SUMMARY

SYNTHESIS AND CHARACTERISATION OF TRANSITION METAL COMPLEXES OF ORGANIC COMPOUNDS CONTAINING HETERO DONOR ATOMS

1.1 INTRODUCTION:

Now that we have presented our effort as per our research plan, it would be worthwhile to recapitulate the important features of the investigations.

In the present work, the synthesis of a number of new heteroligand complexes of Cu(II), Ni(II) and Co(II) with a neutral base and a carboxylic acid/schiff’s base ligand have been successfully carried out. The molecular formulae, structure and geometry of the complexes so synthesized have been determined and confirmed by their elemental analysis, IR spectra, UV spectra and magnetic measurements. Moreover, screening of anti-bacterial and anti-fungal action of the new ligands and the complexes has been carried out to assess their utility as anti-microbial agents against a number of common fungi and bacteria viz. Aspergillus flavus, Aspergillus niger, Aspergillus fumigatus; and Staphylococcus aureus (Gram +ve) and Escherichia coli (Gram −ve).

Whole work has been divided into four chapters. The preliminary intensive survey of literature is reported in Chapter-1.

1.2 SYNTHESIS:

The new ligands synthesized for our present investigations are:

2,2'-dithiodisalicylic acid (DTSA), 2-hydroxybenzalidine anthranilic acid (HBAA), 2-hydroxybenzalidine-2-amino-thiophenol (HBAT) and diphenylamine-2, 2'-dicarboxylic acid (DPDC).

The following ternary complexes of Cu(II), Ni(II) and Co(II) were synthesized:
1.2.1 Complexes of Copper:

1. Cu (dipy.) TDP A. H₂O
2. Cu (dipy.) MBA
3. Cu (dipy.) TDAA⋅H₂O
4. Cu (dipy.) DTSA
5. Cu (dipy.) DTPA
6. Cu (dipy.) PDA⋅H₂O
7. Cu (dipy.) HBAA⋅H₂O
8. Cu (dipy.) HBAT⋅H₂O
9. Cu (dipy.) DNSA
10. Cu (dipy.) DBSA
11. Cu (dipy.) HNA
12. Cu (dipy.) IMDA⋅H₂O
13. Cu (dipy.) DPDC⋅H₂O
14. Cu (phen.) MBA
15. Cu (phen.) DTSA
16. Cu (phen.) DTPA
17. Cu (phen.) PDA⋅H₂O
18. Cu (phen.) HBAA⋅H₂O
19. Cu (phen.) HBAT⋅H₂O
20. Cu (phen.) DNSA
21. Cu (phen.) DBPA

1.2.2 Complexes of Cobalt:

1. Co (dipy.) TDP A. H₂O
2. Co (dipy.) MBA
3. Co (dipy.) TDAA⋅H₂O
4. Co (dipy.) DTSA
5. Co (dipy.) DTPA
6. Co (dipy.) PDA⋅H₂O
7. Co (dipy.) HBAA⋅H₂O
8. Co (dipy.) HBAT⋅H₂O
9. Co (dipy.) DNSA
10. Co (dipy.) DBSA
11. Co (dipy.) HNA
12. Co (phen.) MBA,2H₂O
13. Co (phen.) DTSA
14. Co (phen.) PDA,H₂O
15. Co (phen.) HBAA,H₂O
16. Co (phen.) HBAT,H₂O
17. Co (phen.) DNSA,2H₂O
18. Co (phen.) DBSA,2H₂O

1.2.3 Complexes of Nickel:

1. Ni (dipy.) TDPA,H₂O
2. Ni (dipy.) MBA
3. Ni (dipy.) TDAA,H₂O
4. Ni (dipy.) DTSA
5. Ni (dipy.) DTPA
6. Ni (dipy.) DPA,H₂O
7. Ni (dipy.) HBAA,H₂O
8. Ni (dipy.) HBAT,H₂O
9. Ni (dipy.) DNSA
10. Ni (dipy.) DBSA
11. Ni (dipy.) HNA
12. Ni (phen.) DPDC,H₂O
13. Ni (phen.) MBA
14. Ni (dipy.) DTSA
15. Ni (phen.) PDA,H₂O
16. Ni (phen.) HBAA,H₂O
17. Ni (phen.) HBAT,H₂O
18. Ni (phen.) DNSA
19. Ni (phen.) DBSA,2H₂O

