CHAPTER - I

1.1 INTRODUCTION

In the recent years, studies on the versatile chelating abilities of biologically active neutral bases have assumed great importance in the development of co-ordination chemistry. It is well known that chelates are of immense importance in the fields of chemical analysis\(^{(1)}\), medicine\(^{(2)}\), biology\(^{(3)}\) and industry\(^{(4)}\). When a biological ligand forms a chelate\(^{(5)}\), a substantical alteration in its biological activity is observed.

When a metal coordinates with only one type of ligands, the complex formed is a simple or a binary complex. When, however, the metal is able to co-ordinate with two different types of ligands, the complex formed is a mixed or a ternary one. It may be pointed out that in a binary complex, all the co-ordination sites of a metal may not be occupied by a single ligand molecule. The remaining co-ordination positions, in such cases, are satisfied by the polar molecules\(^{(6,7)}\) of the solvent used for the reaction. But in ternary complexes when all the co-ordination sites are not satisfied by one type of a ligand molecule\(^{(8)}\), the second type of ligand molecule replaces the co-ordinated solvent molecules to form more stable mixed ligand complex species\(^{(9)}\).

Heteroligand ternary complexes may be formed by any one of the following ways—

(i) When two different ligands of almost equal co-ordinating ability with a metal ion are simultaneously added to the solution of the metal ion, simultaneous chelation is said to take place.

\[
M + L_1 + L_2 \xrightleftharpoons{} ML_1 L_2
\]

(ii) When two different types of ligands with very small difference in their co-ordinating abilities are added simultaneously to a solution of the metal ion, almost stepwise ternary complex formation occurs:

\[
M + L_1 + L_2 \xrightleftharpoons{} ML_1 + L_2 \xrightleftharpoons{} ML_1 L_2
\]

(iii) When the two different types of ligands having substantial difference in their co-ordinating abilities are simultaneously added to the solution of metal ion, stepwise ternary complex formation is found to occur:
\[ M + L_1 + L_2 \rightleftharpoons ML_1 + L_2 \rightleftharpoons ML_1 L_2 \]

OR

\[ M + L_1 + L_2 \rightleftharpoons ML_2 + L_1 \rightleftharpoons ML_1 L_2 \]

(iv) Initially, two binary species are formed which may interact at high pH to form hetero-ligand ternary complex.

\[ M + L_1 + L_2 \rightleftharpoons M_xL_1 + M_{(1-x)}L_2 \rightleftharpoons ML_1 L_2 \]

The formation of such ternary complexes is chiefly dependent upon factors such as the ionic potential of the metal ion, basicity and denticity of the ligand, and number of fused rings in the complex. However, the nature of the metal to ligand bond\(^{(10)}\), chelate formation\(^{(11)}\), shape\(^{(12)}\) and configuration\(^{(13)}\) also have a role to play in determining the stability of the heteroligand complexes.

Among other factors which may affect the relative stabilization of ternary species as compared to the binary species, the nature of bonding between ligands of different types\(^{(14-17)}\), asymmetry of the ligand field, nature of the solvent, ionic strength, pH and temperature of the medium are more prominent. A “polarized ion model” has been proposed\(^{(18-20)}\) to account for the greater stability of the ternary species as compared to the parent binary one. Furthermore, this model has enabled the evaluation\(^{(21-24)}\) for force constant, energies and thermodynamic parameters of the equilibria.

The formation and characterization of complex species in solution is best explained through evaluation of their stability constants and thermodynamic parameters. That the stability constants of the mixed ligand complexes are much greater than corresponding binary species and that they are increasingly finding larger applications in analytical and biological fields have lent them immense importance.

A number of physico-chemical techniques may be employed to determine the stability constants of ternary complexes in solution. Some of them are electrometric\(^{(25,26)}\) (pH metric, potentiometric, conductometric, polarographic), spectrophotometric\(^{(27)}\), liquid–liquid extraction\(^{(28)}\) and two phase distribution method\(^{(29)}\). On account of simplicity, speed and accuracy, pH–metric method is most
widely used for determination of the stability or the formation constants of complexes under investigation. The study of heteroligand ternary complex formation is also facilitated by investigations on their magnetic susceptibility, IR, EPR, NMR spectral and thermal properties.

For purposes of co-ordination to form metal chelates, the nature of electron donor atoms attached to the ligand is of vital importance. Ligands with ‘O’, ‘N’, ‘S’ as donor atoms greatly interest us because they are present in almost all biological systems. Irving and Williams\(^{(30)}\) have established the following order of stability of the some transition metal ions with respect to a particular ligand.

\[
\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}
\]

This order is known as Irving Williams order.

