PART -I

SYNTHESIS AND CHARACTERISATION
CHAPTER I

INTRODUCTION

The field of coordination chemistry is one of the most intellectual, attractive and experimentally demanding frontiers in modern chemical sciences. It has grown in a half century from a readily defined and limited area into the most active research field of inorganic chemistry. Coordination compounds brought about a synthetic revolution in inorganic chemistry which leads to novel products of equally novel applications in wide range of areas such as analytical chemistry, fungicides, paints, pigments, polymers, pharmaceuticals, catalysis, and photoconductors. Complexation reactions are used in qualitative as well as in quantitative analysis. There are some extremely sensitive and selective organic reagents for the determination of metal ions. The role of coordination compounds in colorimetric, spectrophotometric and polarographic analysis is also significant.

Transition metal complexes acts as catalyst in many industrial processes like Wacker process, Oxoprocess, Monsanto processes etc. Many enzymes contain a small prosthetic group which is usually a complexed metal ion. Haemoglobin, Myoglobin, Chlorophyll and Cytochrome are some of the most important complex compounds in living systems.
Another exciting application of metal complexes is the photolytic spitting of water producing hydrogen. This process has immense potential for generating non polluting fuel which may be a solution for the fuel crisis. Another important development is the recognition of the vital role of metal complexes in biological systems and in the field of therapy. Many of the complexes and complex formers are known to be used as drugs in certain types of diseases and also for metal detoxification in the case of metal poisoning.

**SCHIFF BASES**

Schiff base complex compounds have taken a wide place in coordination chemistry and have important role in development of inorganic chemistry, biochemistry and environment chemistry. Schiff bases have a chelating structure and are in demand because they are straightforward to prepare and are moderate electron donors with easily tunable electronic and steric effects thus being versatile. These types of complexes with transition and heavy metals are used in organic synthesis, analytical reagent, metal ion catalyst and medicine (Nelson SM, 1980; Fenton DE, 1986; Mukerjee S, 2006). Schiff bases have been extensively studied because of their high potential permutations. Magnetic susceptibility, absorption spectra, elemental analysis, molecular weight determination, conductivity...
and thermal analysis of many Schiff bases and their complexes have been reported (Thomas R, 1982; Khalil MM, 1999; Mukhargee AK, 2004). Several workers have reported that the rapidly developing field of bioinorganic chemistry is centered in the presence of coordination compounds in the living systems (Ashash S, 2006; Jeong T, 2005).

The general preparation of Schiff bases and reports of metal complexes of these types of ligands were first published in the 1860s (Schiff H, 1864; Ettling C, 1840; Hobday MD, 1972). Schiff bases or imines have the general formula RN=CR’ where the R and R’ are alkyl, aryl, cycloalkyl or heterocyclic groups. They are formed by condensation reaction that occurs when aldehydes and some ketones react with primary amines.

Imines play an important role in many biochemical reactions because some of the enzymes use an amine group of an amino acid to react with an aldehyde or ketone to form an imine linkage (Solomons TWG, 1986). It follows then, that when aldehyde or ketones are reacted with diamines in a stoichiometry of 2:1, a diimine compound is produced. N, N’-bis(salicylidine)-ethylenediamine (salenH₂) is a good example of a diimine Schiff base obtained from this type of reaction. Moreover, if dialdehydes or diketones are reacted with a diamine in a stoichiometry of 1:1, a cyclic
compound may be obtained. This type of reaction is used to prepare the mixed donor macro cycles.

Transition metal organic and organometallic chemistry lie at the interface between organic and inorganic chemistry because they look at the interaction between metal ions and organic molecules. The bonding ability of ligands depends on the nature of atoms which act as coordination sites,
their electronegative and steric factors. The possibility of having a lone pair of electrons in either $\pi$ or $sp^2$ hybridised orbital or trigonally hybridised nitrogen in the $C=\text{N}$ group is of the fundamental chemical and biological importance.

Transition metal ion acts as Lewis acids and can bind to lewis bases known as ligands (L) to give a coordination compound, or complex $ML_n$. The ligands bind in the first coordination sphere of the metal, while the second coordination sphere may accommodate such compounds as uncoordinated solvent molecules which act to stabilize the complex. The most common type of coordination complex is $ML_6$, which adopts an octahedral geometry (Sargeson AM, 1984). The ligands occupy the six vertices of the octahedron which allows them to minimize their M-L bonding distances, while maximizing their L-L non bonding distances. Obviously the geometry is named after the number of faces rather than the number of vertices present in the complex (Crabtree RH, 1994).

Complex ions of d-block elements exhibit certain special features when compared with the complexes of other block metals due to the presence of incompletely filled d-orbitals. The special features exhibited are
1. Great variety of colours observed in these complexes

2. Magnetic properties exhibited due to the presence of unpaired electrons

3. Important feature is the large number of possible oxidation states; even zero or negative oxidation states are possible

4. d-block metals bond with certain types of ligands such as CO, which very seldom bond to p-block metals.

All these special characters are exhibited by the d-block elements of the 4th period, that is complexes of eight metals, Ti through Cu.

With a broad range of metal ions and ligands available to form coordination compounds in limitless numbers, the question arises- what makes certain ligands coordinate to certain metal ions. This can be explained by the hard and soft acid base (HSAB) principle whereby hard (Lewis) acids tend to combine with hard (lewis) bases, while soft acids prefer soft bases (Shriver DF, 1994).

Most metal ions in high oxidation states tend to bind saturated ligands where examples of these include \( \text{NH}_3 \), \( \text{H}_2\text{O} \), \( \text{F}^- \) which are known as hard ligands (Sargeson AM, 1984). The hard metal ions such as \( \text{Cr}^{3+} \) and \( \text{Al}^{3+} \)
are low in electron density and require good σ donor ligands. Low oxidation state metals such as Ag⁺, Hg²⁺, which are soft metals, tend to form strong complexes with unsaturated or polarisable ligands, including PPh₃ or C₂H₄ which are all soft ligands. The soft metal binds soft ligands because these metals have excess electron density by virtue of their reduced state. They avoid strong donor ligands and prefer ligands with which they can form covalent bonds, and that have available empty orbitals into which they can donate, also known as back bonding, some of their excess electron density (Sargeson AM, 1984). Ligands are generally nucleophilic because they have available electron lone pairs and the metal ion is electrophilic because it has available d-orbitals to accept those lone pairs.

The chemical character of many ligands can be profoundly altered on binding to the metal. For example in the case of molecular nitrogen metal complex, the nitrogen directly bonded to the metal becomes positively charged and the terminal nitrogen becomes negative, thus activating nitrogen towards chemical reactions (Sargeson AM, 1984).

The properties of the metal ion can also be altered on complex formation. For example Co (III) is very strongly oxidising in a simple compound such as acetate which will even oxidize hydrocarbons. All the oxidizing power can be quenched by binding six ammonia ligands to give
[Co(NH$_3$)$_6$]$^{3+}$ ion which lacks the severe electron deficiency of the acetate because of the presence of six strong σ-donor ligands (Sargeson AM, 1984). These cobalt complexes represent examples of coordination compounds incorporating monodentate ligands. Monodentate ligands have only one donor atom attached to the metal, based on their denticity. Bidentate chelating ligands will be attached by two donor atoms, tridentate by three and so on.

**CHELATE EFFECT**

If the coordinating ligands bear a functional group usually –OH,–SH, or –COOH sufficiently near to the site of condensation, then a very stable five or six membered chelate ring can be formed. Chelated ligands have always played important roles in the field of medicine, catalysis, chemical analysis and geology. These ligands will donate lone pairs of electrons from the donor atoms to the same metal to give a ring compound, referred to as a chelate—from Greek word for ‘claw’. The properties of chelating ligands arise from the ability of the ligand to sequester various metals dictated by the soft or hard nature of the two or more donor atoms. As a general rule, complex containing a five or six membered chelate ring has a higher formation constant than a complex that is otherwise similar, but lacks some or all of the connecting ring structure. For example if we compare the complexes
tris(ethylene-diamine) Nickel(II) \( ([\text{Ni(en)}_3])^{2+} \) and Hexaammine Nickel(II), \( ([\text{Ni(NH}_3)_6])^{2+} \) both are Octahedral Nickel(II) species that contain six nitrogen donors. The formation constants show that \( ([\text{Ni (en)}_3])^{2+} \) is about 10\(^{10}\) times more thermodynamically stable than \( ([\text{Ni(NH}_3)_6])^{2+} \). \( \text{(Cotton FA, 1995)} \).

\[
\begin{align*}
\text{Ni} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3
\end{align*}
\]

\[\text{log } K = 8.6\]

\[
\begin{align*}
\text{Ni} & \quad \text{H}_2\text{N} \\
\text{H}_2\text{N} & \quad \text{NH}_2 \\
\text{H}_2\text{N} & \quad \text{NH}_2
\end{align*}
\]

\[\text{log } k = 18.3\]

The term ‘chelate effect’ refers to the generalisation that chelate ligands form more stable complexes than analogous monodentate ligands \( \text{(Wulsberg G, 1987)} \). Relating this to ring structure, it is the enhanced stability of a complex system containing chelate rings as compared to the stability of a system that is similar but contains none or fewer rings \( \text{(Cotton FA, 1999)} \). In this case, the enthalpy and entropy components of a reaction favour the formation of the chelate complex. In some reactions, the enthalpy component can be unfavourable towards the chelate complex; however this contribution is generally small. Hence it is important to note
that the chelate effect is essentially entropy driven and the thermodynamically favourable formation of a chelate complex is due to the overall increase in the entropy of the system. The entropy of the system is increased because as the chelate complex is formed there will be a displacement of a greater number of molecules into the system increasing the disorder (Cotton FA, 1995, 1999).

Review shows that transition metal complexes of Schiff bases have emerged as highly effective catalyst for various important reactions. Catalysis plays an important role in synthesising a diverse group of molecules for the mass production of drugs and other chemical compounds. In drug developed, often only one of the two mirror images of a compound generally has the desired biological effect, while the other is ineffective or perhaps even harmful.

In order to ensure the safety of the chemical compound, it must be enantiomerically pure. So asymmetric catalysis used for designing a catalyst that is able to selectively control the formation of a desired stereo isomer, where new Schiff bases are playing a central role. Such a pentadentate sulphonamide ligand is reported by Karno et.al. (Karno NG, 2001). It was envisaged that a pentadentate ligand could coordinate to metals and leave
an open coordination site that could bind and activate a substrate in a Lewis acid catalyzed reaction.

Another report by Genet et.al. (Genet JP, 1986) accounts for the use of palladium chiral complexes of Schiff bases in the stereo selective synthesis of α-amino acid. Tridentate Schiff base complexes of ruthenium (III) are used in the oxo transfer from tert ButOOH, to C-H by insertion (Chatterjee D, 2004). Catalysis of hydrocarbon, oxidation of cyclohexene, cyclohexane, cyclohexanol, toluene, tetrahydrofuran has been studied using various O-transfer agents. A mechanism involving intermediary of a high valent Ru(IV)–oxo species is proposed for the catalytic oxidation processes.

Application of Schiff base complexes in the field of catalysis is not only limited to the field of chemical catalysis but it extent even to the field of biological catalysis. In this area, report by Erskine et.al. is very significant (Erskine PT, 1999). They studied about Schiff base complexes formed by the yeast 5-aminolaevulinic acid dehydrates with the inhibitor laevulinic acid which has specific role during catalysis.