where dipy. = 3,3'-dipyridyl, phen. = 4,7-dimethyl-1,10-phenanthroline and TDPA = thiodipropionic acid, MBA = 2-mercaptobenzoic acid,
TDAA = thiodiacetic acid, DTPA = dithiodipropionic acid,
PDA = pyridine–2,6–dicarboxylic acid, DNSA = 3,5–dinitrosalicylic acid,
DBSA = 3,5–dibromosalicylic acid, HNA = 1–hydrox–2–naphthoic acid
IMDA = Iminodiacetic acid apart from the novel ligands referred to in sub–section 1.2

Chapter II of this dissertation reports the synthesis of all the ternary complexes by mixing equimolar amounts of metal acetates and relevant ligands at pH 6–7 by the established methods as reported in literature. All complexes were found to be stable at room temperature, non–hygroscopic and non–ionic in nature.

1.3 Physico–chemical Studies: The heteroligand ternary complexes were subjected to physico–chemical analysis as described in Chapter III and summarized below:

1.3.1 Infrared Spectroscopy: The section 3.1 in Chapter III has been further subdivided into two sub–sections. The first sub–section carried an account of M(II)–dipy.–X type of complexes while the other deals with M(II)–phen.–X type of complexes

where:

\[
\begin{align*}
M(II) & = \text{Cu(II), Co(II) or Ni(II) ion} \\
\text{Dipy} & = 3,3'–\text{dipyridyl} \\
\text{Phen} & = 4,7–\text{dimethyl–1,10–phenanthroline} \\
X & = \text{Dicarboxylic acid / Schiff's base = TDA, MBA, TDAA, DTSA, DTPA, PDA, HBAA, HBAT, DNSA, DBSA, HNA, IMDA and DPDC.}
\end{align*}
\]

1.3.2 Infrared Spectra: A comparison of the IR spectra of the (free ligands) and the (metal complexes) reveals the following vital modifications:

(a) In the region of 3280–3580 cm\(^{-1}\), a broad adsorption band appears in some dipy.– and phen.–metal complexes. They may be attributed to the stretching vibration of O–H in complexes wherein water molecules have coordinated with the metal ion. A moderate band in the region 810–860 cm\(^{-1}\) and 680 – 690 cm\(^{-1}\) due to rocking and bending vibrations supports the above assumption. Further
confirmation of the phenomenon is available from loss in weight of complex at 180°C ruling out presence of lattice water.

(b) In the region around 3300 cm\(^{-1}\) and 1370 cm\(^{-1}\) for the spectra of HBA, HBAT, DNSA and DBSA uncoordinated ligands, the two bands are attributed to O–H phenolic stretching and bending vibrations. The two bands disappear in their dipy- and phen.-metal complexes leading us to conclude that M–O–C bond is formed following deprotonation of the phenolic group.

(c) In the region around 3400 cm\(^{-1}\), a spectral band is observed for free IMDA and DPDC ligands due to N–H stretching frequency. The bands shifts to a lower frequency region in Cu(dipy.) IMDA (3360 cm\(^{-1}\)), Cu(dipy.) DPDC (3370 cm\(^{-1}\)) and Ni(dipy.) DPDC (3340 cm\(^{-1}\)). The lowering of the frequency on complexation is suggestive of metal to ligand bonding taking place through ‘N’ of the –NH group. A moderate band at 1585 cm\(^{-1}\) in IMDA and DPDC free ligands is due to the –NH bending frequency overlapping the frequency of the aromatic ring. Involvement of ‘N’ of –NH in bonding in metal chelates is confirmed by lowering of this frequency on coordination.

(d) In the region around 2930 cm\(^{-1}\) and 2850 cm\(^{-1}\), a moderate band is observed for the free TDPA, TDAA and DTPA ligands due to asymmetric and symmetric CH\(_2\)-S stretching vibrations respectively. In the related metal complexes of dipy. and phen. (with the exception of Ni(dipy.) TDPA in which these frequencies are shifted to higher region by 20 cm\(^{-1}\) and 30 cm\(^{-1}\) respectively) both these frequencies are lowered. It may, therefore, be concluded that ligand is linked to metal via ‘S’ atom of CH\(_2\)-S group.