Studies have revealed that different metal ions prefer to attach to ligands having different types of co-ordination sites. We find that biological systems are no exception to this preference.

1.2 SURVEY OF RELEVANT LITERATURE:

There has never been any doubt about the importance of metal chelates in analytical, industrial, pharmaceutical, biological and medicinal fields\(^{(14)}\). Thus, for example, a chelate of 8-hydroxyquinoline with a suitable metal ion can act as an effective anti-bacterial and anti-fungal agent\(^{(31)}\). The use of oxime-metal chelates\(^{(32)}\) as antimicrobial agents has been investigated by Albert and Magrath\(^{(32)}\). The ‘O’, ‘N’ and ‘S’ donor mixed ligands of some transition metal are gaining increasing importance as anti-virals\(^{(33)}\), antibacterials\(^{(76)}\), anti-fungals\(^{(35)}\), anti-cancers\(^{(78)}\) and also as spray agents\(^{(79)}\) in chromatography. M.M. Jones\(^{(38)}\) has shown that radiation damage to exposed organisms can be reduced by chelates with organic ligands containing –N, –NH\(_2\), –OH, –SH and –COOH as co-ordinating groups. Metal chelates of nitrogen containing ligands\(^{(39-43)}\) display more effective biological activity. Transition metal complexes of some biologically important ligands\(^{(44-47)}\) such as 2,2\(^{1}\)-dipyridyl, o-phenanthroline, 2-picolinic acid, 8-hydroxyquinoline and α-alanine have been cited as potential drugs. Malik, Singh and Tandon\(^{(48)}\) have studied transition metal
simple and mixed complexes of some aminopolycarboxylic acids. The complexes of some medicinally important ligands\(^{49-51}\) such as tetracycline, potassium penicillin, penicillamine, EDTA, dextrin etc. with some transition metals have also been investigated from the clinical point of view.

Analytical chemistry owes a lot to metal chelate formation. Thus, N-hydroxy-N-diphenyl formamidine\(^{52}\) can be usefully employed in the estimation of Cu(II) and Ni(II). Similarly, 7-nitro-8-quinolinol-5-sulphonic acid\(^{53}\) is a useful reagent for quantitative estimation of Cu(II) and Fe(III).

In fact, it is useful to classify heteroligand complexes on the basis of their applications in analysis. The following classification is found advantageous from a number of points of view:

(a) **With one ligand organic base:** Many extractive photometric\(^{54-56}\) and ion exchange\(^{57-59}\) methods make use of such complexes. An example is the study of 2,2'-bipyridyl metal complexes and ligands of varying electronegativities\(^{60-62}\).

(b) **With two different ligands:** A number of catalytic reactions and complexometric titrations\(^{63-69}\) can make use of this type of complexes. Ti(IV)-phosphate molybdate\(^{70}\) and Nb(IV) phosphate molybdate\(^{71-73}\) are the more common examples of this type.

(c) **With three different ligands:** The quarternary heteroligand complexes\(^{74-81}\) of Ni(II), Co(II), Fe(II) and some other transition metals and rare earths represent the formation of this class of complexes. Krishnan et al\(^{82}\) has reported the formation of such complexes of Zn and Cd with chloride, thiocyanate and glycine.

(d) **With one ligand but two different metal ions:** This type of complex formation\(^{83}\) is exhibited by the formation of Ni(II)-EDTA-alkaline earth metal complexes during complexometric analysis. The fact that complexes\(^{84-85}\) of two atoms of the same metal in different oxidation states are coloured is usefully employed in colorimetric analysis\(^{86-87}\).

It is now widely accepted that infra-red and electronic spectra and magnetic studies play a vital role to establish a number of stereo-chemical aspects of metal
complexes. The following lines give a brief review of the magnetic, infra-red and electronic spectral studies of some metal complexes.

1.3 MAGNETIC STUDIES:

Useful input is provided by magnetic susceptibility measurements for forecasting the stereochemistry of transition metal complexes. A number of investigators\textsuperscript{(88-90)} have critically reviewed the role of magnetic measurements in transition metal co-ordination chemistry.

The spin state of the metal ion i.e. whether high, low or intermediate spin state in magnetic measurements mainly depends upon the nature of the donor set present on the ligand. Its abnormal behaviour and variation with temperature in complexes of metals like copper(II), nickel(II) and cobalt(II) can be logically explained\textsuperscript{(91)}. The discussion below summarises the magnetic behaviour of metal complexes with some ligands containing N, S and O as donor atoms.