The next goal of this review is to demonstrate significant progress in the field of Schiff base coordination chemistry as it applies to medicinal field like drug designing, diagnostic tool etc. This aspect has gained momentum
in the development of molecule which have active role in treatment of diseases like cancer, neurological diseases and heart diseases (Cad VT, 2002; Verma M, 2004; Toshihiko Takeuchi, 1998). Report of Cad on synthesis and biological activities of new racemic gossypol and gossypolone and of (+) and (-) enantiomers and their gold complexes is an interesting example. They are stable at room temperature and it was suggested that gossypol and gossypolone dithianes and dithiolanes can be used as prodrug that target tumour cells.

Toshihiko Takeuchi et.al. (Toshihiko 1998) reported the selective inhibition of human α-thrombin by cobalt (III) Schiff base complexes. Human α-thrombin associated with the blood coagulation cascade, converts fibrinogen into fibrin, which ultimately forms blood clots. Cobalt (III) Schiff base complexes of class acacen bind histidine residues in active sites and on enzymes surfaces in a random fashion. Spectroscopic evidence indicates that the binding of these complexes is controlled by axial ligand substitution. They showed that the active site directed peptide linked to cobalt chelate leads to selective irreversible inhibition of thrombin.

Other developing areas of drug research include the study of antimicrobial activity of Schiff bases and enhancement in activity due to complexation. Dashora et.al. reported the synthesis (Dashora R, 1986) of
organo silicon and organo lead complexes of Schiff bases from sulpha drugs. Complexes of the type (CH$_3$)$_2$Si (ONN) (C$_6$H$_5$)$_2$Si (ONN), (C$_6$H$_5$)$_2$Pb (ONN) have been prepared. New (N-indoledene-DL-glycine, N-indolidiene-DL alanine, and N-indolidene-DL-valine were prepared and characterised by Nursen.et.al. (Nursen S, 2003) and their antimicrobial activities tested against different micro-organisms like *B.subtilis*, *S.aureus*, *E.coli* and *C.albicans*. The results of antibacterial screening of the Schiff bases ind-gly, ind-ala, and ind-val, at a concentration of 5000μg/cm$^3$ against all bacteria have been found and results indicate that amino acid Schiff bases shows more activity against *Staphylococcus aureus*, *E.coli* and *Bacillus polymyxa* than *Candida albicans*. Ind-gly was found to be active against both strains of *S.aureus*. *Escherichia coli* and *Bacillus polymyxa* were inhibited by ind-gly. Ind-val was found to be most active of them all. *E.coli* was the most sensitive. The activity of these substances may be due to the presence of electron donating effect.

Acylhydrazine derived furanyl and thienyl Schiff bases and their Cu(II) complexes were prepared and characterised by Zahid Chohan et.al. (Zahid CH, 2000). The Schiff bases and their complexes with different anions were tested for their antibacterial activity against bacterial species.
such as *E.coli, Staphylococcus aureus, Pseudomonas aeruginosa* and *Klebsiella pneumoniae*.

Raman et.al. ([Raman N, 2003](#)) screened Cu(II), Ni(II), Co(II) and Zn(II) complexes of Schiff bases formed by condensation of acetyl acetone and p-anisidine by the diffusion technique using DMSO as solvent. The minimum inhibitory concentration MIC values were calculated at 37°C for a period of 24h. It was found that all the complexes are antimicrobial active and show higher activity than free ligand.

Modern researchers used to imitate the biosynthetic pathways by designing bio mimetic reactions that approximate natural reaction pathways. For example the relationship between redox properties and superoxide dismutase mimetic activity of thiohydrazone Cu (II) complexes was studied by Zdena et.al. ([Zdena DM, 1999](#)). The macro cyclic complexes showed more positive reduction potential and more activity than the open derivatives. From their results it follows that the structure and conformation of ligand has influence on the redox potential of central atom in the coordination compound.

In coherence with advances in analytical chemistry Schiff bases have emerged as cutting edge tools in sophisticated chemical analysis such as
application of polyvinyl chloride membrane (Susan S, 2004). Electrodes based on two complexes of Schiff base 2,2’[4,4’-diphenylmethane bis (nitromethylidyne)] bis phenol, with copper(II) and iron(III) ions, and used for determination of triiodide ions, with lower limits of detection 4X10⁻⁶ and 6X10⁻⁶ mol/dm³, respectively. The proposed electrode has fast response, independent of pH and good selectivity for tri iodide ion over a variety of anions. The electrode is used in the determination of ascorbic acid in vitamin-C tablet.

Copper in alloys can be safely estimated by using the Schiff base method without interference from many, other metals in alloys. Elif Kormal used (Elif K, 2002) N, N’-disalicylidine-1, 3-diaminopropane as selective chelating titrant for copper(II). The stoichiometry of titration reaction and interference effects of some metals ions on titration of copper was studied. There was a good agreement between the results obtained by the proposed titration method and EDTA titration method.

In another report Papi et.al (Papi S, 1994) studied the synthesis, characterisation and application of metal complex of Nickel(II) with Schiff bases, 2-(2-pyridylmethylenamino) phenol (PMAP) and 2-(2-quinolylmethyleneamino) phenol (QMAP). The solution properties of Ni-QMAP were investigated at different pH. The chromophoric properties of the
complex were enhanced with increase in pH, while stability decreased with time. The study of QMAP as a spectrophotometric reagent for the determination of small amounts of nickel was investigated. Dyeing properties of both complexes were investigated on polyamide 66 and the influence of the addition of another phenyl ring to the ligand molecule, the dyeing properties of the complex is also investigated.

Guidelines for the molecular design of non-doping red emissive materials for OLED applications are presented in the investigation of Jia-An Gan et.al. (Jia-An Gan, 2004). They have reported the synthesis of Schiff base derivatives of 1, 8-naphthalimides for non doping OLEDs (Organic Light Emitting Diode) showing tunable emission colour from blue, green to red.

Several Schiff bases and their complexes were synthesised from raceacetophenone (Nair R, 2006) and their antibacterial activity was studied against B.magaterium, E.coli, B.subtilis and antifungal activity against A.awamori. On comparison of activity of ligand and complexes, presence of metal causes more inhibition i.e more activity.

The synthetic, spectroscopic, and biological studies of sixteen ring-substituted 4-phenylthiosemicarbazones and 4-nitrophenylthiosemicarbazones of anisaldehyde, 4-chlorobenzaldehyde, 4-fluoro-benzaldehyde,
and vanillin with ruthenium(III) and rhodium(III) chlorides are reported by Vinod K. et al. (Vinod KS, 2007). Their structures were determined on the basis of the elemental analyses, spectroscopic data (IR, UV, $^1$H and $^{13}$C NMR) along with magnetic susceptibility measurements, molar conductivity and thermogravimetric analyses. On the basis of the above studies, three ligands were suggested to be coordinated to each metal atom by thione sulphur and azomethine nitrogen to form low-spin octahedral complexes with ruthenium (III) while forming diamagnetic complexes with rhodium (III). Both ligands and their complexes have been screened for their bactericidal activities and the results indicate that they exhibit a significant activity.

A series of 2-benzylideneaminonaphthothiazoles were designed and synthesized incorporating the lipophilic naphthalene ring to render them more capable of penetrating various biomembranes. Schiff bases were synthesized by the reaction of naphtha[1,2-$d$]thiazol-2-amine with various substituted aromatic aldehydes. 2-(2'-Hydroxy)-benzylideneaminonaphthothiazole was converted to its Co(II), Ni(II) and Cu(II) metal complexes upon treatment with metal salts in ethanol. All the compounds were evaluated for their antibacterial activities by paper disc diffusion method with Gram positive Staphylococcus aureus and Staphylococcus epidermidis and Gram negative Escherichia coli and Pseudomonas aeruginosa.
bacteria. All the compounds moderately inhibited the growth of Gram positive and Gram negative bacteria. The results obtained validate the hypothesis that Schiff bases having substitution with halogens, hydroxyl group and nitro group at phenyl ring are required for the antibacterial activity while methoxy group at different positions in the aromatic ring has minimal role in the inhibitory activity. The results also indicated that the metal complexes are better antibacterial agents as compared to the Schiff bases (Faizul A, 2007).

Reactions of diphenyllead(IV) chloride with benzil bis(thiosemicarbazone) (L$_1$H$_6$) and benzil bis(4-methyl-3-thiosemicarbazone) (L$_1$MeH$_4$) afforded the first complexes containing the diphenyllead(IV) moiety with bis(thiosemicarbazone) ligands. The new complexes show diverse structural characteristics depending on the ligand and the working conditions. The X-ray structure shows a distorted octahedral geometry around the lead atom, with the ligand molecules acting as NS chelates, but the nitrogen bonded to the metal is different; one of the triazines shows a novel behavior, since the nitrogen atom of the new imine group formed is the one that is bonded to the lead center, being a good example of linkage isomerism (David G, 2007).
SCHIFF BASES OF 2-AMINOPHENOL AND 2-AMINOTHIOPHENOL

Schiff base complexes of 2-Aminophenol and 2-Aminothiophenol are of wide interest because of their higher tendency for chelation stability, diversity of structure and speciality in applications. Tez Can 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 (Tez Can, 1984). The synthesis of several new complexes 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-aminothiophenol have been reported by Sonabati and Bindary (Sonabati AZ, 2000). Ligands and complexes were characterised and the Schiff bases behave as mono basic and tridentate ligands coordinating through oxygen atom of the deprotonated phenolic group, the nitrogen atom of the azomethine group and pyridine.

New complexes of the Vanadium (IV) and oxovanadium (IV) with Schiff base ligands derived from the β diketone and 2-aminophenol with distorted octahedral geometry were characterised (Abdel SD, 1998). The spectroscopic results were used to compute the important ligand field parameters. Vanadium (IV) complexes exhibit promising catalytic activity.
towards the aerobic oxidation of phenylene diamine to the corresponding semi oxide form.

Copper (II) complexes of Schiff bases of 5-nitro salicylaldehyde with 2-aminophenol and 4-aminophenol were prepared by Murty et.al. (Jaya Murty J, 2000). The complex showed mild to moderate activity against common pathogenic organisms. Maya devi et. al. (Mayadevi S, 1997) have synthesised and characterised some transition metal complexes of Schiff base -quinoxaline-2-carboxaline-2-aminophenol. A tetrahedral structure was assigned for Mn(II), Co(II), Ni(II), Cu(II) complexes, but for Fe(III) complex an octahedral dimeric structure was suggested. Pt complexes of 2-aminophenol with salicylaldehyde and 2-hydroxy-1-naphthaldehyde were prepared. The dibasic tridentate nature of the ligands was established on the basis of IR studies. The complexes were found to be non electrolytes, diamagnetic and square planar.

Sanchez et.al. (Sanchez G, 2002) have synthesised new palladium (II) complexes with a tridentate PNO Schiff base ligand of amino phenol. Deprotonation of the Schiff base formed by the condensation of 2-(diphenylphosphino)benzaldehyde with 2-aminophenol in the presence of the appropriate Pd precursor ([Pd(AcO)₂] or [PdCl₂(PhCN)₂] form the corresponding neutral complexes in good yield.
Minu et al. (Minu GB, 2004) have synthesised several Ru (II) Schiff base complexes derived from bis(pyrrole-2-carboxaldehyde)-3,4-toluenediimine, bis (pyrrole-2-carboxaldehyde)-1,2-cyclohexanediimine and bis (pyrrole-2-carboxaldehyde) ethylenediimine. All the complexes were characterised by analytical and spectroscopic methods and were found to be effective catalysts for the oxidation of primary alcohols in the presence of N-methyl morpholine-N-oxide as oxidant.