(e) In the region of 2590 cm\(^{-1}\) and 2550 cm\(^{-1}\) weak spectral bands are observed for MBA and HBAT free ligands. These bands tend to disappear in their respective dipy.- and phen.-metal complexes leading us to the firm conclusion that there is deprotonation of –SH group prior to coordination.
(f) In the regions of 1660 ± 40 cm⁻¹, 1440 ± 40 cm⁻¹ and 920 ± 10 cm⁻¹, the observed frequencies in all the free acid ligands may be attributed $v_{as}$ (CO), $v_{as}$(CO) and $-\text{OH}$ deformation vibrations respectively. In almost all the corresponding dipyr- and phen.-metal complexes, there is a notable shift in CO stretching frequency towards the lower region and disappearance of $-\text{OH}$ deformation vibration. The phenomenon is suggestive of ligand to metal coordination through the carboxylic group.

(g) In the region of 1640 cm⁻¹ and 1635 cm⁻¹, a sharp spectral band is observed for free HBAA and HBAT ligands respectively due to the (C=N) frequency of the azomethine group. In the dipyr.- and phen.-metal complexes, this frequency is lowered by 20–55 cm⁻¹ leading us to infer that ligand to metal coordination is occurring via the ‘N’ of azomethine group.

(h) In the region of 1600 cm⁻¹, a sharp spectral band occurs for uncoordinated dipyr., phen. And PDA due to the $v$(C=N) vibration (py.). In all the respective complexes, a negative shift of the order of 10–80 cm⁻¹ is found. It clearly suggests that the ‘N’ of the pyridine is involved in coordination. A shift in $vC$–N (py.) and pyridine ring deformation vibration confirms the involvement of ‘N’ in ligand to metal linkage.

(i) In the region of 1165 cm⁻¹, a band indicates the presence of pyridine ring in free phen. Ligand. The vibration overlaps with the frequency of the aromatic ring, $-\text{C–C}$ and $-\text{C=C}$ combination. In almost all the corresponding metal ternary complexes, this frequency shifts to a lower side by a magnitude of 10–25 cm⁻¹. It is possibly explained by the coordination of the metal to the ligand through nitrogen of the pyridine ring.

(j) In the region of 590 cm⁻¹ and 650 cm⁻¹, weak to moderate bands for free TDPA and DTSA, in the region of 570 cm⁻¹ for free MBA and TDPA and in the region of 660 cm⁻¹ for DTPA and HBAT free ligands are assigned to $v\text{C–S}$ vibrations. In the corresponding dipyr.- and phen.-metal complexes, this
frequency is invariably lowered by $15 - 40 \text{ cm}^{-1}$. It indicates that coordination occurs through 'S' atom of the ligand.

(k) In the region of 500 cm$^{-1}$ and 510 cm$^{-1}$ a band each for DTSA and DTPA free ligands can be assigned to $v$(S-S) vibrations. In all the related dipy.- and phen.- metal complexes there is a perceptible negative shift in this frequency. Obviously, an M-S bond is definitely present in these ternary complexes.

(l) The appearance of some new bands in the region of 350 - 510 cm$^{-1}$, 300 - 480 cm$^{-1}$ and 260 - 340 cm$^{-1}$ in the coordinated species further confirms our conclusion that metal is linked to ligand via oxygen, nitrogen and sulphur donors, respectively, the three frequencies may be assigned to $v$(M-O), $v$(M-N) and $v$(M-S) vibrations respectively in all the ternary complexes under investigation.

1.3.3 **Magnetic Studies:** Sub-section 3.2 of the chapter has been sub-divided into three parts: each dealing with complexes of Copper(II), Cobalt(II) and Nickel(II) respectively.

It has been observed that the effective magnetic moment values of all the Copper(II) complexes lie between 1.67 to 2.19 B.M. Obviously, unpaired electrons are present in each of them. The values of magnetic moment suggest that these complexes with one unpaired electron may have square planar, tetrahedral or distorted octahedral configuration in their monomeric forms.