There are two distinct ranges into which the magnetic moments of Cu(II) complexes may classified\textsuperscript{(91)}:

(a) complexes with magnetic moments in the range 1.72 – 1.82 B.M.
(b) complexes with magnetic moment in the range 1.92 – 2.20 B.M.

It goes to the credit of Ray and Sen\textsuperscript{(92)} to interpret the results by assuming almost complete quenching of orbital moment of the single unpaired electron raised to the 4p level in the case of dsp\textsuperscript{2} bonding. A number of researchers\textsuperscript{(93-98)} have investigated the copper(II) complexes of tridentate schiff's bases. Mostly, the complexes formed are polymeric with low magnetic moments. This work has recently been complimented by a number of novel attempts\textsuperscript{(99-105)}. A sub-normal magnetic moment of copper(II) observed at the room temperature has been attributed to a partial spin pairing between metal ions. Patel and Fairan\textsuperscript{(106,107)} have studied the magnetic properties of copper(II) complexes at liquid nitrogen temperature. Their results have corroborated the earlier assumptions.

Variation of trans-axial ligand may have an effect on the magnetic properties of compounds\textsuperscript{(108,109)} as revealed by a number of studies on magnetic moments of
copper(II)-carboxylate complexes. In tetrahedral, square planar and distorted octahedral stereochemistry, copper(II) complexes exhibit magnetic moments corresponding to one unpaired spin. The magnetic measurements indicate that the complexes are monomeric. The magnetic moment values in the range 1.70 – 1.94 B.M. endorse the square planar geometry of the complexes.

However, for the cobalt(II) complexes, the effective magnetic moment values range from 5.2 B.M. to lower values depending upon the extent of distortion from octahedral symmetry\(^{(110)}\). Cobalt(II) complexes, such as Co (tch)\(_2\) Cl\(_2\) (where tch = N-substituted thiocarbazide) are polymeric and spin free with magnetic moments\(^{(111)}\) in the range of 4.86–5.16 B.M. Co(II) is known to form complexes of three types. The square planar complexes are paramagnetic with one unpaired electron. Outer orbital tetrahedral or octahedral complexes possess magnetic moments which correspond to three unpaired-electrons. Accordingly, square planar Co(II) complexes are associated with magnetic moment in the range 2.1–2.8 B.M.

In the octahedral complexes of cobalt(II), the three unpaired electrons unquestioningly reside in 3\(^{rd}\) orbitals. However, in some complexes involving inner d-orbitals for hybridization, one electron might be promoted to higher orbital besides pairing of the other two. Consequently, the inner orbital complexes are expected to exhibit magnetic moment corresponding to one unpaired electron and strong reducing properties.

But, in general, both the tetrahedral and the outer orbital formations indicate the presence of three unpaired electrons. The spin only value of magnetic moment value of three unpaired electrons is 3.87 B.M. The higher observed values than this may be due to the orbital contribution.

Syamal\(^{(112)}\) has investigated the magnetic behaviour of nickel(II) complexes of ligands with O, N and S as the donor atoms. The Ni(tch)\(_2\) Cl\(_2\) complex has magnetic moment in the range 3.78 – 3.87 B.M. It is said to be pseudo-tetrahedral with the thiocarbazide being bonded via S atom only. Ni(tch)\(_2\)Cl\(_2\).4H\(_2\)O complex has magnetic moment in the range 3.30 – 3.31 B.M. and is said to possess the shape of a distorted octahedron with thiocarbazide linked to metal through S and terminal N. The complex
has a polymeric structure involving chloro-bridges. It has been noticed\(^{(113)}\) that complexes having magnetic moment in the range 3.09 - 3.18 B.M. are polymeric with S-bridges. Studies have further revealed that Ni(H\(_2\)O)\(_3\)LH\(_2\) complex (where LH\(_2\) = tridentate dibase schiff's base) has \(\mu_{\text{eff}} = 3.0 - 3.2\) B.M. indicating octahedral structure while NiL\(_2\)^\(^1\) (where L\(_2\)^\(^1\) = bidentate monobase schiff's base) complex is diamagnetic and has a square planar structure.

