co(II), Ni(II), Cu(II) and Zn(II) complexes of FAP can be confirmed to octahedral. From all these studies, it is clear that the ligand acts as dianionic tridentate ligand towards metal ion. Above discussion suggest the following structure for these complexes (figure 1.4.3).

\[ M= \text{Co(II), Ni(II), Cu(II) and Zn(II)} \]

Figure 1.4.3 Structure of metal complexes of FAP
CHAPTER 5
STUDIES ON Co(II), Ni(II), Cu(II) AND Zn(II)
COMPLEXES OF FUROIN THIOSEMICARBAZONE
(FTSC)

Transition metal complexes with Schiff bases as ligands have been amongst the most widely studied coordination compounds. The chemistry of transition metal complexes of thiosemicarbazones has been receiving considerable attention largely because of their pharmacological and other properties. The literature review reveals that detailed investigation on synthetic and structural aspects of metal complexes derived from furoin and thiosemicarbazide are rare. So furoin thiosemicarbazone (FTSC) a potential tridentate Schiff base ligand, have been synthesised from furoin and thiosemicarbazide. This ligand forms a variety of complexes with various transition metals. In this chapter, therefore, the results of a brief study of the coordination compounds of Schiff base furoin thiosemicarbazone are discussed.

Preparation of the furoin thiosemicarbazone

The ligand FTSC was prepared by refluxing the ethanolic solution containing equal moles of furoin and thiosemicarbazide for three hours on a water bath. The refluxed solution was concentrated and cooled in an ice bath. The ligand formed was separated by filtration and washed with ethanol and
dried over calcium chloride in a desiccator. The melting point of FTSC was found to be 96°C and it was soluble in ethanol and DMSO mixture.

**Characterisation of the ligand**

The C, H, N, and S content of the ligand were determined using micro analytical technique. The ligand FTSC was further characterised using spectral techniques like electronic and IR spectroscopy. The analytical data obtained are given in table 1.5.1 and were found to be in good agreement with the empirical formula for FTSC.

<table>
<thead>
<tr>
<th>Table 1.5.1 Analytical data for the ligand FTSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTSC</td>
</tr>
<tr>
<td>Found</td>
</tr>
<tr>
<td>Calculated</td>
</tr>
</tbody>
</table>

The UV and IR spectra of the ligand showed the characteristic bands. Based on the above results, the structure of the ligand FTSC was confirmed as shown in the figure 1.5.1.
Synthesis of complexes

To prepare the Co(II), Ni(II), Cu(II) and Zn(II) complexes of FTSC, 0.005mol of the FTSC was first dissolved in a mixture of ethanol and DMSO by boiling. To this clear solution, 0.005mol of hot ethanolic solution of corresponding metal acetates were added slowly along with 0.5-1g of sodium acetate. The above solution was refluxed for 3-4 hours, then concentrated, cooled and filtered. The obtained complexes were dried in a desiccator over anhydrous calcium chloride.

Characterisation of the complexes

The complexes were characterised on the basis of elemental analysis, magnetic measurements, electronic and infrared spectral data, conductance measurements, thermal data and X-ray diffraction technique.
Results and discussion

The complexes are coloured, stable and non hygroscopic solids. They are insoluble in water but slightly soluble in organic solvents like ethanol, methanol and completely soluble in DMSO. The properties, structure and bonding of the complexes have been explained on the basis of information obtained from analytical, physicochemical and spectral investigations.

Elemental analysis

The complexes were analyzed for metal and sulphur content by standard methods. C, H, N and S content were estimated by micro analytical methods. The results of above analysis are summerised in table 1.5.2.