The values of magnetic moment of all the dipy.-Copper(II) complexes except those with MBA, DNSA, DBSA and HNA correspond to octahedral shape. Hence, it has been proposed that all these complexes have octahedral geometry with spin free arrangement.

Lower values of the ternary Cu(II)-dipy. complexes with MBA, DNSA, DBSA and HNA are close to spin only magnetic moment. Hence these complexes are expected to be square planar and paramagnetic. The observed magnetic moment value (1.67 B.M.) for the Cu(dipy.) HBAA$\cdot$H$_2$O complex is too low. Now, this is significant
because the short Cu–Cu distance may allow a direct partial spin–spin coupling through super exchange mechanism.

For the phen.–Cu(II) complexes, the ternary complexes with MBA, DNSA and DBSA, the magnetic moment values are 1.80, 1.79 and 1.77 B.M. respectively. A square planar geometry may be assumed in their case. On the other hand, the complexes with PDA, HBAA and HBAT (all mono hydrates) with magnetic moments of 1.95, 2.13 and 2.19 B.M. respectively may be proposed to have low spin octahedral stereochemistry due to one coordinated water molecule whose presence has been confirmed by elemental analysis. However, the complexes with DTSA and DTPA with magnetic moment of 2.14 B.M. and 1.89 B.M. are hypothesized to be spin free octahedral complexes with paramagnetic character. There is no other way to explain the situation in the absence of water molecules.

In the case of cobalt(II) complexes, under investigation, the magnetic moments vary between 3.81 to 5.37 B.M. respectively revealing the presence of three unpaired electrons. In the complexes of dipy.– and phen.– Co(II), except those of Co(dipy.) with MBA, DNSA, DBSA and HNA, the $\mu_{\text{eff}}$ values lie in the range 4.02 - 5.37 B.M. suggesting a spin free octahedral shape for them. The $\mu_{\text{eff}}$ values of paramagnetic dipy.–Co(II) complexes of MBA, DNSA, DBSA and HNA are 4.15, 4.13, 3.86 and 3.81 respectively. It indicates that these ternary complexes are tetrahedral. Lowering of symmetry in DBSA and HNA complexes is responsible for lower value of their magnetic moment. The negative orbital contribution to paramagnetism may also be the reason for it is a vector quantity. These considerations lead us to conclude that Co(dipy.) DBSA and Co(dipy.) HNA should have distorted tetrahedral configuration around the Co(II) ion.

For the nickel(II) ternary complexes, generally, the magnetic moments are found to range between 2.9 and 3.3 B.M. In our present investigations, the effective magnetic moment values of all the dipy.– and phen.– Ni(II) complexes except Ni(dipy.) MBA, Ni(dipy.) DNSA, Ni(dipy.) HNA and Ni(phen.) MBA are found to lie in the range of 2.84 - 3.23 as expected for spin free complexes with two unpaired
electrons and having octahedral shape. Hence all these spin free paramagnetic complexes except Ni(dipy.) DBSA and Ni(phen.) DNSA must have octahedral geometry. \(sp^3d^2\) hybridisation may be conveniently invoked to explain the stereochemistry. The effective magnetic moment values of MBA, DNSA and HNA complexes of Ni(dipy.) and MBA complexes of Ni(phen.) are found to be 0.99, 1.09, 1.08 and 1.04 B.M. respectively. Thermal population of a triplet lying very close to the singlet ground state accounts for the small paramagnetism in these cases. It is proposed that these complexes have spin paired square planar shape.

The structures as proposed for the mixed complexes of Cu(II), Co(II) and Ni(II) are confirmed by electronic spectral investigations.

**1.3.4 Electronic Spectral Studies:** The sub-section 3.3 of Chapter III deals with the electronic spectral studies of mixed complexes of Cu(II), Co(II) and Ni(II) on an individual basis.