Ni(II) has eight electrons in the 3\(^{rd}\) orbital indicating the possibility of bond formation through sp\(^3\)d\(^2\), sp\(^3\) and dsp\(^2\) hybridisations to yield octahedral, tetrahedral and square planar complexes respectively. Obviously, for dsp\(^2\) hybridisation for square planar complexes, all 3–d electrons are paired and hence the complexes are diamagnetic. In the other tetrahedral and outer orbital octahedral shapes, there are two unpaired electrons and such complexes should show a magnetic moment of 2.8 B.M. or above. It has been observed that \(\mu_{\text{eff}}\) for tetrahedral Ni(II) complexes lies in the range 3.4 - 4.2 B.M. and that for octahedral complexes lies in the range 2.83 - 3.40 B.M. Any distortion from standard octahedral shape, however, increases the magnetic moment.

1.4 ELECTRONIC SPECTRAL STUDIES:

Many problems regarding structure of metal chelates can be tackled by electronic spectral studies of transition metal complexes with information in terms of energy level scheme and chemical bonding. By directing their attention mainly to d–d transitions, a number of researchers\(^{(114-118)}\) have delved into the world of electronic spectra of metal complexes. d–d transitions due to fundamental d–splitting as envisaged by ligand field theory is sufficient to interpret the broad features of the spectra. It is convenient to classify the electronic spectra of N, O and S containing ligands and their complexes into three regions–

(i) 220 – 270 nm
(ii) 270 – 350 nm
(iii) 350 – 500 nm
Two main peaks are observed in the first two regions. They may be attributed to \( \pi - \pi^* \) and \( n - \pi^* \) transitions associated probably with N, O or S functions of the ligand.\(^{(119,120)}\) In the third region, metal to ligand transfer bands and some crystal field d-d transitions are observed.\(^{(121)}\)

A number of workers\(^{(122-124)}\) have made attempts in the recent years to establish a relationship between magnetic and electronic spectral properties of metal complexes. Yamada and co-workers\(^{(125)}\) have studied the electronic spectra of Cu(II) complexes with schiff's bases. Square planar Ni(II)-schiff's base complexes have an interesting electronic absorption spectra\(^{(126)}\). They do not show any appreciable absorption below 18000-20000 cm\(^{-1}\). Thus, it becomes possible to distinguish square planar complexes of Ni(II) from their tetrahedral and octahedral counterparts on account of their inability of absorption below 18000 cm\(^{-1}\) due to very large crystal field splitting. In penta-coordinated environs, the ground energy state of Ni(II) splits into a large number of terms on lowering the symmetry.\(^{(127)}\) The Ni(II) complexes with salicyldiamine ligands\(^{(128)}\) display four absorption bands at 8000, 10000, 13000 and 16000 cm\(^{-1}\). It has helped in postulating that they are five co-ordinated. Ni(II) chelates exhibit two bands around 16200 and 17500 cm\(^{-1}\) confirming square planar shape\(^{(129)}\). Similar results were obtained for Cu(II) and Pd(II) complexes\(^{(130)}\).

Reviews of special characteristics of a number of Cu(II), Ni(II) and Co(II) complexes with special reference to the factors affecting the spin multiplicity in the ground state have been published by some authors\(^{(131-134)}\). It is an established fact that the electronic spectra of low spin square planar Ni(II) complexes is vastly different from that of high spin tetrahedral or octahedral species and no transition occurs below 10 \( \kappa \kappa \) in square planar Ni(II) species\(^{(135)}\). In a square planar complex, the energy difference between d\(x^2-y^2\) orbital and the next lowest orbital is greater than 10 \( \kappa \kappa \) due to large crystal field splitting. For a square planar complex three absorption bands corresponding to \( ^1A_1g \rightarrow ^1A_2g, ^1A_1g \rightarrow ^1B_1g \) and \( ^1A_1g \rightarrow ^1E_g \), transitions are expected.
1.5 INFRA–RED SPECTRAL STUDIES:

IR spectral studies present a versatile technique. It helps unveil a number of stereochemical aspects of metal complexes. The spectra originate from different modes of vibrations in molecules when they absorb energy in the infra–red region. The consequent molecular vibration and rotation of absorbing groups yield absorption bands. When a ligand is linked to some other atom or a metal, its vibrating system, bond length, bond angles and intra–atomic forces are expected to change. As such, the infra–red spectrum of a co–ordinated ligand differs from that of the free ligand. It is possible to correlate the change in spectral characteristics with change in geometry. However, the interpretation of all vibrations in a molecule is extremely difficult. Even then, some of them can be analysed and interpreted to suit the extent and scope of our investigations. Thus IR spectral studies can successfully distinguish cis and trans forms.\[^{135}\]

