CHAPTER IV
RESULTS AND DISCUSSION

4.1 SOLUTION EQUILIBRIA

As outlined under the scope of the present investigation, the first part of this Chapter mainly describes the reliable stability constants for the M(II)-thiophenal (A)-amino acids (B) Schiff base complex systems [where M(II) = Co(II)/Ni(II)/Cu(II)/Zn(II) and B = val/phe/trp/thr/gln/glu/asp/his] at 25 ± 0.1 °C and \( \mu = 0.1 \text{ mol dm}^{-3} \) KNO\(_3\). For M(II)-thiophenal (A) systems, the auxiliary data of the stability constants have been determined under the present experimental conditions.

4.1.1 Binary metal complexes of thiophenal (A)

\[
\begin{array}{c}
\text{Thiophenal (A)} \\
\begin{array}{c}
\text{H} \\
\text{S} \\
\text{O} \\
\text{C}
\end{array}
\end{array}
\]

The pH titration data of Co(II), Ni(II), Cu(II) and Zn(II) with thiophenal binary systems are given in Tables 4.1.1a-d and the stability constant values are reported in Table 4.1.1e. In the M(II)-thiophenal binary systems, all the four metal ions form MA and MA\(_2\) types of complexes in addition to HA species. The stability constant (Table 4.1.1e) data evaluated in M(II)-thiophenal systems suggest that the ligand thiophenal coordinates with the metal ion in a bidentate manner through thiophene ring sulphur and carbonyl oxygen atoms. It is evidenced that the observed \( \log \beta_{MA} \) values of 1.75, 1.94, 2.51 and 1.65 respectively for Co(II), Ni(II), Cu(II) and Zn(II)-thiophenal systems are comparable with those in the corresponding complexes of furfural, where the ligand is bidentate and binds through ring oxygen and carbonyl
oxygen atoms [117]. Sari et al [142] have potentiometrically studied Co(II), Ni(II) and Cu(II) complexes involving thiophene-2-carbaldehyde and DL-alanine, DL-valine and DL-phenylalanine and found that the ligands bind through ring sulphur, azomethine nitrogen and carboxylato oxygen atoms. In addition, numbers of solid complexes of thiophene analogues ligands have been reported that the ring sulphur atom also takes part in coordination [143-148]. Because softer sulphur atom can easily coordinate with borderline Co(II), Ni(II), Cu(II) and Zn(II) metal ions. The \( \log K_{MA}^{MA} \) values in Table 4.1.1e clearly indicate that both the ligands in MA\(_2\) species are bidentate.

**Species distribution**

The species distribution diagrams (Figs. 4.1.1.1a-h) for M(II)-thiophenal (A) binary systems indicate that the complex formation is favoured over HA species. MA species predominates in the pH range 4-7. In M(II)-thiophenal systems, formation of MA species is favoured comparatively at lower pH in 1:2 than 1:1 solution. MA\(_2\) species predominates above pH 6 in both 1:1 and 1:2 solution.

**4.1.2 Binary metal complexes of amino acids (B)**

Binary complexes of metal ions with amino acids, L-valine (val), L-phenylalanine (phe), DL-tryptophan (trp), L-threonine (thr), L-glutamine (gln), L-glutamic acid (glu), L-aspartic acid (asp) and L-histidine (his) have been studied by many researchers [74-79]. For M(II)-amino acids (B) systems, the binary stability constant values for chosen amino acids at the present experimental conditions values were taken from the literature [149, 150]. The stability constant values are listed in Tables 4.1.2a-c. Generally, it has been observed that MB species of the M(II)-amino acid complexes begins to form in the lower pH range of 5.5. At higher pH values the concentration of the MB\(_2\) species are high.
**Binary metal complexes of amino acid with non-polar side chain (val and phe)**

The binary stability constant values clearly indicate that val and phe binds the metal ion in a glycine like mode both in its 1:1 and 1:2 complexes. Thus, they are potentially bidentate. It forms HB, H$_2$B, MB, MB$_2$ and MB$_3$ types of species with Co(II) and Ni(II) ions. Cu(II) and Zn(II) form only MB and MB$_2$ types of complexes in addition to HB and H$_2$B.

**Binary metal complexes of amino acids with polar uncharged side chain (trp, thr and gln)**

tryptophan (trp)

threonine (thr)

glutamine (gln)
The ligands, trp, thr and gln act as a potentially bidentate. They form HB, $H_2B$, MB and $MB_2$ types of species with all the four metal ions. The ligands, thr and gln contain a hydroxyl oxygen and amide group nitrogen or oxygen respectively as possible third donor atoms. However, the stability constant values (Tables 4.1.2 a-c) reveal that the above ligands bind the metal ion in a bidentate manner. This demonstrates that the –OH group of thr and –CONH$_2$ group of gln do not take part in coordination.

**Binary metal complexes of amino acids with acidic side chain (glu and asp)**

![Glutamic Acid (glu) and Aspartic Acid (asp)](image)

The ligands glu and asp are potentially tridentate and they bind through the metal ion viz amino and two carboxylato groups. The stability constant values (Tables 4.1.2a-c) are higher than bidentate amino acids indicating the possibility of their tridentate binding.

**Binary metal complexes of amino acid with basic side chain (his)**

![Histidine (his)](image)
The M(II)-his systems show higher log K values for the MB and MB\textsubscript{2} complexes compared to those in the corresponding M(II)-gly/ala/val/phe systems [142]. This demonstrates the tridentate coordination of his in its MB and MB\textsubscript{2} complexes. The ligand his binds the metal ion through the imidazole and amino nitrogen atoms and carboxylato oxygen atom.

4.1.3 Ternary metal complexes of thiophenal (A) and amino acids (B)

*Schiff base* (AB) metal complexes involving thiophenal (A) and amino acids (B)

This section deals with the Schiff base metal complexes of eight \(\alpha\)-amino acids \textit{viz.} val, phe, trp, thr, gln, glu, asp and his with thiophenal. The metal ions chosen are Co(II), Ni(II), Cu(II) and Zn(II). The formation constant of the protonated (HAB) and deprotonated (AB) Schiff bases are given in the Table 4.1.3.

4.1.3.1 M(II)-thiophenal-val systems

The stability constant values for the Schiff base complexes of the M(II)-thiophenal-val systems are given in Table 4.1.3.1.

4.1.3.1.1 Co(II)-thiophenal-val system

This system was investigated in the pH range of 6.2 to 8.3. The experimental and the computed pH titre values are given in Table 4.1.3.1.1. Three ternary complex species \textit{viz.} CoAB, CoAB\textsubscript{2} and CoA\textsubscript{2}B\textsubscript{2} in addition to the binary species HA, CoA, CoA\textsubscript{2}, HB, H\textsubscript{2}B, CoB, CoB\textsubscript{2} and CoB\textsubscript{3} have been detected. The pH values of the experimental and computed for the system coincide indicating the achievement of the best-fit.

The stepwise formation of various species is shown in Scheme 1. The upward arrows are for the acquisition of val to the metal ion and downward arrows are for the addition of thiophenal. The numbers marked over the arrows are the stepwise
formation constant for the particular step. This scheme shows the preferential formation of ternary species over binary analogues.

![Scheme 1]

**Scheme 1**

**Stability and structure of CoAB species**

The complex CoAB may be a mixed ligand complex rather than a Schiff base species. If it is so, the overall formation constant of the CoAB mixed ligand complex using the eqn. \( \log \beta_{\text{MA}} = \frac{1}{2} ( \log \beta_{\text{MA}_2} + \log \beta_{\text{MB}_2} ) + 0.3010 \) would be 6.02 log units. But the experimental \( \log \beta_{\text{CoAB}} \) value is 8.71 log units. This large enhancement in the stability value confirms that the CoAB species is a Schiff base complex and not a mixed ligand complex. The enhanced stability of the Schiff base complex over the mixed ligand complex is due to the enhancement of the entropy due to the fusion of two independent ring systems. The higher \( \log \beta_{\text{CoAB}} \) value indicates that Schiff base ligand AB is tridentate in CoAB Schiff base complex binding through imino nitrogen, thiophene ring sulphur and carboxylato oxygen resulting in a stable two five membered chelate rings.

The following equilibrium reactions explain the preferential formation of Schiff base complex over binary species.
From the formation constants, it is obvious that val binds more strongly than thiophenal. The log K value for the addition of thiophenal to CoB is more than that for CoB from CoB. The addition of val to CoA results in the log K value of 6.96. This is 5.26 log units greater than the log K value for the formation of CoA2 from CoA. This confirms the preferential formation of Schiff base species over binary.

**Stability and structure of CoAB₂ species**

The experimental log β_{CoAB₂} value of 13.04 is higher than the expected value of 9.01 obtained using the eqn. log β^*_{MB₂} = ½ log β_{MA₂} + log β_{MB₂} + 0.3010 which indicates CoAB₂ species to be a mixed ligand Schiff base complex of stoichiometry, Co(AB)B. If CoAB₂ is a mixed ligand species of the type CoA(B)₂, the value would be comparatively low. Following equilibrium reactions are necessary to consider the formation of this complex.

\[
\text{Co(val)} + \text{val} \rightleftharpoons \text{Co(val)}_2 \quad \log K = 3.54
\]

\[
\text{Co(val)} + \text{thiophenal} \rightleftharpoons \text{Co(thiophenal-val)} \quad \log K = 4.27
\]

\[
\text{Co(thiophenal)} + \text{thiophenal} \rightleftharpoons \text{Co(thiophenal)}_2 \quad \log K = 1.70
\]

\[
\text{Co(thiophenal)} + \text{val} \rightleftharpoons \text{Co(thiophenal-val)} \quad \log K = 6.96
\]

The above data show that, the formation of CoAB₂ from MB₂ and A is preferred compared to CoB₃ from the binary complex formation. This is due to the formation of Schiff base ligand. In CoAB₂, the Schiff base ligand can bind in a tridentate manner and val (B) can bind bidentatedly.
Stability and structure of CoA₂B₂ species

The most stable species in this system is CoA₂B₂. The \( \log \beta_{\text{CoA}_2\text{B}_2} \) value is 14.85. CoA₂B₂ species can be considered either as a mixed ligand Co(A)₂(B)₂ complex or Co(AB)₂ Schiff base complex. If it is a mixed ligand complex the calculated stability constant value by the eqn.

\[
\log 
\beta^{*}_{\text{MA}_2\text{B}_2} = \log 
\beta_{\text{MA}_2} + \log 
\beta_{\text{MB}_2} + 0.3010
\]

would be 11.73, which is lesser than the experimental value of 14.85. Therefore, CoA₂B₂ can be represented as a Schiff base complex of the type Co(AB)₂, where the Schiff base (AB) is tridentate. The extra stability of the Schiff base complex is due to the formation of four five membered chelate rings and enhancement in the entropy. In the Schiff base complex systems of Co(II), Ni(II) and Zn(II) with N-salicylidene-L-valinate also, M(AB)₂ complex species has been reported [85].

Species distribution

The concentration of various species formed in the complex formation process were directly obtained as computer outputs and the species distribution curves of the systems were constructed by plotting percentage concentration of various possible species formed versus pH of solution during complexation and the diagrams are given in Figs. 4.1.3.1.1a & b. The concentration of Schiff base complex species CoAB is found to be maximum (~78%) at around the pH 7.0. CoA₂B₂ species predominates in 1:2 solution rather than in 1:1 solution. In 1:2 solution, CoAB₂ species is formed above pH 7.5 and the formation of the species is favoured with increase of pH.

Electronic spectra

Electronic spectra of the Schiff base species CoAB and Co(AB)₂ were recorded at pH 7.1 and pH 8.5 respectively in the 1:1 and 1:2 solution Figs. 4.1.3.1.1c
The CoAB species has an absorption maximum at 620 nm. This absorption can be attributed to the transition $^4A_2 \text{(F)} \rightarrow ^4T_1 \text{(P)}$ due to tetrahedral geometry [135]. This tetrahedral geometry is possible by the tridentate binding of (AB) and the completion of the coordination sphere by a solvent molecule. The Co(AB)$_2$ species system has two bands at 560 and 692 nm respectively which are due to the octahedral transitions $^4T_{1g} \text{(F)} \rightarrow ^4T_{1g} \text{(P)}$ and $^4T_{1g} \text{(F)} \rightarrow ^4A_2 \text{(F)}$ for Co(II) [135]. This is possible by the tridentate binding of both (AB) ligands.

### 4.1.3.1.2. Ni(II)-thiophenal-val system

Ni(II)-thiophenal-val system has been investigated in the pH range of 6.8 to 9.0. The experimental and computed pH titration data are given in Table 4.1.3.1.2. NiAB, NiAB$_2$ and NiA$_2$B$_2$ ternary species were detected in addition to HA, NiA, NiA$_2$, HB, H$_2$B, NiB, NiB$_2$ and NiB$_3$ binary species. The stability constants are reported in Table 4.1.3.1. The preferential formation of ternary species over binary is indicated by Scheme 2.

**Scheme 2**

*Stability and structure of NiAB species*

The important equilibrium reactions to be considered are given below.
Ni(val) + val $\leftrightarrow$ Ni(val)$_2$ \( \log K = 3.86 \)

Ni(val) + thiophenal $\leftrightarrow$ Ni(thiophenal-val) \( \log K = 5.09 \)

Ni(thiophenal) + thiophenal $\leftrightarrow$ Ni(thiophenal)$_2$ \( \log K = 1.89 \)

Ni(thiophenal) + val $\leftrightarrow$ Ni(thiophenal-val) \( \log K = 8.41 \)

The NiAB species may be a mixed ligand complex of thiophenal and val. If it is so, the calculated stability constant value should be 6.78 log units. But the experimental value is 10.35. Therefore, NiAB can be considered as a Schiff base complex of the type Ni(AB), where (AB) is the Schiff base, thiophenal-val. The extra stability of the Schiff base complex is due to the formation of two fused five membered rings. From the stability constant values, it becomes clear that a tridentate ligand is favoured over two bidentate ligand in the coordination sphere. Similar to the Co(II) system, the Schiff base ligand binds the metal ion through thiophene ring sulphur, imino nitrogen and carboxylato oxygen atoms.

**Stability and structure of NiAB$_2$ species**

Equilibrium reactions necessary for the NiAB$_2$ species are given below.

Ni(val)$_2$ + val $\leftrightarrow$ Ni(val)$_3$ \( \log K = 3.23 \)

Ni(val)$_2$ + thiophenal $\leftrightarrow$ Ni(thiophenal-val)val \( \log K = 5.51 \)

Ni(thiophenal-val) + val $\leftrightarrow$ Ni(thiophenal-val)val \( \log K = 4.28 \)

The calculated $\log \beta$ value for the formation of NiAB$_2$ is 11.34 log units. But the experimental value is 14.63. Thus, NiAB$_2$ can be considered as the mixed ligand complex of Schiff base ligand (AB) and B. From the equilibrium reactions, it is clear that addition of thiophenal to Ni(val)$_2$ is preferred over the addition of val with Ni(thiophenal-val). This is due to the more probable interaction of thiophenal with two molecules of val present in the coordination sphere that leading to the formation of Schiff base.
The log K value for the addition of val to Ni(AB) is 4.28 log units greater than that for the formation of NiB$_2$ from NiB. This enhancement is due to the formation of an additional chelate ring in the system. Thus, it can be concluded that one of the two val ligands form Schiff base ligand (AB) and the other val binds independently giving the stoichiometry of the NiAB$_2$ species to be Ni(AB)B.

**Stability and structure of NiA$_2$B$_2$ species**

The most stable species in this system is NiA$_2$B$_2$. The log $\beta_{\text{NiA}_2\text{B}_2}$ value is 16.91. NiA$_2$B$_2$ species can be considered as a mixed ligand Ni(A)$_2$(B)$_2$ complex or Ni(AB)$_2$ Schiff base complex. If it is a mixed ligand complex the calculated stability constant value would be 13.25, which is lesser than the experimental value of 16.91. Therefore, NiA$_2$B$_2$ can be represented as a the Schiff base complex of the type Ni(AB)$_2$, where the Schiff base (AB) is tridentate. The extra stability of the Schiff base complex is due to the formation of four five member chelate rings and enhancement in the entropy.

**Species distribution**

The species distribution diagrams are given in Figs. 4.1.3.1.2a & b. In the 1:1 solution, NiAB species predominates in the pH range ~7.5. NiB$_2$ and NiB$_3$ are present in the higher pH. In 1:2 solution, NiA$_2$B$_2$ species predominates compared to that of Schiff base species NiAB$_2$ and NiAB at pH 8.0, where ~80 % of the total metal ion has been found to be present.

**Electronic spectra**

The 1:1 and 1:2 Ni (II) systems were recorded at pH 7.5 and 8.4 respectively for recording the spectra of NiAB and Ni(AB)$_2$ species [Figs. 4.1.3.1.2c & d]. NiAB species has absorption at 628 nm for the transition $^3$T$_1$ (F) $\rightarrow$ $^3$T$_1$ (P) indicating its tetrahedral geometry [135]. As indicated above, (AB) binds the metal ion in tridentate
mode and the fourth position can be completed by solvent water molecule. In 1:2 solution for Ni(AB)$_2$ species, three absorptions were observed at 390 nm, 705 nm and ~1100 nm respectively for the transitions $^{3}A_{2g}$ (F) $\rightarrow$ $^{3}T_{1g}$ (P), $^{3}A_{2g}$ (F) $\rightarrow$ $^{3}T_{1g}$ (F) and $^{3}A_{2g}$ (F) $\rightarrow$ $^{3}T_{2g}$ (F). These transitions are for the octahedral geometry of Ni(II) [135].

This is possible by the tridentate binding of both (AB) ligands.

4.1.3.1.3 Cu(II)-thiophenal-val system

The pH titration data are given in Table 4.1.3.1.3. The ternary species CuAB and CuAB$_2$ were detected in addition to HA, CuA, CuA$_2$, HB, H$_2$B, CuB and CuB$_2$ binary species. Schematic representation of the preferential formation of ternary species over binary is given in Scheme 3.

![Scheme 3](image)

**Stability and structure of CuAB species**

The equilibrium reactions for the formation of CuAB complex are given below.

\[
\begin{align*}
\text{Cu(val)} + \text{val} & \rightleftharpoons \text{Cu(val)$_2$} & \log K = 6.29 \\
\text{Cu(val)} + \text{thiophenal} & \rightleftharpoons \text{Cu(thiophenal-val)} & \log K = 7.10 \\
\text{Cu(thiophenal)} + \text{thiophenal} & \rightleftharpoons \text{Cu(thiophenal)$_2$} & \log K = 2.31 \\
\text{Cu(thiophenal)} + \text{val} & \rightleftharpoons \text{Cu(thiophenal-val)} & \log K = 12.68
\end{align*}
\]

The observed log $\beta$ value for CuAB is 15.19, which is higher than the calculated stability constant value of 9.90 for simple mixed ligand complex CuAB,
indicating the species to be Schiff base complex. As in the case of the corresponding Co(II) and Ni(II) complexes, the Schiff base would be tridentate in the Cu(AB) species also.

**Stability and structure of CuAB$_2$ species**

Equilibrium reactions necessary for the CuAB$_2$ species are given below.

\[
\begin{align*}
\text{Cu(val)$_2$} & \quad + \quad \text{thiophenal} \quad \rightarrow \quad \text{Cu(thiophenal-val)}\text{val} \quad \log K = 4.07 \\
\text{Cu(thiophenal-val)} & \quad + \quad \text{val} \quad \rightarrow \quad \text{Cu(thiophenal-val)}\text{val} \quad \log K = 3.26
\end{align*}
\]

The calculated log $\beta$ value for the formation of CuAB$_2$ is 17.09 log units. But the experimental value is 18.45. Thus, CuAB$_2$ can be considered as the mixed ligand complex of Schiff base ligand (AB) and B. From the equilibrium reactions, it is clear that addition of thiophenal to Cu(val)$_2$ is preferred over the addition of val with Cu(thiophenal-val). This is due to the more probable interaction of thiophenal with two molecules of val present in the coordination sphere that leading to the formation of Schiff base.

The log K value for the addition of B to Cu(AB) is 3.03 log units greater than that for the formation of CuB$_2$ from CuB. This enhancement is due to the formation of an additional chelate ring in the system. Thus, it can be concluded that one of the two val ligands forms Schiff base ligand (AB) and the other val binds independently giving the stoichiometry of the CuAB$_2$ species to be Cu(AB)B.

**Species distribution**

The species distribution diagrams are presented in Figs. 4.1.3.1.3a & b. In 1:1 solution, CuAB is the predominant species whereas CuAB$_2$ is the predominant species in 1:2 solution. The concentration of CuAB species has been found to be $\sim$87 % at pH 7.4.
**Electronic spectra**

The Electronic spectrum of CuAB complex shows a broad band at ~642 nm (Fig. 4.1.3.1.3c). This corresponds to $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ transitions for square planar Cu(II) complex [135].