Besides the traditional applications, Schiff bases have emerged as analytical tool for precise determination of traces in even physiological systems as the application of Al(III) complex (Sanchez G, 2002) with salicylidene-o-aminophenol to the fluorometric determination of nucleic acids is a very good development in this field. In buffer medium of hexamethylene tetramine-HCl at pH 5.9 the Al (III) complex with salicylidene –o-aminophenol has a fluorescence peak at 508nm with excitation at 410nm. When nucleic acid coexists, it reacts with the complex within 8minutes at room temperature to produce a non fluorescent product, resulting in decrease of fluorescence intensity of the aluminium complex. On basis of this a new flourimetric method for nucleic acids determination is proposed. Compared with some established fluorometric methods, this procedure is sensitive, selective, reliable and reproducible.
Investigation on new transition metal chelates of 3-methoxysalicyledene-2- aminothiophenol Schiff base have carried out by Soliman et.al. (Soliman AA, 1999) Co (II), Cu(II), and Zn(II) complexes of the Schiff base was prepared and characterised by elemental analysis, IR, NMR, thermo gravimetric analysis, conductometric and magnetic measurements. The Schiff base act as bivalent anion with tridentate ONS donors derived from the phenolic oxygen, azomethine nitrogen and thiophenolic sulphur. The formulae were found to be [ML.H₂O] and ML₂] for the 1:1 and 1:2 non electrolyte complexes, respectively. The thermal decomposition of the complex follows first order and complexes show ligand field transitions at 815 and 760nm at room temperature and are consistent with a pseudo tetrahedral kinetics and thermodynamic parameters of the decomposition were calculated.

Subrata Mandal. et.al have reported (Subatra M, 1995) synthesis and characterisation of CuN₂S₂ complexes for modelling the blue protein active sites. Two new tetradentate ligands have been synthesised by Schiff base condensation of di isobutyraldehyde disulphide with mercaptoethylamine L₁ and 2-aminothiophenol L₂ respectively and then reducing the imine linkage with sodium borohydride in refluxing methanol. In the free ligand
the thiolate sulphur is protected with t-butyl groups, which are cleaved in the presence of Cu (II) salts to give neutral CuN₂S₂ complexes.

The condensation of o-aminothiophenol with 2-thiophene-dicarboxaldehyde yields 2-thiazolin derivative, rather than the expected Schiff base. However, upon reaction with metal ions, the thiazoline rearranges to the expected thiolate Schiff base. Complexes of Schiff base with Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), Ag(I), and Pd(II) were isolated and characterised (Tayim HA, 1983). Schiff base derived from the reaction of 2,5-thiophene-dicarboxaldehyde and o- amino-benzenethiol gave 2,5-bis(benzothiazolidin-2-yl)thiophene. Schiff base reacted as neutral ligand with Pb(II) and as dianionic species with Cu(II), Cd(II), Zn(II) (Salameh AS, 1983).

Complexes of Ni(II), Co(II), Cu(II), Zn(II), Pd(II), Pb(II), with Schiff base derived from isatin and 2-aminothiophenol were synthesised and characterised by elemental analysis, molar conductance, magnetic moment and spectroscopic methods (Khalifa MA, 1996). Schiff bases derived from 5-nitrosalicylaldehyde and the amines, o-and p-aminophenols o-aminothiophenol and sulfanilic acid were prepared and characterised. These complexes were tested for antibacterial activity against common pathogens and showed mild to moderate activity (Murty JJ, 1998).
Synthesis, spectroscopic characterisation, redox and biological screening studies of some Schiff bases transition metal complexes derived from salicylidine -4-aminophenol and aminophenol and 2-aminothiophenol were studied by Raman et.al. (Raman N, 2001). Ruthenium(II) complexes with tetradentate Schiff base ligands derived by condensing o-aminophenol or o-aminothiophenol with glyoxal has been carried out. (Viswanathan P, 2006). An octahedral geometry was proposed for the complexes and it was effective catalyst for the oxidation of benzyl alcohol to benzaldehyde using N-methyl morpholine-N-oxide as co-oxidant.

The Schiff base has been prepared by condensing 4-[N.N-dimethylamino] benzaldehyde with o-aminophenol in ethanolic media, form new metal complexes with Ni(II), Fe(II) and Cr (III) ions. The elemental analysis data exhibit the formation of 1:1 [M:L] ratio. IR spectral data display that the complexation occurs through oxygen atom or the hydroxyl group in the o-aminophenol and the nitrogen atom of azo-methine group (Maihub AA, 2007).

SCHIFF BASES OF DIKETONES AND HYDROXY KETONES

Tetradentate Schiff base ligands can conveniently be synthesised by condensing α-diketones, β-diketones, aldehydes with various diamines.
Tetradentate Schiff bases with N₂O₂, N₃O, N₄ and N₂S₂ donor sets have been widely studied for their ability to coordinate with metal ions. Classical examples that have been most widely examined with N₂O₂ donor set are the derivatives of acetylacetone with various diamines.

Recently large number of biologically active quadridentate ligands and its complexes has been reported. Gillian F. Morgan and coworkers (Gillian F, 1990) characterised the structural features of the new brain imaging agent ⁹⁹Tc [TcO(L)], a novel technetium complex with N₃O donor set, currently undergoing clinical trial evaluation for cerebral perfusion.

Rameswar Shukla and Bharadwaj have synthesised a new tetradentate Schiff base ligand by the condensation of diisobutyraldehyde disulphide with 2-aminophenol (Rameswar S, 1993). The ligand forms mononuclear manganese (II) complex with imine and phenolate ligation, which is relatively rare.

![Chemical structure](image)

Tropolone, o-quinone, 9, 10-phenanthrenequinone etc. are formally 1,2-diketones. In many respects their coordination chemistry resembles that of the more familiar congener acetylacetone. An important feature is its ability to provide stable paramagnetic ligands upon reduction. Its relevance to bacterial photosynthesis attracts special attention.

The electronic structure of these congeners is such that it is capable of undergoing successive one electron reduction and the close similarity between the complexes of their compounds can be appreciated by considering the redox equation given below.
It was noted earlier that the planar, rigid nature and small bite angle of 1, 2-diketones favours twist rearrangement pathways in metal complexes. The synthesis of quadridentate diimine chelates usually require the combination of one equivalent of a dicarbonyl compound and 2 equivalents of a primary amine, or one equivalent of a diamine and two equivalent of a carbonyl compound.

Simple α-diimines are hydrolytically unstable, but can be stabilised as metal complexes by the virtue of formation of chelated 5-membered rings (Krumhotz P, 1954). The α-diketones and gloxal undergo metal template reactions with amines to yield complexes of multidentate ligands. The same reactions occur with amino alcohols and amino thiols (Thomson MC, 1965; Elder MS, 1968).
Template reactions between α-diketones and diamines have been used for the synthesis of complexes of macro cyclic ligands (Jackel SC, 1972, Welsh WA, 1977).

A variety of primary amines undergo reaction with substituted aldehydes or ketones to yield the related imines, which can be used as the ligands in the metal complexes. The imine carbon is more susceptible to nucleophilic attack, and hence to the hydrolytic cleavage; so the imine formation is reversible. Therefore, it is often more desirable to prepare such metal complexes directly from the amine and the aldehyde or ketone, in the presence of the metal ion (Jackel SC, 1980; Lindoy LF, 1971).
The prior coordination of the carbonyl group to the metal ion results in the activation of the carbonyl carbon to amine nucleophilic attack. But it would be impossible for a precoordinated amine to act as a nucleophile and hence no kinetic template effect is involved. Numerous macrocyclic chelated compounds have been prepared by this method.

It is noteworthy that dicarbonyl compounds undergo reactions with diamines to yield heterocyclic compounds rather than α-diimines. However, in the presence of suitable metal ions the tautomeric α-diimines structure is reoriented and stabilised through the formation of five membered chelate rings (Stoufer RC, 1960). Dihydrazones of α-diketones can form low spin tris complexes with iron (II) ion. Thus the complex with biacetyl dihydrazone is well characterised and related tris complexes derived from benzil and glyoxal were also low-spin (Busch DH, 1956). While bis complexes of the type [FeX₂ (NN)₂] are paramagnetic with magnetic moment of 3 B.M.

Considerably much work has been carried on the low spin bis and tris complexes of bidentate and tridentate Schiff base of diketones. The facile template synthesis can be used to prepare free ligand by subsequent demetallation with EDTA.
Schiff bases, especially multidentate and macrocyclic ones are strong ligands for Zn. Derivatives of diketones form tetradeinate Zn complexes in which the ligand controls the stereochemistry of the complexes and provides numerous examples of unusual geometry about the metal atom, thus illustrating the coordination flexibility of these ions. The diimine formed by the condensation of benzil with ethylenediamine or 1,2-diamino benzene has been shown to have tetrahedral structure.

Neutral complexes of Cu(II), Ni(II), Co(II), and Zn(II) have been synthesised (Raman N, 2002) from benzil and 2-aminobenzyl alcohol and their antimicrobial activity was carried out. Most complexes have higher activity compared to the free base.

A series of antibacterial and antifungal compounds derived from various amino acids and diketone and their metal complexes were synthesised and characterised (Chohan ZH, 2006). The ligands and the complexes were screened for their antibacterial and antifungal activity. The results show metal (II) complexes are more active than the free ligands.

Schiff base derived from the reaction of the aldehydes, 3-hydroxybenzaldehyde and 5-nitrosalicylaldehyde with amines, aniline, and o-aminothiophenol and their complexes with Co(II), Ni(II) were reported.
The chemical shifts of the different protons in the NMR spectra of the prepared Schiff bases were also reported (Kolwalker SD, 1996; Issa YM, 1998).

Thiosemicarbazones of aromatic o-hydroxy aldehydes and ketones have attracted considerable interest because of their potential biological properties (West DX, 1990) and catalytic activities (Barber DE, 1992). These aromatic thiosemicarbazones most often coordinate as the dianion on loss of the phenoxy hydrogen and thiosemicarbazones to form mononuclear [M(ONS)X] (ONS represents the dianionic thiosemicarbazone) ligand coordinated via the phenoxy oxygen, azomethine nitrogen and thiolato sulphur and X represents a neutral molecule such as ammonia or pyridine (Sorianco M, 1985).

Palladium complexes of 2-hydroxyacetophenone N-ethyl thiocarbzone have been studied with regard to their structural and biological properties. The complexes were found to be triangular, trinuclear complex with bridging thiosemicarbazonato sulphur atoms (Dimitra KD, 1997).

Vanadium (IV) complexes have an ability to catalyse the generation of ROS, so diverse vanadium complexes with different ligands linked to metal
by carbon, nitrogen or oxygen atoms were synthesised. Among the various complexes, Bromo Hydroxyl acetophenone complex was found to have a potent sperm immobilizing activity and hence may be used as a contraceptive agent (Osmond JD, 1999).

Mixed ligand complexes of alkaline earth metals with 5-chlorosalicyaldehyde and o-hydroxyacetophenone have been prepared and characterised (Prasad RN, 2002). In recent years complexation studies of these metal ions have been undertaken following the recognition of various important roles of these metal ions in biological system.

In order to investigate the electronic, steric and geometric effect of a methyl group on imine carbon three optically active Schiff-base ligands of 2-hydroxyacetophenone with (1R,2R)-(−)1,2-diaminocyclohexane, (1S,2S)-(−)1,2-diphenylethlenediamine or R(+)-2,2’-diamino-1,1’-binaphthalene were prepared and characterised (Wen TG, 2002).