Magnetic measurements

The Co(II) complexes possess magnetic moment values of 4.8 BM as expected for the octahedral Co(II) complexes. The complex of Ni(II) have magnetic moment value of 3.3 BM which are in accordance with octahedral complex. The magnetic moment values of Cu(II) possess normal values of 1.9 BM as expected for octahedral Cu(II). The magnetic susceptibility measurements support the diamagnetic nature of the Zn(II) complex.
Table 1.5.2 Microanalytical, magnetic and conductance data of metal complexes of furoin thiosemicarbazone

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>M%</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>S%</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
<th>$\Omega^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(FTSC)</td>
<td>Greenish</td>
<td>15.32</td>
<td>36.05</td>
<td>3.91</td>
<td>10.95</td>
<td>8.15</td>
<td>4.8</td>
<td>17.39</td>
</tr>
<tr>
<td>(H$_2$O)$_3$</td>
<td>black</td>
<td>(15.48)</td>
<td>(35.01)</td>
<td>(4.51)</td>
<td>(11.14)</td>
<td>(8.51)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(FTSC)</td>
<td>Greenish</td>
<td>15.61</td>
<td>36.15</td>
<td>3.85</td>
<td>10.02</td>
<td>9.20</td>
<td>3.3</td>
<td>17.60</td>
</tr>
<tr>
<td>(H$_2$O)$_3$</td>
<td>black</td>
<td>(15.42)</td>
<td>(35.03)</td>
<td>(4.24)</td>
<td>(11.14)</td>
<td>(8.51)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cu(FTSC)</td>
<td>Greenish</td>
<td>16.83</td>
<td>35.02</td>
<td>3.98</td>
<td>10.85</td>
<td>8.02</td>
<td>6.55</td>
<td></td>
</tr>
<tr>
<td>(H$_2$O)$_3$</td>
<td>black</td>
<td>(16.69)</td>
<td>(34.56)</td>
<td>(4.19)</td>
<td>(11.02)</td>
<td>(8.40)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Zn(FTSC)</td>
<td>Greenish</td>
<td>16.53</td>
<td>35.02</td>
<td>3.38</td>
<td>10.05</td>
<td>7.79</td>
<td>D</td>
<td>5.89</td>
</tr>
<tr>
<td>(H$_2$O)$_3$</td>
<td>black</td>
<td>(17.09)</td>
<td>(34.42)</td>
<td>(4.17)</td>
<td>(10.95)</td>
<td>(8.36)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

D- Diamagnetic M- Metal, $\Omega^{-1}$. Molar conductance in ohm$^{-1}$cm$^2$mol$^{-1}$. Calculated values are given in parenthesis.
**Molar conductance**

Molar conductance of $10^{-3}$ M solutions of Co(II), Ni(II), Cu(II) and Zn(II) complexes in DMSO were found to be in the range of 5-18 ohm$^{-1}$cm$^2$mol$^{-1}$, indicating their non electrolytic nature$^{156}$.

**Infrared spectral studies**

The important infrared absorption frequencies obtained for the ligand FTSC and its complexes are given in the table 1.5.3. IR spectra of the ligand FTSC show bands at 1650 and 760cm$^{-1}$ corresponding to C=N and C=S stretching respectively$^{166}$. FTSC exists in thioketo form in the solid state as evidence from the IR spectral data. However, in solution, the ligand can exists in the thioketo (I) and thioenol (II) forms.

![Chemical structure of FTSC](image)

In the deprotonated form it is potentially a tridentate ligand coordinating through N and the thiolate S forming five membered chelate ring.
The band at 850 cm\(^{-1}\) is attributed to \(\nu\)C=S in the ligand. But in the case of complexes this band disappears and new band in the region 700-600 cm\(^{-1}\) due to \(\nu\)C-S would be taken as evidence of the ligand coordinating via thioenol\(^{167}\). The appearance of bands near 500 cm\(^{-1}\) and 481 cm\(^{-1}\) due to M-N and M-O vibrations indicate the bonding of the ligand to central metal atom\(^{162}\). A broad feature at 3455-3310 cm\(^{-1}\) in the spectra of complexes attributed to the hydroxyl stretching mode of water molecule. In addition a medium band approximately at 870-950 cm\(^{-1}\) suggests that water molecules are coordinated\(^{161}\).

