CHAPTER - 2

ADVANCED SUMMARY OF THE PRESENT INVESTIGATION

As reported previously, the metal ions selected for the present investigation are divalent Cobalt (d⁷), divalent Nickel (d⁸), divalent Copper (d⁹), divalent Cadmium (d¹⁰) and divalent Mercury (d¹⁰). Their halides, nitrates and thiocyanates were reacted with the ligands containing different donor atoms as indicated below. In addition, some anionic and neutral complexes were synthesised and these were again made to react with different nitrogen donor ligands to obtain new type of heteroligand complexes. The ligands used in the present investigation contain nitrogen, oxygen and sulphur as donor atoms and these are listed below.

Nitrogen Ligands:

Pyridine, 4-methyl pyridine, piperidine, morpholine, quinoline, isoquinoline, quinaldine, diethylamine, aniline, ethylenediamine, ortho phenanthroline, ortho tolidine and 2,2'-bipyridyl.

Oxygen Ligands:

Benzil, benzoin, benzilic acid, ortho-dihydroxy benzene (catechol) and anthranilic acid either independently or in the form of condensation derivatives.
Sulphur Ligands:

Substituted amino benzothiazoles and hydrazine dithiourea.

Polydentate Ligands: (Involving oxygen, Nitrogen and Sulphur donor atoms).

The polydentate ligands mentioned below were for the first time synthesised by us and attempts have been made to study their complexation behaviour.

Tetradentate Schiff's base derived from benzoin and ortho tolidine, benzil and ortho tolidine, and benzil and ethylenediamine.

Tridentate Schiff's base derived from benzil and anthranilic acid, benzil and cyano acetic ester and both benzoin and benzil with substituted amino benzothiazoles.

Bidentate Schiff's base derived by reacting salicylaldehyde with either 2-amino-6-methyl benzothiazole or 2-amino-6-chloro benzothiazole. Besides above, the hydrazine dithiourea was also synthesised from hydrazine hydrate.

The reaction of these ligands with the above metal salts and some of their complexes have been carried out under appropriate condition and several new compounds were isolated in a pure condition as is evident from their analytical data. Conductance measurements were carried out in acetone, and dimethyl formamide medium (10^{-3} M) using Toshniwal conductivity bridge type CL.0102. Magnetic
susceptibility measurements were made at room temperature on solid specimens using 'Gouy method'. Infrared spectra were recorded on KBr phase using Perkin-Elmer-221 and Beckman IR-12 spectrophotometer operating in the region 200 to 5000 cm$^{-1}$. Electronic absorption spectra were obtained in chloroform and dimethylformamide solutions using Hilger-Watt Uvispeck spectrophotometer in the 300-1200 nm region. X-ray powder photographs of some of the complexes were also studied.

The results obtained in the above investigations have been written under the Chapters 4 to 9.

A general survey of transitional metal complexes has been briefly reviewed in Chapter-3 and a general description of analytical and physical methods used is included in Chapter-10. As regards to the application sides of the complexes synthesised, the antifungal studies of some of the complex compounds have been carried out by bioassay method against two rice pathogens, Pyricularia oryzae, Cav and Helminthosporium oryzae, BrdeHaan. The results and discussions of this study is incorporated in the separate Chapter-9.

The complexes of the metal ions Co(II), Ni(II), Cu(II), Hg(II) and Cd(II) synthesised and characterised with different ligands are listed below. The details of these complexes are discussed in detail in Chapters 4 to 8.
Table 1: Complexes of Cobalt(II):

1. Complexes with tetradentate Schiff's bases:

\[ \text{[CoLX}_2\text{]}, \text{ where } \text{L is the tetradentate Schiff's base derived (a) benzoin and ortho-tolidine, (b) benzil and ortho-tolidine and (c) benzil and ethylenediamine; } \text{X = H}_2\text{O} \]

2. Complex with tridentate Schiff's base:

\[ \text{[CoL}_3\text{X}_3\text{]} \text{ where } \text{L = tridentate Schiff's base derived from benzil and anthranilic acid; X = H}_2\text{O}. \]

3. Complexes with bidentate ligands:

\[ \text{[CoL}_2\text{X}_2\text{]}, \text{[CoL}_2\text{B}_2\text{]} \text{ and } \text{[CoL}_2\text{Y}_2\text{]}, \text{ where L = bidentate Schiff's base ligand derived from salicylaldehyde with either 2-amino-6-methyl benzothiazole or 2-amino-6-chloro benzothiazole, L' = ortho-tolidine, L" = hydrazine dithioura, X = Cl}^- \text{ or SCN}^- \text{, B = H}_2\text{O and Y = Cl}^- \text{, SCN}^- \text{ or NO}_3^- \cdot \]