### 4.1.3.1.4 Zn(II)-thiophenal-val System

The experimental and computed pH titration values are given in Table 4.1.3.1.4. This system was studied in the pH range 6.4 - 7.9. In this system ZnAB, ZnAB$_2$ and ZnA$_2$B$_2$ ternary complexes in addition to HA, ZnA, ZnA$_2$, HB, H$_2$B, ZnB and ZnB$_2$ have been found to be present. Schematic representations of preferential formation of ternary species over binary are given in Scheme 4.

![Scheme 4](image)

**Stability and structure of ZnAB species**

The following equilibrium reactions explain the preferred formation of Schiff base complex ZnAB

- $\text{Zn(val)} + \text{val} \rightleftharpoons \text{Zn(val)}_2$ \hspace{1cm} $\log K = 4.00$
- $\text{Zn(val)} + \text{thiophenal} \rightleftharpoons \text{Zn(thiophenal-val)}$ \hspace{1cm} $\log K = 5.00$
- $\text{Zn(thiophenal)} + \text{thiophenal} \rightleftharpoons \text{Zn(thiophenal)}_2$ \hspace{1cm} $\log K = 1.68$
- $\text{Zn(thiophenal)} + \text{val} \rightleftharpoons \text{Zn(thiophenal-val)}$ \hspace{1cm} $\log K = 7.10$
The calculated stability constant value for the ZnAB mixed ligand complex is 6.34 log units, which is less than the experimental value of 8.75. This indicates ZnAB to be a Schiff base complex species rather than a simple mixed ligand complex. The Schiff base (AB) is a tridentate ligand and can bind the metal ion through thiophene ring sulphur, imino nitrogen and carboxylato oxygen atoms.

**Stability and structure of ZnAB₂ species**

The formation of ZnAB₂ complex can be explained by the following equilibrium reactions.

\[ \text{Zn(val)}_2 + \text{thiophenal} \rightleftharpoons \text{Zn(thiophenal-val)} \quad \log K = 4.34 \]

\[ \text{Zn(thiophenal-val)} + \text{val} \rightleftharpoons \text{Zn(thiophenal-val)val} \quad \log K = 5.34 \]

ZnAB₂ complex has a high stability constant value of 13.09 log units. This indicates that ZnAB₂ species can also be considered as a mixed ligand complex, Zn(AB)B like the MAB₂ species in Co(II) and Ni(II) systems discussed earlier. In this species, the Schiff base ligand coordinates in tridentate mode and val binds in a bidentate manner.

**Stability and structure of ZnA₂B₂ species**

The stability constant value for ZnA₂B₂ is 14.95 log units. This higher value can be accounted by considering ZnA₂B₂ species to be the bis (Schiff base) complex Zn(AB)₂ with octahedral structure, similar to the MA₂B₂ species in the corresponding Co(II) and Ni(II) systems described earlier.

**Species distribution**

The species distribution diagrams are given in Figs. 4.1.3.1.4a & b. ZnAB is the dominant species in the pH range of 6.9 - 8.0. ZnAB₂ and ZnA₂B₂ species are formed in the higher pH range and their concentration increase with increase of pH. A considerable amount of total metal ion has been found to be present in the form of
ZnAB species in 1:1 solution in a wide range of pH. A maximum of 65% of the total metal ion has been found to be present in the form of ZnAB species in 1:1 solution.

4.1.3.1.5 Stability enhancement in the Co(II), Ni(II), Cu(II) and Zn(II) thiophenal-val systems

Hopgood et al [65] formulated an equation to calculate the stabilization factor, $\Delta \log K_{MAB}$.

$$\Delta \log K_{MAB} = \log \beta_{MAB} - (\log \beta_{MA} + \log \beta_{MB})$$

The calculated values of $\Delta \log K_{MAB}$ for Co(II), Ni(II), Cu(II) and Zn(II) systems are 2.52, 3.15, 4.59 and 2.35 respectively. This shows that the enhancement in the stability of the Schiff base complexes of thiophenal-val systems follow the Irving - Williams order of stability [151].

$$\text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}$$
4.1.3.2 M(II)-thiophenal-phe systems

The stability constant for the Schiff base complexes of the M(II)-thiophenal-phe systems are given in Table 4.1.3.2.

4.1.3.2.1 Co(II)-thiophenal-phe system

This system was investigated in the pH range of 6.3 to 8.5. The experimental and the computed pH titre values are given in Table 4.1.3.2.1. Three ternary complex species viz. CoAB, CoAB₂ and CoA₂B₂ in addition to the binary species HA, CoA, CoA₂, HB, H₂B, CoB, CoB₂ and CoB₃ have been identified. The experimental pH values coincide with those of computed values indicating the achievement of the best-fit.

The stepwise formation of various species is shown in Scheme 5. This scheme proves the preferential formation of ternary species over binary analogues.

Scheme 5

**Stability and structure of CoAB species**

The complex CoAB may either be a mixed ligand complex or a Schiff base species. If former is the case, then the overall formation constant of the CoAB mixed ligand complex would be 6.03 log units. But the larger experimental log β_{CoAB} value of 8.52 log units confirms the CoAB species as a Schiff base complex and not a mixed ligand complex. The enhanced stability of the Schiff base complex over the
mixed ligand complex is due to the enhancement of the entropy due to the fusion of two independent ring systems. The high $\log \beta_{\text{CoAB}}$ value indicates the Schiff base ligand AB is tridentate.

The following equilibrium reactions explain the preferential formation of Schiff base complex over binary species.

\[
\begin{align*}
\text{Co(phe)} + \text{phe} & \rightleftharpoons \text{Co(phe)}_2 \\ 
\text{Co(phe)} + \text{thiophenal} & \rightleftharpoons \text{Co(thiophenal-phe)} \\ 
\text{Co(thiophenal)} + \text{thiophenal} & \rightleftharpoons \text{Co(thiophenal)}_2 \\ 
\text{Co(thiophenal)} + \text{phe} & \rightleftharpoons \text{Co(thiophenal-phe)} 
\end{align*}
\]

From the formation constants, it is clear that phe binds more strongly than thiophenal. The log K value for the addition of thiophenal to CoB is more than that for CoB$_2$ from CoB. The addition of phe to CoA results in the log K value of 6.77. This is 5.07 log units greater than the log K value for the formation of CoA$_2$ from CoA. This confirms the preferential formation of Schiff base species over binary.

**Stability and structure of CoAB$_2$ species**

The experimental $\log \beta_{\text{CoAB}}$ value of 12.95 is higher than that the calculated value of 10.04 expected if CoAB$_2$ is a mixed ligand species of the type CoA(B)$_2$. This indicates CoAB$_2$ species to be a mixed ligand Schiff base complex of stoichiometry, Co(AB)B. Following equilibrium reactions are necessary to consider the formation of this complex.

\[
\begin{align*}
\text{Co(phe)}_2 + \text{phe} & \rightleftharpoons \text{Co(phe)}_3 \\ 
\text{Co(phe)}_2 + \text{thiophenal} & \rightleftharpoons \text{Co(thiophenal-phe)phe} \\ 
\text{Co(thiophenal-phe)} + \text{phe} & \rightleftharpoons \text{Co(thiophenal-phe)phe} 
\end{align*}
\]

The above data show that, the formation of CoAB$_2$ is preferred compared to CoB$_3$ from the binary complex formation. This is due to the formation of Schiff base
ligand. In CoAB₂, the Schiff base ligand can bind in a tridentate manner and phe (B) can bind bidentatedly.

**Stability and structure of CoA₂B₂ species**

The most stable species in this system is CoA₂B₂. The \( \log \beta_{\text{CoA}_2 \text{B}_2} \) value is 15.07. CoA₂B₂ species can be considered as a mixed ligand Co(A)₂(B)₂ complex or Co(AB)₂ Schiff base complex. If it is a mixed ligand complex the calculated stability constant value would be 11.76, which is lesser than the experimental value of 15.07. Therefore, CoA₂B₂ can be represented as a the Schiff base complex of the type Co(AB)₂, where the Schiff base (AB) is tridentate. The extra stability of the Schiff base complex is due to the formation of four five membered chelate rings and enhancement in the entropy.

**Species distribution**

The species distribution diagrams are given in Figs. 4.1.3.2.1a & b. The concentration of Schiff base complex species CoAB is found to be maximum (~ 87 %) at pH 7.3. CoA₂B₂ species predominates (~ 78 %) in 1:2 solution rather than in 1:1 solution.

**Electronic spectra**

Electronic spectra of the Schiff base species CoAB and Co(AB)₂ were recorded at pH 7.2 and pH 7.9 respectively in the 1:1 and 1:2 solution (Figs. 4.1.3.2.1c & d). The CoAB species has an absorption maximum at 642 nm. This absorption can be attributed for the transition \( ^4 \text{A}_2 (F) \rightarrow ^4 \text{T}_1 (P) \) due to tetrahedral geometry [135]. This tetrahedral geometry is possible by the tridentate binding of (AB) and the completion of the coordination sphere by a solvent water molecule. The Co(AB)₂ species system has two bands one at 628 nm and other at 756 nm, which are
due to the octahedral transitions $^{4}T_{1g} (F) \rightarrow ^{4}T_{1g} (P)$ and $^{4}T_{1g} (F) \rightarrow ^{4}A_{2} (F)$ for Co(II) [135]. This is possible by the tridentate binding of both (AB) ligands.

4.1.3.2.2. Ni(II)-thiophenal-phe system

Ni(II)-thiophenal-phe system has been investigated in the pH range of 6.5 to 8.9. The experimental and computed pH titration data are given in Table 4.1.3.2.2. NiAB, NiAB$_2$ and NiA$_3$B$_2$ ternary species have been identified in addition to HA, NiA, NiA$_2$, HB, H$_2$B, NiB, NiB$_2$ and NiB$_3$ binary species. The preferential formation of ternary species over binary is indicated by Scheme 6.

![Scheme 6](image)

**Stability and structure of NiAB species**

The important equilibrium reactions to be considered are given below.

\[
\begin{align*}
\text{Ni(phe)} + \text{phe} & \rightleftharpoons \text{Ni(phe)}_2 & \log K = 4.35 \\
\text{Ni(phe)} + \text{thiophenal} & \rightleftharpoons \text{Ni(thiophenal-phe)} & \log K = 4.86 \\
\text{Ni(thiophenal)} + \text{thiophenal} & \rightleftharpoons \text{Ni(thiophenal)}_2 & \log K = 1.89 \\
\text{Ni(thiophenal)} + \text{phe} & \rightleftharpoons \text{Ni(thiophenal-phe)} & \log K = 8.07
\end{align*}
\]

The calculated stability constant value is expected to be 6.97 log units for the NiAB species when existing as mixed ligand complex of thiophenal and phe. But the experimental value is 10.01. Hence, the species would be considered as a Schiff base
complex of the type Ni(AB), where (AB) is the Schiff base, thiophenal-phe. Formation of two fused five membered rings leads to the extra stability of the Schiff base complex. From the stability constant values, it becomes clear that a tridentate ligand is favoured over two bidentate ligands in the coordination sphere. The Schiff base binds in a same manner as in the Co(II) systems.

**Stability and structure of NiAB$_2$ species**

Equilibrium reactions necessary for the NiAB$_2$ species are given below.

\[
\begin{align*}
\text{Ni(phe)$_2$} & + \quad \text{phe} \quad \leftrightarrow \quad \text{Ni(phe)$_3$} & \log K = 2.55 \\
\text{Ni(phe)$_2$} & + \quad \text{thiophenal} \quad \leftrightarrow \quad \text{Ni(thiophenal-phe)phe} & \log K = 5.02 \\
\text{Ni(thiophenal-phe)} & + \quad \text{phe} \quad \leftrightarrow \quad \text{Ni(thiophenal-phe)phe} & \log K = 4.51
\end{align*}
\]

The larger experimental log β value of 14.52 over the calculated value of 11.72 log units for the formation of Ni(A)(B)$_2$ demonstrates NiAB$_2$ as the mixed ligand complex of Schiff base ligand (AB) and B. From the equilibrium reactions, it is apparent that addition of thiophenal to Ni(phe)$_2$ is preferred over the addition of phe with Ni(thiophenal-phe). This is due to the more probable interaction of thiophenal with two molecules of phe present in the coordination sphere leading to the formation of Schiff base.

The log K value for the addition of phe to Ni(AB) is 4.51 log units greater than that for the formation of NiB$_2$ from NiB. This enhancement is due to the formation of an additional chelate ring in the system and leads to the conclusion that one of the two phe ligands forms Schiff base ligand (AB) and the other binds independently giving the stoichiometry of the NiAB$_2$ species to be Ni(AB)B.
**Stability and structure of NiA₂B₂ species**

Similar to CoA₂B₂ species of thiophenal-val system, NiA₂B₂ can also be represented as Ni(AB)₂ Schiff base complex species. Both (AB) bind in a tridentate manner giving a coordination number of six to the metal ion.

**Species distribution**

The species distribution diagrams are shown in Figs. 4.1.3.2.2a & b respectively. In the 1:1 solution, NiAB species predominates in the pH range 6.8 - 7.5. NiAB₂ and NiA₂B₂ species are present in low concentrations. In 1:2 solution, NiA₂B₂ species predominates among the Schiff base species, NiAB₂ and NiAB. Approximately 73 % of total metal ion has been found to be present in the form of NiA₂B₂ at pH 7.8 in 1:2 solution.

**Electronic spectra**

The 1:1 and 1:2 Ni(II) systems were recorded at pH 7.0 and 8.0 respectively for recording the spectra of NiAB and Ni(AB)₂ species [Figs. 4.1.3.2.2c & d]. NiAB species has absorption at 628 nm for the transition \(^3T_1 (F) \rightarrow ^3T_1 (P)\) indicating its tetrahedral geometry [135]. As indicated above, (AB) binds the metal ion in tridentate mode and the fourth position can be completed by solvent water molecule. In 1:2 solution for Ni(AB)₂ species, three absorptions were observed at 390 nm, 708 nm and ~1100 nm respectively for the transitions \(^3A_2g (F) \rightarrow ^3T_{1g} (P)\), \(^3A_2g (F) \rightarrow ^3T_{1g} (F)\) and \(^3A_2g (F) \rightarrow ^3T_{2g} (F)\). These transitions are for the octahedral geometry of Ni(II) [135]. This is possible by the tridentate binding of both (AB) ligands

**4.1.3.2.3 Cu(II)-thiophenal-phe system**

The pH titration data are given in Table 4.1.3.2.3. The ternary species CuAB and CuAB₂ were detected in addition to HA, CuA, CuA₂, HB, H₂B, CuB and CuB₂ binary species. The Schematic representation of the preferential formation of ternary species over binary is given in Scheme 7.
Stability and structure of CuAB species

The following are the equilibrium reactions for the formation of CuAB complex.

- \( \text{Cu(phe)} + \text{phe} \rightleftharpoons \text{Cu(phe)}_2 \quad \log K = 6.40 \)
- \( \text{Cu(phe)} + \text{thiophenal} \rightleftharpoons \text{Cu(thiophenal-phe)} \quad \log K = 7.01 \)
- \( \text{Cu(thiophenal)} + \text{thiophenal} \rightleftharpoons \text{Cu(thiophenal)}_2 \quad \log K = 2.31 \)
- \( \text{Cu(thiophenal)} + \text{phe} \rightleftharpoons \text{Cu(thiophenal-phe)} \quad \log K = 12.55 \)

The log \( \beta \) value for CuAB is 15.06, which is higher than the stability constant value of 9.94 for simple mixed ligand complex Cu(A)(B), indicating the species to be Schiff base complex. As in the case of the corresponding Co(II) and Ni(II) complexes, the Schiff base would be tridentate in the Cu(AB) species.

Stability and structure of CuAB\(_2\) species

The formation of CuAB\(_2\) complex can be explained by the following equilibrium reactions.

- \( \text{Cu(phe)}_2 + \text{thiophenal} \rightleftharpoons \text{Cu(thiophenal-phe)phe} \quad \log K = 4.00 \)
- \( \text{Cu(thiophenal-phe)} + \text{phe} \rightleftharpoons \text{Cu(thiophenal-phe)phe} \quad \log K = 3.26 \)

CuAB\(_2\) complex has a high stability constant value of 18.32 log units. This indicates that CuAB\(_2\) species can also be considered as a mixed ligand complex,
Cu(AB)B like the MAB$_2$ species in Co(II) and Ni(II) systems discussed earlier. In this species, the Schiff base ligand coordinates in tridentate mode and phe binds in a bidentate manner. The sixth position is occupied by a solvent molecule and form octahedral geometry.

**Species distribution**

The species distribution diagrams are presented in Figs. 4.1.3.2.3a & b. In both 1:1 and 1:2 solutions, CuAB is the predominant species in the pH range of 6.8 to 8.5 in which the concentration of the species is almost same. CuAB$_2$ species is formed comparatively at a higher pH.

**Electronic spectra**

The Electronic spectrum of CuAB complex shows a broad band at ~ 630 nm (Fig. 4.1.3.2.3c). This corresponds to $^2$B$_{1g}$ → $^2$A$_{1g}$ transitions for square planar Cu(II) complex [27].

### 4.1.3.2.4 Zn(II)-thiophenal-phe System

The experimental and computed pH titration values are given in Table 4.1.3.2.4. The system was studied in the pH range 6.2 - 8.4. In this system, ZnAB, ZnAB$_2$ and ZnA$_2$B$_2$ ternary complexes have been found to be present in addition to HA, ZnA, ZnA$_2$, HB, H$_2$B, ZnB and ZnB$_2$. Schematic representations of preferential formation of ternary species over binary are given in Scheme 8.
Stability and structure of ZnAB species

The following equilibrium reactions explain the preferred formation of Schiff base complex ZnAB.

\[
\begin{align*}
Zn(phe) + phe & \rightleftharpoons Zn(phe)\_2 \quad \log K = 3.93 \\
Zn(phe) + thiophenal & \rightleftharpoons Zn(thiophenal-phe) \quad \log K = 4.47 \\
Zn(thiophenal) + thiophenal & \rightleftharpoons Zn(thiophenal)\_2 \quad \log K = 1.68 \\
Zn(thiophenal) + phe & \rightleftharpoons Zn(thiophenal-phe) \quad \log K = 7.17
\end{align*}
\]

The calculated stability constant value for the ZnAB mixed ligand complex is 6.11 log units, which is less than the experimental value of 8.82. This indicates ZnAB to be a Schiff base complex species rather than a simple mixed ligand complex. The Schiff base (AB) is a tridentate ligand and can bind the metal ion through thiophene ring sulphur, imino nitrogen and carboxylato oxygen atoms.

Stability and structure of ZnAB\(_2\) species

The formation of ZnAB\(_2\) complex can be explained by the following equilibrium reactions.

\[
\begin{align*}
Zn(phe)\_2 + thiophenal & \rightleftharpoons Zn(thiophenal-phe)phe \quad \log K = 4.82 \\
Zn(thiophenal-phe) + phe & \rightleftharpoons Zn(thiophenal-phe)phe \quad \log K = 4.28
\end{align*}
\]

ZnAB\(_2\) complex has a high stability constant value of 13.10 log units which indicates that ZnAB\(_2\) species can also be considered as a mixed ligand complex, Zn(AB)B like the MAB\(_2\) species and in Co(II), Ni(II) and Cu(II) systems discussed earlier. Same mode of binding for both Schiff base and phe would be possible.

Stability and structure of ZnA\(_2\)B\(_2\) species

The stability constant value for ZnA\(_2\)B\(_2\) is 15.01 log units. This higher value can be accounted by considering ZnA\(_2\)B\(_2\) to be a species containing two Schiff base
molecules coordinated to the metal ion with octahedral structure, similar to the MA₂B₂ species in the corresponding Co(II) and Ni(II) systems described earlier.

**Species distribution**

The species distribution diagrams are given in Figs. 4.1.3.2.4a & b. A considerable amount of total metal ion has been found to be present in the form of ZnAB in the pH range of 6.8 - 7.2. ZnA₂B₂ and ZnAB₂ species are formed in the higher pH range and their concentration increases with increase of pH. There is an increase in concentration of the species ZnA₂B₂ in 1:2 solution in comparison to 1:1 solution at pH 8.