In the case of Cu(II) complexes, one invariably expects the existence of broad asymmetric band. The two degenerate states \(^2E_g\) and \(^2T_{2g}\) are also split when distorted octahedral complex is formed. Three shoulder bands occur in the region 11510 – 12026 cm\(^{-1}\), 17300 – 18540 cm\(^{-1}\) and 26960 – 27419 cm\(^{-1}\) corresponding to transitions \(^2B_{1g} \rightarrow ^2A_{1g} (v_1)\), \(^2B_{1g} \rightarrow ^2B_{2g} (v_2)\) and \(^2B_{1g} \rightarrow ^2E_g (v_3)\) respectively for the Cu(dipy.) TDAAC, Cu(dipy.) HBAA, Cu(dipy.) IMDA and Cu(phen.) DTPA mixed complexes. Logically, therefore, these complexes have distorted octahedral environment around the metal ion. \(v_2/v_1\) ratio values fall in the region 1.49 – 1.54 as per the requirement for this shape for Cu(II) complexes. Further, sufficiently high degree of covalent character is indicated by the \(\beta\) and \(\beta\%\) values. With increase in energy of \(^2A_{1g}\), all three bands may merge together due to small difference in energy to yield a broad symmetrical band.

On the other hand, in case of Cu(dipy.) MBA, Cu(dipy.) DNSA, Cu(dipy.) DBSA, Cu(dipy.) HNA, Cu(phen.) DNSA and Cu(phen.) DBSA ternary complexes, a broad spectral band in the region 16210 to 18940 cm\(^{-1}\) corresponding to \(^2B_{1g} \rightarrow ^2A_{1g}\) transition is observed. Incidentally, this transition has been reported for square planar
CuO$_2$N$_2$ chromophore. In the remaining Cu(II) complexes under investigation, a single electronic spectral band in the lower region of 13980 – 16020 cm$^{-1}$ is observed. This band corresponds to $^2E_g \rightarrow ^2T_{2g}$ transition to indicate octahedral configuration. In fact, as reported earlier in Chapter III, the calculated D$q$ and LFSE values also reaffirm the existence of octahedral environment around Cu(II) ion in all these complexes.

Three spectral bands in the region 5920 – 17230 cm$^{-1}$ observed for Co(II) dipy complexes of MBA, DNSA, DBSA and HNA indicate tetrahedral stereochemistry as these bands may be attributed to $^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$ ($v_1$), ($F$) $\rightarrow ^4T_{1g}(F)$ ($v_2$) and $^4A_{2g}(F) \rightarrow ^4T_{1g}(P)$ ($v_3$) transitions respectively. The ratio $v_2/v_1$ in the range 2.37 – 2.42 confirms tetrahedral geometry of these Co(II) complexes. The phen – Co(II) complexes with MBA, HBAA and DBSA are hypothesized to have distorted octahedral geometry for in their case, three spectral bands lie in the range 8425 – 20360 cm$^{-1}$ which are assigned to $^3A_{1g}(F) \rightarrow ^3T_{2g}(F)$ ($v_1$), $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ ($v_2$) and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ ($v_3$) transitions. Lower values of $v_2/v_1$ ratio around 1.7 allowed us to assign distorted octahedral geometry to these complexes of Co(II).

In the remaining Co(II) complexes, the three bands are observed in the region of 8016 – 8786 cm$^{-1}$, 14456 – 16118 cm$^{-1}$ and 18200 – 21380 cm$^{-1}$ for the transitions referred to in the previous paragraph. The $^4A_{2g}$ is comparatively very weak and is observed as a shoulder band in most of these cases. The ratio $v_2/v_1$, D$q$, B, $\beta$ & LFSE values are well within the reported range for octahedral cobalt(II) complexes. There is a clear indication of greater covalent character from the $\beta$% values.

No transition is found to occur below 10000 cm$^{-1}$ in low spin square planar Ni(II) complexes. It has been observed that Ni(phen.) MBA complex and MBA, DNSA and HNA; complexes of dipy. exhibit spectral bands in the range 18130 – 18620 cm$^{-1}$, 28790 – 29900 cm$^{-1}$ and 34170 – 35170 cm$^{-1}$ which are assigned to $^1A_{1g} \rightarrow ^1E_u$ ($v_1$), $^1A_{1g} \rightarrow ^1A_{2u}$ ($v_2$) and $^1A_{1g} \rightarrow ^1B_{1u}$ ($v_3$) transitions respectively. One, therefore, arrives at tetrahedral geometry of these complexes. As in tetrahedral Ni(II) complexes a spectral band below 10 KK is expected and the remaining fall in the
range of 15000 - 19000 cm\(^{-1}\) due to \(3^3T_1 \rightarrow 3^3A_2\), \(3^3T_1 \rightarrow 3^3A_2\) and \(3^3T_1 \rightarrow 3^3T_1(P)\) transitions respectively, the complexes Ni(dipy.) DBSA and Ni(phen.) DNSSA should possess tetrahedral geometry. In their cases the spectral bands fall in the region 8470 - 8650 cm\(^{-1}\), 15340 - 15560 cm\(^{-1}\) and 19530 - 19660 cm\(^{-1}\) respectively. The Dq, B, \(\beta\), LFSE and \(v_2/v_1\) values for these complexes also agree with those found in literature for tetrahedral complexes.