4. Complexes with substituted aminobenzothiazoles:

\[ \text{[Co(L or L')}_2\text{X}_2\text{]} \text{ and } \text{[CoL}_2\text{]}(\text{ClO}_4)_2 \text{ where L = 2-amino-6-methyl benzothiazole, L' = 2-amino-6-chloro benzothiazole and X = Cl}^- \text{, Br}^- \text{, SCN}^- \text{, NO}_3^- \text{, OAc}^-. \]

5. Mixed ligand anionic complexes:

\[ \text{[L}_2\text{][COCl}_4\text{Y]} \text{ and } \text{[L][COCl}_3\text{B]} \text{, where L = monomethyl ammonium ion, Y = ethylene diamine, ortho phenanthroline and 2,2'-bipyridyl, B = Aniline, Pyridine or \text{\gamma-Picoline.}} \]
6. Mixed ligand adduct Complexes:

\[ [\text{COL}_2B_2], \text{ where } H_2L = \text{ orthodihydroxy benzene (Catechol) and } B = \text{ Pyridine, } \gamma\text{-Picoline, Quinoline or isoquinoline.} \]

The total number of Cobalt(II) complexes synthesised is 27.

The complexes listed above belong to tetra-, hexa- and penta-coordinated varieties. The complexes with tetradentate Schiff's bases as well as with tridentate Schiff's base are all indicated to have octahedral configuration. Complexes of the composition \([\text{COLX}_2]\) and \([\text{COL}^\prime\text{Y}_2]\) with bidentate ligands have been assigned tetrahedral symmetry on the basis of elemental analysis, conductance, magnetic susceptibility, infrared and electronic spectral data. The thiocyanato group in both type of complexes is deduced to be terminal N-bonded. The nitrato-group is found to be monodentate in the complex \([\text{COL}^\prime(\text{NO}_3)_2]\). The ortho-tolidine complex of Cobalt(II) is found to have octahedral symmetry around the metal ion.

The complexes listed in catagory 4 above, having the compositions \([\text{COL}(L \text{ or } L')_2X_2]\) and \([\text{COL}_4] (\text{ClO}_4)_2\) are reported to have tetrahedral symmetry as is indicated from the infrared and electronic spectral data. In the complexes the nitrate group is monodentate and the thiocyanate group is terminal N-bonded. The conductance data indicate the perchlorate complex to be ionic and this has been corroborated by the appearance of bands in the infrared spectra of the complex.
Complexes having the compositions \([L]_2[COCl_4Y]\)
and \([L][COCl_3B]\) as listed under category five are 2:1 and 1:1 electrolytes as is indicated from the conductance data. The later type of complexes are reported to be penta-coordinated on the basis of analytical reports. X-ray Powder photographic data of some anionic complexes suggest cubic structure. Lastly, the mixed ligand adduct complexes are all octahedral and the different physico-chemical studies corroborate the fact.

Table - 2 : Complexes of Nickel(II) :

1. Complexes with tetridentate Schiff's bases :

\([\text{Ni}LX_2]\), where \(L\) is the tetridentate Schiff's bases mentioned previously in Table-1 under Cobalt(II) complexes.

2. Complexes with tridentate Schiff's bases :

\([\text{Ni}LX_3]\) and \([\text{Ni}L'X_3]\), where \(L\) is the Schiff's base derived from benzil and anthranilic acid, \(L' = \) Schiff's base derived from benzil and cyano acetic ester; \(X = H_2O\) in both cases.

3. Complexes with bidentate ligands :

\([\text{Ni}(L \text{ or } L')_2X_2]\) and \([\text{Ni}L''B_2]\), where \(L = \) Schiff's base derived from salicylaldehyde and 2-amino-6-methyl benzothiazole, \(L' = \) Schiff's base derived from salicylaldehyde and 2-amino-6-chloro benzothiazole, \(L'' = \) ortho tolidine, \(X = \text{Cl}^-\) or \(\text{SCN}^-\) and \(B = H_2O\.\)
4. Complexes with substituted amino benzothiazoles:

\[
[\text{Ni}(L \text{ or } L')_2X_2] \text{ and } [\text{Ni}(L \text{ or } L')_4\text{ClO}_4)_2,
\]
where \( L = 2\text{-amino-6-methyl benzothiazole} \), \( L' = 2\text{-amino-6-chloro benzothiazole} \) and \( X = \text{Cl}^-, \text{SCN}^-, \text{NO}_3^- \).