### 4.1.3.2.5 Stability enhancement in the Co(II), Ni(II), Cu(II) and Zn(II) thiophenal-phe systems

The calculated $\Delta \log K_{MAB}$ values for Co(II), Ni(II), Cu(II) and Zn(II) systems are 2.32, 2.92, 4.50 and 2.82 respectively. The stability constant values of all the complex species in the systems follow Irving-Williams order of series with respect to metal ions.

$$\text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}$$
4.1.3.3 M(II)-thiophenal-trp systems

The stability constant values for the Schiff base complexes of the M(II)-thiophenal-trp systems are given in Table 4.1.3.3.

4.1.3.3.1 Co(II)-thiophenal-trp system

The pH titration data are given in Table 4.1.3.3.1. Three ternary complex species CoAB, CoAB$_2$ and CoA$_2$B$_2$ were identified in addition to the binary species HA, CoA, CoA$_2$, HB, CoB, CoB$_2$ and CoB$_3$. A schematic representation of preferential formation of ternary species over binary is given in Scheme 9.

![Scheme 9]

Stability and structure of CoAB, CoAB$_2$ and CoA$_2$B$_2$ species

The calculated stability constant value for the CoAB mixed ligand complex is 6.04 log units, which is less than the experimental value of 8.82. This shows that CoAB in the thiophenal-trp is a Schiff base complex species. Further, the log $\beta_{CoAB}$ value (Table 4.1.3.3) of Co(II)-thiophenal-trp system is comparable to that in the Co(II)-thiophenal-val system (Table 4.1.3.1). This indicates that thiophenal-trp and thiophenal-val systems have similar structures in CoAB i.e. the Schiff base (AB) in thiophenal-trp system can bind Co(II) in a tridentate manner through thiophene ring sulphur, imino nitrogen and carboxylato oxygen atoms.
The $\log K_{\text{CoAB}}^\text{CoAB}$ value of Co(II)-thiophenal-trp system is 0.63 units greater than $\log K_{\text{CoB}}^\text{CoB}_2$. This enhancement is not large enough to consider the tridentate binding of the trp unit through indole nitrogen as the additional coordinating site. But this may be ascribed due to the stacking interaction between aromatic moieties present in the ligands [152-154]. In Co(AB)B complex of Co(II)-thiophenal-trp system, the Schiff base (AB) is tridentate and the trp B binds the metal ion through amino nitrogen and carboxylato oxygen atoms in bidentate manner. Besides this difference, the Co(II)-thiophenal-trp system and the corresponding thiophenal-val system behave in the same manner. Hence the indole moiety of trp does not seem to exert any steric effect on the mode of binding and structure of the Schiff base complexes.

The $\log \beta_{\text{CoA}_2\text{B}_2}$ value for Co(II)-thiophenal-trp system is 15.02. Schiff base complex species of the type Co(AB)$_2$ would be indicated by this higher value. Tridentate binding for the Schiff base AB through imino nitrogen, thiophene sulphur and carboxylato oxygen atoms would also be revealed.

Species distribution

The species distribution diagrams are given in Figs. 4.1.3.3.1a & b. The CoAB is the predominating of all the species in the pH range 6.8 to 7.6 in 1:1 solution. CoAB$_2$ is formed after pH 7.5. In this system, an appreciable amount of metal ion has been found to be present in the form of CoA$_2$B$_2$ species in 1:2 solution at higher pH.

Electronic spectra

Electronic Spectrum for CoAB in 1:1 solution was recorded at pH 7.3. It has peak at 590 nm. This corresponds to the tetrahedral environment for Co(II). The spectrum for Co(AB)$_2$ species in 1:2 solution was recorded at pH 8.2 and has two absorption maximum at 598 and 703 nm respectively. These absorptions are due to octahedral environment for Co(II).
4.1.3.3.2 Ni(II)-thiophenal-trp system

The pH titration data (Table 4.1.3.3.2) point out the presence of three ternary species NiAB, NiAB₂ and NiA₂B₂ in addition to the binary species HA, NiA, NiA₂, HB, H₂B, NiB, NiB₂ and NiB₃. A schematic representation of the preferential formation of ternary species in this system is shown in Scheme 10.

Scheme 10

Stability and structure of NiAB, NiAB₂ and NiA₂B₂ species

The experimental logβ value for NiAB is 10.42 units, which is higher than the calculated simple mixed ligand stability constant value of 6.77. This implies that NiAB is a Schiff base species and not a mixed ligand complex. The logβ values for the NiAB, NiAB₂ and NiA₂B₂ are comparable with the corresponding values in thiophenal-val system. Therefore the mode of binding in these systems can be similar i.e. the Schiff base ligand in thiophenal-trp system is tridentate and binds the metal through thiophene sulphur, imino nitrogen and carboxylato oxygen atoms as in the thiophenal-val system and the indole nitrogen is not involved in coordination in the former. The trp in the NiAB₂ binds the metal ion through amino nitrogen and carboxylato oxygen atoms.
Species distribution

The species distribution diagrams in Figs. 4.1.3.2a & b show that a significant amount (88 %) of metal ion has been found to be present in the form of NiAB at pH 7.3 in 1:1 solution. The NiAB₂ species is present at higher pH range. NiA₂B₂ is predominant in 1:2 solution.

Electronic Spectra

Electronic Spectrum for NiAB in 1:1 solution was recorded at pH 7.2. It has peak at 658 nm. This corresponds to the tetrahedral environment for Ni(II). The spectrum for Ni(AB)₂ species in 1:2 solution was recorded at pH 7.9 and has three absorption maximum at 389 nm, 724 nm and ~1100 nm. These absorptions are due to octahedral environment for Ni(II).

4.1.3.3 Cu(II)-thiophenal-trp system

The pH titration data are given in Table 4.1.3.3. CuAB and CuAB₂ species were detected in addition to HA, CuA, CuA₂, HB, H₂B, CuB and CuB₂. The preferential formation of ternary species over binary complexes is evident from Scheme 11.

![Scheme 11](image)

Stability and structure of CuAB and CuAB₂ species

Calculated mixed ligand stability constant value for CuAB species is 9.89. This is lesser than the experimental $\log \beta_{CuAB}$ value of 15.33. This shows that CuAB
is the Schiff base complex and not a mixed ligand complex of the type Cu(A)(B). The log $\beta_{\text{CuAB}}$ value of this system is comparable with that of 15.19 in Cu-thiophenal-val system. Thus, the Schiff base is tridentate in the thiophenal-trp system. The trp in the CuAB$_2$ binds the metal ion through amino nitrogen and carboxylato oxygen atoms as in the case of Ni(II) system.

**Species distribution**

The species distribution diagram is given in Figs. 4.1.3.3.3a & b. The species distribution diagram of 1:1 and 1:2 solution show that CuAB is the predominant species. At higher pH, CuAB$_2$ is the predominant species.

**Electronic spectra**

The Electronic spectrum of CuAB complex shows a broad band at ~ 636 nm. This corresponds to $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ transitions for square planar Cu(II) complex.

**4.1.3.3.4 Zn(II)-thiophenal-trp system.**

The pH titration data are given in Table 4.1.3.3.4. The ternary species ZnAB, ZnAB$_2$ and ZnA$_2$B$_2$ in addition to the binary species HA, ZnA, ZnA$_2$, HB, H$_2$B, ZnB and ZnB$_2$ were detected. The preferred formation of the ternary complexes over binary analogues is clearly depicted in Scheme 12.

![Scheme 12](image-url)
Stability and structure of ZnAB, ZnAB₂ and ZnA₂B₂ species

The calculated mixed ligand stability constant value of 6.12 for ZnAB is less than the log β_{ZnAB} value of 8.95. This shows that ZnAB is the Schiff base species. The overall stability constant values for ZnAB, ZnAB₂ and ZnA₂B₂ species of thiophenal-trp system are comparable with those in thiophenal-val system. This indicates the similarity between these two systems in the mode of binding as well as the structure of the species.

Species distribution

The species distribution diagrams are given in Figs. 4.1.3.3.4 a & b. ZnAB and ZnA₂B₂ species are predominant in 1:1 and 1:2 solution respectively. ZnAB₂ is formed after pH 7.

4.1.3.3.5 Stability enhancement in the Co(II), Ni(II), Cu(II) and Zn(II)-thiophenal-trp systems

The calculated values of the stabilization factor, Δ log K_{MAB} for Co(II), Ni(II), Cu(II) and Zn(II)-thiophenal-trp systems are 2.61, 3.43, 4.84 and 3.00 respectively. This clearly indicates the enhancement in the stability of the Schiff base complexes of the thiophenal-trp systems and they follow Irving - Williams order of stability.

Co(II) < Ni(II) < Cu(II) > Zn(II)
4.1.3.4 M(II)-thiophenal-thr systems

The stability constant values for the Schiff base complexes of the M(II)-thiophenal-thr systems are given in Table 4.1.3.4.

4.1.3.4.1 Co(II)-thiophenal-thr system

The pH titration data are given in Table 4.1.3.4.1. Three ternary complexes CoAB, CoAB₂ and CoA₂B₂ in addition to the binary species HA, CoA, CoA₂, HB, H₂B, CoB and CoB₂ have been identified. The Scheme 13 shows the stepwise formation constants of various species involved in the system.

![Scheme 13](image)

**Stability and structure of CoAB, CoAB₂ and CoA₂B₂ species**

This scheme shows that the formation of ternary species is favoured over that of the binary. The experimental \( \log \beta_{\text{CoAB}} \) value is 9.25. The calculated mixed ligand stability constant value for CoAB is 6.35. This low value suggests that CoAB is the Schiff base species rather than mixed ligand complex. As compared to Co(II)-thiophenal-val system, the stability constant value for CoAB species of Co(II)-thiophene-thr is higher by 0.54 log units. This enhancement is less to consider the involvement of the additional coordination site of hydroxyl group in thr. But this increment can be accounted by considering the molecular recognition caused by intermolecular hydrogen bonding formed between the free hydroxyl groups of the neighbouring complex species [155]. The Schiff base is tridentate and binds through
thiophene ring sulphur and carboxylato oxygen and imino nitrogen similar to that of Co(II)-thiophenal-val system.

The $\log \beta_{\text{CoAB}_2}$ value is 13.59 log units. This higher value confirms CoAB$_2$ as a Schiff base complex. It is a mixed ligand complex of the type Co(AB)B. The formation constant for the CoAB$_2$ species of thiophenal-thr is 0.55 log units higher than that in the corresponding species of thiophenal-val system. This increment is not enough to consider an additional coordination site in thiophenal-thr as compared to thiophenal-val system. But this increment can be accounted by considering the molecular recognition through intermolecular hydrogen bonding between free hydroxyl groups of the neighbouring complexes. Again, the $\log K_{\text{CoAB}}^{\text{CoAB}_2}$ value is 0.44 units higher than $\log K_{\text{CoB}_2}^{\text{CoB}}$. This is not accountable for an additional donor site in thr, but this may also be due to molecular recognition through hydrogen bonding.

The stability constant value of CoA$_2$B$_2$ species of Co(II)-thiophenal-thr system is 0.84 log units higher than that of the similar species in Co(II)-thiophenal-val system. This additional stability is small to consider the coordination of the hydroxyl groups of both thr moieties. If both the hydroxyl groups also take part in coordination, it will give a coordination number eight to the metal ion, which is not possible for transition metal ions, in general. Therefore, both the Schiff bases AB coordinate in tridentate mode. But the possibility of -OH coordination by displacing carboxylato group can be visualized due to the following fact. The -OH group is a soft base than -COO$^-$ group at higher pH and 3d metal ions are known to prefer softer bases particularly at higher pH conditions. Ramanujam et al [156] on their studies of the Co(II), Ni(II) and Zn(II) complexes with N-salicylidene-L-serinate system have reported the coordination of hydroxyl group displacing the carboxylato group in the
bis(Schiff base) complexes of the type M(AB)\textsubscript{2}. Palanichamy \textit{et al} [157] also have reported similar change in the coordination site in the N-salicylidene-L-threoninate systems with Ni(II) and Zn(II). Thus, the most probable mode of binding in the Co(AB)\textsubscript{2} complex of Co(II)-thiophenal-thr system is through thiophene ring sulphur, imino nitrogen and the hydroxyl oxygen atoms to form two five membered chelate ring.

\textit{Species distribution}

The species distribution diagrams (Figs. 4.1.3.4.1a & b) demonstrate that the formation of Schiff base species is preferred to binary complexes. The CoAB species is predominant in 1:1 solution and reaches a maximum of ~ 90 \% in the pH range of 6.4 to 7.3. CoAB\textsubscript{2} species is formed after pH 7.5 and reaches a maximum of 77 \% after pH 7.8. In 1:2 solution, CoA\textsubscript{2}B\textsubscript{2} species reaches a maximum of ~ 21 \% at ~ pH 8.1.

\textit{Electronic spectra}

Electronic spectra of the Schiff base species CoAB and Co(AB)\textsubscript{2} were recorded at pH 6.5 and pH 8.9 respectively in the 1:1 and 1:2 solution. The CoAB species has an absorption maximum at 628 nm. This absorption can be attributed to the transition \( ^4 \text{A}_2 \text{ (F)} \rightarrow ^4 \text{T}_1 \text{ (P)} \) due to tetrahedral geometry. This tetrahedral geometry is possible by the tridentate binding of (AB) and the completion of the coordination sphere by a solvent molecule. The two bands obtained for Co(AB)\textsubscript{2} species at 564 and 694 nm are due to the octahedral transitions \( ^4 \text{T}_{1g} \text{ (F)} \rightarrow ^4 \text{T}_{1g} \text{ (P)} \) and \( ^4 \text{T}_{1g} \text{ (F)} \rightarrow ^4 \text{A}_2 \text{ (F)} \) respectively. This is possible by the tridentate binding of both (AB) ligands.
4.1.3.4.2 Ni(II)-thiophenal-thr system

The analysis of the pH titration data (Table 4.1.3.4.2) indicates the formation of three ternary species NiAB, NiAB$_2$ and NiA$_2$B$_2$ along with HA, NiA, NiA$_2$, HB, H$_2$B, NiB and NiB$_2$ binary species. The preferential formation of ternary complex species over binary analogues is apparent from Scheme 14.

![Scheme 14](image)

**Scheme 14**

**Stability and structure of NiAB, NiAB$_2$ and NiA$_2$B$_2$ species**

The higher experimental stability constant value of 10.88 for NiAB compared to the calculated value of 7.10 for the simple mixed ligand species indicates that NiAB is Schiff base complex. As in the case of CoAB thiophenal-thr species, the Schiff base ligand AB binds the metal ion through thiophene ring sulphur, imino nitrogen and carboxylato oxygen atoms in the NiAB species.

Similar to CoAB$_2$ species of thiophenal-thr system, NiAB$_2$ is also a mixed ligand complex of the Schiff base AB and B, Ni(AB)B. The Schiff base is tridentate and thr is bidentate. The $\log \beta_{\text{NiA}B_2}$ value is 17.65. This higher value indicates that NiA$_2$B$_2$ is a Schiff base complex species. As discussed in the Co(II)-thiophenal-thr system, a change in the coordination sites can also be expected for the Ni(AB)$_2$ complex of thiophenal-thr.
Species distribution

The Figs. 4.1.3.4.2a & b consist of the species distribution diagrams. NiAB and NiA₂B₂ are predominant in both the 1:1 and 1:2 solution. The NiAB species is found to have maximum concentration between pH 7.1 to 7.4 in 1:1 solution. In 1:2 solution, the NiA₂B₂ species is the predominant species. NiAB₂ species is formed only at pH 6.5.

Electronic spectra

The 1:1 and 1:2 Ni(II) systems were recorded at pH 7.97 and 8.14 for NiAB and Ni(AB)₂ species respectively. NiAB species has absorption at 632 nm for the transition \( ^3T_1 (F) \rightarrow ^3T_1 (P) \) indicating its tetrahedral geometry. As indicated above, (AB) binds the metal ion in tridentate mode and the fourth position can be completed by solvent water molecule. In 1:2 solution for Ni(AB)₂ species, three absorptions were observed at 393 nm, 713 nm and \(~1100 \) nm respectively for the transitions \( ^3A_{2g} (F) \rightarrow ^3T_{1g} (P) \), \( ^3A_{2g} (F) \rightarrow ^3T_{1g} (F) \) and \( ^3A_{2g} (F) \rightarrow ^3T_{2g} (F) \). These transitions are for the octahedral geometry of Ni(II). This is possible by the tridentate binding of both (AB) ligands.

4.1.3.4.3 Cu(II)-thiophenal-thr system

This system has been studied in the pH range of 6.0 to 8.2 and the pH titration data are given in Table 4.1.3.4.3. The ternary species CuAB and CuAB₂ were detected in addition to the binary species HA, CuA, CuA₂, HB, H₂B, CuB and CuB₂. Scheme 15 clearly shows the preferential formation of ternary complex over binary complex.
Stability and structure of CuAB and CuAB$_2$ species

The higher experimental $\log \beta_{\text{CuAB}}$ value of 16.19 compared to the calculated $\log \beta_{\text{CuAB}}$ value of 9.91 for the simple mixed ligand complex shows that CuAB is a Schiff base complex species. The $\log \beta_{\text{CuAB}}$ of the titled system is 16.19, which is 1.00 log unit higher than that in the Cu(II)-thiophenal-val system. This indicates that the Schiff base AB of Cu(II)-thiophenal-thr coordinates in a tetradentate manner through thiophene ring sulphur, carboxylato and hydroxyl oxygens and imino nitrogen atoms. Similar to CoAB$_2$ and NiAB$_2$ species of thiophenal-thr system, CuAB$_2$ is also a mixed ligand complex of the Schiff base AB and B, Cu(AB)B. The Schiff base is tridentate and thr is bidentate.

Species distribution

Species distribution diagrams are presented in Figs. 4.1.3.4.3a & b. The CuAB species is predominant in the 1:1 and 1:2 solution and found to have a maximum concentration of $\sim$ 85% over a wide range of pH. A significant amount of total metal ion has been found to be present in the form of CuAB$_2$ pH above 8.0.

Electronic spectra

The Electronic spectrum of CuAB complex shows a broad band at $\sim$ 638 nm. This corresponds to $^2B_{1g} \rightarrow ^2A_{1g}$ transitions for square planar Cu(II) complex.
4.1.3.4.4 Zn(II)-thiophenal-thr system

The experimental and computed pH titre values of this system are given in Table 4.1.3.4.4. The Zn(II)-thiophenal-thr system forms three ternary complexes ZnAB, ZnAB₂ and ZnA₂B₂ in addition to the binary species HA, ZnA, ZnA₂, HB, H₂B, ZnB and ZnB₂. The preferential formation of the various ternary species over binary analogues is clear from Scheme 16.

![Scheme 16]

**Stability and structure of ZnAB, ZnAB₂ and ZnA₂B₂ species**

The calculated mixed ligand stability value for ZnAB is 6.22, which is less than the experimental value of 9.44. This indicates ZnAB to be a Schiff base species. The $\log \beta_{ZnAB}$ value of this system is higher than that in Zn(II)-thiophenal-val system by 0.69 log units. This enhancement is not large enough to consider the tetradentate binding of the Schiff base AB including the hydroxyl group. But this may be ascribed due to the molecular recognition. Thus, the Schiff base AB is only tridentate and binds through imino nitrogen, thiophene ring sulphur and carboxylato oxygen atoms. Similar to Co(II)/Ni(II)/Cu(II)-thiophenal-thr systems, ZnAB₂ complex of Zn(II)-thiophenal-thr is a mixed ligand complex of Schiff base AB and B as Zn(AB)B. The experimental $\log \beta_{ZnAB₂}$ value is 13.78. The enhanced stability is not because of the involvement of hydroxyl group for coordination, but can be accounted by
considering molecular recognition. The Schiff base AB is tridentate and thr is bidentate. The sixth position would be occupied by solvent molecule to have octahedral geometry.

The \( \log \beta_{ZnA_2B_2} \) value for the title system is 15.78, which is higher than the corresponding thiophenal-val system by 0.83 log units. Similar to the MA_2B_2 species of Co(II)/Ni(II)-thiophenal-thr systems, in the ZnA_2B_2 species also a change of coordination site is possible with Schiff base AB binding through imino nitrogen, thiophene ring sulphur and hydroxyl oxygen atoms.

**Species distribution**

From Figs.4.1.3.4.4a & b show that ZnAB is predominant in the 1:1 solution in the pH range of 6.8 and 7.4. About 90% of the total metal ion has been found to be present in the form of ZnAB. In the 1:2 solution, ZnA_2B_2 is the predominant species at higher pH. ZnAB_2 is formed after pH 7.0.