**Table 1. 5. 3 Characteristic Infrared absorption frequencies (cm\(^{-1}\)) of metal complexes of furoin thiosemicarbazone**

<table>
<thead>
<tr>
<th>Substance</th>
<th>(\nu)H(_2)O</th>
<th>(\nu)C=N</th>
<th>(\nu)M-N</th>
<th>(\nu)M-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand FTSC</td>
<td>-</td>
<td>1650</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Co(FTSC) (H(_2)O)(_3)]</td>
<td>3299</td>
<td>1644</td>
<td>501</td>
<td>481</td>
</tr>
<tr>
<td>[Ni(FTSC) (H(_2)O)(_3)]</td>
<td>3310</td>
<td>1641</td>
<td>510</td>
<td>476</td>
</tr>
<tr>
<td>[Cu(FTSC) (H(_2)O)(_3)]</td>
<td>3453</td>
<td>1646</td>
<td>512</td>
<td>481</td>
</tr>
<tr>
<td>[Zn(FTSC) (H(_2)O)(_3)]</td>
<td>3418</td>
<td>1644</td>
<td>508</td>
<td>481</td>
</tr>
</tbody>
</table>
Electronic spectra

The electronic spectra of Co(II) complex exhibited a peak at 570nm, which was taken as evidence to support the presence of Co(II) in octahedral geometry\textsuperscript{169,170}. Ni(II) complexes also characterised by two peaks one at 564nm and other 390nm. These two peaks are due to the $^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(F)$ and $^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(P)$ transitions of octahedral geometry\textsuperscript{171}. The octahedral geometry of Cu(II) complex is clear from the absorption peak at 619nm.

Thermal analysis

Thermal analysis of the prepared complexes was carried out and the mass loss considerations of the decomposition indicate that the complexes have been converted to corresponding metal oxides. Detailed kinetic analysis of these complexes is described in Part II.

X-ray diffraction

The copper and zinc complexes have well defined crystalline patterns as seen in the X-ray diffraction pattern as shown in the figure 1.5.2. But Co(II) and Ni(II) complexes does not have characteristic peaks indicating the amorphous nature of the complexes. The thermal decomposition products of the complexes were subjected to X-ray analysis and found that the residues are corresponding metal oxides. The detailed X-ray diffraction studies of the selected complexes are described in part III.
Figure 1.5.2 X-ray diffraction patterns of the ligand FTSC and its Co(II), Ni(II), Cu(II) and Zn(II) complexes

Based on these observations, the structure of the Co(II), Ni(II), Cu(II) and Zn(II) complexes of FTSC can be confirmed to be octahedral. From all these studies, it is clear that the ligand acts as dianionic tridentate ligand towards metal ion. The proposed structure of the complexes is shown in the figure 1.5.3.
Figure 1.5.3 Structure of metal complexes of ligand FTSC

$M = \text{Co(II), Ni(II), Cu(II) and Zn(II)}$
CHAPTER 6
STUDIES ON Co(II), Ni(II), Cu(II) AND Zn(II) COMPLEXES OF FUROIN SEMICARBAZONE (FSC)

Semicarbazone is the one of the widely studied nitrogen and oxygen donor ligand like thiosemicarbazone. They are capable of acting as neutral or charged ligand moieties. Detailed survey of literature indicates that no reports were published about metal complexes containing the Schiff base, furoin semicarbazone. So a potential tridentate Schiff base ligand, furoin semicarbazone, derived from furoin and semicarbazide hydrochloride and its transition metal complexes have been synthesised and studied for the first time.

**Preparation of the furoin semicarbazone**

Equal moles of hot ethanolic solutions of furoin and semicarbazide hydrochloride were mixed and refluxed for three hours on a water bath. The ligand was separated out from the refluxed solution after concentration, cooling and filtration. The ligand FSC was soluble in ethanol, DMSO mixture.
Characterisation of the ligand

The ligand FSC was characterised on the basis of elemental analysis and spectral data. The analytical data is given in the table 1.6.1 and were found to be in agreement with the empirical formula for FSC.