The remaining nickel(II) complexes exhibit three spin allowed transitions in the regions 8760 - 12680 cm\(^{-1}\), 16440 - 20980 cm\(^{-1}\) and 20100 - 27500 cm\(^{-1}\) due to \(3^3A_{2g} \rightarrow 3^3T_{2g}(P)\) \((v_1)\), \(3^3A_{2g} \rightarrow 3^3T_{1g}(P)\) \((v_2)\) and \(3^3A_{2g} \rightarrow 3^3T_{1g}(P)\) \((v_3)\) transitions respectively to indicate octahedral geometry. The Dq, B, \(\beta\), LFSE and \(v_2/v_1\) values fall in the range 8760 - 12680, 633 - 713, 0.61 - 0.66, 30 - 43 and 1.81 - 1.91 respectively further confirm the octahedral stereochemistry of these complexes of Ni(II) except Ni(dipy.) PDA, Ni(phen.) DTSA, Ni(phen.) HBAA and Ni(Phen.) DBSA ternary complexes. In these exceptions, lower values of \(v_2/v_1\) (1.64 - 1.68) indicate that they possess distorted octahedral configuration. The \(\beta\)% values lie in the range 51 - 63%.

Obviously, the metal–ligand bond has partial covalent character.

Magnetic susceptibility studies as described in sub-section 3.2 reinforce our conclusions on the structures of various ternary complexes of Cu(II), Co(II) and Ni(II).

1.4. Antimicrobial studies on synthesized ligands and the ternary complexes have been reported in Chapter IV. The ligands and the complexes were screened for their biocidal activity on fungi (A. flavous, A. fumigatus and A. niger) and bacteria (S. aureus and E. coli) by means of agar diffusion method.

A comparative study of the results so obtained reveals that, in general, the metal complexes are biologically more active than the ligands alone. The TDPA–dipyridine complexes except Ni(dipy.) TDPA and PDA–dipyridine complexes except Cu(dipy.) PDA fail to show any activity against Aspergillus flavus and A. niger. Co(dipy.) DBSA exhibits extremely weak antimicrobial activity against A. flavus, A. niger and test bacteria. It is possible to attribute the inactivity of Ni(dipy.) DTSA
complex towards test fungi and of Co(dipy.) DTSA towards test bacteria to the combined bioactive effect of the metal ion, the ligands and the trace elements present in the bacteria and fungi species.

In the case of Phen.–Cu(II) complexes of MBA, HBAT and DNSA very poor activity against Staphylococcus aureus and Escherichia coli may be attributed to the bioactive action of Cu(II) and poor antibacterial activity of phen. Very poor activity amounting to virtual inactivity of Cu(II) DNSA complexes of dipy.– and phen.– against all bacteria and fungi may be due to NO2− present in DNSA acting as a nutrient. If the geometry and charge distribution around the periphery of the pores of the fungal or bacterial cell wall, it is believed that penetration of the toxic agent is not possible and biocidal activity does not occur. That some of the mixed ligands are less toxic than their free ligands may be explained on this basis.