**4.1.3.4.5 Stability enhancement in the Co(II), Ni(II), Cu(II) and Zn(II)-thiophenal-thr systems**

The stabilization factor values, \( \Delta \log K_{MAB} \) obtained for Co(II), Ni(II), Cu(II) and Zn(II) Schiff base systems with thiophenal-thr are 2.75, 3.52, 5.72 and 3.07 respectively. This shows that the enhancement of stabilities of the Schiff base complexes of the thiophenal-thr systems follow the Irving-Williams order of stability with respect to metal ions.

\[ \text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}. \]
4.1.3.5 M(II)-thiophenal-gln systems

The stability constant for the Schiff base complexes of the M(II)-thiophenal-gln systems are given in Table 4.1.3.5

4.1.3.5.1 Co(II)-thiophenal-gln system

The pH titration data are given in Table 4.1.3.5.1. In this system three ternary species viz. CoAB, CoAB₂ and CoA₂B₂ were detected along with the HA, CoA, CoA₂, HB, H₂B, CoB and CoB₂ binary species. The schematic representation of preferential formation of ternary species over binary analogues is given in Scheme 17.

![Scheme 17](image)

Stability and structure of CoAB, CoAB₂ and CoA₂B₂ species

The \( \log \beta_{CoAB} \) value is 9.15, which is higher than the calculated mixed ligand complex \( \log \beta_{CoAB} \) value of 6.06. Therefore CoAB can be considered as Schiff base complex. Further \( \log \beta_{CoAB} \) value of Co(II)-thiophenal-gln system is 0.44 log units higher than that in the corresponding thiophenal-val system. This increment is not enough for an additional coordination site indicating the non-participation of amide group in coordination. This slight enhancement may be due to the molecular recognition between the amide groups of the neighbouring complex species which leads to inter molecular association by forming hydrogen bond between them [157]. Thus, CoAB is a Schiff base complex species where (AB) is tridentate, binding
through thiophene ring sulphur, carboxylato oxygen and imino nitrogen atoms. The fourth position would be occupied by solvent molecule to have tetrahedral geometry. Though the Schiff base ligand has four electron rich atoms viz. thiophene, carboxylato, imino and amide groups for coordination due to stability reasons the amide nitrogen is not involved in the coordination. Instead, it is engaged in molecular recognition.

The log\(\beta_{\text{CoAB}}\) value is 13.49. This higher value indicates the formation of Schiff base between thiophenal and gln and the CoAB\(_2\) species can be represented as mixed ligand Co(AB)B. The log\(\beta_{\text{CoAB}}\) value in thiophenal-gln system is 0.45 units greater than that in thiophenal-val system. This small increment is not enough to suggest an additional donor site for gln and this increment can be explained by considering the molecular recognition.

The log\(\beta_{\text{CoA,B}}\) value in the title system is 15.55. This higher value implies that it is a Schiff base complex. Moreover, the stability constant value of CoA\(_2\)B\(_2\) species in thiophenal-gln system is 0.70 log units greater than that in the corresponding thiophenal-val system. This increment is due to intermolecular hydrogen bonding between free amide groups. The species distribution diagrams clearly show that formation of the Schiff base complex species is preferred to binary complexes.

**Species distribution**

The species distribution diagrams are presented in Figs. 4.1.3.5.1a & b. The CoAB and CoA\(_2\)B\(_2\) complexes are predominant both in 1:1 and 1:2 solution. CoAB\(_2\) is found to form at high pH 7.0. In 1:1 solution, ~ 92% of the total metal ion is present as CoAB. The maximum concentration of CoA\(_2\)B\(_2\) is 88% in 1:2 solution at pH 8.1.
Electronic spectra

Electronic spectra of the Schiff base species CoAB and Co(AB)$_2$ were recorded at pH 6.6 and pH 8.9 respectively in the 1:1 and 1:2 solution. The CoAB species has an absorption maximum at 617 nm. This absorption can be attributed to the transition $^4A_2$ (F) $\rightarrow$ $^4T_1$ (P) due to tetrahedral geometry. This tetrahedral geometry is possible by the tridentate binding of (AB) and the completion of the coordination sphere by a solvent molecule. The Co(AB)$_2$ species system has two bands at 550 and 678 nm respectively which are due to the octahedral transitions $^4T_{1g}$ (F)$\rightarrow$ $^4T_{1g}$ (P) and $^4T_{1g}$ (F)$\rightarrow$ $^4A_2$ (F) for Co(II). This is possible by the tridentate binding of both (AB) ligands.

4.1.3.5.2 Ni(II)-thiophenal-gln system

During the analysis of the pH titration data in Table 4.1.3.5.2, three types of the ternary complex species NiAB, NiAB$_2$ and NiA$_2$B$_2$ in addition to the binary species HA, NiA, NiA$_2$, HB, H$_2$B, NiB and NiB$_2$ have been detected. The preferential formation of the ternary complexes over binary species is clearly brought out by considering the stepwise formation of various species given in scheme 18.

![Scheme 18](image)

**Stability and structure of NiAB, NiAB$_2$ and NiA$_2$B$_2$ species**

The overall formation constant for the species NiAB is 10.75 log units. The calculated mixed ligand complex stability value for NiAB is 6.94. This large value
indicates the presence of inter ligand interaction leading to the formation of Schiff base ligand (AB). The stability constant value for the NiAB species in the Ni(II)-thiophenal-gln system is higher than that in Ni(II)-thiophenal-val system by 0.40 log units. This enhancement is less for considering the involvement of the amide group of gln in coordination. This enhancement can be accounted by considering the presence of molecular recognition between the amide groups of the neighbouring complex species leading to molecular association through intermolecular hydrogen bonding. Thus the Schiff base ligand AB binds the metal ion in a tridentate mode.

Similar to that of CoAB$_2$ of thiophenal-gln system, NiAB$_2$ species can also be represented as Ni(AB)B. The log $\beta_{\text{NiAB}_2}$ value for thiophenal-gln system is 0.65 units higher than that for the corresponding species in thiophenal-val system. This enhancement is not sufficient to account for an additional donor site of gln over val. The increase in the stability can be accounted by considering intermolecular hydrogen bonding.

The difference in log $\beta_{\text{NiA}_2\text{B}_2}$ values in thiophenal-gln and thiophenal-val systems is 0.67. This can also be enlightened by considering the molecular recognition as described in the case of Co(II) system. Both the Schiff base ligands in Ni(AB)$_2$ can be considered to be coordinated in a tridentate mode through their imino nitrogen, carboxylato oxygen and thiophene ring sulphur atoms.

Species distribution

The species distribution diagrams are presented in Figs. 4.1.3.5.2a & b. The species distribution diagram in 1:1 solution shows that NiAB is the predominant species. NiAB$_2$ is found to form above pH 7 and its concentration increases with increase of pH. NiA$_2$B$_2$ is the dominant species with a maximum concentration of 74 % in 1:2 solution.
**Electronic spectra**

The 1:1 and 1:2 Ni(II) systems were recorded at pH 7.97 and 7.63 for NiAB and Ni(AB)\(_2\) species respectively. NiAB species has absorption at 635 nm for the transition \(^3T_1\) (F) \(\rightarrow\) \(^3T_1\) (P) indicating its tetrahedral geometry. As indicated above, (AB) binds the metal ion in tridentate mode and the fourth position can be completed by solvent water molecule. In 1:2 solution for Ni(AB)\(_2\) species, three absorptions were observed at 396 nm, 715 nm and ~1009 nm respectively for the transitions \(^3A_{2g}\) (F) \(\rightarrow\) \(^3T_{1g}\) (P), \(^3A_{2g}\) (F) \(\rightarrow\) \(^3T_{1g}\) (F) and \(^3A_{2g}\) (F) \(\rightarrow\) \(^3T_{2g}\) (F). These transitions are for the octahedral geometry of Ni(II). This is possible by the tridentate binding of both (AB) ligands.

4.1.3.5.3 Cu(II)-thiophenal-gln system

The experimental and computed titre values are given in Table 4.1.3.5.3. Ternary complexes of the types CuAB and CuAB\(_2\) have been detected in addition to the binary species HA, CuA, CuA\(_2\), HB, H\(_2\)B, CuB and CuB\(_2\). The species distribution diagrams are given in Figs. 4.1.3.5.3a & b. The Scheme 19 indicates the preferential formation of ternary species over binary.

![Scheme 19](image-url)
Stability and structure of CuAB and CuAB$_2$ species

The log $\beta_{\text{CuAB}}$ value is 16.12. This is higher than the mixed ligand complex stability constant value of 9.81. This higher log $\beta_{\text{CuAB}}$ designates that CuAB is Schiff base complex species. The overall formation constant value for CuAB species of Cu(II)-thiophenal-gln system is higher than that in the Cu(II)-thiophenal-val system by 0.93 units indicating possible molecular recognition between the free amide groups of the neighbouring complex species leading to intermolecular association due to the formation of hydrogen bond between them. Thus, the Schiff base AB binds in a tridentate manner through imino nitrogen, thiophene sulphur and carboxylato oxygen atom and amide group of gln does not take part in coordination.

The comparable CuAB$_2$ values of 19.42 and 18.45 in Cu(II)-thiophenal-gln and val systems respectively indicate that CuAB$_2$ species in the former system can be represented as Cu(AB)B, where Schiff base (AB) is tridentate and gln (B) coordinates independently.

Species distribution

The species distribution diagrams are presented in Figs. 4.1.3.5.3a & b. In the 1:1 and 1:2 solutions, CuAB is the predominant species, accounting a maximum of ~90 % of the total metal ion in this form. The formation of CuAB$_2$ starts comparatively at higher pH.

Electronic spectra

The Electronic spectrum of CuAB complex shows a broad band at ~ 642 nm. This corresponds to $^2$B$_{1g}$ → $^2$A$_{1g}$ transitions for square planar Cu(II) complex.
4.1.3.5.4 Zn(II)-thiophenal-gln system

The pH titration data are given in Table 4.1.3.5.4. Three types of ternary complexes *viz.* ZnAB, ZnAB$_2$ and ZnA$_2$B$_2$ in addition to the binary species HA, ZnA, ZnA$_2$, HB, H$_2$B, ZnB and ZnB$_2$ have been detected. The Scheme 20 clearly shows that the ternary complex formation is preferred to the binary species.

![Scheme 20](image)

**Stability and structure of ZnAB, ZnAB$_2$ and ZnA$_2$B$_2$ species**

The overall formation constant value for ZnAB species is 9.29 log units. This higher value compared to the calculated mixed ligand stability constant value of 6.14 log units indicates ZnAB to be a Schiff base complex species. Moreover, log $\beta_{ZnAB}$ value is greater by 0.54 as compared to that in Zn(II)-thiophenal-val system. The enhancement may be explained by considering intermolecular hydrogen bonding. Similar to MAB$_2$ species of Co(II)/Ni(II)/Cu(II)-thiophenal-gln system, ZnAB$_2$ is also a mixed ligand complex of the Schiff base AB and B, Zn(AB)B where the Schiff base (AB) binds the metal ion in a tridentate manner. The slightly higher log $\beta_{ZnA_2B_2}$ value in the Zn(II)-thiophenal-gln system compared to that in thiophenal-val system can be explained by considering molecular recognition.
Species distribution

The species distribution diagrams are given in Figs. 4.1.3.5.4a & b. ZnAB and ZnA₂B₂ are found to be predominant in both 1:1 and 1:2 solution. ZnAB₂ is found to form around pH 7.0.

4.1.3.5.5 The stability enhancement in the Co(II), Ni(II), Cu(II) and Zn(II)-thiophenal-gln systems

The stabilization factor values, Δ log K_MAB for the title systems are 2.96, 3.64, 5.87 and 3.09 respectively for Co(II), Ni(II), Cu(II) and Zn(II) systems. This follows the Irving - Williams order of stability: Co(II)<Ni(II)<Cu(II)>Zn(II).

4.1.3.6 M(II)-thiophenal-glu systems

The stability constant for the Schiff base complexes of the M(II)-thiophenal-glu systems are given in Table 4.1.3.6

4.1.3.6.1 Co(II)-thiophenal-glu system

The experimental and computed pH titre values are given in Table 4.1.3.6.1. In this system three ternary species CoAB, CoAB₂ and CoA₂B₂ were detected along with HA, CoA, CoA₂, HB, H₂B, CoB and CoB₂ binary species. A schematic representation of preferential formation of ternary species is given in Scheme 21.

\[ \text{Scheme 21} \]
**Stability and structure of CoAB, CoAB₂ and CoA₂B₂ species**

The experimental \( \log \beta_{\text{CoAB}} \) value is 9.55. This is higher than the stability constant value of simple mixed ligand complex of 6.38. Therefore, CoAB can be considered as a Schiff base complex species. Further, \( \log \beta_{\text{CoAB}} \) of this system is higher than that in thiophenal-val system by 0.84 units. This enhancement may be due to the interaction of \( \gamma \)-carboxyl group with the metal ion of the neighbouring complex. In addition to that, \( \log \beta_{\text{CoAB}} \) is comparable with that for the similar species of thiophenal-thr and thiophenal-gln systems. This clearly shows that the Schiff base in Co(II)-thiophenal-glu system functions as a tridentate ligand. Apparently, the \( \gamma \)-carboxyl group is not involved is coordination. Similar to thiophenal-gln Schiff base ligand, thiophenal-glu is also a potentially tetradentate. Though it can bind through thiophene ring sulphur, imino nitrogen, \( \alpha \)-carboxylato oxygen and \( \gamma \)-carboxyl oxygen atoms, it behaves as a tridentate ligand through thiophene ring sulphur, imino nitrogen and \( \alpha \)-carboxylato oxygen due to stability factor. The \( \gamma \)-carboxyl group is involved in molecular recognition.

The \( \log \beta_{\text{CoAB₂}} \) value is 13.55. As in the other systems, this species may be represented as Co(AB)B. The above value is 0.51 higher than that in the thiophenal-val system. This enhancement is not enough to consider an additional donor site in glu. Further the \( \log \beta_{\text{CoAB₂}} \) is higher than the \( \log \beta_{\text{CoB₂}} \) value by 0.66 units. These enhancements in the stability constant value may be due to the interaction between \( \gamma \)-carboxylato group and metal ion of the neighbouring complex. This leads to the conclusion that the Schiff base AB is tridentate in Co(AB)B.

The \( \log \beta_{\text{CoA₂B₂}} \) value in Co(II)-thiophenal-glu system is 15.65, which is comparable with that in Co(II)-thiophenal-gln system. This species can be represented
as Co(AB)$_2$, where each Schiff base (AB) is tridentate. Moreover, if AB is tetrar Dentate, it will lead to an effective coordination number of eight to the metal ion, which is improbable for 3d-transition metal ions, in general.

**Species distribution**

The species distribution diagrams are presented in Figs. 4.1.3.6.1a & b. CoAB and CoA$_2$B$_2$ species are predominant in 1:1 and 1:2 solution respectively. The concentration of CoA$_2$B$_2$ is ~ 86% over a extensive range of pH. CoAB$_2$ is formed at pH 7.1 in 1:2 solution.

**Electronic spectra**

Electronic spectra of the Schiff base species CoAB and Co(AB)$_2$ were recorded at pH 6.6 and pH 8.5 respectively in the 1:1 and 1:2 solution. The CoAB species has an absorption maximum at 626 nm. This absorption can be attributed to the transition $^4A_2$ (F) $\rightarrow$ $^4T_1$ (P) due to tetrahedral geometry. This tetrahedral geometry is possible by the tridentate binding of (AB) and the completion of the coordination sphere by a solvent molecule. The Co(AB)$_2$ species system has two bands at 555 and 688 nm respectively which are due to the octahedral transitions $^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$ (P) and $^4T_{1g}$ (F) $\rightarrow$ $^4A_2$ (F) for Co(II).

**4.1.3.6.2 Ni(II)-thiophenal-glu system**

The pH titration data are given in Table 4.1.3.6.2. NiAB, NiAB$_2$ and NiA$_2$B$_2$ ternary species were detected along with the binary species HA, NiA, NiA$_2$, HB, H$_2$B, NiB and NiB$_2$. The preferential formation of ternary species over binary is clearly shown by Scheme 22.
Stability and structure of NiAB, NiAB$_2$, and NiA$_2$B$_2$ species

The log $\beta_{\text{NiAB}}$ value is 11.19 and this is higher than that for mixed ligand complex value of 7.61. Thus, NiAB is a Schiff base species rather than mixed ligand complex. The log $\beta_{\text{NiAB}_2}$ and log $\beta_{\text{NiA}_2\text{B}_2}$ values are 15.38 and 17.70 and these values are 0.75 and 0.79 log units higher than those in the thiophenal-val system respectively. Further Ni(II)-thiophenal-glu system resembles Co(II)-thiophenal-glu system. Thus, the Schiff (AB) in Ni(II)-thiophenal-glu system binds the metal ion in tridentate manner through thiophene sulphur and $\alpha$-carboxylato oxygen and imino nitrogen atoms whereas $\gamma$-carboxylato group is not involved in coordination. The glu ligand in Ni(AB)B is bidentate. Like Co(II)-thiophenal-glu system, the slight enhancement in the stability in the Ni(II)-thiophenal-glu system may be accounted by considering interaction between $\gamma$-carboxylato group and Ni(II) of the neighbouring complex.

Species distribution

The species distribution diagrams are given in Figs.4.1.3.6.2a & b. In 1:1 solution, the maximum percentage of NiAB is found to be ~ 93 % of the total Ni(II) ion. In 1:2 solution, the maximum concentration of NiAB is decreased to 61 %. The NiA$_2$B$_2$ predominates in 1:2 solution. NiAB$_2$ species is present in higher pH range.
The species distribution diagrams clearly indicate that the Schiff base complexes are more preferred compared to binary complex species.

**Electronic spectra**

The 1:1 and 1:2 Ni(II) systems were recorded at pH 7.40 and 7.46 for NiAB and Ni(AB)₂ species respectively. NiAB species has absorption at 630 nm for the transition \( ^3T_1 (F) \rightarrow ^3T_1 (P) \) indicating its tetrahedral geometry. As indicated above, (AB) binds the metal ion in tridentate mode and the fourth position can be completed by solvent water molecule. In 1:2 solution for Ni(AB)₂ species, three absorptions were observed at 393 nm, 710 nm and \(~1100\) nm respectively for the transitions \( ^3A_{2g} (F) \rightarrow ^3T_{1g} (P) \), \( ^3A_{2g} (F) \rightarrow ^3T_{1g} (F) \) and \( ^3A_{2g} (F) \rightarrow ^3T_{2g} (F) \). These transitions are for the octahedral geometry of Ni(II). This is possible by the tridentate binding of both (AB) ligands.

4.1.3.6.3 Cu(II)-thiophenal-glu system

The pH titration data are given in Table 4.1.3.6.3. The ternary species CuAB and CuAB₂ were detected in addition to the binary species HA, CuA, CuA₂, CuB and CuB₂. Scheme 19 shows the preferential formation of ternary complex species involved in this system.

![Scheme 23](image-url)
Stability and structure of CuAB and CuAB\textsubscript{2} species

The overall formation constant for CuAB species of thiophenal-glu system is 16.41 log units. This is higher than simple mixed ligand stability constant value of 10.36. Hence, CuAB can be considered as a Schiff base complex species. The $\log \beta_{\text{CuAB}}$ value in this system is comparable with that in the Cu(II)-thiophenal-gln/thr systems, indicating similar mode of coordination. The $\log \beta_{\text{CuAB}_2}$ value of 20.20 obtained in the Cu(II)-thiophenal-glu system is higher than that of 18.45 in Cu(II)-thiophenal-val system. This higher value suggests the tetradentate coordination of the Schiff base (AB) in the CuAB\textsubscript{2} species of Cu(II)-thio-glu system.

Species distribution

The species distribution diagrams (Figs.4.1.3.6.3a & b) for both the 1:1 and 1:2 solution shows that the Schiff base complex CuAB is the dominating one.

Electronic spectra

The Electronic spectrum of CuAB complex shows a broad band at ~ 636 nm. This corresponds to $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ transitions for square planar Cu(II) complex.

4.1.3.6.4 Zn(II)-thiophenal-glu system

Table 4.1.3.6.4 consists of the experimental and computed pH values. This system has three types of ternary complexes \textit{viz.} ZnAB, ZnAB\textsubscript{2} and ZnA\textsubscript{2}B\textsubscript{2} along with the binary species HA, ZnA, ZnA\textsubscript{2}, HB, H\textsubscript{2}B, ZnB and ZnB\textsubscript{2}. The preferential formation of the ternary complex over binary analogues is clearly depicted by Scheme 24.
Stability and structure of ZnAB, ZnAB₂ and ZnA₂B₂ species

The $\log \beta_{ZnAB}$ value is 9.51, which is higher than that of 6.67 for the simple mixed ligand complex. Therefore, ZnAB can be considered as a Schiff base species. As in the case of Co(II)/Ni(II)-thiophenal-glu systems, Zn(II)-thiophenal-glu also forms ZnAB₂ and ZnA₂B₂ species with the respective $\log \beta$ values of 13.78 and 15.81. These values are comparable with those in the similar species of Zn(II)-thiophenal-gln/thr system indicating similar mode of binding in all these systems. Thus, the Schiff base AB in ZnAB₂ in the Zn(II)-thiophenal-glu system is tridentate and $\gamma$-carboxylato group is not involved in coordination. In the Zn(AB)_2 complex, both (AB) ligands are tridentate.