5. Mixed ligand complexes of bis-(benzilato) Nickel(II):

\[
[\text{NiL}_2\text{B}_2], \text{ where } HL = \text{benzilic acid and } B = \text{Pyridine, } \gamma\text{-Picoline, Quinoline or iso-quinolone and }
\]

6. Mixed ligand anionic complexes:

\[
[L]_2[\text{NiCl}_4B], [L]_2[\text{NiCl}_4\text{(morph})_2] \text{ and } [L][\text{NiCl}_3](\text{Py}),
\]
where \( L = \text{monomethyl ammonium cation} \),

\( B = \text{ethylene diamine, ortho-phenanthroline and } 2,2'\text{-bipyridyl} \),

\( \text{Morph} = \text{morpholine and } \text{Py} = \text{Pyridine} \)

The total number of Nickel(II) complexes synthesised is 27.

The nickel(II) complexes listed above are mostly of octahedral type. The Nickel(II) complexes with substituted amino benzothiazoles having the compositions \([\text{Ni}(L \text{ or } L')_2X_2]\) and \([\text{Ni}(L \text{ or } L')_4\text{ClO}_4)_2\) are reported to have square planar and tetrahedral symmetries respectively on the basis of magnetic moment and electronic spectral studies. The presence of ionic perchlorate group, and the bonding modes of the thiocyanate and nitrate groups have been assigned from conductance and infrared data.
Conductance data reveal the anionic mixed ligand complexes of the composition $[L]_2[NiCl_4 B]$ and $[L]_2[NiCl_4 (morph)_2]$ to be 2:1 electrolyte, whereas the complex $[L][NiCl_3(Py)_2]$ is a 1:1 electrolyte. Further, analytical results suggest the complex $[L][NiCl_3(Py)_2]$ to be penta-coordinated.

Table - 3 : Complexes of Copper(II) :

1. **Complexes with tetradentate Schiff's bases** :

   $[CuL]$, where $L =$ Schiff's base derived from
   (a) benzoin and ortho-tolidine, (b) benzil and ortho-tolide, and (c) benzil and ethylene diamine.

2. **Complexes with tridentate Schiff's bases** :

   $[CuL_2]$ and $[CuL'_2]$, where $L =$ Schiff's base derived from benzil and anthranilic acid, $L' =$ Schiff's base derived from benzil and cyano acetic ester.

3. **Complexes with bidentate ligands** :

   $[CuLX_2]$, $[CuL'_2]$ and $[CuL''Y_2]$, where $L =$ Schiff's bases derived from salicylaldehyde and substituted amino benzothiazoles, $L' =$ ortho-tolidine, $L'' =$ hydrazine dithiourea, $X = Cl^-$ or $SCN^-$ and $Y = Cl^-$, $SCN^-$ or $NO_3^-$.  

4. **Complexes with substituted amino benzothiazoles** :

   $[Cu(L \text{ or } L')_2X_2]$ and $[CuL'_4](ClO_4)_2$, where $L =$ 2-amino-6-methyl benzothiazole, $L' =$ 2-amino-6-chloro
benzothiazole and X = Cl\(^-\), OAc\(^-\) or NO\(_3\)^-.

5. **Mixed ligand adduct complexes** :

\[\text{[CuL}_2\text{X}_2]\], where \(\text{H}_2\text{L} = \text{ortho dihydroxy benzene} \) (Catechol) and X = Pyridine, \(\gamma\)-Picoline or Piperidine.

6. **Mixed ligand anionic complexes** :

\[\text{[L}]_2[\text{CuCl}_4\text{B}_2], [\text{L}]_2[\text{CuCl}_4\text{B}'], \text{and [L][CuCl}_3\text{B}'']\]

where, L = monomethyl ammonium cation, B = Pyridine, \(\gamma\)-Picoline, quinoline, piperidine, aniline and dimethylamine, B' = 1,10-Phenanthroline, 2,2'-bipyridyl and ethylenediamine, B'' = quinaldine and morpholine.

In total 33 complexes of Copper(II) are synthesised.

Most of the complexes listed above have square planar geometry and the rest have either distorted octahedral or pseudo tetrahedral configuration. The characterisations were based upon analysis, conductance, magnetic susceptibility, infrared and electronic spectral data. The geometry of some representative complexes have also been studied by X-ray powder photographic measurements.