Novel Pd\textsuperscript{II} and Pt\textsuperscript{II} complexes of substituted o-hydroxyacetophenone-glycine have been synthesized, and characterized by conductivity measurements, IR, UV and NMR spectra. The spectral data indicate that the ligands are monobasic bidentate, coordinating through imino nitrogen and the carboxylate group. A four coordinate square planar configuration has
been proposed for all the complexes. The ligands, as well as their Pd$^{II}$ and Pt$^{II}$ complexes, exhibit potent cytotoxic activity against Ehrlich ascites tumour cells in vitro, but appear to be more active in vivo (Offiong E, 2004).

Several hexacoordinated ruthenium (III) complexes with appropriate Schiff bases having the donor groups (O,N) viz., o-hydroxy acetophenone ethylenediimine, o-hydroxy acetophenone propylenediimine, o-hydroxy acetophenone tetramethylenediimine and o-hydroxy acetophenone orthophenylenediimine in 1:1 molar ratio. All the complexes have been characterised on the basis of elemental analyses and spectral (IR, electronic and EPR), electrochemical and magnetic moment data. The antibacterial activities was tested for these complexes and found to be active (Thangadurai T, 2002).

A new complex of Cu with 2'-hydroxy-5'-methyl-acetophenone (HMAP) and triphenylphosphine (PPh$_3$) was prepared by the electrochemical oxidation of Cu in acetonitrile solutions. The final product, (MAP)Cu(PPh$_3$)$_2$, was crystallized from bulk solution and characterized by microanalysis, IR, Raman, $^1$H NMR together with x-ray crystallographic determinations. The results showed that the complex was a chelate structure in which Cu(I) ion was coordinated with two oxygen atoms of the
deprotonated ligand of MAP anion to form a six member ring, and two PPh$_3$ molecules participated in the coordination (Yaxian Yuan, 2005).

The synthesis of Cu(II) complexes derived from Schiff base ligands obtained by the condensation of 2-hydroxybenzaldehyde or terephthalic aldehyde with 4-amino-antipyrine is reported. The newly prepared compounds were characterized by 1H-NMR, UV-VIS, IR and ESR spectroscopy. The determination of the antimicrobial activity of the ligands and of the complexes was carried out on samples of *Escherichia coli*, *Klebsiella pneumoniae*, *Acinetobacter boumanii*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Candida sp*. The qualitative and quantitative antimicrobial activity test results proved that all the prepared complexes are very active, especially against samples of *Ps. aeruginosa*, *A. Boumanii*, *E. coli* and *S. aureus* (Tudor Rosu, 2006).

The metal complexes of UO[II] and Th[IV] with Schiff bases derived from 2-aminopyridine and acetophenone/o-hydroxy acetophenone/o-amino acetophenone have been synthesized and characterized on the basis of elemental analyses, conductivity, IR, electronic and [1]H NMR spectral studies. The evidences show that the complexes with acetophenone and o-hydroxy acetophenone Schiff bases exhibit coordination number eight while coordination number ten with o-amino acetophenone Schiff bases. A
comparative study of testicular atrophy in albino rats by the chelating agents and the corresponding UO[II] and Th[IV] complexes was carried out. A considerable reduction in the testes weight and weight of some accessory sex organs was observed. The effect is more with the complexes than with the ligands (Gudasi KB, 2006).

Scope of the Present Investigation

Generally an extensive study of co-ordination compounds has centered on the behaviour of metal ions rather than the attached Schiff base ligands. But the properties of such ligands can be modified by the co-ordination to the metal ions. An overview of Schiff base metal chelates reveals that only few works have been carried out in the area of hydroxy ketones as well as 1,2-diketones. Such class of ketones together with aminophenols and aminothiols, act as the building blocks of many poly and macrocyclic ligand systems of Schiff bases and their metal chelates. The present investigation has been designed to provide some modern and advanced results in this field.

In the present work, some new ligands namely 2-Hydroxyacetophenone 2-Aminothiophenol (HAPATP), 2-Hydroxyacetophenone 2-Aminophenol (HAPAP), Benzil 2-Aminothiophenol (BATP), Benzil
Aminophenol (BAP) have been synthesised and characterised. Their complexes with traditional transition metal ions such as Co(II), Ni(II), Cu(II) and Zn(II) were also isolated and characterised by various physico-chemical methods like UV, IR, NMR Spectra, Molar conductance and Magnetic data. The thermal decomposition character of some representative complexes in static air atmosphere have been studied by TGA technique. Analysis of the TG curves provides some probable structural assignments for each stages of decomposition. These results also support the proposed geometry of the complexes.
CHAPTER II
MATERIALS, METHODS AND INSTRUMENTS

In this chapter a concise report of the general reagents employed for the present study are given. It also gives the theory and techniques of the analytical and physical methods used for the characterisation of the ligands and complexes synthesised. Materials methods and instruments for antitumor and antibacterial studies were given as a separate chapter in Part III and Part IV.

Materials

Analar grade samples of 2-Hydroxyacetophone, Benzil, 2-Aminothiophenol and 2-Aminophenol supplied by E-Merck, BDH (India), Glaxo, Sigma Company, USA were used for the preparation of ligands, the metal source used for the synthesis of the complexes are acetates of Co(II), Ni(II), Cu(II) and Zn(II). Solvents like chloroform, carbon tetrachloride, dimethylformamide and dimethylsulphoxide were used as such, but the LR grade ethanol, methanol and acetone were purified by standard procedures (Weissberger A, 1956; Vogel AI, 1962). Specroscopic grade samples of the solvents were employed for the spectral measurements.
Methods

The following procedures were employed to test the purity of ligands and characterisation of their metal complexes.

CHN Analysis

Carbon, Hydrogen and Nitrogen content of the ligands and their metal complexes were determined by microanalysis on a Heraous-CHN-O-rapid analyser.

Estimation of Metals

Standard methods (Vogel AI, 1978) like volumetric, gravimetric, pyrolitic techniques were adopted for the estimation of metal content. The atomic absorption spectroscopy is also used for the confirmation of the metal percentage in selected samples.

For the volumetric and gravimetric estimations a common methods was used for decomposing the metal complexes. About 0.2gm of the complex was digested with concentrated nitric acid-perchloric acid mixture followed by Conc.HCl. The resultant solution was then quantitatively made up to 100 ml by using a definite volume of the solution, the metal content of the complex was estimated.
Amount of copper was determined iodometrically by the addition of KI and subsequent titration of liberated iodine by standard sodium thiosulphate. The amount of Cobalt was estimated volumetrically by complexometric titration using standard EDTA solution and Xylenol Orange indicator. Gravimetrically Nickel was estimated by precipitating as dimethyl glyoximate. By complexometric titration using standard EDTA and Eriochrome Black-T indicator, the amount of zinc metal was estimated.

Almost all of these metals were estimated by pyrolysis method. About 0.2 gm of each complex was weighed out in a silica crucible and heated strongly. During the heating all the organic particles in the chelate was burnt of and the metallic oxide left behind was weighed. From the weight of the oxide metal percentage was calculated.

**Estimation of Sulphur**

Sulphur content in the complexes was estimated after oxidising it with nitric acid to sulphate. The sulphate was then determined gravimetrically (Furman NH, 1962) as BaSO₄.
**Molar Conductance**

Molar conductance measurements of the complexes were carried out in methanol, ethanol and double distilled water at 28 ± 2°C using a solution of 10^{-3} M concentration. The conductance measured can be used to find the electrolytic or non electrolytic nature of complexes.

**Magnetic Moment**

Magnetic susceptibilities of the complex were determined at room temperature by using a Gauy Balance (Lewis J, 1963). Diamagnetic Corrections were applied using Pascal’s Constants taking into consideration of the magnetic contribution of various atoms and structural units (Earnshaw N, 1968). The effective magnetic moment ($\mu_{\text{eff}}$) was calculated using the equation

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi' M \times T}$$

$\chi'M = $ molar susceptibility corrected for diamagnetism and $T = $ absolute temperature.

The theoretical magnetic moments were calculated using the formula

$$\mu_{\text{eff}} = g \sqrt{S \times (S+1)}$$
Electronic Spectra

The UV - Visible spectra of the ligands and complexes were recorded on a Shimadzu recording spectrophotometer using methanol, ethanol or distilled water as the solvent. Electronic spectral studies were carried out to supplement the information obtained from the magnetic measurements.

The ligands which are mainly organic compounds have absorption in the UV region and hence do have bands in the region of 200 to 350nm of the electromagnetic spectrum. In some cases these bands extends over to a higher wavelength region due to conjugation. But upon complexation with transition metal ions, due to interaction with the metal ion, there will be interesting change in the electronic properties of the system. For each complex the peak was assigned to a particular d-d transition and charge transfer spectra from metal to ligand (M→L) or ligand to metal (L→M) can be observed. These information can be processed to obtain the structure and geometry of the compounds (Lever ABP, 1984).

Infrared Spectra

The IR Spectroscopy is commonly used as a characterisation technique for metal complexes. The IR Spectra of the ligands and metal complexes were recorded in the range of 4000-400 cm⁻¹ on a Schimadzu-IR -
470 infrared spectrometer by KBr disc technique. The importance of IR spectroscopy lies in the fact that the characteristic infrared absorption bands of a group occur at about the frequency irrespective of the molecule in which the group is present.

**Thermogravimetric Analysis**

The thermogram of complexes were recorded non isothermally using a sample weight of 5mg in static air atmosphere at a rate of heating $10^\circ$ or $15^\circ$C min$^{-1}$. Each mass loss consideration from the TG plot can be assigned to the decomposition of volatilisation of a particular group. The careful examination of such steps during the heating of each complex can be found to be in good agreement with the proposed structure.

**NMR Spectra**

NMR Spectra of some selected ligands and complexes (Zn Complexes of HAPATP and BAP) were carried out on BruckerDPX 300 MHz Machine using DMSO as solvent. In each case the spectra were analysed by considering the standard chemical shift values.
Instruments

The instruments used for the present investigations are given below.

1. Heraous – CHN – O – rapid analyser

2. Toshniwal conductivity bridge.


4. Shimadzu UV-1602 Spectrophotometer

5. Shimadzu IR 470 Infrared Spectrophotometer

6. Hitachi R – 600 Spectrometer

7. Varian E4 Band Spectrometer


9. Brucker DPX – 300 MHz Machine
CHAPTER III

TRANSITION METAL COMPLEXES OF 2-HYDROXY ACETOPHENONE 2-AMINO THIOPHENOL (H$_2$L$^1$)

New vistas have opened up in the field of co-ordination chemistry with the designing of structure of complexes by the influence of metal ions (Busch DN, 1963). A perusal of literature showed major developments have been achieved in the research of co-ordination compounds with special emphasis on metal complexes of Schiff bases containing nitrogen, oxygen and sulphur atoms as donors (Djebar SS, 1997). This may be due to their stability, pharmacological activity and potential applications in many fields.

The Schiff bases derived from 2-Hydroxy acetophenone are very interesting due to their ability to form various types of metal complexes. Biological activity of complexes derived from amino thiophenol has been extensively studied with respect to their antiviral, antitumor and antibacterial activities (Thanga Durai TD, 2002). In view of the importance of this class of complexes we have attempted to synthesize a novel ligand 2-Hydroxy acetophenone 2-Aminothiophenol (HAPATP), and to explore its structure and possibilities as an active biological agent.
In this chapter we have described our results of the brief study of the transition metal complexes of the Schiff base derived from 2-Hydroxy acetophenone and 2-Aminothiophenol.