The comparative study of MIC values of the ternary complexes of the three metals under investigation reveals that nickel(II) complexes show maximum biocidal activity against the test bacteria and fungi as phen.–complexes. In the case of dipy. complexes, the biocidal activity is dependent upon the nature of ligand and the metal under test conditions.
SYNTHESIS AND CHARACTERISATION OF TRANSITION METAL COMPLEXES OF ORGANIC COMPOUNDS CONTAINING HETERO DONOR ATOMS

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1. INTRODUCTION:

The introduction of sulphur and nitrogen atoms in the structure of organic compounds has often resulted in important consequences in their behaviour towards metal ions. Many investigations have been undertaken of the interaction of transition metal ions with ligands, containing sulphur and nitrogen as donor atoms. These sulphur, nitrogen or sulphur, nitrogen and oxygen containing ligands are of prime importance in biological systems i.e. exhibit anticancer\(^1\), antiviral\(^2\), antibacterial\(^3\) and antifungal\(^4\) properties. Recently the role of coordination compounds in water pollution control has been discussed by some workers\(^5\). It has been shown by these workers that on complexation, the metal goes into the coordination sphere and properties of the complexes are most of the time differ from those of free metal ion. If the stability of the complexes is high enough, the toxic effect due to free metal ion in the aquatic system can be reduced to a great extent.

2. PRESENT STATE OF KNOWLEDGE:

Transition metal complexes constitute a group which has been most widely studied in coordination chemistry. New possibilities have arisen in practice and in research due to the advancement of ligand field theory and application of group
theory to coordination, chemistry and development of various techniques such as IR including far IR, UV, visible, ESR, magnetic and electronic spectral studies.

In Schiff bases since nitrogen atom of the azomethine group has a lone pair of electrons and the double bond has electron donating character. Compounds containing the azomethine group gained prominence as pharmacologically important substance. They possess medicinal properties. Pfeiffer and his workers\(^{(6)}\) in a series of papers produced a prodigious number and variety of complexes. The first attempt to establish the structure of schiff base complexes was made by Stackelberg\(^{(7)}\) who deduced molecular structure with the help of space group theory density determination, and packing considerations. Generally survey of literature reveals that much stress has been laid on the transition metal complexes of schiff bases. The phenomenal rise in the investigation of the properties of the metal schiff base complexes is due to their ease of preparation, their diverse properties and their use as a model for biological reactions.

Investigations in thiosemicarbazones\(^{(8-10)}\) have been mainly carried out from the synthetic view point and very little is known about their physico chemical aspects viz. their role as chelating agents and their use as a colormetric reagents.

3. **BROAD OUTLINES OF THE WORK:**

Scanty knowledge about the nature of chemical bond in coordination compounds, particularly about their physico chemical behaviour pointed towards the necessity and importance of undertaking systematic studies in these compounds.

Recently Verma et.al\(^{(11-16)}\) described the synthesis of certain hydrazides and related products. Such compounds have shown antitubercular activity. The activity\(^{(17-19)}\) of these compounds can be increased manifold by substituting halogeno and nitro group. But these authors have not studied\(^{(20-21)}\) the effect of metal ion complexes prompted by these findings and as a part of our general search for pharmacologically active compounds it was contemplated by
synthesize and study the chelating behaviour of some \( N, O, S \) containing ligands.\(^{22-26}\)

4. **THE PROBLEM UNDER INVESTIGATION WILL BE DONE ON THE FOLLOWING LINES:**

1. The preparation of some organic compounds (Schiff bases hydroxy acids, as well amine compounds).
2. Their characterization by different physico chemical methods.
3. Isolation of the complexes with less familiar transition and inner transition metal ions of the above mentioned compounds.
4. Chemical analysis, IR spectra and magnetic measurements will be used to determine the stoichiometry and the various sites of attachment as well as the oxidation state of metal ion involved.
5. Further attempts will be made to calculate various ligand field parameters by recording the electronic spectra of isolated complexes.
6. Evaluation of different ligand field parameters and to suggest possible stereochemistry around the metal ions.

5. **INSTRUMENTS TO BE USED:**

Infra red spectrophotometer, Guoy's balance, (to measure the magnetic susceptibility) will be used.

6. **IMPORTANCE AND UTILITY OF WORK:**

Acyclic and cyclic ligands containing multi coordination sites have been synthesized which usually coordinate to two similar or different cations mainly ligands of this type have \( \mathrm{N}_2\mathrm{O}_4 \) sites. Later on these ligands systems can be extended to systems containing seven coordination sites. The interest in the latter type of ligands arises from the need of the uranyl cations to coordinate with five donating atoms to complete its seven coordination sphere.
REFERENCES