Species distribution

The species distribution diagrams are given in Figs.4.1.3.6.4a & b. The species distribution diagrams clearly show that ZnAB and ZnA₂B₂ are the predominant species in both 1:1 and 1:2 solution respectively.

4.1.3.6.5 Stability enhancement in the Co(II), Ni(II), Cu(II) and Zn(II)-thiophenal-glu systems

The stabilization factor values, $\Delta \log K_{MAB}$ in the title systems are 2.44, 3.15, 4.15 and 2.76 respectively and follow the Irving-Williams order of stability:

Co(II) < Ni(II) < Cu(II) > Zn(II)
4.1.3.7 M(II)-thiophenal-asp systems

The stability constant values for the Schiff base complexes of the M(II)-thiophenal-asp systems are given in Table 4.1.3.7.

4.1.3.7.1 Co(II)-thiophenal-asp system

The experimental and computed pH titre values are given in Table 4.1.3.7.1. Three ternary species CoAB, CoAB$_2$ and CoA$_2$B$_2$ are detected in addition to HA, CoA, CoA$_2$, HB, H$_2$B, CoB and CoB$_2$ binary species. The preferential formation of ternary complex species over binary species is evident from Scheme 25.

![Scheme 25](image)

**Stability and structure of CoAB, CoAB$_2$ and CoA$_2$B$_2$ species**

The $\log \beta_{CoAB}$ value in the system is 9.91. This higher value compared to that of 7.12 for the simple mixed ligand complex implies the formation of Schiff base complex. Moreover, the $\log \beta_{CoAB}$ value for the title system is 1.20 units greater than that for the similar species of Co(II)-thiophenal-val system. This demonstrates that (AB) in the CoAB species of Co(II)-thiophenal-asp system is tetradentate and can bind the metal ion through thiophene ring sulphur, imino nitrogen and two carboxylato oxygen atoms. This would result in the formation of two five membered and one six membered rings. The formation of the multi-ring system will naturally enhance the stability of the complex.
The $\log_\beta_{\text{CoAB}_2}$ value in thiophenal-asp system is 14.19. This species can be represented as a mixed ligand complex of the type Co(AB)B. Further its stability constant value is 1.15 log units higher than that for the corresponding species of thiophenal-val system. Moreover, if the Schiff base AB is tetradeinate and asp is tridentate, it will lead to the coordination number of seven for Co(II), which is less possible for 3d-metal ions, in general. Hence, it is more appropriate to suggest that in Co(AB)B species of thiophenal-asp system, the Schiff base (AB) is tetradeinate and asp behaves as bidendate ligand binding through amino nitrogen and $\alpha$-carboxylato oxygen atoms.

The $\log_\beta_{\text{CoA}_2\text{B}_2}$ value for the Co(AB)$_2$ complex is 16.11. In this species, both (AB) can bind tridentately through the thiophene sulphur, imino nitrogen and carboxylato oxygen present in the $\beta$-position to the imino nitrogen. Such a mode of binding will result in a structure where each Schiff base AB will form five and six membered rings, with an overall structure of two five and are six membered rings.

**Species distribution**

The species distribution diagrams (Figs.4.1.3.7.1a & b) of the 1:1 and 1:2 solution clearly indicate that the Schiff base species are preferred to binary species. In the 1:1 solution, CoAB species predominates around pH 7.2. The maximum concentration of CoAB is $\sim$ 92%. CoAB$_2$ and CoA$_2$B$_2$ are present in appreciable concentration above pH 7.5 in 1:2 solution.

**Electronic spectra**

The $\lambda_{\text{max}}$ value for CoAB in 1:1 solution is 625 nm at pH 6.8. This value corresponds to tetrahedral geometry for Co(II) ion. For CoA$_2$B$_2$ species, spectrum was recorded for 1:2 system of Co(II) at pH 8.3 and has two bands, one at 763 nm and the other at 583 nm. These bands correspond to octahedral geometry for CoA$_2$B$_2$. 
4.1.3.7.2 Ni(II)-thiophenal-asp system

The system was studied in the pH range of 6.6 to 8.6 (Table 4.1.3.7.2). Three ternary species NiAB, NiAB$_2$ and NiA$_2$B$_2$ were detected in addition to HA, NiA, NiA$_2$, HB, H$_2$B, NiB and NiB$_2$ binary species. The preferential formation of the ternary complexes is obvious from Scheme 26.

![Scheme 26](image)

**Stability and structure of NiAB, NiAB$_2$ and NiA$_2$B$_2$ species**

The NiAB species can be a mixed ligand or Schiff base complex species. The calculated overall formation constant value for the mixed ligand complex is 8.53 log units. But the experimental log $\beta_{NiAB}$ value is 12.01 log units. This large enhancement in the stability constant value indicates that the NiAB species is a Schiff base complex. The higher log$\beta_{NiAB}$ of 12.01 in the thiophenal-asp system compared to that of 10.35 in thiophenal-val system indicates that the Schiff base (AB) in the former system is tetradequate.

The log$\beta_{NiAB_2}$ value of 17.33 in the title system is higher than that of 14.86 for NiAB$_2$ mixed ligand complex. Therefore NiAB$_2$ can be represented as a mixed Schiff base AB and B, Ni(AB)B. The Schiff base AB would be tetradequate and asp, B would be bidentate, so that the coordination number of the metal would be six.
The log $\beta$ value for NiA$_2$B$_2$ species is 19.32 and this species can be represented as Ni(AB)$_2$. If both AB are tetradeinate, the coordination number would be eight, which is less probable for the transition metal complexes. Hence each (AB) can bind in a tridentate mode involving thiophene ring sulphur, imino nitrogen and carboxylato oxygen atom present at the $\alpha$-position to the imino nitrogen giving a coordination number six to the metal.

Species distribution

The species distribution diagrams are given in Figs.4.1.3.7.2a & b. NiAB is present to a maximum of $\sim$ 90% at pH 7.0. In the 1:2 solution, NiAB is found to be predominant between pH 7.1 and 7.3. Above pH 7.5, the NiA$_2$B$_2$ complex is the dominant one.

Electronic spectra

The Electronic spectrum for the NiAB species in the 1:1 solution of Ni(II)-thiophenal-asp was recorded at pH 7.13. The $\lambda_{\text{max}}$ value is 667 nm. This value indicates that NiAB has tetrahedral geometry. The spectrum for the NiA$_2$B$_2$ species in the 1:2 solution was recorded at pH 8.21. It shows three bands at 358 nm, 637 nm and $\sim$1100 nm. These absorptions indicate the octahedral geometry for Ni(AB)$_2$.

4.1.3.7.3 Cu(II)-thiophenal-asp system

The experimental and computed pH titre values are given in Table 4.1.3.7.3. Analysis of the experimental data shows the presence of the ternary species CuAB and CuAB$_2$ along with HA, CuA, CuA$_2$, HB, H$_2$B, CuB and CuB$_2$ binary species. A schematic representation to show the preferential formation of ternary species is given in Scheme 27.
Scheme 27

**Stability and structure of CuAB and CuAB₂ species**

The \( \log \beta \) value for CuAB is 17.17. This is a higher value compared to the overall stability constant value of 10.44 of simple mixed ligand complex. Therefore, CuAB can be considered as a Schiff base species. Like Co(II)/Ni(II)-thiophenal-aspartate systems, the Schiff base AB in the Cu(II)-thiophenal-aspartate is tertradentate and coordinates through thiophene ring sulphur, imino nitrogen and two carboxylate oxygens. Same mode of binding for the Schiff base ligand molecules would be expected in CuAB₂ as in the case of Co(II)/Ni(II)-thiophenal-aspartate systems by considering \( \log \beta \) values.

**Species distribution**

Figs. 4.1.3.7.3a & b consists of the species distribution diagrams. CuAB is the predominant species and concentration reaches a maximum of 92% at pH 7.2. At higher pH, CuAB₂ species is present in higher concentration.

**Electronic spectra**

The Electronic spectrum for this system was recorded at pH 6.7. The \( \lambda_{\text{max}} \) value for CuAB is 650 nm. This value corresponds to square planar environment for Cu(II).
4.1.3.7.4 Zn(II)-thiophenal-asp system

The pH titration data of the title system are given in Table 4.1.3.7.4. This system forms three ternary complexes ZnAB, ZnAB$_2$ and ZnAB$_3$ in addition to the binary species HA, ZnA, ZnA$_2$, HB, H$_2$B, ZnB and ZnB$_2$. The Scheme 28 shows the stepwise formation constants of various binary and ternary species present in this system which clearly shows that the ternary complex formation is preferred.

![Scheme 28](image)

**Stability and structure of ZnAB, ZnAB$_2$ and ZnA$_2$B$_2$ species**

ZnAB species may be a mixed ligand complex of thiophenal and asp. If it is so, the stability constant value should be 6.89 log units. But, the experimental value is 10.11. Therefore, ZnAB can be considered as a Schiff base complex Zn(AB). As in the other systems, the Schiff base (AB) could be tetradentate. The log $\beta_{ZnAB}$ value is 14.48. This higher value indicates the formation of Schiff base. Here, the Schiff base AB can be tetradentate and the asp would be bidentate through amino nitrogen and $\alpha$-carboxylato oxygen as in the case of MAB$_2$ species in the corresponding Co(II)/Ni(II) systems.

The ZnA$_2$B$_2$ species with the log $\beta$ value of 16.44 is a bis(Schiff base) complex Zn(AB)$_2$. As in other similar systems, both the Schiff base ligands could coordinate tridentately.
**Species distribution**

The species distribution diagrams are given in Figs.4.1.3.7.4a & b. In the 1:1 solution, the Schiff base complex ZnAB predominates between pH 6.8 and 7.6. The maximum concentration of ZnAB is ~ 93 %. The concentration of Zn(AB)B species increases above pH 7.5. After pH 7.5, ZnA₂B₂ is the dominating species in 1:2 solution.

**4.1.3.7.5 Stability enhancement in the Co(II), Ni(II), Cu(II) and Zn(II)-thiophenal-asp systems**

The stabilization factor values, Δ log K\textsubscript{MAB} obtained in the title systems are 2.26, 2.98, 5.96 and 2.78 respectively. This shows the enhancement of stabilities of the Schiff base complexes of the thiophenal-asp systems to follow the Irving-Williams order of stability.

Co(II) < Ni(II) < Cu(II) > Ni(II).
4.1.3.8 M(II)-thiophenal-his systems

The stability constant values for the Schiff base complexes of the M(II)-thiophenal-his systems are given in Table 4.1.3.8.

4.1.3.8.1 Co(II)-thiophenal-his system

The pH titration data are given in Table 4.1.3.8.1. Three types of ternary complexes viz. CoAB, CoAB₂ and CoA₂B₂ in addition to HA, CoA, CoA₂, HB, H₂B, H₃B, CoB and CoB₂ binary species have been detected in this system. The preferential formation of the ternary complexes over binary species is clearly brought out by considering the stepwise formation of various species given in Scheme 29.

Scheme 29

Stability and structure of CoAB, CoAB₂ and CoA₂B₂ species

The $\log \beta_{\text{CoAB}}$ value for the title system is 13.22 units. This higher value compared to the stability constant value of 8.96 for the simple mixed ligand complex demonstrates that CoAB is a Schiff base complex species. The Schiff base ligand is tetradeptate and can coordinate through imino and imidazole nitrogen atoms, thiophene ring sulphur and carboxylato oxygen atoms.

The calculated stability constant value for simple mixed ligand complex CoAB₂ is 15.89, which is lesser than the experimental value of 17.40 for the CoAB₂ species. This indicates that CoAB₂ is a Schiff base complex species and can be represented as Co(AB)B. If the Schiff base AB and histidinate B are respectively
considered as tetra and tridentate, it will lead to the coordination number of seven. This is not possible for 3d-metal ions. Hence, there must be some change in the mode of coordination. The better description of the binding mode is that the Schiff base AB binds Co(II) in tetradienate mode and his is linked bidentately through amino and imidazole nitrogen.

The CoA$_2$B$_2$ species can be represented as Co(AB)$_2$. Both the ligands, AB cannot bind tetradienate, because it would lead to the improbable coordination number of eight for Co(II). There are two possibilities to maintain the maximum coordination number of six to the metal ion. In the first case, one AB would be tetradienate, while the second AB will be bidentate. However, a more reasonable structure will be the one where both Schiff base ligands will be tridentate, utilising the thiophene ring sulphur, imino nitrogen and imidazole nitrogen for coordination.

**Species distribution**

The species distribution diagrams in Figs.4.1.3.8.1a & b show that CoAB predominates in the 1:1 solution. The concentration of CoAB$_2$ species is in appreciable amount in the pH near 8.4. The CoA$_2$B$_2$ dominates after pH 8.5 in 1:2 solution.

**Electronic spectra**

The Electronic spectrum for the CoAB species in the 1:1 solution of Co(II)-thiophenal-his was recorded at pH 7.0. It has a peak at 638 nm. This value corresponds to the tetrahedral environment for Co(II). Spectrum for CoA$_2$B$_2$ species was recorded in 1:2 solution at pH 8.0. There are two bands at 759 nm and 601 nm. These absorptions are due to octahedral environment for Co(II).
**4.1.3.8.2 Ni(II)-thiophenal-his system**

The experimental and computed pH values are listed in Table 4.1.3.8.2. NiAB, NiAB₂ and NiA₂B₂ ternary species are detected along with the binary species HA, NiA, NiA₂, HB, H₂B, H₃B, NiB and NiB₂. A schematic representation of the various species involved in the system is given in Scheme 30. This clearly shows that the ternary complexes are more stable than the binary analogues.

![Scheme 30](image)

**Stability and structure of NiAB, NiAB₂ and NiA₂B₂ species**

The overall stability constant value for NiAB is 15.32 log units, which is higher than the calculated mixed ligand stability constant value of 9.89. This implies that NiAB is a Schiff base complex and not a simple mixed ligand species. The Schiff base AB would be tetradentate as in the corresponding Co(II) system.

The log β\textsubscript{NiAB₂} value of 21.01 is higher than that of 17.56 for the simple mixed ligand species indicating NiAB₂ to be a Schiff base complex species and can be represented as Ni(AB)B. As in the case of Co(II)-thiophenal-his system, it can be expected that AB is tetradentate and his (B) is bidentate. The observed higher log β value of 23.31 for NiA₂B₂ compared to that for the simple mixed ligand stability constant value of 19.47 indicates that NiA₂B₂ is a Schiff base complex of the type Ni(AB)₂, where both Schiff base ligands coordinate in tridentate mode.
Species distribution

Figs. 4.1.3.8.2a & b consist of the species distribution diagrams. In 1:1 solution, NiAB is the dominant species and the concentration reaches a maximum of ~ 93% at pH 7.2. NiAB₂ species is found to be in considerable amount at higher pH region. NiA₂B₂ is present in more amounts in the 1:2 solution and ~ 90% of the total metal ion has been found to be in this form near pH 8.3.

Electronic spectra

Spectrum for NiAB in 1:1 solution was recorded at pH 7.35. It has peak at 647 nm. This corresponds to the tetrahedral environment for Ni(II). The spectrum for Ni(AB)₂ species in 1:2 solution was recorded at pH 8.05 and has three absorption maximum at 323 nm, 604 nm and 878 nm. These absorptions are due to octahedral environment for Ni(II).

4.1.3.8.3 Cu(II)-thiophenal-his system

The pH titration data are given in Table 4.1.3.8.3. The ternary complex species CuAB and CuAB₂ in addition to the binary species HA, CuA, CuA₂, HB, H₂B, H₃B, CuB and CuB₂ have been detected. The stepwise formation constants of the different complex species detected are given in Scheme 31 which clearly demonstrates the preferential formation of the ternary complexes.

![Scheme 31](image-url)
**Stability and structure of CuAB and CuAB₂ species**

The higher \( \log \beta_{\text{CuAB}} \) value of 18.88 compared to that of 11.41 for the simple mixed ligand complex indicates that CuAB is a Schiff base complex and the Schiff base ligand can bind in a tetradentate manner as in the corresponding Co(II) and Ni(II) systems. The \( \log \beta_{\text{CuAB₂}} \) value of 23.52 is higher than that of 20.11 for the simple mixed ligand species indicating CuAB₂ to be a Schiff base complex species and can be represented as Cu(AB)B. As in the case of Co(II)/Ni(II)-thiophenal-his system, it can be expected that AB is tetradentate and his (B) is bidentate.

**Species distribution**

The species distribution diagrams are shown in Figs.4.1.3.8.3a & b. CuAB and CuAB₂ species predominates in 1:1 and 1:2 solutions respectively. The maximum concentration of CuAB is \( \sim 92 \% \) in the 1:1 solution and 80 \% in 1:2 solution.

**Electronic spectra**

The Electronic spectrum for CuAB was recorded at pH 6.8. The peak was at 641 nm. This value corresponds to square planar geometry for Cu(II) ion.

**4.1.3.8.4 Zn(II)-thiophenal-his system**

The experimental and computed pH values are given in Table 4.1.3.8.4. Three ternary complex species \( \text{viz.} \) ZnAB, ZnAB₂ and ZnA₂B₂ were detected in addition to the binary species HA, ZnA, ZnA₂, HB, H₂B, H₃B, ZnB and ZnB₂. The preferential formation of the Schiff base complexes over binary species has been brought out by Scheme 32.
**Stability and structure of ZnAB, ZnAB\(_2\) and ZnA\(_2\)B\(_2\) species**

The log \(\beta_{ZnAB}\) value is 12.15, which is higher than the calculated mixed ligand stability constant value of 7.85. This indicates ZnAB to be the Schiff base complex species. The Schiff base AB can be tetradentate as in the case of Co(II), Ni(II) and Cu(II) complexes. As in the case of Co(II)/Ni(II)/Cu(II)-thiophenal-his systems, ZnAB\(_2\) can be represented as Zn(AB)B, where the Schiff base AB is tetradentate and B is bidentate. In the case of Zn(AB)\(_2\) species, both the Schiff bases AB are tridentate.

**Species distribution**

The species distribution diagrams in Figs.4.1.3.8.4a & b show that ZnAB predominates between pH 6.7 and 7.6 in 1:1 solution. The ZnAB\(_2\) is found to be formed in the higher pH level in 1:1 solution. The concentration of ZnA\(_2\)B\(_2\) is maximum at pH 8.4 in 1:2 solution.

4.1.3.8.5 **Stability enhancement in the Co(II), Ni(II) Cu(II) and Zn(II)-thiophenal-his systems**

The stabilization factor values, \(\Delta \log K_{MAB}\) calculated for M(II)-thiophenal-his systems are 4.55, 4.81, 6.39 and 3.94 for Co(II), Ni(II), Cu(II) and Zn(II) respectively. The systems follow Irving - Williams’s order of stability:

\[
\text{Co(II)} < \text{Ni(II)} < \text{Cu(II)} > \text{Zn(II)}
\]
4.1.3.9 Stability enhancement in the Co(II), Ni(II) Cu(II) and Zn(II) - thiophenal-amino acid systems

The preferential formation of Schiff base complex over the simple mixed ligand complex is effectively elucidated by comparing the observed stability constant values of the Schiff base complexes MAB, MAB$_2$ and MA$_2$B$_2$ with the calculated stabilities of the simple mixed ligand complexes. The expected stability constants are calculated using the following equations.

$$\log \beta_{\text{MAB}}^{*} = \frac{1}{2} (\log \beta_{\text{MA}}^{*} + \log \beta_{\text{MB}}^{*}) + 0.3010$$

$$\log \beta_{\text{MAB}} = \frac{1}{2} \log \beta_{\text{MA}} + \log \beta_{\text{MB}} + 0.3010$$

$$\log \beta_{\text{MA}_2\text{B}_2} = \log \beta_{\text{MA}} + \log \beta_{\text{MB}} + 0.3010$$

The experimental stability constants (log $\beta$) and computed stability constants (log $\beta^*$) are given in Tables 4.1.3.9a-d. The higher experimental log $\beta$ values compared to the corresponding log $\beta^*$ indicate preferential formation of the Schiff base complexes over the simple mixed ligand complexes.
4.2 SOLID STATE STUDIES

This part describes the synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes involving thiophenal-val (L^1), thiophenal-phe (L^2) and thiophenal-his(L^3) Schiff base ligands. Antimicrobial and DNA cleavage studies for these ligands and their metal complexes have also been discussed.