**Table - 4 : Complexes of Cadmium(II) :**

1. **Complexes with tetradeutate Schiff's bases** :

\[\text{[CdL]}\], where L is the tetradeutate Schiff's base derived by reacting (a) benzoin with ortho-tolidine, (b) benzil with ortho-tolidine and (c) benzil with ethylene
2. Complexes with dicyandiamide:

\[ \text{[CdL}_2\text{X}_2] \text{ and [CdL}_4\text{]}(\text{ClO}_4)_2, \text{ where, L = dicyandiamide and X = Cl}^-, Br^-, I^-, SCN^-, NO_3^- \text{ and OAc}^- \].

3. Complexes with tetrathiocyanato Cadmium(II) with unidentate ligands:

\[ [\text{Me}_4\text{N}]_2[\text{Cd(SCN)}_4\text{L}_2] \text{ and [Me}_4\text{N}]_2[\text{Cd(SCN)}_4\text{L}'] \]
where \( \text{Me}_4\text{N} = \text{tetramethyl ammonium ion}, \text{ L = 4-methylpyridine or isoquinoline, L'} = \text{Quinoline, Pyridine or thiourea.} \)

In total, 15 complexes of Cadmium(II) are synthesised.

The Cadmium(II) complexes with the Schiff's bases and dicyandiamide are presumably tetrahedral. The 4-methyl pyridine and iso-quinoline adduct complexes of tetrathiocyanato Cadmium(II) are indicated to be hexacoordinated, whereas the other three adduct complexes of tetrathiocyanato Cadmium(II) are penta-coordinated. Although the possibility of a trigonal bipyramidal symmetry is suggested for these penta-coordinated complexes, only the X-ray crystallographic studies can elucidate whether they are trigonal bipyramidal or square pyramidal.
Table - 5 : Complexes of Mercury(II) :

1. Complexes with tetradentate Schiff's bases :

\([HgL], \) where \(L = \) Schiff's bases as reported in Table-1 previously.

2. Complexes with tridentate Schiff's bases :

\([HgLCl], \) and \([HgL'C1], \) where \(L = \) Schiff's bases derived by reacting benzoin with 2-amino-6-methyl benzothiazole and 2-amino-6-chloro benzothiazole, \(L' = \) Schiff's bases derived by reacting benzil with 2-amino-6-methyl benzothiazole and 2-amino-6-chloro benzothiazole.

3. Complexes with bidentate ligands :

\([HgL_2] \) and \([HgL'X_2], \) where \(L = \) ortho-tolidine, \(L' = \) hydrazine dithiourea and \(X = Cl^-, Br^-, SCN^- \) and \(NO_3^- \).

4. Complexes with substituted amino benzothiazoles :

\([HgL_2X_2], \) where \(L = 2\)-amino-6-chloro benzothiazole and 2-amino-6-methyl benzothiazole, \(X = Cl^-, Br^-, I^-, SCN^- , NO_3^- \) and \(OAc^- \).

In total, 22 complexes of Mercury(II) are synthesised.

All the Mercury(II) complexes listed above are suggested to have tetrahedral symmetry. The fungitoxicity of some of these Mercury(II) complexes exhibited encouraging results against the fungal organisms Pyricularia oryzae, Cav. and Helminthosporium oryzae, Brde Haan. Coordination and behaviour of the groups like thiocyanate,
nitrates and acetates have been given in detail from the occurrence of characteristic infrared bands.

Apart from the evidence obtained for bonding of the ligand donor atoms to the metal, the infrared spectra gave definite evidence for the presence of the following:

(i) $\gamma(M-O)$, $\gamma(M-N)$, $\gamma(M-S)$ and $\gamma(M-Cl)$
(ii) Nature of bonding of the thiocyanate group
(iii) Presence of coordinated water molecule and
(iv) $\gamma(C=C)$, $\gamma(C=O)$, $\gamma(C-O)$, $\gamma(C=N)$, $\gamma(C=S)$, $\gamma(N-H)$, $\gamma(C-S)$ and $\gamma(C=\equiv N)$ etc.

Electronic spectra and magnetic moment data have been extensively used in case of Co(II), Ni(II) and Cu(II) complexes to provide information regarding probable stereochemistry of the complexes.

Most of the work in the present investigation has either been published or accepted for publication in various journals. A list of these communications are mentioned below. Reprints of the published papers are duly appended at the end.

1. Complexes of Co(II), Ni(II), Cu(II), Hg(II) and Cd(II) with tetradeutate Schiff's base ligand - Acta Chimica, (Hungary) - accepted for publication.


6. Complexes of Co(II), Ni(II), Hg(II) and Cd(II) with tetratdentate Schiff's base - J. Inorg. Nucl. Chem. - accepted for publication.


10. Complexes of Co(II), Ni(II) and Cu(II) with tridentate Schiff's bases - Acta Chimica (Hungary) - Communicated.