It has been settled that the frequencies due to C=N bond lie between the frequencies of C=O and C=C bands. It has further been determined that when amine–nitrogen is uncoordinated, the electron density in the C=N region is less.\[^{136}\] Conjugate systems containing −C=N and −C=C bands show one or more rather strong bands in the region 1700–1500 cm\(^{-1}\). Obviously, they can be attributed to stretching motion of the double band. However, in specific −C=C and −C=N linkages it is usually not possible to identify such bands.\[^{137,138}\]

The study of infra–red spectra of Ga–thiocyanate with 2,2\(^{1}\)–dipyridyl and 1,10–phenanthroline\[^{139}\] in the range 250 – 4000 cm\(^{-1}\) reveals characteristic bands at 470, 485, 2050 – 2120 and 3200 – 3400 cm\(^{-1}\). They may be ascribed to the deformation and valence vibration of NCS, CN and OH groups respectively. A band shift at 1300–1600 cm\(^{-1}\) indicated the co–ordination bond between Ga and N in the NCS group. Dipyridyl and o–phenanthroline adducts with divalent metal derivatives were also subjected to infra–red spectral analysis. It was found that distortion from octahedral symmetry was greater for the dipyridyl complexes than that for o–phenanthroline complexes. From the point of view of the metal used, it is greater for Cd than Zn and Mg.
The number of studies\(^{140-148}\) on mixed ligand complexes of transition metals with neutral bases have registered a tremendous increase in the recent years. The study\(^{149-154}\) of the Cu(II) complexes has been particularly favoured on account of the fact that it displays a variety of coordination shapes. In fact, Gazo et al.\(^{155}\) have gone into the factors that are responsible for the configurations assumed by the Cu(II) complexes.

Heteroligand complexes of some transition and rare earth metals with 4,4\(^{-}\)-bipyridyl and 2,9-dimethyl-1,10-phenanthroline were subjected to molecular structure studies by some researchers\(^{156-162}\).

Czakis and Danuta\(^{163}\) were able to isolate Bi(III), Sb(III), Sn(IV) and Sn(II) complexes with 2,2\(^{-}\)-dipyridyl and 4,4\(^{-}\)-dipyridyl (BiCl\(_3\).2HCl, SbCl\(_3\).2HCl, BiCl\(_3\).2HCl, SnCl\(_2\).Z.2HCl, SnCl\(_2\).Z.2HCl, SnBr\(_3\).A, SnBr\(_3\).Z) where A and Z represent 2,2\(^{-}\)-dipyridyl and 4,4\(^{-}\)-dipyridyl respectively. They discussed the infra-red spectra of these complexes to assign their characteristics.

The 4,4\(^{-}\)-dipyridyl complexes with Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) thiocyanates have also been prepared and then studied spectroscopically\(^{164}\). It was observed that 4,4\(^{-}\)-bipyridyl forms a 1:1 complex with all the metal thiocyanates. It also acts as a bidentate ligand bridging two metal atoms. Co(II), Ni(II), Zn(II) and Cd(II) thiocyanate complexes are polymeric pseudo-octahedral species with both 4,4\(^{-}\)-bipyridyl and the thiocyanate group acting as bridging ligands. The 1:1 Hg(II) thiocyanate 4,4\(^{-}\)-bipyridyl complex is supposed to be polymeric, four co-ordinated species with both 4,4\(^{-}\)-bipyridyl and thiocyanate ligands acting as bridging groups.

The donor acceptor compounds of bivalent mercury cyanide with 2,2\(^{-}\)-bipyridyl, 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline have also been synthesized and investigated\(^{165}\). Mercuric cyanide complexes of the type Hg(CN)\(_2\)L with donor ligands (L) are formed in ethanol. The infra-red spectra reveals that v(CN) shifts to lower frequency (\(\Delta v \sim 30 \text{ cm}^{-1}\)) and decreases in intensity on formation of the complex. Both v(Hg–CN) and \(\delta\)(Hg–CN) shift to lower frequency on complex formation. It is possible to correlate these shifts with the strength of the donor atoms. Above 200 cm\(^{-1}\), the v(Hg–CN) vibration is not detectable.
Melnik et al\textsuperscript{(166)} have carried out magnetic and spectroscopic studies of 4,4'-bipyridyl adducts with Cu(II) isobutyrate. They concluded that the adducts have a binuclear structure in which Cu\textsubscript{2}[(CH\textsubscript{3})\textsubscript{2} CHCO\textsubscript{2}] units are linked together by 4,4'-bipyridyl ligand through N atom at axial positions.