4.2.1 Synthesis of Schiff base ligands

Schiff base ligands, thiophenal-val (L^1), thiophenal-phe (L^2) and thiophenal-his(L^3) were prepared by refluxing thiophene-2-carboxaldehyde and valine/phenylalanine/histidine in 1:1 molar ratio in methanol by following the procedure given in Sec. 3.3.1(Scheme33).

4.2.2 Characterization of Schiff base ligands
The results of analytical and physical data of the Schiff base ligands are given in Table 4.2.1. All the Schiff bases are air sensitive in nature and soluble in common organic solvents like MeOH, EtOH, DMF, DMSO and CH$_3$CN.

**4.2.2.1 IR spectra**

The IR spectrum of the Schiff base ligands are shown in Figs. 4.2.2.1 and the spectral data are given in Table 4.2.2.1.

The IR spectrum of thiophenal-val shows a high intensity band at 1616 cm$^{-1}$ range is due to the imino $>$C=N stretching frequency. The strong bands were observed at 1581 and 1389 cm$^{-1}$, which can be attributed to asymmetric and symmetric carboxyl stretching frequencies respectively [134]. In addition, a band seen at 846 cm$^{-1}$ can be assigned to C-S stretching frequency of the thiophene ring[143-148].

The spectrum of thiophenal-phe shows a characteristic $>$C=N stretching frequency band at 1630 cm$^{-1}$ indicating the presence of azomethine group. The strong bands observed at 1588 and 1403 cm$^{-1}$, which can be attributed to asymmetric and symmetric carboxyl stretching frequencies respectively [134]. Further, a band seen at 839 cm$^{-1}$ can be ascribed to C-S stretching frequency[143-148].

The spectrum of thiophenal-his shows a characteristic $>$C=N stretching frequency band at 1629 cm$^{-1}$ indicating the presence of azomethine group. The strong bands observed at 1589 and 1409 cm$^{-1}$, which can be attributed to asymmetric and symmetric carboxyl stretching frequencies respectively [134]. Further, a band seen at 832 cm$^{-1}$ can be ascribed to C-S stretching frequency[143-148].

**4.2.2.2 Electronic spectra**
The electronic spectra of the Schiff base ligands were recorded in methanol solution at room temperature are given in Figs. 4.2.2.2 and the spectral data are given in Table 4.2.2.2.

The electronic spectrum of thiophenal-val shows a broad band at 300 nm, which is assigned to $\pi-\pi^*$ transition of the C=N chromophore. In addition, the intense absorption at higher energy, 250 nm, is presumably from the $\pi-\pi^*$ transition of the thiophene ring of the Schiff base.

The spectrum of thiophenal-phe shows a broad band at 310 nm, which is assigned to $\pi-\pi^*$ transition of the C=N chromophore. In addition, the intense absorption at higher energy, 240 nm, is presumably from the $\pi-\pi^*$ transition of the thiophene ring of the Schiff base. This band is probably broadened because of overlap with $\pi-\pi^*$ transition of the benzene ring of the Schiff base.

The spectrum of thiophenal-his shows a broad band centered at 275 nm, which is assigned to $\pi-\pi^*$ transition of the C=N chromophore. This band is probably broadened because of overlap with $\pi-\pi^*$ transition of the thiophene ring of the Schiff base.

### 4.2.3 Synthesis of Schiff base metal complexes

The Co(II), Ni(II), Cu(II) and Zn(II) Schiff base complexes were synthesized by the reaction of metal chlorides with thiophenal-val (L$^1$/), thiophenal-phe (L$^2$/), thiophenal-his (L$^3$/) in 1:1 (M:L) ratio in aqueous methanol medium by refluxing for
about 2 hrs (Sec. 3.3.2). The results of analytical and physical data of the Schiff base complexes are given in Table 4.2.3a-c. The complexes are stable towards air and moisture. All the complexes are partially soluble in DMF, MeCN and DMSO and insoluble in other common organic solvents. Elemental analysis values are in close harmony with the values calculated for molecular formula assigned to these complexes. Thus, the complexes can be represented by the formula MLCl, where L is the Schiff base ligand.

4.2.4 Characterization of Schiff base metal complexes

4.2.4.1 Molar conductance

The molar conductance of all the complexes was measured in DMSO using 10^{-3} M solutions at room temperature. From the conductance data (Table 4.2.3a-c), it has been observed that all the complexes are non-electrolytic in nature[158].

*Silver nitrate test*

When the complexes were treated with silver nitrate solution, no white precipitate was obtained. It shows the absence of chloride ions outside the coordination sphere in the complexes.

The complexes were heated with a mixture of concentrated nitric acid and hydrogen peroxide to dryness. After decomposing the complexes, a residue was obtained which is then treated with silver nitrate solution when white silver chloride was obtained. It demonstrates the presence of coordinated chloride ions in the complexes.

4.2.4.2 Infrared spectra

The important IR spectral data of ML^1, ML^2 and ML^3 complexes are given in Table 4.2.4.2a-c

*M(II)-L^1 complexes*
The IR spectrum of Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff baseligand \( L^1 \) are shown in Fig. 4.2.4.1.

**Co(II)-\( L^1 \) complex**

The IR spectrum of the free ligand \( L^1 \) shows the characteristic \( >\text{C}=\text{N} \) band in the 1616 cm\(^{-1} \) region which is shifted to lower frequencies (1602 cm\(^{-1} \)) in the spectrum of Co(II) complex confirming the coordination of \( >\text{C}=\text{N} \) group to Co(II) ion. The complex also displays bands at 1571 and 1389 cm\(^{-1} \) region due to the asymmetric and symmetric stretching vibration of the carboxylato group respectively, which is slightly lower than that of free Schiff base ligand indicating the linkage between the metal ion and carboxylato oxygen atom. The immense difference between \( v_{as}(\text{COO}^-) \) and \( v_s(\text{COO}^-) \) (~200 cm\(^{-1} \)) indicates the monodentate binding nature of the carboxylato group in the complexes [134, 159]. The IR spectrum of the free Schiff base ligand exhibits a sharp band at 846 cm\(^{-1} \), due to the \( \nu(\text{C-S}) \). On complexation, this band is shifted to a lower frequency in the 819 cm\(^{-1} \) range indicating the coordination of the thiophene sulphur atom to the metal ion. The new bands in the low frequency region at 468 and 530 cm\(^{-1} \) in the spectrum of the complex which are not present in the spectrum of the free ligand are assigned to stretching frequencies of (M-N) and (M-O) bonds respectively [160, 161].

**Ni(II)-\( L^1 \) complex**

The IR spectrum of the free ligand \( L^1 \) shows the characteristic \( >\text{C}=\text{N} \) band in the 1616 cm\(^{-1} \) region which is shifted to lower frequencies (1609 cm\(^{-1} \)) in the spectrum of Ni(II) complex confirming the coordination of \( >\text{C}=\text{N} \) group to Ni(II) ion. The complex also displays bands at 1575 and 1383 cm\(^{-1} \) region due to the asymmetric and symmetric stretching vibration of the carboxylato group respectively, which is slightly lower than that of free Schiff base ligand indicating the linkage between the metal ion.
and carboxylato oxygen atom. The monodentate binding nature of the carboxylato group in the complexes is indicated by the large difference between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ (~200 cm$^{-1}$)[134, 159]. The IR spectrum of the free Schiff base ligand exhibits a sharp band at 846 cm$^{-1}$, due to the $\nu$(C-S). On complexation, this band is shifted to a lower frequency in the 812 cm$^{-1}$ range indicating the coordination of the thiophene sulphur atom to the metal ion. The characterization bands in the region of 475 and 532 cm$^{-1}$ in the spectrum of the complex which are not present in the spectrum of L$^1$ are assigned to stretching frequencies of (M-N) and (M-O) bonds respectively [160, 161].

$Cu(II)$-$L^1$ complex

The IR spectrum of the free ligand ($L^1$) shows the characteristic >C=N band in the 1616 cm$^{-1}$ region which is shifted to lower frequencies (1609 cm$^{-1}$) in the spectrum of Cu(II) complex confirming the coordination of >C=N- group to Cu(II) ion. The complex also displays bands at 1574 and 1382 cm$^{-1}$ region due to the asymmetric and symmetric stretching vibration of the carboxylato group respectively, which is slightly lower than that of free Schiff base ligand indicating the linkage between the metal ion and carboxylato oxygen atom. The large difference between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ (~200 cm$^{-1}$) designates the monodentate binding nature of the carboxylato group in the complexes[134, 159]. The IR spectrum of the free Schiff base ligand exhibits a sharp band at 846 cm$^{-1}$, due to the $\nu$(C-S). On complexation, this band is shifted to a lower frequency in the 825 cm$^{-1}$ range indicating the coordination of the thiophene sulphur atom to the metal ion. The novel bands observed in the region of 448 and 537 cm$^{-1}$ in the spectrum of the complex are assigned to stretching frequencies of (M-N) and (M-O) bonds respectively[160, 161].

$Zn(II)L^1$ complex
The IR spectrum of the free ligand (L\textsuperscript{1}) shows the characteristic >C=N band in the 1616 cm\textsuperscript{-1} region which is shifted to lower frequencies (1603 cm\textsuperscript{-1}) in the spectrum of Zn(II) complex confirming the coordination of >C=N- group to Zn(II) ion. The complex also displays bands at 1570 and 1381 cm\textsuperscript{-1} region due to the asymmetric and symmetric stretching vibration of the carboxylato group respectively, which is slightly lower than that of free Schiff base ligand indicating the linkage between the metal ion and carboxylato oxygen atom. The large difference between $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ (~200 cm\textsuperscript{-1}) points out the monodentate binding nature of the carboxylato group in the complexes\cite{134, 159}. The IR spectrum of the free Schiff base ligand exhibits a sharp band at 846 cm\textsuperscript{-1}, due to the $\nu$(C-S). On complexation, this band is shifted to a lower frequency in the 815 cm\textsuperscript{-1} range indicating the coordination of the thiophene sulphur atom to the metal ion. The spectrum of the complex indicates two fresh bands observed in the low frequency region at 429 and 549 cm\textsuperscript{-1} which are assigned to stretching frequencies of (M-N) and (M-O) bonds respectively \cite{160, 161}.

Thus, the IR spectral studies show that the ligand coordinates the metal ions in a tridentate manner, capable of binding through thiophene sulphur, azomethine nitrogen and carboxylato oxygen atoms. This type of coordination is also supported by the results obtained in solution studies as discussed in Sec. 4.1.3.1.1-4

**M(II)-L\textsuperscript{2} complexes**

The IR spectrum of Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff base ligand L\textsuperscript{2} are shown in Fig 4.2.4.2.2.

**Co(II)-L\textsuperscript{2} complex**

The IR spectrum of the free ligand (L\textsuperscript{2}) shows the characteristic >C=N band in the 1630 cm\textsuperscript{-1} region which is shifted to lower frequencies (1622 cm\textsuperscript{-1}) in the spectrum of Co(II) complex confirming the coordination of >C=N- group to Co(II) ion. The
complex also displays bands at 1580 and 1382 cm$^{-1}$ region due to the asymmetric and symmetric stretching vibration of the carboxylato group respectively, which is slightly lower than that of free Schiff base ligand indicating the linkage between the metal ion and carboxylato oxygen atom. The monodentate binding nature of the carboxylato group in the complexes is indicated by the great difference between $\nu_{\text{as}}$(COO$^-$) and $\nu_{\text{s}}$(COO$^-$) (~200 cm$^{-1}$). The IR spectrum of the free Schiff base ligand exhibits a sharp band at 839 cm$^{-1}$, due to the $\nu$(C-S). On complexation, this band is shifted to a lower frequency in the 819 cm$^{-1}$ range indicating the coordination of the thiophene sulphur atom to the metal ion. The characterization bands observed in the region of 468 and 544 cm$^{-1}$ in the spectrum of the complex are assigned to stretching frequencies of (M-N) and (M-O) bonds respectively.

$\text{Ni(II)}$-$L^2$ complex

The IR spectrum of the free ligand ($L^2$) shows the characteristic $>\text{C}=\text{N}$ band in the 1630 cm$^{-1}$ region which is shifted to lower frequencies (1622 cm$^{-1}$) in the spectrum of Ni(II) complex confirming the coordination of $>\text{C}=\text{N}$- group to Ni(II) ion. The complex also displays bands at 1582 and 1381 cm$^{-1}$ region due to the asymmetric and symmetric stretching vibration of the carboxylato group respectively, which is slightly lower than that of free Schiff base ligand indicating the linkage between the metal ion and carboxylato oxygen atom. The monodentate binding nature of the carboxylato group in the complexes is shown by the huge difference between $\nu_{\text{as}}$(COO$^-$) and $\nu_{\text{s}}$(COO$^-$) (~200 cm$^{-1}$). The IR spectrum of the free Schiff base ligand exhibits a sharp band at 839 cm$^{-1}$, due to the $\nu$(C-S). On complexation, this band is shifted to a lower
frequency in the 825 cm\(^{-1}\) range indicating the coordination of the thiophene sulphur atom to the metal ion. The complex gives rise to two new bands in the low frequency region at 551 cm\(^{-1}\) and 475 cm\(^{-1}\) which can be assigned to stretching frequencies of (M-O) and (M-N) bonds respectively.

**Cu(II)-L\(_2\) complex**

The IR spectrum of the free ligand (L\(^2\)) shows the characteristic >C=N band in the 1630 cm\(^{-1}\) region which is shifted to lower frequencies (1616 cm\(^{-1}\)) in the spectrum of Cu(II) complex confirming the coordination of >C=N- group to Cu(II) ion. The complex also displays bands at 1580 and 1382 cm\(^{-1}\) region due to the asymmetric and symmetric stretching vibration of the carboxylato group respectively, which is slightly lower than that of free Schiff base ligand indicating the linkage between the metal ion and carboxylato oxygen atom. The large difference between \(\nu_{as}(COO^-)\) and \(\nu_s(COO^-)\) (~200 cm\(^{-1}\)) reveals the monodentate binding nature of the carboxylato group in the complexes. The IR spectrum of the free Schiff base ligand exhibits a sharp band at 839 cm\(^{-1}\), due to the \(\nu(C-S)\). On complexation, this band is shifted to a lower frequency in the 819 cm\(^{-1}\) range indicating the coordination of the thiophene sulphur atom to the metal ion. In the lower frequency region the weak bands observed at 558 and 461 cm\(^{-1}\) have been assigned to \(\nu(M-O)\) and \(\nu(M-N)\) vibrations, respectively.

**Zn(II)-L\(_2\) complex**

The IR spectrum of the free ligand (L\(^2\)) shows the characteristic >C=N band in the 1630 cm\(^{-1}\) region which is shifted to lower frequencies (1603 cm\(^{-1}\)) in the spectrum of the Zn(II) complex confirming the coordination of >C=N- group to Zn(II) ion. The Zn(II) complex also displays bands at 1570 and 1381 cm\(^{-1}\) region due to the asymmetric and symmetric stretching vibration of the carboxylato group respectively, which is slightly lower than that of free Schiff base ligand indicating the linkage
between the metal ion and carboxylato oxygen atom. The large difference between $\nu_{as}(\text{COO}^-)$ and $\nu_{s}(\text{COO}^-)$ (~200 cm$^{-1}$) indicates the monodentate binding nature of the carboxylato group in the complexes. The IR spectrum of the free Schiff base ligand exhibits a sharp band at 846 cm$^{-1}$, due to the $\nu$(C-S). On complexation, this band is shifted to a lower frequency in the 815 cm$^{-1}$ range indicating the coordination of the thiophene sulphur atom to the metal ion. In the lower frequency region the weak bands observed at 549 and 429 cm$^{-1}$ have been assigned to $\nu$(M-O) and $\nu$(M-N) vibrations, respectively.

From the IR spectral data, it would be concluded that the ligand L$^2$ coordinates the metal ions through thiophene sulphur, azomethine nitrogen and carboxylato oxygen atoms in a tridentate manner. This mode of binding for the ligand is comparable to the results obtained from solution equilibria as discussed in Sec.4.1.3.2.1-4

$M(II)$-$L^3$ complexes

The IR spectrum of Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff base ligand L$^3$ are shown in Fig 4.2.4.2.3

$Co(II)$-$L^3$ complex

The IR spectrum of the free ligand (L$^3$) demonstrates the characteristic $>\text{C}=\text{N}$ band in the 1629 cm$^{-1}$ region which is shifted to lower frequencies (1622 cm$^{-1}$) in the spectrum of Co(II) complex confirming the coordination of $>\text{C}=\text{N}$- group to Co(II) ion. The complex also displays bands at 1574 and 1382 cm$^{-1}$ region due to the asymmetric and symmetric stretching vibration of the carboxylato group respectively, which is slightly lower than that of free Schiff base ligand indicating the linkage between the metal ion and carboxylato oxygen atom. The monodentate binding nature of the carboxylato group in the complexes is revealed by the large difference between
ν\text{as}(\text{COO}^-) \text{ and } ν\text{s}(\text{COO}^-) (\sim 200 \text{ cm}^{-1})$. The IR spectrum of the free Schiff base ligand exhibits a sharp band at 832 cm\(^{-1}\), due to the ν(C-S). On complexation, this band is shifted to a lower frequency in the 825 cm\(^{-1}\) range indicating the coordination of the thiophene sulphur atom to the metal ion. In the lower frequency region, the weak bands observed at 537 and 461 cm\(^{-1}\) would be assigned to ν(M-O) and ν(M-N) vibrations, respectively.

**Ni(II)-L\text{\textsuperscript{3}} complex**

The IR spectrum of the free ligand (L\text{\textsuperscript{3}}) shows the characteristic >C=N band in the 1629 cm\(^{-1}\) region which is shifted to lower frequencies (1620 cm\(^{-1}\)) in the spectrum of Ni(II) complex confirming the coordination of >C=N- group to Ni(II) ion. The complex also displays bands at 1581 and 1382 cm\(^{-1}\) region due to the asymmetric and symmetric stretching vibration of the carboxylato group respectively, which is slightly lower than that of free Schiff base ligand indicating the linkage between the metal ion and carboxylato oxygen atom. The monodentate binding nature of the carboxylato group in the complexes is revealed by the appreciable difference between ν\text{as}(\text{COO}^-) \text{ and } ν\text{s}(\text{COO}^-) (\sim 200 \text{ cm}^{-1})$. The IR spectrum of the free Schiff base ligand exhibits a sharp band at 832 cm\(^{-1}\), due to the ν(C-S). On complexation, this band is shifted to a lower frequency in the 825 cm\(^{-1}\) range indicating the coordination of the thiophene sulphur atom to the metal ion. The presence of M-O and M-N bonds may be inferred by the new bands in the spectrum of Ni(II) complex in the low frequency region at 551 cm\(^{-1}\) and 461 cm\(^{-1}\) respectively.

**Cu(II)-L\text{\textsuperscript{3}} complex**

The IR spectrum of the free ligand (L\text{\textsuperscript{3}}) shows the characteristic >C=N band in the 1629 cm\(^{-1}\) region which is shifted to lower frequencies (1616 cm\(^{-1}\)) in the spectrum of Cu(II) complex confirming the coordination of >C=N- group to Cu(II) ion. The
complex also displays bands at 1581 and 1375 cm\(^{-1}\) region due to the asymmetric and symmetric stretching vibration of the carboxylato group respectively, which is slightly lower than that of free Schiff base ligand indicating the linkage between the metal ion and carboxylato oxygen atom. The monodentate binding nature of the carboxylato group in the complexes is revealed by the considerable difference between \(\nu_{as}(\text{COO}^-)\) and \(\nu_{s}(\text{COO}^-)\) (~200 cm\(^{-1}\)). The IR spectrum of the free Schiff base ligand exhibits a sharp band at 832 cm\(^{-1}\), due to the \(\nu(\text{C-S})\). On complexation, this band is shifted to a lower frequency in the 826 cm\(^{-1}\) range indicating the coordination of the thiophene sulphur atom to the metal ion. The presence of M-O and M-N bonds may be substantiated by the new bands in the low frequency region at 564 cm\(^{-1}\) and 454 cm\(^{-1}\) respectively.