**Synthesis of the Ligand**

The ligand 2-Hydroxyacetophenone2-Aminothiophenol was prepared in ethonolic medium from 2-Hydroxyacetophenone and 2-Aminothiophenol. An ethanolic solution of 2-Hydroxy acetophenone (0.01 mol) was mixed with and ethanolic solution of 2-Aminothiophenol (0.01 mol) and was refluxed for two hours on a water bath. The pale yellow precipitate formed was filtered, washed and dried over anhydrous CaCl₂. The melting point was found to be 105°C.

**Characterisation of the Ligand**

The ligand 2-Hydroxy acetophenone 2-Aminothiophenol (HAPATP) was characterized on the basis of elemental analysis and spectral data as given in the Table I.3.1 and I.3.2. The UV, IR and NMR studies of the ligands showed the characteristic bands. Based on the above results the structure of the ligand was confirmed as

![2-Hydroxy acetophenone 2-Aminothiophenol](image)

2-Hydroxy acetophenone 2-Aminothiophenol
STUDIES ON Co (II), Ni(II), Cu(II) AND Zn(II) COMPLEXES OF 2-HYDROXY ACETOPHENONE 2-AMINO THIOPHENOL- HAPATP (H₂L¹)

Preparation and characterization Co (II), Ni(II), Cu(II) and Zn(II) complexes of 2-Hydroxyacetophenone 2-Aminothiophenol- HAPATP (H₂L¹) are described in this part.

Synthesis of the Complexes

The complexes were prepared by slowly adding a hot aqueous solution of the metal acetate to a refluxing ethanolic solution of the ligand containing sodium acetate (0.5 gm), until the metal ligand ratio reached 1:1. The reaction mixture was refluxed for 1 hour and the complexes were precipitated. The precipitated complexes filtered, washed with water and alcohol and dried over anhydrous calcium chloride.

Co(II), Ni(II), Cu(II) and Zn(II) complexes were prepared by this method.

Characterisation of the Complexes

The complexes were characterized on the basis of elemental analysis, UV, IR and NMR spectral data, magnetic studies, conductance measurements and thermal studies as given in the Tables I.3.1 and I.3.2.
Results and Discussion

All the complexes are coloured, photostable and non hygroscopic. They are soluble in DMSO and in other common organic solvents. On the basis of elemental analysis Co(II), Ni(II), Cu(II) and Zn(II) complexes can be represented by the general formula ML(H₂O)₃ where M is the metal and L is the ligand moiety.

The analytical data of these complexes are presented in the Table I.3.1. The room temperature, magnetic moments and molar conductivities of the complexes are also given in the same table. Important IR spectral bands of the ligands and complexes are also given in the Table I.3.2.

Elemental Analysis

The complexes were analysed for metal and sulphur by standard methods (Vogel AI, 1978; Furman NH, 1962). The percentages of carbon, hydrogen and nitrogen were estimated by micro analytical methods. The results are given in the Table I.3.1.

Molar Conductance

Conductance measurements of these complexes in methanol at a concentration of 10⁻⁴ M at room temperature are in the range of 2-10 ohm⁻¹.
1 \text{cm}^2\text{mol}^{-1}. The very low values indicate that these complexes behave as non-electrolytes and are neutral in nature (Geory WJ, 1971).

**Magnetic Measurements**

Magnetic susceptibility of the complexes was determined by Gouy balance. The measurements were made at room temperature and instrument was standardized using Hg [Co(NCS)$_4$] as calibrant (Figgis BN, 1958). Table I.3.1 shows effective magnetic moment values calculated from the corrected magnetic susceptibility. Some indications of the structures and geometries of the complexes can be obtained from these magnetic moment values (Dutta RL, 1992).

Octahedral and tetrahedral Co(II) complexes differ in their magnetic properties. In high spin octahedral complexes of Co(II), the ground term is $^4T_{1g}$ which results in considerable orbital contributions. It is reported that octahedral high spin geometry can be assigned to Co(II) complexes if the measured value of the magnetic moment is in the range of 4.7-5.2 BM (Lewis J, 1963; King EA, 1968). The expected magnetic moment is the spin only value for the three unpaired electrons ie 3.87BM. Here the Co(II) complex shows a magnetic moment of 4.82BM rather above the spin only value indicates octahedral geometry.
Ni(II) complex has a magnetic moment value of 3.5 BM, which is near to the normal range observed for octahedral Ni(II) complexes. This shows the presence of two unpaired electrons with the electronic configuration of \( t_2^6e_g^2[3A_2] \). Therefore an octahedral geometry can be assigned to the Ni(II) complex (Lewis J, 1963; Masoud MS, 1991).

The Cu(II) complexes usually have a distorted octahedral stereochemistry. A few are known with squareplanar or approximately tetrahedral geometry. In regular octahedral Cu(II) complexes ground term is \( ^3E_g \) and hence no orbital contribution is expected. The spin only magnetic moment values corresponding to one unpaired electron is 1.73BM but the observed values fall in the range 1.80-2.10BM. This is due to spin orbit coupling. In regular tetrahedral Cu(II) complexes, the ground term being a triplet state, orbital contribution is expected. So theoretically predicted magnetic moment value is 2.2BM (Figgis BN, 1958). But the reported values are in the range of 1.95-2BM (Kumar NRS, 1999). In our study the Cu(II) Complex gave a magnetic moment value of 1.96BM which indicates an octahedral geometry for the complex. The Zn(II) Complex was found to be diamagnetic.
Electronic Spectra

The electronic spectra of all the complexes of HAPATP are recorded in DMSO. Octahedral geometries are commonly found in Co(II) Complexes and such complexes are pale pink in colour. In the octahedral Co(II) complex, $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ transitions occur in the region 1250-1000nm and 700-500nm respectively (Bhara B, 1971). In the present case the electronic spectrum of Co(II) Complex shows bands at 1066nm and 665nm which can be assigned to the d-d transitions of octahedral geometry. Low intensity of bands and the pink colour of the complex support octahedral geometry.

Studies by Jorgensen (Jorgenson CK, 1956) revealed that in the case of Ni(II) octahedral complexes, the d-d transitions are observed in the ranges of 1100-900nm [$3A_{2g}(F) \rightarrow 3T_{2g}(F)$], 650-500nm [$3A_{2g}(F) \rightarrow 3T_{1g}(F)$] and 400-350nm [$3A_{2g}(F) \rightarrow 3T_{1g}(P)$]. Most of the tetrahedral complexes of Ni(II) has intense blue colour due to the presence of an absorption band in the red part of the visible region (Solimann AA, 1999). In the present investigation Ni(II) complexes of HAPATP shows three absorption band at 444nm, 580nm and 900nm which can be attributed to an octahedral geometry (Angela K, 2007).
For octahedral Cu(II) complexes only a single band due to the transition $^2E_g \rightarrow ^2T_{2g}$ (D) would result but the observed band is very broad and clearly contain several components which is a result of tetragonal distortion due to Jahn –Teller Effect (Sutton, 1968). In the case of Cu(II) complex of HAPATP, an absorption band at 694nm is assigned to a slightly distorted octahedral geometry for the complex. In the case of Zn(II) complex d-d transitions are not possible and the bands observed ~ 400nm are due to charge transfer.

**Infrared Spectra**

Infrared spectra of the ligand and complexes were examined in detail. The significant vibrational bands and their assignments are given in the Table I.3.2. IR Spectra of the ligand (HAPATP) show the absence of bands corresponding to $\nu$ NH$_2$ and $\nu$C=O. Instead of this a new prominent band at 1550-1690 cm$^{-1}$ due to azomethine linkage appeared in the ligand indicating the condensation of ketonic group with amino group (Nakomoto K, 1970). A peak ~3400 cm$^{-1}$ and ~1300 cm$^{-1}$ corresponds to $\nu$(OH) stretching and bending vibrations. A weak band ~2550 cm$^{-1}$ corresponds to the $\nu$(SH) vibration. Bands at ~760 cm$^{-1}$ probably indicate the C-S symmetric vibrations and this band is shifted to lower frequencies in all the complexes. The band at 1612 cm$^{-1}$ is the characteristic of the azomethine group (>C=N) present in
the free ligand. A downfield shifting in this frequency region (1570-1595 cm\(^{-1}\)) can be observed in all the complexes indicating that the ligand is coordinated to the metal through azomethine nitrogen. This also indicates the reduction of electron density in the azomethine ligand. Broad and strong band around 3300-3400 cm\(^{-1}\) indicates coordinated water molecules present in the complexes. In the chelates of Co(II), Ni(II) and Cu(II), coordinated nature of water molecules is further supported by the appearance of new bands of medium intensity between 750-850 cm\(^{-1}\) \textit{(Clothup NB, 1975)}). The weak \(\nu\) (SH) vibration band at 2552 cm\(^{-1}\) in the ligand disappears in the complexes showing the participation of SH group in chelation. The C-O band which appear \(\sim 1246\) cm\(^{-1}\) in the ligand is shifted to lower frequency in the complexes indicating the co-ordination of the metal through phenolic oxygen. The new band found in complexes in the range 540-560 cm\(^{-1}\) are assigned to \(\nu\)(M-N) stretching mode. The \(\nu\)(M-S) bands of the complexes appear in the range 450-500 cm\(^{-1}\) and the new bands in the region 420-440 cm\(^{-1}\) are correspond to \(\nu\)(M-O) stretching vibrations \textit{(Ferrare R, 1971)}. The above data indicate that the ligand is dianionic tridentate ligand (ONS) coordinating to the metal through the deprotonated thiophenol, deprotonated phenol and azomethine nitrogen.
NMR Spectra

Proton NMR spectra has been useful in establishing the nature and structure of Schiff bases and complexes in solution. In the case of HAPATP complexes the $^1$H NMR Spectra of diamagnetic Zn Complex, $[\text{ZnL}^1(\text{H}_2\text{O})_3]$ was compared with free ligand. The ligand gave a singlet at 12.5$\delta$ corresponding to OH protons, another singlet at 5.1$\delta$ corresponding to SH, and a singlet at $\delta$ 2.5 for the methyl protons. Aromatic multiplet was observed at the range 6.9-7.4 $\delta$ corresponding to 8 aromatic protons. In NMR spectra of the diamagnetic Zn complex it was found that the singlets due to SH and OH protons disappeared indicating the removal of these protons by chelation with Zinc (Soliman AA, 1999).