Metal chelates with 2,2'-bipyridyl and 2,9-dimethyl-1,10-phenanthroline have also been investigated by Thomas et al\textsuperscript{(167)}. They proposed the structures of the binary complexes formed on the basis of electronic, IR and ESR spectra. High covalent character for out of plane π-bending and low covalent character for σ-bonding was deduced from the ESR data. Ternary complexes of Cu(II) with o-phenanthroline and o-donor ligands have been synthesized and investigated\textsuperscript{(168)} on the basis of IR and electronic spectral measurements. The Cu(phen)\textsubscript{2} species has great affinity for O-donor ligands to form chelate rings of various sizes. As the chelate ring increases in size, IR spectra indicates that Cu–O bond is weakened. In comparison, Cu–N bond is less sensitive to ring size. The ternary complexes of Cu(II) with 2,2'-dipyridyl and 1,10-phenanthroline along with amino acids like glycine, alanine, valine, tyrosine have been synthesized and characterized by magnetic moment, UV, IR and ESR spectral data and polarography\textsuperscript{(169)}. Higher absorption frequencies were observed for phenanthroline ternary complexes due to Cu–O and Cu–N stretching as well as greater reduction potentials.

With homophthalic and tetrachlorophthalic acids as primary ligands and quinoline, isoquinoline, pyridine, 2-aminopyridine, 2-picoline, o-phenanthroline and bipyridyl as secondary ligands, a series of ternary complexes of Co(II) and Ni(II) have been prepared and characterized on the basis of elemental analysis, conductance, magnetic moment, IR and electronic spectral studies\textsuperscript{(170)}. Co(II) forms tetrahedral complexes with dipyridyl and o-phenanthroline while those of Ni(II) are square planar in the case of homophthalic acid. It has been proposed that all other complexes have octahedral configuration.

The structural studies on the basis of IR and electronic spectral data of the heteroligand complexes of Ti, V, Cr, Mo, Mn with 2,2'-dipyridyl and 1,10-phenanthroline have been made by a number of investigators\textsuperscript{(171–178)}. They have
made efforts to confirm the structure on the basis of magnetic measurements. By using strong and broad metal–chlorine bands, it becomes possible to determine co-ordination number and oxidation state of metal ions in some complexes.\(^{(179)}\)

Further, there have been extensive investigations\(^{(180}-^{189)}\) on the iron complexes with 1,10-phenanthroline, 2,2\(^{1}\)-bipyridyl, 5-nitro-1,10-phenanthroline and with pyridine-2,6-dicarboxylic acid (picolinic acid). Polymeric structures have been proposed\(^{(189)}\) for some thiocynate complexes of transition metals with 2,2\(^{1}\)-bipyridyl.

d-d transition studies on the mixed chelate complexes of Ni(II) with acetylacetone and aromatic diamine ligands have revealed\(^{(190)}\) that the inter-ligand interactions affect the energy of \(^{3}\)T\(_{2g}\) \(-\) \(^{3}\)A\(_{2g}\) transitions. It was possible to characterize and study heteroligand complexes of Ni(II) with 2,2\(^{1}\)-dipyridyl and amino acids by thermal analysis, IR and electronic spectroscopy\(^{(191},^{192)}\).

Elemental analysis, IR, UV, NMR and visible spectral studies have enabled investigators\(^{(193},^{194})\) to isolate and characterize ternary complexes of Co(II) with 2,2\(^{1}\)-dipyridyl, ethylenediamine, propylendiamine with some bidentate ligands with NN, OO, NO donor pairs. Mixed complexes of rhodium with a natural base and dicarboxylic acids, pyridine-2,6-dicarboxylic acid or iminodiacetic acid were studied by Nozi et al\(^{(195)}\) on the basis of IR spectra. They proposed structures for the chelates and attempted to validate them on the basis of magnetic susceptibility measurements.

Shukla and Rajkamat\(^{(196)}\) have studied the hetero-ligand complexes of Cu(II) - Ni(II) and Co(II) phthalates with aromatic amines and diamines. Padhy and Patel\(^{(1)}\) isolated, characterized and studied similar complexes of Ni(II) phthalate with S and N donor ligands like naphthylthiourea, 1,10-phenanthroline, morpholine, 3,5-lutidine piperidine and benzylamine. The occurrence of \(\nu(M-O)\) around 510 cm\(^{-1}\) provided evidence for the formation of M–O bond. It could be assumed that 1,10-phenanthroline co-ordinates through both of its N atoms. That morpholine co-ordinates to the metal ion through its N atom was indicated by bands at 3270 cm\(^{-1}\)
(\nuNH), 1130 \text{ cm}^{-1} (\nuC-N-C) and 1010 \text{ cm}^{-1} (\nuC-O-C) compared to those at 3325 \text{ cm}^{-1}, 1142 \text{ cm}^{-1} and 1110 \text{ cm}^{-1} of the free ligand morpholine.