**Zn(II)L\(^3\) complex**

The IR spectrum of the free ligand (L\(^3\)) shows the characteristic >C=N band in the 1629 cm\(^{-1}\) region which is shifted to lower frequencies (1619cm\(^{-1}\)) in the spectrum of Zn(II) complex confirming the coordination of >C=N- group to Zn(II) ion. The Zn(II) complex also displays bands at 1581 and 1382 cm\(^{-1}\) region due to the asymmetric and symmetric stretching vibration of the carboxylato group respectively, which is slightly lower than that of free Schiff base ligand indicating the linkage between the metal ion and carboxylato oxygen atom. The noticeable difference between \(\nu_{as}(\text{COO}^-)\) and \(\nu_{s}(\text{COO}^-)\) (~200 cm\(^{-1}\)) indicates the monodentate binding nature of the carboxylato group in the complexes. The IR spectrum of the free Schiff base ligand exhibits a sharp band at 832 cm\(^{-1}\), due to the \(\nu(\text{C-S})\). On complexation, this band is shifted to a lower frequency in the 826 cm\(^{-1}\) range indicating the coordination of the thiophene sulphur atom to the metal ion. The new bands in the low
frequency region at 562 cm\(^{-1}\) and 461 cm\(^{-1}\) confirm the M-O and M-N bonds respectively.

Thus, the IR spectral studies demonstrate that the ligand thiophenal-his coordinates the metal ion in a tridentate manner, capable of binding through thiophene sulphur, azomethine nitrogen and carboxylato oxygen atoms. This kind of binding of the ligand coincides with the results obtained in solution studies as discussed in Sec. 4.1.3.8.1-4

4.2.4.3 Electronic spectra

The electronic spectra of the ML\(^1\), ML\(^2\) and ML\(^3\) complexes were recorded at room temperature in DMSO solution and the spectral data are given in Table 4.2.4.3.a-c

**M(II)-L\(^1\) complexes**

The electronic spectrum of Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff base ligand L\(^1\) are shown in Figs. 4.2.4.3.1. The spectrum of tetrahedral Co(II) complexes is reported to have only one absorption band in the visible region due to \(^4\)\(A_2(F) \rightarrow ^4\)\(T_1(P)\) transition [135]. The spectrum of CoL\(^1\)Cl complex has only one band in the visible region at 520 nm, which indicates tetrahedral geometry for the complex.

The spectrum of NiL\(^1\)Cl complex shows an intense absorption band at 510 nm, which is due to the \(^3\)\(T_1(F) \rightarrow ^3\)\(T_1(P)\) transition indicating tetrahedral geometry [135].

The spectrum of CuL\(^1\)Cl complex exhibits a broad band centered at 750 nm due to \(^2\)\(B_{1g} \rightarrow ^2\)\(A_{1g}\) transition corresponding to square planar geometry [135].
Zn(II) complex does not exhibit any d-d electronic transition due to its completely filled d$^{10}$ electronic configuration. However, four coordinate Zn(II) complexes would have tetrahedral geometry.

**M(II)-L$^2$ complexes**

The electronic spectrum of ML$^2$ complexes is given in Figs. 4.2.4.3.2. The spectrum of CoL$^2$Cl complex shows band in the 525 nm region which is attributable to $^4A_2$(F)$\rightarrow^4T_1$(P) transition, which favours tetrahedral geometry[135].

The spectrum of NiL$^2$Cl complex shows d-d band at 650 nm, which is due to $3T_1$(F)$\rightarrow^3T_1$(P) transition observed for tetrahedral Ni(II) complexes[135].

The copper complex of L$^2$ displays a broad band in the 575 nm region which can be assigned to $^2B_{1g} \rightarrow ^2A_{1g}$ transition, indicating that Cu(II) complex has square planar geometry[135].

Zn(II) complex does not exhibit any d-d electronic transition due to its completely filled d$^{10}$ electronic configuration. However, four coordinate Zn(II) complexes would have tetrahedral geometry.

**M(II)-L$^3$ complexes**

The electronic spectrum of ML$^3$ complexes is given in Figs. 4.2.4.3.3. The spectrum of Co(II)-L$^3$ complex shows a band at 600 nm region which is attributable to $^4A_2$(F)$\rightarrow^4T_1$(P) transition, which favours its tetrahedral geometry [135]

The spectrum of Ni(II)-L$^3$ complex gives a band at 625 nm, which is due to $^3T_1$(F)$\rightarrow^3T_1$(P) transition observed for tetrahedral Ni(II) complexes [135].
The copper complex of L³ displays a broad band in the 630 nm region which can be assigned to 2B₁g → 2A₁g transition, indicating that Cu(II) complex has square planar geometry [135].

Zn(II) complex do not exhibit d-d electronic transition due to the completely filled d orbital. Four coordinate Zn(II) complexes would have tetrahedral geometry.

**4.2.4.4 Magnetic measurements**

The magnetic moment values of ML¹, ML² and ML³ complexes are given in Table 4.2.4.4a-c

**M(II)-L¹ complexes**

Tetrahedral Co(II) with a 4A₂ ground state has been reported to have magnetic moments in the range of 4.2-4.8 B.M. The present Co(II) complex has a magnetic moment of 4.48 B.M indicating its tetrahedral geometry [162].

Generally, square planar Ni(II) complexes are diamagnetic while tetrahedral complexes have moments in the range 3.2-4.1 B.M. The present NiL¹Cl complex reported herein has a room temperature magnetic moment value of 3.37 B.M, which is within the normal range observed for tetrahedral Ni(II) complex [163].

The magnetic moment value of the CuL¹Cl complex was observed to be 1.87 B.M, which corresponds to that of dsp² hybridization of Cu(II) and have square planar arrangement for the complex and it is monomeric and paramagnetic [164].

As expected Zn(II) complex is diamagnetic, the complex is suggested to be tetra coordinated probably having tetrahedral geometry based on analytical, IR and conductance data.
**M(II)-L² complexes**

The CoL²Cl complex has a magnetic moment of 4.42 B.M, which is in agreement with the reported value for tetrahedral Co(II) complex.

The present NiL²Cl complex reported herein has a room temperature magnetic moment value of 3.31 B.M, which is within the normal range observed for tetrahedral Ni(II) complex.

The magnetic moment value of the CuL²Cl complex was observed to be 1.96 B.M, which indicates that the complex is monomeric and paramagnetic.

ZnL²Cl complex with d¹⁰ electronic configuration is diamagnetic and would have tetrahedral geometry.

**M(II)-L³ complexes**

The CoL³Cl complex has a magnetic moment of 4.58 B.M, which is in agreement with the reported value for tetrahedral Co(II) complex.

The NiL³Cl complex reported herein has a room temperature magnetic moment value of 3.62 B.M, which is within the normal range observed for tetrahedral Ni(II) complex.

The magnetic moment value of the CuL³Cl complex was observed to be 2.01 B.M, which indicates that the complex is monomeric and paramagnetic.

Zn(II) complex is diamagnetic as expected for d¹⁰ systems and would have tetrahedral geometry.

Thus, the findings are in agreement with the results obtained from the electronic spectra of the complexes. Based on the above studies, one can deduce the probable structure of the Schiff base complexes are shown in Scheme 34.
4.2.4.5 Electrochemical studies

All cyclic voltammograms were recorded in acetonitrile solution at a scan rate of 100 mVs$^{-1}$ in the potential range +2.0 to -2.0V. The electrochemical data of ML$_1$, ML$_2$ and ML$_3$ complexes are summarized in Table 4.2.4.5a-c

**M(II)-L$_1$ complexes**

The cyclic voltammograms of L$_1$ complexes are given in Fig. 4.2.4.5.1. The cyclic voltammogram of CoL$_1$Cl complex shows a well defined redox process corresponding to the formation of the quasi-reversible Co(II)/Co(I) couple. The
cathodic peak at −0.754 V versus Ag/AgCl and the associated anodic peak at −0.591 V corresponds to the Co(II)/Co(I) couple. The peak to peak separation (ΔEp = 0.163 V) indicates a quasi-reversible one electron transfer process.

The NiL₁Cl complex does not show any peak in this potential range under similar conditions indicating the complex is electrochemically inactive.

The CuL₁Cl complex displayed two reduction couples at +0.066 V and -0.806 V versus Ag/AgCl with the corresponding anodic waves at +0.345 and at -0.612 V on the reverse scan. The peak separation values (ΔEp = 279 & 194 mV) indicate totally quasi-reversible character for the one electron transfer reaction of metal-based Cu(II)/Cu(I) and Cu(I)/Cu(0) couples.

The ZnL₁Cl complex does not show any peak in this potential range under similar conditions indicating the complex is electrochemically inactive.

**M(II)-L² complexes**

The cyclic voltammograms of L² complexes are given in Fig 4.2.4.5.2. The redox property of CoL²Cl displayed reduction peak at Epc -0.329 V. During the reverse scan the oxidation peak occurs in the potential range Epa -0.10 V. The peak to peak separation (ΔEp) is 319 mV indicating the process to be quasi-reversible Co(II)/Co(I) couple.

The NiL²Cl complex does not show any peak in this potential range under similar conditions indicating the complex is electrochemically inactive.

The CuL²Cl complex displayed a cathodic peak at -0.862 V versus Ag/AgCl with the corresponding anodic wave at -0.634 V on the reverse scan. The peak
separation value (ΔEp= 0.228 V) indicates a totally quasi-reversible character for the one electron transfer reaction of metal-based Cu(II)/Cu(I) couple.

The ZnL²Cl complex does not show any peak in this potential range under similar conditions indicating the complex is electrochemically inactive.

*M(II)-L³ complexes*

The cyclic voltammograms of L³ complexes are given in Fig4.2.4.5.3. The cyclic voltammogram of the CoL³Cl complex shows a well defined redox process corresponding to the formation of the quasi-reversible Co(II)/Co(I) couple. The cathodic peak at −0.872 V versus Ag/AgCl and the associated anodic peak at −0.640 V corresponds to the Co(II)/Co(I) couple. The peak to peak separation (ΔEp = 0.232 V) indicates a quasi-reversible one electron transfer process.

The redox property of the NiL³Cl complex displayed an anodic and associated cathodic peaks at -0.898 and -0.746 V respectively, corresponding to the formation of the quasi-reversible(ΔEp = 0.152 V) one electron reduction Ni(II)/Ni(I) couple.

The CuL³Cl complex displays a cathodic peak at -0.866 V versus Ag/AgCl with the corresponding anodic wave at -0.656 V on the reverse scan. The peak separation value (ΔEp=0.210 V) indicates a totally quasi-reversible character for the one electron transfer reaction of metal-based Cu(II)/Cu(I) couple.

The ZnL³Cl complex does not show any peak in this potential range under similar conditions indicating the complex is electrochemically inactive.

4.2.4.6 Thermal analysis

Thermogravimetric studies have been made in the temperature range 35-900 °C. The thermal stability data of the complexes are listed in Tables 4.2.4.6a-c

*M(II)-L¹ complexes*
The thermograms of $L^1$ complexes are shown in Figs. 4.2.4.6.1. Thermal decomposition curves of $CoL^1Cl$, $NiL^1Cl$, $CuL^1Cl$ and $ZnL^1Cl$ complexes show a similar sequence of two decomposition steps. The thermograms show no weight loss up to $300^\circ C$, indicating the absence of water molecule in the complexes. The first stage of decomposition starts at 300 and ends with $550^\circ C$ corresponding to $\sim 60\%$ weight loss. The weight loss may be due to the loss of chloride ion and partial decomposition of coordinated ligand. This step is accompanied by an endothermic peak at 350-550$^\circ C$ range. The next exothermic step of the thermal degradation that occurs between $550–700^\circ C$ ($\sim 20\%$ weight loss) corresponds to the removal of remaining organic ligand moiety leaving a metal oxide residue.

$M(II)-L^2$ complexes

The thermograms of $L^2$ complexes are shown in Figs. 4.2.4.6.2. Thermal decomposition curves of $CoL^2Cl$, $NiL^2Cl$, $CuL^2Cl$ and $ZnL^2Cl$ complexes show a similar sequence of two decomposition steps. The thermograms show no weight loss up to $300^\circ C$, indicating the absence of water molecule in the complexes. The first stage of decomposition starts at 298 and ends with $500^\circ C$ corresponding to $\sim 60\%$ weight loss. The weight loss may be due to the loss of chloride ion and partial decomposition of coordinated ligand. This step is accompanied by an endothermic peak at 350-550$^\circ C$ range. The next exothermic step of the thermal degradation that occurs between $510–680^\circ C$ ($20\%$ weight loss) corresponds to the removal of remaining organic ligand moiety leaving a metal oxide residue.

$M(II)-L^3$ complexes

The thermograms of $L^3$ complexes are shown in Fig. 4.2.4.6.3. Thermal decomposition curves of the $CoL^3Cl$, $NiL^3Cl$, $CuL^3Cl$ and $ZnL^3Cl$ complexes show a similar sequence of two decomposition steps. The thermograms show no weight loss
upto 300°C, indicating the absence of water molecule in the complexes. The first stage of decomposition starts at 310 and ends with 475°C corresponding to ~60% weight loss. The weight loss may be due to the loss of chloride ion and partial decomposition of coordinated ligand. This step is accompanied by an endothermic peak at ~400-420°C range. The next exothermic step of the thermal degradation that occurs between 460–650°C (20% weight loss) corresponds to the removal of remaining organic ligand moiety leaving a metal oxide residue.

4.2.5 Biological studies

4.2.5.1 Antimicrobial studies

Antimicrobial activities of the ligands [Table 4.2.5.1] and their complexes have been carried out against the bacteria species, *Escherichia coli*, *Pseudomonasaeruginosa*, *Klebsiella pneumoniae*, *proteus vulgaris*, and *Staphylococcus aureus*; fungal species, *Aspergillus niger* and *Candida albicans*. The results of the antimicrobial activities are summarized in Table 4.2.5.1a-c Antimicrobial activity images of Schiff base ligands and their metal complexes are presented in Figs. 4.2.5.1a & b.

In general, metal complexes are more efficacy than the free ligands towards the microorganisms. Such increased activity for the metal chelates as compared to the free ligands can be explained on the basis of chelation theory [69]. The mechanism of toxicity of the complexes with the ligand may be ascribed to the increase of the lipophilic nature of the complexes arising from chelation. Chelation considerably reduces the polarity of the metal ion because of the partial sharing of its positive charge with the donor groups and possible π-electron delocalization over the chelate.
ring. Such chelation could increase the lipophilic character of the central metal atom, which subsequently favors the permeation through the lipid layer of cell membrane. The difference in antimicrobial activity is due to nature of metal ion and also cell membranes [165]. The mode of action of antimicrobials may involve different targets in pathogens, e.g. interference with the cell wall synthesis and damage to the cytoplasmic membrane, as a result of which cell permeability may be altered leading to cell death. The enhanced activity of the complexes can also be explained on the basis of their high solubility, fineness of the particles, size of the metal ion and the presence of bulkier organic moieties [166, 167]. Further, it increases the delocalization-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and restricts further multiplicity of the microorganisms.

In the present study, the antimicrobial activity of the ligands and their metal complexes indicate that the complexes acquire higher growth compared to those of ligands as seen in earlier reports [168]. However, the bioactivity of the compound varies with metal ions which form complexes with different Schiff base ligands.

**Thiophenal-val (L^1) and its complexes**

The Schiff base ligand, thiophenal-val (L^1) and Cu(II) complex have less activity against most of the microbes. Zn(II) complex has moderate activity against *E. coli* with medium inhibitory zone, while very sensitive against *S. aureus* with high inhibitory zone. Ni(II) complex is effective against *P. aeruginosa* whereas higher antimicrobial activity has been exhibited by Co(II) complex for *E. coli* and moderate activity towards *P. aeruginosa*. The activity of all the complexes is almost same.
against the fungal species *C.albicans*. The bioactivity of the thiophenal-val (L^1) and its complexes are found to be in the order: Co(II)>Ni(II)>Zn(II)>Cu(II)>ligand.

**Thiophenal-phe (L^2) and its complexes**

As seen in Table 4.2.5.1b, it can be demonstrated that the newly prepared Schiff base, thiophenal-phe (L^2) and its metal complexes show a higher effect on *C.albicans*. The Schiff base and its metal complexes are more toxic on *C.albicans* than *A. niger*, probably due to the presence of phenyl group, which might interact with the double membrane. The bioactivity of the thiophenal-phe (L^2) and its complexes is found to be in the order: Ni(II)>Co(II)>Cu (II)>Zn(II)>ligand.

**Thiophenal-his (L^3) and its complexes**

From Table 4.2.5.1c, it is evident that thiophenal-his (L^3) complexes have more activity against most of the microbes compared to that of other Schiff base complexes. The bioactivity of all the complexes is same against *K.pneumoniae*, *P.vulgaris* and *C.albicans*. This may be due to the presence of heterocyclic imidazole ring there in. In addition, the higher inhibition of microbial growth can be ascribed to the uncoordinated hetero atoms and carboxylic moieties. In the thiophenal-his (L^3) complexes, the ligand have uncoordinated donor atoms, which enhance the activity of the complexes by bonding with trace elements present in microorganism. This may combine with the uncoordinated site and inhibit the growth of microorganism. The bioactivity of the thiophenal-his (L^3) and its complexes are found to be in the order: Cu(II)>Co(II)>Zn>Ni(II)>ligand.

Antimicrobial activity of all the complexes at low concentration towards the microbes is very low. The activity of the Schiff base ligands and their complexes increases with the increasing concentration because the concentration plays a vital role in increasing the degree of inhibition. The mode of action of the complexes may
involve the formation of the hydrogen bond through the azomethine group (>C=N) with the active centers of the cell constituents resulting in the interference with normal cell process.

4.2.5.2 DNA cleavage studies

Gel electrophoresis experiments using pUC19 DNA were performed with Schiff base ligands and their complexes in the presence of H₂O₂ as oxidant. At micromolar concentrations for 2hrs incubation periods, the ligands exhibit no significant cleavage activity in the presence of H₂O₂. The nuclease activity is greatly enhanced by the incorporation of metal ions with the respective Schiff base ligands. From Fig.4.2.5.2b, it is evident that the complexes cleave DNA more efficiently in the presence of oxidant, which may be due to the formation of hydroxyl free radicals. The production of hydroxyl free radical is due to the reaction between the metal complex and oxidant. These hydroxyl free radicals participate in the oxidation of the deoxyribose moiety, followed by the hydrolytic cleavage of the sugar phosphate backbone [169]. The more pronounced nuclease activity in the metal complexes in the presence of H₂O₂ as oxidant may be due to the increased production of hydroxyl radicals [170]. The production of hydroxyl radical due to the reaction between the metal complex and oxidant may be explained as shown below.

\[
\begin{align*}
M(II)L + e^- & \rightarrow M(I)L \\
M(I)L + O_2 & \rightarrow M(II)L + O_2^- \\
2O_2^- + 2H^+ & \rightarrow H_2O_2 + O_2 \\
M(I)L + H_2O_2 & \rightarrow M(II)L + OH^- + OH^* \\
O_2^- + H_2O_2 & \rightarrow O_2 + OH^- + OH^*
\end{align*}
\]
The cleavage efficiency was measured by determining the ability of the complex to convert the Supercoiled DNA to nicked (open circular) form or sheared form. As can be seen from Fig.4.2.5.2a-c, there is a considerable increase in the intensity of bands for open circular form in the case of samples.
4.3 COMPUTATIONAL STUDIES

4.3.1 Computational studies of Schiff base ligands

In this part, the results and discussion related to the computational studies of Schiff base ligands viz. thiophenal-valine (val)/ phenylalanine (phe)/ tryptophan (trp)/ threonine (thr)/ glutamine (gln)/ glutamic acid (glu)/ aspartic acid (asp)/histidine (his) are discussed.

4.3.1.1 Thiophenal-val

The numbering pattern, 3-D structure and electrostatic potential diagram of thiophenal-val are shown in Figs. 4.3.1.1a-d. The parameters such as bond lengths, bond angles, atomic charges and Mulliken electron population are given in Tables 4.3.1.1a-c. The geometrical parameters are in good agreement with the experimental values. The Schiff base thiophenal-val is a non-planar molecule. Based on the Mulliken charge density [171-173], it was observed that thiophenal-val has four electronegative hetero atoms viz. S₁, N₇, O₁₀ and O₁₁. The carboxylato group can take part in coordination either through O₁₀ or O₁₁. But O₁₀ is the carbonyl oxygen of carboxylato group. Therefore the coordination through O₁₀ can be neglected. Thus, the possible donor atoms in thiophenal-val are S₁, N₇ and O₁₁. Thus, it can function as a potentially tridentate ligand.
The Mulliken electron population of thiophenal-val shows that the thiophene ring sulphur (S₁) can coordinate through σ orbital, azomethine nitrogen (N₇) through pₓ orbital and carboxylato oxygen (O₁₁) through pₓ orbital.