TG Studies

Cu(II) and Zn(II) complexes of HAPATP were subjected to thermal studies by non isothermal method. A three stage decomposition was observed for Cu(II) Complex whereas Zn(II) Complex undergoes a two stage decomposition. The observed mass loss in TG studies, agrees fairly well with the values calculated from pyrolitic experiments. Probable assignments of each decompositions are discussed in Part II.
The complexes can be represented by the following structure based on the above results.

\[ M = \text{Co(II), Ni(II), Cu(II) and Zn(II)} \]
Table I.3.1

Microanalytical, magnetic and conductance data of transition metal chelates of 2-Hydroxyacetophenone 2-Aminothiophenol (H$_2$L$^1$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
<th>S %</th>
<th>M %</th>
<th>$\mu_{\text{eff}}$</th>
<th>B.M</th>
<th>ohm$^{-1}$cm$^{2}$mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$L$^1$</td>
<td>68.40</td>
<td>(69.10)</td>
<td>5.2</td>
<td>(5.34)</td>
<td>5.2</td>
<td>(5.76)</td>
<td>12.5</td>
<td>(13.16)</td>
</tr>
<tr>
<td>CoL$^1$(H$_2$O)$_3$</td>
<td>47.9</td>
<td>(47.46)</td>
<td>4.7</td>
<td>(4.80)</td>
<td>4.02</td>
<td>(3.95)</td>
<td>9.1</td>
<td>(9.049)</td>
</tr>
<tr>
<td>NiL$^1$(H$_2$O)$_3$</td>
<td>47.23</td>
<td>(47.49)</td>
<td>4.56</td>
<td>(4.80)</td>
<td>4.01</td>
<td>(3.95)</td>
<td>9.4</td>
<td>(9.04)</td>
</tr>
<tr>
<td>CuL$^1$(H$_2$O)$_3$</td>
<td>47.02</td>
<td>(46.85)</td>
<td>4.15</td>
<td>(4.74)</td>
<td>3.92</td>
<td>(3.90)</td>
<td>8.9</td>
<td>(8.92)</td>
</tr>
<tr>
<td>ZnL$^1$(H$_2$O)$_3$</td>
<td>47.2</td>
<td>(46.61)</td>
<td>4.65</td>
<td>(4.71)</td>
<td>3.93</td>
<td>(3.88)</td>
<td>8.79</td>
<td>(8.87)</td>
</tr>
</tbody>
</table>

Calculated values are given in the parenthesis; D-diamagnetic, M –metal, L-ligand

Table I.3.2

Characteristic Infrared absorption frequencies (cm$^{-1}$) of transition metal chelates of 2-Hydroxyacetophenone 2-Aminothiophenol (H$_2$L$^1$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$H$_2$O cm$^{-1}$</th>
<th>$\nu$C=N cm$^{-1}$</th>
<th>$\nu$C-O cm$^{-1}$</th>
<th>$\nu$C-S cm$^{-1}$</th>
<th>$\nu$M-N cm$^{-1}$</th>
<th>$\nu$M-O cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$L$^1$</td>
<td>3379br</td>
<td>1612s</td>
<td>1246m</td>
<td>763m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(H$_2$L$^1$)(H$_2$O)$_3$</td>
<td>3308br</td>
<td>1585s</td>
<td>1230m</td>
<td>747m</td>
<td>540m</td>
<td>420w</td>
</tr>
<tr>
<td>Ni(H$_2$L$^1$)(H$_2$O)$_3$</td>
<td>3316br</td>
<td>1587s</td>
<td>1230m</td>
<td>750m</td>
<td>542m</td>
<td>428w</td>
</tr>
<tr>
<td>Cu(H$_2$L$^1$)(H$_2$O)$_3$</td>
<td>3329br</td>
<td>1580s</td>
<td>1226m</td>
<td>749m</td>
<td>520w</td>
<td>422w</td>
</tr>
<tr>
<td>Zn(H$_2$L$^1$)(H$_2$O)$_3$</td>
<td>3304br</td>
<td>1590s</td>
<td>1227m</td>
<td>742m</td>
<td>560m</td>
<td>438m</td>
</tr>
</tbody>
</table>

br – broad, s-strong, m-medium, w-weak
Figure I.3.1: Infra red spectra of HAPATP (H$_2$L$^1$)
Figure I.3.2: Infra red spectra of [ZnL₁(H₂O)₃]
A survey of literature showed that there have been numerous studies on the Schiff bases and metal complexes derived from 2-Aminophenol. However little information is available on metal complexes of Schiff bases derived from 2-Hydroxyacetophenone and 2-Aminophenol. Hence it is considered to be worthwhile and interesting to investigate the properties, structures and geometries of the ligand 2-Hydroxyacetophenone 2-Aminophenol and its complexes with metal ions such as Co(II), Ni(II), Cu(II) and Zn(II).

The present study described the synthesis of a new tridentate Schiff base ligand derived from 2-Hydroxyacetophenone and 2-Aminophenol.

**Synthesis of the ligand**

For the preparation of the ligand $\text{H}_2\text{L}^2$, an ethanolic solution of 2-hydroxyacetophenone (0.01 mol) was reflexed with an ethanolic solution of 2-aminophenol (0.01 mol) for about 3 hours on a water bath. The product formed was filtered and washed with very dilute alcohol. It was dried over
anhydrous CaCl$_2$. The melting point of the ligand H$_2$L$^2$ was found to be 121°C.

**Characterisation of the ligand**

CHN analysis, IR and UV spectral data and thermal data were used for the characterisation of the ligand HAPAP. The calculated percentages of carbon, hydrogen and nitrogen were found to be in good agreement with observed values. Results are given in the Tables I.4.1 and I.4.2.

Bases on the above results the proposed structure of the ligand is given below.

![Structure of HAPAP](image)

2-Hydroxyacetophenone 2-Aminophenol
STUDIES On Co(II), Ni(II), Cu(II) AND Zn(II) COMPLEXES OF 2-HYDROXYACETOPHENONE 2-AMINOPHENOL - HAPAP (H₂L²)

Synthesis of the Complexes

The complexes are prepared by adding a hot aqueous solution of the metal acetate slowly to a refluxing ethanolic solution of the ligand. The resulting solution was refluxed for two hours and then cooled. The separate complex was filtered washed with alcohol and dried.

Characterisation of the Complexes

The complexes were characterised on the basis of elemental analysis, UV and IR spectral data, magnetic studies, conductance measurements and thermal data.

Results and Discussion

All the complexes are coloured, stable and non hygroscopic powdered solids. They are insoluble in water but soluble in organic solvents like methanol, ethanol, acetone, DMSO, etc. The properties of the complexes were analysed on the basis of information obtained from analytical, physiochemical and spectral investigations
Elemental Analysis

The complexes were analysed for metal by standard methods. Carbon, hydrogen and nitrogen were estimated by microanalytical methods. Results are summarized in tables.

Molar Conductance

The conductance measurements in methanol were carried out at a concentration of $10^{-4}$ M at room temperature and the data are included in the Table I.4.1. All the chelates exhibited very low values of molar conductance ($<10 \text{ ohm}^{-1} \text{ cm}^{2} \text{ mol}^{-1}$) which indicate their non electrolytic nature.

Magnetic Measurements

The details of the methods for the theoretical prediction by magnetic behaviour of the complexes are already explained in the Chapter III. The observed magnetic moment values are summarised in Table I.4.1.

The magnetic moments for the spin free octahedral Co(II) complex ($4T_{1g}$) is higher than the spin only values and it may be due to orbital contributions of the ground state and first excited state. It is reported that the octahedral high spin geometry can be assigned to Co(II) complexes if the observed magnetic moment values are in the range of 4.7 – 5.2BM (Wilkins
RG, 1969). In the case of Co(II) complex of HAPAP shows a magnetic moment of 4.94BM prefers an octahedral geometry. The complex of Ni(II) have a magnetic moment value of 3.4BM which is very close to the value of octahedral geometry (Wilkins RG, 1969). The magnetic moment observed for Cu(II) complex of HAPAP was 1.9BM as expected for octahedral geometry. The Zn(II) complex was found to be diamagnetic.

**Electronic Spectra**

The electronic spectral data were found to be in good agreement with the conclusions arrived from magnetic susceptibility measurements.

In the present study Co(II) complex of HAPAP shows the absorption bands of 476nm and 562nm which can be assigned to the transitions \([^4T_{1g}(F) \rightarrow ^{4}T_{2g}(P), ^{4}T_{1g}(F) \rightarrow ^{4}A_{2g}(F)]\) respectively. This suggests an octahedral geometry for the complex.

For Ni(II) complex two bands correspond to 564nm and 972nm were obtained. These data supports an octahedral geometry for the complex. In the case of Cu(II) complex absorption band was found to be at 678nm and can be assigned to the d-d transitions in an octahedral environment (Waters JM, 1964). For the Zn(II) complex of HAPAP d-d transitions are not possible and the band observed at 399nm is due to charge transfer.
Infra Red Spectra

The infrared spectra of the ligand gave the azomethine stretching band at 1603 cm\(^{-1}\) and the broad band due to O-H stretching frequency ~3405cm\(^{-1}\). The bands at 1368cm\(^{-1}\) and 1254cm\(^{-1}\) corresponds to the bending vibrations of O-H and C-O respectively. The IR spectra of the complexes were compared with that of the free ligand to resolve the changes that might have taken place during complexation. The ligand exhibit broad medium intensity bands in the 2700-2450cm\(^{-1}\) range, which are assigned to the intra molecular hydrogen bonding, O-H…N, vibrations. This situation is common for aromatic azo methine compounds containing ortho -OH groups and in complexes this band disappeared completely (Khedry AM, 2005; Ben Saber SM, 2005). The band at 1603cm\(^{-1}\) is the characteristic of the azomethine group present in the free ligand. The lowering of this frequency region to 1585cm\(^{-1}\) observed in Cu(II) and Zn(II) complexes of the ligand indicates the involvement of azomethine nitrogen in co-ordination (Mahapatra BI, 1987). The same phenomenon can also be observed in cobalt and nickel complexes of the ligand (Table I.4.2). Presence of a broad band around 3378cm\(^{-1}\) in Co(II), Ni(II), Cu(II) and Zn(II) complexes corresponds to the OH stretching of co-ordinated water which is further supported by new bands at 871-894cm\(^{-1}\). New bands in the range 420-432cm\(^{-1}\) and 520-540 cm\(^{-1}\) also appeared
in all the complexes. These bands are due to the formation of M-O and M-N bonds (Ferrare R, 1971).

**TG Studies**

Complexes of Cu(II) and Zn(II) were subjected to thermal studies by non-isothermal method. The observed mass loss values from the TG curves were in good agreement with the values obtained from pyrolytic experiments. Probable assignments of each decompositions are discussed in Part II.

Bases on the above results an Hexa co-ordinated structure is assigned to all the metal complexes of HAPAP under study. The general structure of the complexes can be represented as follows.

\[
\begin{align*}
\text{OH}_2 & \quad \text{H}_2\text{O} \\
\text{M} & \quad \text{OH}_2 \\
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{C} \\
& \quad \text{CH}_3
\end{align*}
\]

\[\text{M} = \text{Co(II), Ni(II), Cu(II) and Zn(II)}\]
Table I.4.1

Microanalytical, magnetic and conductance data of transition metal chelates of 2-Hydroxyacetophenone 2-Aminophenol (H₂L²)

<table>
<thead>
<tr>
<th>Compound</th>
<th>C %</th>
<th>H %</th>
<th>N%</th>
<th>M%</th>
<th>μ\text{eff}</th>
<th>B.M</th>
<th>ohm⁻¹ cm² mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂L²</td>
<td>73.61 (74.00)</td>
<td>5.24 (5.7)</td>
<td>6.06 (6.16)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoL²(H₂O)₃</td>
<td>48.42 (49.71)</td>
<td>4.78 (5.03)</td>
<td>4.23 (4.14)</td>
<td>17.01 (17.43)</td>
<td>4.94</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>NiL²(H₂O)₃</td>
<td>48.5 (49.74)</td>
<td>4.95 (5.03)</td>
<td>4.3 (4.14)</td>
<td>16.82 (17.38)</td>
<td>3.4</td>
<td>3.73</td>
<td></td>
</tr>
<tr>
<td>CuL²(H₂O)₃</td>
<td>48.20 (49.04)</td>
<td>4.46 (4.96)</td>
<td>3.9 (4.08)</td>
<td>17.92 (18.54)</td>
<td>1.9</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>ZnL²(H₂O)₃</td>
<td>47.56 (48.78)</td>
<td>4.4 (4.93)</td>
<td>4.11 (4.06)</td>
<td>17.9 (18.98)</td>
<td>D</td>
<td>5.1</td>
<td></td>
</tr>
</tbody>
</table>