<table>
<thead>
<tr>
<th>FSC</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found</td>
<td>53.87</td>
<td>5.04</td>
<td>15.56</td>
</tr>
<tr>
<td>Calculated</td>
<td>53.0</td>
<td>4.42</td>
<td>16.87</td>
</tr>
</tbody>
</table>

The UV and IR spectra of the ligand showed the characteristic bands. Based on the above results, the structure of the ligands FSC was confirmed and shown in the figure 1.6.1

![Figure 1.6.1 Structure of Schiff base furoin semicarbazone](image-url)
Synthesis of complexes

Co(II), Ni(II), Cu(II) and Zn(II) complexes were prepared by mixing ethanolic solutions of metal acetate (0.005mol), semicarbazide hydrochloride (0.005mol) and furoin (0.005mol) in the presence of sodium acetate (0.5-1.0 gm). The resulting solution was refluxed for about 3-4 hours, concentrated and kept overnight in an ice bath. The complex formed was filtered using a vacuum pump and washed with ethanol, dried in a desiccator over anhydrous calcium chloride.

Characterisation of the complexes

The complexes were characterised on the basis of elemental analysis, magnetic measurements, electronic and infrared spectral data, conductance measurements, thermal data and X-ray diffraction technique.

Results and discussion

The complexes were insoluble in water but slightly soluble in organic solvents like ethanol, methanol and completely soluble in DMSO. The complexes were coloured and non hygroscopic solid.

Elemental analysis

The complexes were analysed for metal and sulphur by standard methods. C, H, N content of the complexes were determined by micro
analytical methods. The results of analysis are tabulated in and given in the

table 1.6.2.

**Molar conductance**

The low molar conductance values obtained for the four complexes
i.e. 5-15 ohm$^{-1}$cm$^2$ mol$^{-1}$, for 10$^{-3}$ M solutions in DMSO at room temperature
indicate the non electrolytic nature of complexes.

**Magnetic measurements**

The magnetic moment values obtained for the complexes are tabulated
in table 1.6.2. The octahedral geometry of the Co(II) complex was confirmed
from the measured magnetic moment value of 4.5 BM$^{157}$. The magnetic
moment value of Ni(II) complex was 2.9 BM which is in agreement with its
octahedral geometry. Cu(II) complex of FSC registered magnetic moment
value of 2.0 BM, therefore octahedral structure can be assigned to Cu(II)
complex$^{158}$. As expected the Zn(II) complex was found to be diamagnetic.
Table 1.6.2 Micro analytical, magnetic and conductance data of metal complexes of furoin semicarbazone

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>M%</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
<th>$\Omega^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(FSC)(H$_2$O)$_3$]</td>
<td>Greenish black (16.16)</td>
<td>16.95</td>
<td>35.06</td>
<td>4.9</td>
<td>11.05</td>
<td>4.5</td>
<td>10.00</td>
</tr>
<tr>
<td>[Ni(FSC)(H$_2$O)$_3$]</td>
<td>Greenish black (16.10)</td>
<td>16.85</td>
<td>35.96</td>
<td>4.80</td>
<td>12.01</td>
<td>2.9</td>
<td>8.06</td>
</tr>
<tr>
<td>[Cu(FSC)(H$_2$O)$_3$]</td>
<td>Greenish black (17.20)</td>
<td>16.57</td>
<td>36.85</td>
<td>4.93</td>
<td>11.20</td>
<td>2.0</td>
<td>15.23</td>
</tr>
<tr>
<td>[Zn(FSC)(H$_2$O)$_3$]</td>
<td>Greenish black (17.62)</td>
<td>18.04</td>
<td>36.01</td>
<td>4.72</td>
<td>10.90</td>
<td>D</td>
<td>5.63</td>
</tr>
</tbody>
</table>

D- Diamagnetic M- Metal, $\Omega^{-1}$. Molar conductance in ohm$^{-1}$cm$^2$mol$^{-1}$. Calculated values are given in the parenthesis.
Infrared spectral studies

The characteristic IR absorption bands of ligand FSC and its complexes are summarised in table 1.6.3.