Elemental analysis, magnetic moment and infra-red spectral studies were undertaken\textsuperscript{198} to investigate the mixed ligand oxovanadium(V) complexes with dipicolinic acid and some monobasic bidentate N and O donor ligands such as picolinic acid, nicotinic acid, isonicotinic acid, glycine and aminophenol. The complex VO (dipic) (dipic.H) is a seven co-ordinate monomeric species.

Walton et al\textsuperscript{199} have used spectral and magnetic susceptibility measurements at the room temperature to study Cu(II) complexes with PDA. They have also studied related complexation to form Ni(dipic).3H\textsubscript{2}O which reacts with mono-, bi- and tridentate N donor ligands such as pyridine, 2-picoline, 2,2\textasciitilde{}dipyridyl and 1,10-phenanthroline to yield six coordinate species.\textsuperscript{200-205}

A variety of analytical tools such as elemental analysis, IR, UV, NMR and X-ray diffraction have been utilized to study the mixed ligand complexes of some rare earths. The neutral\textsuperscript{206-212} chelates of lanthanides with picolinic acid–N–oxide (Pic.AOH) was isolated and characterized for the first time by Navneetham et al\textsuperscript{213} on the basis of elemental analysis, IR and electronic spectra. The complexes with the composition Ln (Pic AO).3.H\textsubscript{2}O (where Ln = La, Pr, Nd, Ho, Yb) were shown to be having bidentate bonding of ligands to the lanthanon ions having co-ordination number of six.

Saxena and Srivastava\textsuperscript{214} have prepared and studied complexes of Co(II), Ni(II) and Cu(II) with schiff's bases derived from 2-furylglyoxal and p-toluidine. These complexes were tested for antibacterial activity against a number of micro-organisms.

The X-ray diffraction and microbiological studies of tris (2,2\textasciitilde{}bipyridyl) nickel(II) tungstate hexahydrate and tungstomonoaquobis (2,2\textasciitilde{}bipyridyl) cobalt(II) mono- hydrate complexes were carried out by Khare and Co–workers\textsuperscript{215}. Toxicity study of these complexes against four pathogenic bacteria was also made. They were shown to possess considerable antibacterial activity against all the four pathogens under investigation.
Schiff bases\textsuperscript{(216)} are an important class of ligands in coordination chemistry and have many applications in different fields. The chemistry of Schiff base complexes continues to attract many researchers\textsuperscript{(217-218)} because of their wide applications in food industry, dye industry, analytical chemistry, catalysis, antimicrobial activity, agrochemical activity, and pharmacological applications\textsuperscript{(219)}. Semicarbazones of aromatic and unsaturated carbonyl compounds, have anti convulsant properties and their advantage over the analogous thiosemicarbazones is their lesser neurotoxicity\textsuperscript{(220)}. Semicarbazones have an inhibitory effect on nitric oxide synthesis, which protects the vascular system.

It is well known that various organic ligands possess strong antibacterial\textsuperscript{(221)} herbicidal, insecticidal and fungicidal properties. It has also been reported\textsuperscript{(222)} that the activity of biometals is very often altered through the formation of chelates with different biologically relevant ligands\textsuperscript{(223)}. It is suggested that the compounds having antimicrobial activity\textsuperscript{(224)} may act either by killing the microbe or blocking their active sites.\textsuperscript{(225)} In addition to this the antimicrobial activity of the compounds also depends upon the nature of the microorganisms. During the last decade group IV transition metal chemistry has made a major contribution to provide effective complexes for novel metal assisted organic transformations\textsuperscript{(226)}. The transmetallation of classical "carbanions" using fitanating agents produces new reagents, which display a high degree of chemo-, regio-, and stereo selectivity.\textsuperscript{(227-228)} The interest in coordination chemistry of such compounds is increasing continuously with the preparation of organic ligands containing a variety of donor groups and is multiplied many folds when the ligands have biological importance. Keeping all these facts into considerations, we have synthesized and screened some biologically potent ligands and their metal complexes.\textsuperscript{(229,230)}

1.6 **RESEARCH PLAN:**

An extensive survey of literature indicated that gaps still exist in the work on solid state chemistry of mixed ligand complexes of certain metals. In addition, vibration spectroscopic studies of heteroligand complexes of Cu(II), Ni(II) and Co(II) are few and far between. The reasons are not far to seek.
(a) it is difficult to make definite assignments in large sized molecules for they have large number of vibrations.