Calculated values are given in the parenthesis; D-diamagnetic, M –metal, L-ligand

Table I.4.2

Characteristic Infrared absorption frequencies (cm⁻¹) of transition metal chelates of 2-Hydroxyacetophenone 2-Aminophenol (H₂L²)

<table>
<thead>
<tr>
<th>Compound</th>
<th>νH₂O cm⁻¹</th>
<th>νC=O cm⁻¹</th>
<th>νC=N cm⁻¹</th>
<th>νM-N cm⁻¹</th>
<th>νM-O cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂L²</td>
<td>3405 br</td>
<td>1603 s</td>
<td>1254 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoL²(H₂O)₃</td>
<td>3378 br</td>
<td>1579 m</td>
<td>1225 m</td>
<td>520 m</td>
<td>420 w</td>
</tr>
<tr>
<td>NiL²(H₂O)₃</td>
<td>3380 br</td>
<td>1586 s</td>
<td>1217 m</td>
<td>524 m</td>
<td>424 w</td>
</tr>
<tr>
<td>CuL²(H₂O)₃</td>
<td>3378 br</td>
<td>1585 s</td>
<td>1216 m</td>
<td>540 m</td>
<td>421 w</td>
</tr>
<tr>
<td>ZnL²(H₂O)₃</td>
<td>3385 br</td>
<td>1585 s</td>
<td>1226 m</td>
<td>525 m</td>
<td>432 w</td>
</tr>
</tbody>
</table>

br-broad, s-strong, m-medium, w-weak
CHAPTER V

TRANSITION METAL COMPLEXES OF BENZIL 2-AMINOTHIOPHENOL (H₂L³)

The interest in the clinical use of sulphur containing chelating agents as vehicles for delivery of metals to various sites in biological systems as led to the study of Schiff bases derived from Aminothiophenol and Diketones. The properties and reactivity of Schiff base complexes derived from 1,2 Diketones and Aminothiophenols attracts many chemist due to their biological activity as antitumor, antifungal and antiviral agents. So it was thought worthwhile to study the interaction of the ligand Benzil 2-Aminothiophenol with some transition metals.

In this chapter we have described the synthesis of a new tetradeinate Schiff base ligand obtained from Benzil and 2-Aminothiophenol. This ligand produces various metal complexes with different transition metal ions such as Co(II), Ni(II), Cu(II) and Zn(II).

Synthesis of the Ligand

For the preparation of the ligand Benzil 2-Aminothiophenol (H₂L³) an ethanolic solution of Benzil (0.01 mol) was refluxed with an ethanolic
solution of 2-Aminothiophenol (0.02 mol) for two hours on a waterbath. When the light yellow crystals of the Schiff base began to separate the solution was cooled in ice, filtered washed and recrystallised from ethanol. The melting point of the compound was found to be 118°C.

**Characterisation of the Ligand**

Free ligand has been studies to obtain an insight into their structure and for comparison with their metal complexes. Elemental and spectral studies were carried out to characterise the compound these details are given in the Table I.5.1 and I.5.2. The calculated percentages of carbon, hydrogen and nitrogen were found to be in good agreement with the observed values.

Bases on the above results the structure of the ligand BATP can be given as follows.

![Benzil 2-Aminothiophenol (BATP)]
STUDIES ON Co(II), Ni(II), Cu(II) AND Zn(II) COMPLEXES OF BENZIL AMINOTHIOPHENOL -BATP (H₂L₃)

Synthesis of the Complexes

The metal complexes were prepared by adding an aqueous solution of the metal acetate to a refluxing ethanolic solution of benzil (0.01 mol) and 2-aminothiophenol (0.02 mol) continued the process for further two hours. The separated complexes were filtered, washed with very dilute alcohol and dried over anhydrous CaCl₂.

Co(II), Ni(II), Cu(II) and Zn(II) complexes of the ligand H₂L₃ were prepared by the above method.

Characterisation of the Complexes

The complexes were characterised on the basis of elemental analysis, UV and IR Spectral data, magnetic studies, conductance measurements and thermal data.

Results and Discussion

The nature of carbonyl and amine compounds favours the formation of Schiff base at equilibrium. When these compounds are aromatic the equilibrium favours the formation of the Schiff base since this brings two
aromatic rings in conjugation. The metal complexes of Benzil 2-Aminothiophenol are coloured, stable and non hygroscopic solids. They are insoluble in water but soluble in all organic solvents. The properties, structure and bonding of these complexes have been explained. On the basis of the information obtained from analytical, physicochemical and spectral investigations.

**Elemental Analysis**

The complexes were analysed for metal and sulphur by standard methods. Carbon hydrogen and nitrogen were estimated by microanalytical methods. The results of this analysis are summarised in Table I.5.1.

**Molar Conductance**

The conductance measurements in methanol were carried out at a concentration of 10^{-4} M at room temperature and the data are included in the Table I.5.1. All these chelates exhibit a very low value of molar conductance which indicates the non-electrolytic nature of all the complexes.

**Magnetic Measurements**

The observed magnetic moment values of the prepared complexes are summarised in Table I.5.1. Co(II) ion in octahedral ground state (^{4}T_{1g})
possesses considerable orbital contribution with a magnetic moment in
between 4.7-5.2BM. For tetrahedral Co(II) complex the ground term 4A_{2g}
have no orbital contribution. But due to spin orbit coupling the magnetic
moment values vary in the range 4.4-4.7BM. In the present case the magnetic
moment of 5.1BM indicates that Co(II) ion is in an octahedral environment
(Lewis J, 1963). The magnetic moment values of 3.12BM for Ni(II) complex is
in accordance with octahedral complexes. Cu(II) complex of BATP possesses
normal magnetic moment value of 1.92BM as expected for octahedral Cu(II)
complexes. The Zn(II) complex is purely diamagnetic.

**Electronic Spectra**

The electronic spectra and the magnetic moments support the
stereochemistry of the complexes. In the spectra of Co(II) complex the bands
at 990nm and 520nm are associated to the transitions 4T_{1g}(F) \rightarrow 4T_{2g}(F) and
4T_{1g}(F) \rightarrow 4T_{1g}(P) respectively. These transitions are specified to the Co(II) ion
in the field of octahedral symmetry.

For the Ni(II) complex two d-d transitions correspond to 634nm and
1010nm were observed, hence an octahedral stereochemistry can be assigned
for the complex (Jorgenson, 1956). The octahedral geometry of Cu(II)
complex is clear from the absorption band at 638nm. For the Zn(II) complex
of BATP d-d transitions are not possible and the bands obtained ~390nm are
due to charge transfer (Lever ABP, 1984).

Infra Red Spectra

The ligand BATP shows bands at 1669cm\(^{-1}\) and 2589cm\(^{-1}\), which are
due to C=N stretching and S-H stretching respectively. The band at 742cm\(^{-1}\)
is probably due to C-S stretching (Koji N, 1962). Absence of bands in the
region 1705-1725cm\(^{-1}\) characteristic of C=O vibrations of 1,2diketones also
indicate the involvement of carbonyl group in Schiff base formation. The IR
spectra of the complexes were compared with that of the ligand to determine
the changes that might have taken place during complexation. The band at
1669cm\(^{-1}\) is characteristic of the azomethine group present in the free ligand.
Lowering of this frequency, to the region (1622-1630cm\(^{-1}\)), observed in all the
complexes indicates the involvement of the C=N group in co-ordination. The
stretching vibrations of S-H have no valuable help since they exhibit weak
bands both in ligand and complexes but the participation of S-H group in
chelation is confirmed from the shift of C-S stretching frequency of the
ligand from 742cm\(^{-1}\) to lower frequencies in the complexes. The bands
ranging from 515-543cm\(^{-1}\) and 460-470cm\(^{-1}\) are due to the presence of M-N
and M-S bonds respectively. Presence of a broad band around 3400cm\(^{-1}\) in
the case of metal complexes may be due to O-H stretching of co-ordinated
water. The characteristic frequency of free acetate ions at 1550 and 1455 are
absent in all the complexes. The non conducting nature and stochiometry of complexes indicate the absence of acetate ion. New bands corresponding to co-ordinated water also appears in all the complexes.

Therefore from the IR spectrum it is concluded that the ligand BATP behaves as a dianionic tetradeutate ligand co-ordinates to the metal ion via deprotonated thiophenol and also azomethine group.

**TG Studies**

Cu (II) and Zn(II) complexes of BATP were subjected to thermogravimetric analysis. The mass loss data obtained from TG curves were compared with the data obtained from pyrolytic experiments. Both values well agree with in the limits of experimental error.

All the above results suggest octahedral structure for the Co(II), Ni(II), Cu(II) and Zn(II) complexes of BATP and is given as follows.

\[ \text{M} = \text{Co(II), Ni(II), Cu(II) and Zn(II)} \]
Table I.5.1

Microanalytical, magnetic and conductance data of transition metal chelates of Benzil 2-Aminothiophenol (H_2L_3)

<table>
<thead>
<tr>
<th>Compound</th>
<th>C %</th>
<th>H %</th>
<th>N%</th>
<th>S%</th>
<th>M%</th>
<th>μ_{eff}</th>
<th>B.M</th>
<th>ohm^{-1} cm^2 mol^{-1}.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2L_3</td>
<td>73.52</td>
<td>5.17</td>
<td>5.98</td>
<td>15.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(73.58)</td>
<td>(4.71)</td>
<td>(6.6)</td>
<td>(15.09)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoL_3(H_2O)_2</td>
<td>60.02</td>
<td>4.10</td>
<td>5.32</td>
<td>12.59</td>
<td>10.98</td>
<td>5.1</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(60.35)</td>
<td>(4.25)</td>
<td>(5.41)</td>
<td>(12.38)</td>
<td>(11.39)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiL_3(H_2O)_2</td>
<td>59.83</td>
<td>4.02</td>
<td>5.61</td>
<td>12.25</td>
<td>11.1</td>
<td>3.12</td>
<td>5.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(60.38)</td>
<td>(4.25)</td>
<td>(5.41)</td>
<td>(12.38)</td>
<td>(11.36)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuL_3(H_2O)_2</td>
<td>58.20</td>
<td>3.9</td>
<td>5.22</td>
<td>12.94</td>
<td>12.95</td>
<td>1.92</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(59.82)</td>
<td>(4.21)</td>
<td>(5.36)</td>
<td>(13.03)</td>
<td>(12.81)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnL_3(H_2O)_2</td>
<td>58.93</td>
<td>4.12</td>
<td>5.25</td>
<td>12.59</td>
<td>12.07</td>
<td>D</td>
<td>6.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(59.61)</td>
<td>(4.20)</td>
<td>(5.34)</td>
<td>(12.22)</td>
<td>(12.49)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calculated values are given in the parenthesis; D-diamagnetic, M –metal, L-ligand

Table I.5.2

Characteristic Infrared absorption frequencies (cm\(^{-1}\)) of transition metal chelates of Benzil 2-Aminothiophenol (H_2L_3)

<table>
<thead>
<tr>
<th>Compound</th>
<th>νH_2O</th>
<th>νC=N</th>
<th>ν C-S</th>
<th>νM-S</th>
<th>νM-N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
<td>cm(^{-1})</td>
</tr>
<tr>
<td>H_2L_3</td>
<td>3450 br</td>
<td>1669 s</td>
<td>742 m</td>
<td>467 w</td>
<td>525 w</td>
</tr>
<tr>
<td>CoL_3(H_2O)_2</td>
<td>3370 br</td>
<td>1630 s</td>
<td>727 m</td>
<td>468 w</td>
<td>525 w</td>
</tr>
<tr>
<td>NiL_3(H_2O)_2</td>
<td>3375 br</td>
<td>1629 s</td>
<td>716 m</td>
<td>468 w</td>
<td>525 w</td>
</tr>
<tr>
<td>CuL_3(H_2O)_2</td>
<td>3373 br</td>
<td>1622 s</td>
<td>716 m</td>
<td>468 m</td>
<td>515 m</td>
</tr>
<tr>
<td>ZnL_3(H_2O)_2</td>
<td>3382 br</td>
<td>1625 s</td>
<td>720 m</td>
<td>470 m</td>
<td>543 m</td>
</tr>
</tbody>
</table>

br-broad, s-strong, m-medium, w-weak
An overview of co-ordination chemistry reveals that only few works have been carried out in the area of Schiff bases involving 1,2 diketones and aminophenols. In the present work tetradeionate Schiff base ligand, Benzil 2-Aminophenol containing ONNO donor groups have been synthesised for the first time. This ligand produces various metal ions such as Co(II), Ni(II), Cu(II) and Zn(II).