### Table 1.6.3 Characteristic Infrared absorption frequencies (cm\(^{-1}\)) of metal complexes of furoin semicarbazone

<table>
<thead>
<tr>
<th>Substance</th>
<th>(\nu)(_{\text{H}_2\text{O}})</th>
<th>(\nu)(_{\text{C}=\text{N}})</th>
<th>(\nu)(_{\text{M}-\text{N}})</th>
<th>(\nu)(_{\text{M}-\text{O}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand FSC</td>
<td>_</td>
<td>1672</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td>([\text{Co(FSC)} (\text{H}_2\text{O})_3])</td>
<td>3390</td>
<td>1654</td>
<td>515</td>
<td>482</td>
</tr>
<tr>
<td>([\text{Ni(FSC)} (\text{H}_2\text{O})_3])</td>
<td>3436</td>
<td>1639</td>
<td>505</td>
<td>487</td>
</tr>
<tr>
<td>([\text{Cu(FSC)} (\text{H}_2\text{O})_3])</td>
<td>3448</td>
<td>1647</td>
<td>511</td>
<td>489</td>
</tr>
<tr>
<td>([\text{Zn(FSC)} (\text{H}_2\text{O})_3])</td>
<td>3390</td>
<td>1645</td>
<td>508</td>
<td>481</td>
</tr>
</tbody>
</table>

The infrared spectroscopic results provide support for the molecular constitution of these complexes. Most of the bands in the spectrum of the ligands undergo frequency shifts and intensity changes during complex formation. In the case of ligand FSC, the band which appeared at 1672 cm\(^{-1}\) may be due to the presence of \(\text{C}=\text{N}\) band and there may be overlapping of \(\text{C}=\text{O}\) band in the same region. In all complexes new band appears around 1000cm\(^{-1}\) due to \(\nu\)\(_{\text{C}-\text{O}}\). This may be due to enolisation and subsequent coordination of carbonyl group\(^{167}\). The participation of azomethine nitrogen in complex formation has been indicated by the shift of band at 1672cm\(^{-1}\).
towards lower frequencies for about 25-35 cm⁻¹ during complex formation¹⁶⁰. The appearance of bands near 500 cm⁻¹ and 480 cm⁻¹ due to M-N and M-O vibrations indicates the bonding of the ligand to central metal atom¹⁶³. The broad bands at 3450-3390 cm⁻¹ along with medium band at 870-950 cm⁻¹ suggest that water molecules are coordinated to central metal atom¹⁶⁶.

**Electronic spectra**

The octahedral geometry of the Co(II) complex was shown by the exhibited peaks at 1077 nm and 544 nm¹⁶⁹,¹⁷⁰. Ni(II) complex also characterised by two peaks, one at 972 nm and other at 561 nm. These two peaks are due to the $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ transitions of octahedral geometry¹⁷¹. The electronic spectrum of Cu(II) complexes showed peaks at 636 nm which support a distorted octahedral geometry.

**Thermal analysis**

The metal complexes were investigated for their thermal behavior during non isothermal heating. The mass residue obtained was corresponding to mass of metal oxides. Detailed kinetic analysis of the TG traces of selected complexes is described in Part II

**X-ray diffraction**

The X-ray diffraction patterns obtained for the ligand and complexes are given in figure 1.6.2. Cu(II) and Ni(II) complexes only showed
crystalline nature. Zn(II), Co(II) complexes and FSC are amorphous in nature. The analysis of thermal decomposition residues confirms the formation of oxides. The detailed x-ray diffraction analysis of selected complexes is described in part III.

Figure 1.6.2 X-ray diffraction patterns of the ligand FSC and its metal complexes.
Based on these observations, the structure of the Co(II), Ni(II), Cu(II) and Zn(II) complexes of FSC can be confirmed to be octahedral. From all these studies, it is clear that the ligand acts as dianionic tridentate towards metal ion. Above discussion suggest the following structure for the complexes (figure 1.6.3).

\[ M = \text{Co(II), Ni(II), Cu(II) and Zn(II)} \]

Figure 1.6.3 Structure of metal complexes of FSC
REFERENCES