(b) it is very time consuming to carry out complete coordinate analysis.

(c) it was not possible to record the Raman spectra on account of insolubility of the species in organic solvents, distinct colour and decomposition in laser beam. Consequently, the investigator is left with an incomplete vibrational spectral pattern.

On account of the constraints, the earlier workers circumscribed themselves and carried out investigations on the basis of elemental analysis and magnetic moment studies. As a result, the studies of mixed ligand complexes of Cu(II), Ni(II) and Co(II) were neglected from the point of view of IR and electronic spectroscopy.

Factors such as aromaticity of the ligand, number of chelate rings, possibility of band formation, coordination behaviour of polydentate ligands, flexibility of the ligand are vital in establishing the role of coordination to the metal ions and also to determine the stability/reactivity of the complex.

Thus, in order to gain a better insight into the molecular structure of such complexes, it was thought worthwhile to carry out investigation on the following lines:

1.6.1 SYNTHESIS OF NEW COMPOUNDS TO ACT AS LIGANDS:

(i) \( 2,2^l \)-dithiodisalicylic acid (DTSA) –

\[
\text{COOH} \quad \text{HOOC} \\
\begin{array}{c}
\text{S} \\
\text{S} \\
\text{benzene} \\
\text{benzene}
\end{array}
\]

(ii) Diphenylamine-\( 2,2^l \)-dicarboxylic acid (DPDC)

\[
\begin{array}{c}
\text{COOH} \\
\text{NH} \\
\text{COOH}
\end{array}
\]
iii) 2-hydroxy benzilidene–2-amino thiophenol (HBAT)

(iv) 2-hydroxy benzilidene–anthranilic acid (HBAA)

1.6.2 CHARACTERISATION OF THE NEW LIGANDS:

It was done on the basis of

(i) elemental analysis

(ii) infra-red spectral analysis.

1.6.3 SYNTHESIS OF HETEROLIGAND COMPLEXES M(II)–B–H₂A:

In these complexes,

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

B = 3,3¹–dipyridyl (dipy.)

4, 7–dimethyl–1,10–phenanthroline (phen.)

H₂A = 2–mercaptobenzoic acid (MBA)

thiodipropionic acid (TDPA)

thiodiacetic acid (TDAA)

2, 2¹–dithiosalicylic acid (DTSA)

Dithiodipropionic acid (DTPA)

2–hydroxybenzilidene–2–aminathiophenol (HBAT)

3, 5–dinitrosalicylic acid (DNSA)

3, 5–dibromosalicylic acid (DBSA)

1–hydroxy–2–naphthoic acid (HNA)

Iminodiacetic acid (IMDA)

2–hydroxybenzilidene–2–aminophenol (HBAA)

Diphenylamine–2,2¹–dicarboxylic acid (DPDC)
Pyridine-2, 6-dicarboxylic acid (PDA).

A consolidated list of synthesized ternary complexes of the three metal ions is given below.

<table>
<thead>
<tr>
<th>Cu(dipy.)</th>
<th>TDPA</th>
<th>Co(dipy.)</th>
<th>TDPA</th>
<th>Ni(dipy.)</th>
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<td>PDA</td>
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<td>DNSA</td>
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<tr>
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<td>IMDA</td>
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<td>MBA</td>
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<td>DTSA</td>
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<td>Co(phen.)</td>
<td>DBSA</td>
<td>Ni(phen.)</td>
<td>DBSA</td>
</tr>
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</table>

6.4 CHARACTERISATION OF SYNTHESISED METAL CHELATES:

The metal chelates as synthesized in the previous step were characterized on the basis of following data—

(i) elemental analysis
(ii) infra-red spectral studies
(iii) magnetic susceptibility measurements
(iv) electronic spectral data.

1.6.5 STUDY OF ANTIMICROBIAL ACTIVITY:

A study and screening of ligands and the hetero-ligand complexes prepared was carried out for biocidal activity against a number of micro-organisms like fungi: Aspergillus flavus, Aspergillus niger, Aspergillus fumigatus, Aspergillus nidulans, Aspergillus sydowii, Aspergillus terreus and Aspergillus fursaum and bacteria: Staphylococcus aureus (Gram +ve) and Escherichia coli (Gram -ve).
CHAPTER-I
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