Detailed investigations on synthesis structural and biological aspects of the ligand Benzil aminophenol and its metal complexes are described in this chapter.

**Synthesis of the Ligand**

A hot ethanolic solution of Benzil (0.01 mol) was added drop wise to a stirred solution of 2-Aminophenol (0.02 mol) dissolved in ethanol. The mixture was refluxed for three hours and then cooled. The precipitate found was filtered, washed with alcohol and then dried over anhydrous CaCl\textsubscript{2}. Melting point of H\textsubscript{2}L\textsuperscript{4} was found to be 131°C.
Characterisation of the Ligand

The ligand BAP was characterised on the basis of elemental analysis and spectral data. The UV, IR and NMR spectra of the ligand show characteristic bands. Based on the above results the structure of the ligand was confirmed as given below.

Benzil 2-Aminophenol
STUDIES ON Co(II), Ni(II), Cu(II) AND Zn(II) COMPLEXES OF BENZIL 2-AMINOPHENOL – BAP (H₂L⁴)

Synthesis of the Complexes

The complexes were prepared by refluxing an aqueous solution of the metal acetate with an ethanolic solution of the ligand. Sodium acetate (1gm) was added and the resulting solution was again refluxed for 3 hours on a waterbath. The separated complex was filtered, washed with very dilute alcohol and dried well. The metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) were prepared by this method.

Characterisation of the Complexes

The complexes were characterised on the basis of elemental analysis, UV, IR and NMR spectral data, magnetic studies, conductance measurements and thermal data. These results are given in the Tables I.6.1 and I.6.2.

Results and Discussion

The metal complexes of Benzil 2-Aminophenol are coloured, stable and non hygroscopic solids. They are insoluble in water but soluble in organic solvents.
**Elemental Analysis**

The complexes were analysed for metal percentage by standard methods. Percentages of carbon, hydrogen and nitrogen were estimated by microanalytical methods. The analytical data obtained is summarized in Table I.6.1.

**Molar Conductance**

Conductance measurements of metal complexes of BAP in methanol at a concentration of $10^{-4}$ M at room temperature are in the range of 2-10 ohm$^{-1}$cm$^2$mol$^{-1}$. The very low values indicate that these complexes behave as non-electrolytes and are neutral in nature.

**Magnetic Measurements**

The values of magnetic moments of the complexes of BAP are tabulated in Table I.6.1. The room temperature, magnetic moments of Co(II) complexes was found to be 4.98BM. The observed magnetic moment for spin free octahedral Co(II) have excess of spin only value and it may be due to orbital contributions of both ground state ($^3t_{2g}^2e_g$) and the first excited state ($^4t_{2g}^3e_g$). It is reported that an octahedral high spin geometry can be assigned to Co(II) complexes it the measured $\mu_{eff}$ value is in the range of 4.7-5.2BM. Ni(II) complex exhibited a magnetic moment value of 3.28BM which is very
close to the spin only value of octahedral complexes. Hence an octahedral geometry can be assigned to the Ni(II) complex of BAP.

Cu(II) complex of BAP showed a magnetic moment value of 2.02BM. This value corresponds to one unpaired electron of the d⁹ electronic configuration which supports the expected octahedral geometry around the metal ion. This value also shows the absence of any antiferromagnetic interaction. As expected, the remaining Zn(II) complex was found to be diamagnetic.

**Electronic Spectra**

The electronic absorption spectra of the ligand BAP (H₂L⁴) exhibits two bands lying around 438nm and 312nm. These bands are due to n→π* and π→π* transitions. These bands were shifted to higher energy in the complexes which indicates the involvement of the Schiff base in co-ordination.

The electronic spectrum of Co(II) complex gives only one characteristic band at 574nm due to ⁴T₁g(F) → ⁴T₂g(F) transitions. Ni(II) complex shows two d-d transitions at 877nm and 598nm, which can be assignable to ³A₂g(F) → ³T₂g(F) and ³A₂g(F) → ³T₁g(F) transitions. Cu(II) complex showed an absorption maxima at about 650nm which supports a
slightly distorted octahedral geometry. Zn(II) complex of BAP do not show any characteristic d-d transition bands.

**Infra Red Spectra**

The IR spectral data of the Schiff base ligand BAP (H₂L₄) and its metal complexes are presented in Table I.6.2. The spectra of the complexes were compared with that of the free ligand to determine the co-ordination sites which involved in chelation. There were some guide peaks in the spectra of the ligand, which were helpful in achieving this goal. In the case of BAP the band found at 1672 cm⁻¹ is due to the presence of azomethine linkage. The broad bands at ~3400 cm⁻¹ and ~1305 cm⁻¹ were respectively due to O-H stretching and bending vibrations. The shifting of C=N stretching band to lower frequency in the range of 1612-1630 cm⁻¹ indicating its participation in metal co-ordination. All the complexes showed peaks at 3300-3350 cm⁻¹ corresponding to the O-H stretching frequency of the co-ordinated water molecules. From IR spectra of the ligand and, complexes it is very clear that the bands were absent in the region of 1705-1725 cm⁻¹ indicates the absence of carbonyl stretching vibrations. The ligand exhibit a broad less intense band in the region 2650-2500 cm⁻¹ indicates the possibility of intra molecular hydrogen bonding between O-H and azo methine nitrogen. This band disappeared completely in complexes implies the involvement of O-H and
>C=N in chelation. New bands are found in the spectrum of the complexes in the region 540-568 cm\(^{-1}\) and 424-433 cm\(^{-1}\) indicate the presence of M-N and M-O bonds respectively. The C-O bond in the free ligand at 1250 cm\(^{-1}\) is shifted to lower frequency indicating the participation of phenolic group in the complex formation.

IR data showed that the ligand is tetradeutate dianionic ligand coordinating to the metal ion through two azomethine nitrogen and two deprotonated phenolic oxygen atoms.

**NMR Spectra**

The NMR spectra of the Schiff base ligand BAP was recorded in DMSO solution using TMS as internal standard. The spectra of the diamagnetic Zn(II) complex was examined in comparison with that of the free ligand. The singlet at 10.2 ppm corresponding to O-H protons in the free ligand disappears in Zn(II) complex indicates the co-ordination. A multiplet at 6.5-7.5 ppm corresponds to aromatic protons. An additional peak at 3.36 ppm showed the presence of two co-ordinated water, whose intensity corresponds to four hydrogen.
TG Studies

Cu(II) and Zn(II) complexes of BAP were subjected to thermal studies by non isothermal method. The thermogram of complexes were recorded using a sample weight of 5mg in static air atmosphere. A three step decomposition was observed for Cu(II) Complex whereas Zn(II) Complex decomposes in two steps above 120°C. The probable assignments for each decomposition are described in Part II.

On the basis of the above results these complexes can be represented by the following structure.

\[ M = \text{Co(II), Ni(II), Cu(II) and Zn(II)} \]
Table I.6.1
Microanalytical, magnetic and conductance data of transition metal chelates of Benzil 2-Aminophenol (H₂L₄)

<table>
<thead>
<tr>
<th>Compound</th>
<th>C %</th>
<th>H %</th>
<th>N%</th>
<th>M%</th>
<th>μeff B.M</th>
<th>ohm⁻¹ cm² mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂L₄</td>
<td>79.17(79.5)</td>
<td>5.4(5.10)</td>
<td>6.84(7.14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoL₄(H₂O)₂</td>
<td>63.9(64.33)</td>
<td>4.12(4.53)</td>
<td>5.5(5.77)</td>
<td>12.02(12.15)</td>
<td>4.98</td>
<td>3.80</td>
</tr>
<tr>
<td>NiL₄(H₂O)₂</td>
<td>63.79(64.36)</td>
<td>4.06(4.53)</td>
<td>5.84(5.77)</td>
<td>11.97(12.11)</td>
<td>3.28</td>
<td>6.8</td>
</tr>
<tr>
<td>CuL₄(H₂O)₂</td>
<td>62.5(63.73)</td>
<td>4.22(4.49)</td>
<td>5.5(5.71)</td>
<td>12.56(12.97)</td>
<td>2.02</td>
<td>3.92</td>
</tr>
<tr>
<td>ZnL₄(H₂O)₂</td>
<td>63.0(63.49)</td>
<td>4.28(4.47)</td>
<td>5.54(5.69)</td>
<td>12.78(13.30)</td>
<td>D</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Calculated values are given in the parenthesis; D-diamagnetic, M –metal, L-ligand

Table I.6.2
Characteristic Infrared absorption frequencies (cm⁻¹) of transition metal chelates of Benzil 2-Aminophenol (H₂L₄)

<table>
<thead>
<tr>
<th>Compound</th>
<th>νH₂O cm⁻¹</th>
<th>νC=O cm⁻¹</th>
<th>νC=N cm⁻¹</th>
<th>νM-O cm⁻¹</th>
<th>νM-N cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂L₄</td>
<td>3400 br</td>
<td>1672 s</td>
<td>1250 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoL₄(H₂O)₂</td>
<td>3341 br</td>
<td>1630 s</td>
<td>1228 m</td>
<td>424 w</td>
<td>540 w</td>
</tr>
<tr>
<td>NiL₄(H₂O)₂</td>
<td>3356 br</td>
<td>1625 s</td>
<td>1224 m</td>
<td>433 m</td>
<td>563 m</td>
</tr>
<tr>
<td>CuL₄(H₂O)₂</td>
<td>3350 br</td>
<td>1625 s</td>
<td>1227 m</td>
<td>433 m</td>
<td>564 w</td>
</tr>
<tr>
<td>ZnL₄(H₂O)₂</td>
<td>3344 br</td>
<td>1612 s</td>
<td>1227 m</td>
<td>430 m</td>
<td>568 w</td>
</tr>
</tbody>
</table>

br-broad, s-strong, m-medium, w-weak.
Figure I.6.1: Infra red spectra of BAP [H:L^4]
Figure I.6.2: Infra red spectra of $\text{[CuL}^4\text{(H}_2\text{O)}_2\text{]}$
References


111. Wilkins RG, Lewis G. The magneto Chemistry or Complex compounds in co-ordination Chemistry, Interscience, New York, 1969.