The dipole moment values, HOMO, LUMO, band gap, ionization potential and number of filled levels of thiophenal-val are given in Tables 4.3.1.1d & e. As can be seen in Table 4.3.1.1d, thiophenal-val contributes the dipole moment along all the three axes and higher value has been observed for y-axis compared with x and
This would be due to the non-planar nature of the molecule. The total dipole moment value indicates that thiophenal-val is soluble in polar solvents. Based on ionization potential and band gap, it can be concluded that thiophenal-val is stable and a hard molecule. It has thirty-eight filled orbitals.

4.3.1.2 Thiophenal-phe

The numbering pattern, 3-D structure, and electrostatic potential diagram of thiophenal-phe are shown in Figs. 4.3.1.2a-d. The parameters such as bond lengths, bond angles, atomic charges, and Mulliken electron population are given in Tables 4.3.1.2a-c. The geometrical parameters are in good agreement with the experimental values. The Schiff base thiophenal-phe is a non-planar molecule. Based on the Mulliken charge density, it was observed that thiophenal-phe has four electronegative hetero atoms viz. S₁, N₇, O₁₀, and O₁₁. The carboxylato group can take part in coordination either through O₁₀ or O₁₁. But O₁₀ is the carbonyl oxygen of carboxylato group. Therefore the coordination through O₁₀ can be neglected. Thus, the possible donor atoms in thiophenal-phe are S₁, N₇, and O₁₁. Thus, it can function as a potentially tridentate ligand. The Mulliken electron population of thiophenal-phe shows that the thiophene ring sulfur (S₁) can coordinate through s orbital, azomethine nitrogen (N₇) through pₓ orbital and carboxylato oxygen (O₁₁) through pₓ orbital.

The dipole moment values, HOMO, LUMO, band gap, ionization potential, and number of filled levels of thiophenal-phe are given in Tables 4.3.1.2d & e. As can be seen in Table 4.3.1.2d, thiophenal-phe contributes the dipole moment along all the three axes and higher value has been observed for y-axis compared with x and z-axis. This may be due to the non-planar nature of the molecule. The total dipole moment value indicates that thiophenal-phe is soluble in polar solvents. Based on ionization potential...
and band gap, it can be concluded that thiophenal-pheis stable and a hard molecule. It has forty six filled orbitals.

4.3.1.3 Thiophenal-trp

The numbering pattern, 3-D structure and electrostatic potential diagram of thiophenal-trp are shown in Figs. 4.3.1.3a-d. The parameters such as bond lengths, bond angles, atomic charges and Mulliken electron population are given in Tables 4.3.1.3a-c. The geometrical parameters are in good agreement with the experimental values. The Schiff base thiophenal-trp is a non-planar molecule. Based on the Mulliken charge density, it was observed that thiophenal-trphas five electronegative hetero atoms viz. S₁, N₇, O₁₀, O₁₁ and N₂₁. The indolering nitrogen, N₂₁ has a hydrogen atom attached to it. Therefore the binding possibility of N₂₁ to the metal ion can be neglected. Similarly, the carboxylato group can take part in coordination either through O₁₀ or O₁₁. But O₁₀ is the carbonyl oxygen of carboxylato group. Therefore the coordination through O₁₀ can be neglected. Thus, the possible donor atoms in thiophenal-trp are S₁, N₇ and O₁₁. Thus, it can function as a potentially tridentate ligand. The Mulliken electron population of thiophenal-trp shows that the thiophene ring sulphur (S₁) can coordinate through s orbital, azomethine nitrogen (N₇) through pz orbital and carboxylato oxygen (O₁₁) through py orbital.

The dipole moment values, HOMO, LUMO, band gap, ionization potential and number of filled levels of thiophenal-trp are given in Tables 4.3.1.3d & e. As can be seen in Table 4.3.1.3d, thiophenal-trp contributes the dipole moment along all the three axes and higher value has been observed for y-axis compared with z and x-axis. This may be due to the non-planar nature of the molecule. The total dipole moment value indicates that thiophenal-trp is soluble in polar solvents. Based on ionization potential
and band gap, it can be concluded that thiophenal-trpis stable and a hard molecule. It has fifty three filled orbitals.

4.3.1.4 Thiophenal-thr

The numbering pattern, 3-D structure and electrostatic potential diagram of thiophenal-thr are shown in Figs. 4.3.1.4a-d. The parameters such as bond lengths, bond angles, atomic charges and Mulliken electron population are given in Tables 4.3.1.4a-c. The geometrical parameters are in good agreement with the experimental values. The Schiff base thiophenal-thr is a non-planar molecule. Based on the Mulliken charge density, it was observed that thiophenal-thr has four electronegative hetero atoms viz. S₁, N₇, O₁₀, O₁₁ and O₁₄. The carboxylato group can take part in coordination either through O₁₀ or O₁₁. But O₁₀ is the carbonyl oxygen of carboxylato group. Therefore the coordination through O₁₀ can be neglected. Thus, the possible donor atoms in thiophenal-thr are S₁, N₇, O₁₁ and O₁₄. Thus, it can function as a potentially tetradentate ligand. The Mulliken electron population of thiophenal-thr shows that the thiophene ring sulphur (S₁) can coordinate through s orbital, azomethine nitrogen (N₇) through pₓ orbital and both carboxylato oxygen (O₁₁) and hydroxyl oxygen (O₁₄) through s orbital.

The dipole moment values, HOMO, LUMO, band gap, ionization potential and number of filled levels of thiophenal-thr are given in Tables 4.3.1.4d & e. As can be seen in Table 4.3.1.4d, thiophenal-thr contributes the dipole moment along all the three axes and higher value has been observed for x-axis compared with y and z-axis. This may be due to the non-planar nature of the molecule. The total dipole moment value indicates that thiophenal-thr is soluble in polar solvents. Based on ionization potential and band gap, it can be concluded that thiophenal-thr is stable and a hard molecule. It has thirty eight filled orbitals.
4.3.1.5 Thiophenal-gln

The numbering pattern, 3-D structure and electrostatic potential diagram of thiophenal-gln are shown in Figs. 4.3.1.5a-d. The parameters such as bond lengths, bond angles, atomic charges and Mulliken electron population are given in Tables 4.3.1.5a-c. The geometrical parameters are in good agreement with the experimental values. The Schiff base thiophenal-gln is a non-planar molecule. Based on the Mulliken charge density, it was observed that thiophenal-gln has six electronegative hetero atoms viz. $S_1$, $N_7$, $O_{10}$, $O_{11}$, $O_{15}$ and $N_{16}$. The carboxylato group can take part in coordination either through $O_{10}$ or $O_{11}$. But $O_{10}$ is the carbonyl oxygen of carboxylato group. Therefore the coordination through $O_{10}$ can be neglected. Thus, the possible donor atoms in thiophenal-gln are $S_1$, $N_7$, $O_{11}$, $O_{15}$ and $N_{16}$. However, it has been well documented that the amide group cannot take part in coordination. Thus, it can function as a potentially tridentate ligand. The Mulliken electron population of thiophenal-gln shows that the thiophene ring sulphur ($S_1$) can coordinate through $s$ orbital, azomethine nitrogen ($N_7$) through $p_z$ orbital and carboxylato oxygen ($O_{11}$) through $p_x$ orbital.

The dipole moment values, HOMO, LUMO, band gap, ionization potential and number of filled levels of thiophenal-gln are given in Tables 4.3.1.5d & e. As can be seen in Table 4.3.1.5d, thiophenal-gln contributes the dipole moment along all the three axes and higher value has been observed for $z$-axis compared with $x$ and $y$-axis. This may be due to the non-planar nature of the molecule. The total dipole moment value indicates that thiophenal-gln is soluble in polar solvents. Based on ionization potential and band gap, it can be concluded that thiophenal-gln is stable and a hard molecule. It has forty three filled orbitals.

4.3.1.6 Thiophenal-glu
The numbering pattern, 3-D structure and electrostatic potential diagram of thiophenal-glu are shown in Figs. 4.3.1.6a-d. The parameters such as bond lengths, bond angles, atomic charges and Mulliken electron population are given in Tables 4.3.1.6a-c. The geometrical parameters are in good agreement with the experimental values. The Schiff base thiophenal-glu is a non-planar molecule. Based on the Mulliken charge density, it was observed that thiophenal-glu has six electronegative hetero atoms viz. S1, N7, O10, O11, O15 and O16. As discussed earlier, the carboxylato group can coordinate only through hydroxyl oxygen. Thus, the possible donor atoms in thiophenal-glu are S1, N7, O11 and O16. Thus, it can function as a potentially tetradentateligand. The Mulliken electron population of thiophenal-glu shows that the thiophene ring sulphur (S1) can coordinate through s orbital, azomethine nitrogen (N7) through p_z orbital and both carboxylato oxygen O11 through s orbital and O16 through p_z orbital.

The dipole moment values, HOMO, LUMO, band gap, ionization potential and number of filled levels of thiophenal-glu are given in Tables 4.3.1.6d & e. As can be seen in Table 4.3.1.6d, thiophenal-glu contributes the dipole moment along all the three axes and higher value has been observed for y-axis compared with x and z-axis. This may be due to the non-planar nature of the molecule. The total dipole moment value indicates that thiophenal-glu is soluble in polar solvents. Based on ionization potential and band gap, it can be concluded that thiophenal-glu is stable and a hard molecule. It has forty three filled orbitals.

4.3.1.7 Thiophenal-asp

The numbering pattern, 3-D structure and electrostatic potential diagram of thiophenal-asp are shown in Figs. 4.3.1.7a-d. The parameters such as bond lengths, bond angles, atomic charges and Mulliken electron population are given in Tables
4.3.1.7a-c. The geometrical parameters are in good agreement with the experimental values. The Schiff base thiophenal-asp is a non-planar molecule. Based on the Mulliken charge density, it was observed that thiophenal-asphas six electronegative hetero atoms viz. S$_1$, N$_7$, O$_{10}$, O$_{11}$, O$_{14}$ and O$_{15}$. As discussed earlier, the carboxylato group can coordinate only through hydroxyl oxygen. Thus, the possible donor atoms in thiophenal-asp are S$_1$, N$_7$, O$_{11}$ and O$_{15}$. Thus, it can function as a potentially tetradentateligand. The Mulliken electron population of thiophenal-asp shows that the thiophene ring sulphur (S$_1$) can coordinate through s orbital, azomethine nitrogen (N$_7$) through p$_z$ orbital and carboxylato oxygens O$_{11}$ & O$_{15}$ through s orbital.

The dipole moment values, HOMO, LUMO, band gap, ionization potential and number of filled levels of thiophenal-asp are given in Tables 4.3.1.7d & e. As can be seen in Table 4.3.1.7d, thiophenal-asp contributes the dipole moment along all the three axes and higher value has been observed for y-axis compared with z and x-axis. This may be due to the non-planar nature of the molecule. The total dipole moment value indicates that thiophenal-asp is soluble in polar solvents. Based on ionization potential and band gap, it can be concluded that thiophenal-asp is stable and a hard molecule. It has forty filled orbitals.

4.3.1.8 Thiophenal-his

The numbering pattern, 3-D structure and electrostatic potential diagram of thiophenal-his are shown in Figs. 4.3.1.8a-d. The parameters such as bond lengths, bond angles, atomic charges and Mulliken electron population are given in Tables 4.3.1.8a-c. The geometrical parameters are in good agreement with the experimental values. The Schiff base thiophenal-his is a non-planar molecule. Based on the Mulliken charge density, it was observed that thiophenal-hishas six electronegative hetero atoms viz. S$_1$, N$_7$, O$_{10}$, O$_{11}$, N$_{14}$ and N$_{16}$. As discussed earlier, the carboxylato
group can coordinate only through $O_{11}$. The hetero atoms in the imidazole group of thiophenal-his can have the possibility of coordination with metal ions using $N_{14}$ and $N_{16}$. However, it has been well documented that the imidazole group can take part in coordination only through $N_{14}$. Further, $N_{16}$ atom has a hydrogen atom attached to it. Hence, it can be concluded that the imidazole group of thiophenal-his can coordinate the metal ion through $N_{14}$ atom. Thus, the possible donor atoms in thiophenal-his are $S_1$, $N_7$, $O_{11}$ and $N_{14}$. Thus, it can function as a potentially tetradentateligand.

The Mulliken electron population of thiophenal-his shows that the thiophene ring sulphur ($S_1$) can coordinate through $s$ orbital, azomethine nitrogen ($N_7$) through $p_z$ orbital and $O_{11}$ and $N_{14}$ through $p_y$ and $s$ orbitals respectively.

The dipole moment values, HOMO, LUMO, band gap, ionization potential and number of filled levels of thiophenal-his are given in Tables 4.3.1.8d & e. As can be seen in Table 4.3.1.8d, thiophenal-his contributes the dipole moment along all the three axes and higher value has been observed for $z$-axis compared with $y$ and $x$-axis. This may be due to the non-planar nature of the molecule. The total dipole moment value indicates that thiophenal-his is soluble in polar solvents. Based on ionization potential and band gap, it can be concluded that thiophenal-his is stable and a hard molecule. It has forty four filled orbitals.

### 4.3.2 Computational studies of Ni(II)-thiophenal-valcomplex

The 3-D structures of Ni(II)-AB for all the eight systems *viz.* thiophenal-val, thiophenal-phe, thiophenal-trp, thiophenal-thr, thiophenal-gln, thiophenal-asp, thiophenal-glu and thiophenal-his with minimum steric energy are presented in Figs. 4.3.2.1-8. For the selected Ni(II)-thiophenal-val system, the Huckel energy on the atoms as well as the geometrical parameters such as bond lengths and bond angles...
have been generated. A comparative account of these parameters for AB and NiAB has been discussed.

4.3.2.1 Huckel charges

The Huckel charges of the Ni(II)-thiophenal-val system have been offered in Table 4.3.2.1. The formal charge of +2 on the Ni(II) on coordination with the imino nitrogen, thiophenering sulphur, carboxylato and aquo oxygen atoms changes to -0.825eV which indicates effective coordination of Schiff base with the metal ion. When Schiff base coordinates with the Ni(II) metal, the charge on thiophene ring sulphur atom has been increased from 0.8817 to 2.14577. The charge on the imino nitrogen atom has also been increased from -0.336889 to 0.30525. The overall charge around the central metal ion is ~ 1.2672. These values show that the NiAB Schiff base complex is quite stable.

4.3.2.2 Bond lengths and Bond angles

The bond lengths and bond angles of the coordinating atoms in Ni(II)-thiophenal-val system have been presented in Table 4.3.2.2&3. In NiAB complex, the bond lengths between the imino nitrogen atom and Ni(II) and the carboxylato oxygen atoms and Ni(II) are close to each other and they are near to the expected values. The bond length between the thiophenesulphur atom and Ni(II) is higher indicating that the bond is little weaker.

The bond angle values in NiAB suggest that the structure is not perfectly tetrahedral or square planar. In order to have minimum steric energy, it attains a distorted tetrahedral shape.
SUMMARY AND CONCLUSION

The present investigation deals with the solution equilibria, solid state and computational studies of some Schiff base ligands and their metal complexes. The equilibrium studies by batchwise pH titration method were carried out for thirty two Schiff base metal complex systems viz. M(II)-thiophenal-val/phe/trp/thr/gln/glu/asp/his \([M = \text{Co, Ni, Cu and Zn}]\). All the studies were carried out at 25 ± 0.1°C and \(\mu = 0.1 \text{ mol dm}^{-3} \text{KNO}_3\). The pH-titration data have been analyzed with the aid of the computer program ‘SCOGS’. Twelve Schiff base metal complex systems viz. M(II)-thiophenal-val, thiophenal-phe and thiophenal-his \([M = \text{Co, Ni, Cu and Zn}]\) were synthesized and characterized by elemental analysis, molecular weight determination, infra red, electronic spectra, magnetic measurements, cyclic voltammetry and thermal analysis. Antimicrobial and DNA cleavage studies for these ligands and their metal complexes have also been carried out. The computational studies of Schiff base ligands viz. thiophenal-valine (val)/ phenylalanine (phe)/ tryptophan (trp)/ threonine (thr)/ glutamine (gln)/ glutamic acid (glu)/ aspartic acid (asp)/ histidine (his) are discussed.

In the Introductory Chapter of the thesis has a short introduction about solution chemistry, synthesis and characterization, computation and biological studies of Schiff base metal complexes. A brief review related to the present study is incorporated in the Chapter II. This Chapter ends with scope of the present investigation. The Chapter III describes the general experimental methods and analytical procedures used. The fourth Chapter deals with Results and Discussion. This Chapter is divided into three parts. The first part comprises the solution equilibria of thirty two Schiff base metal complex systems viz. M(II)-thiophenal(A)-amino acids (B) \([M(II) = \text{Co/Ni/Cu/Zn and } B = \text{val/phe/trp/thr/gln/glu/asp/his}]\) by
batchwise pH titration method at 25 ± 0.1 °C and µ = 0.1mol.dm⁻³ (KNO₃). The second part deals with synthesis, characterization and biological activities of thiophenal-val, thiophenal-phe and thiophenal-his and their Co(II), Ni(II), Cu(II) and Zn(II) complexes. The third part deals with the computational studies of Schiff base ligands \( \text{viz.} \) thiophenal-valine (val)/ phenylalanine (phe)/ tryptophan (trp)/ threonine (thr)/ glutamine (gln)/ glutamic acid (glu)/ aspartic acid (asp)/ histidine (his) are discussed. At the end, a bibliography containing selective and relevant references is included.

The present investigation leads to the following major conclusions.

1. Analysis of pH titration data of the M(II)-thiophenal systems revealed the presence of MA and MA₂ species in addition to HA species. From the values of stability constants, it is concluded that the ligand thiophenal coordinates with the metal ion in a bidentate manner through thiophene ring sulphur and carbonyl oxygen atoms.

2. Three types of ternary complexes of stoichiometry MAB, MAB₂ and MA₂B₂ have been detected in the complex systems under investigation. In all the cases, the experimentally calculated stability constant values were found to be much higher compared to those calculated on the assumption that they are simple mixed ligand complexes. This trend has been accounted by considering inter-ligand interaction between thiophenal and amino acid forming stable Schiff base complexes. Thus, MAB, MAB₂ and MA₂B₂ complexes are Schiff base metal complexes.

3. The results on MAB complexes in Co(II)/Ni(II)/Zn(II)-thiophenal-val/phe/trp/thr/gln/glu systems indicate that the Schiff base (AB) is tridentate.
The slightly higher stability constant values in thiophenal-thr/gln/glu systems over that in thiophenal-val system can be accounted by considering molecular recognition in the former systems. The trend in the log $\beta$ values in Co(II)/Ni(II)/Zn(II)-thiophenal-asp/his systems demonstrate the tetradebate binding of the Schiff base ligand in MAB. In the CuAB species in Cu(II)-thiophenal-val/phe/trp systems the results indicate that (AB) is tridentate. However, Cu(II)-thiophenal-thr/gln/glu/asp/his systems, the Schiff base binds in tetradebate manner.

4. Co(II)/Ni(II)/Zn(II)-thiophenal-val/phe/trp/thr/gln/glu/asp/his systems showed the presence of $\text{MAB}_2$ species, where also the experimental stability constant values are higher than log $\beta$ value for simple mixed ligand species of the type $\text{MA(B)}_2$. This indicates that $\text{MAB}_2$ species is a mixed ligand Schiff base complex of the type $\text{M(AB)B}$. In the thiophenal-val/phe/trp/thr/gln/glu systems, the results indicate that the Schiff base (AB) is tridentate and ligand B is bidentate and in Co(II)/Ni(II)/Zn(II)-thiophenal-asp/his systems, (AB) is tetradebate and B is bidentate. In Cu(II)-thiophenal-val/phe/trp systems, the results point out that the Schiff base (AB) is tridentate and ligand B is bidentate whereas Cu(II)-thiophenal-thr/gln/glu/asp/his systems, (AB) is tetradebate and B is bidentate.

5. $\text{MA}_2\text{B}_2$ type of species has been detected in Co(II)/Ni(II)/Zn(II) -thiophenal-val/phe/trp/thr/gln/glu/asp/his systems and these complexes can be represented as $\text{M(AB)}_2$. The results clearly show that in all these complexes, both the Schiff base ligands bind in a tridentate manner. In thiophenal-thr systems, the results specify a change in the coordination site with the hydroxyl group replacing the carboxylato group.
6. Electronic spectral studies carried out for MAB species in the Co(II)/Ni(II)-thiophenal-val/phe/trp/thr/gln/glu/asp/his systems show that M(II) has tetrahedral geometry and Cu(II) metal complexes have square planar geometry. The same studies for the MA$_2$B$_2$ species show that MA$_2$B$_2$ has octahedral geometry.

7. The calculated values of $\Delta \log K_{MAB}$ for Co(II), Ni(II), Cu(II) and Zn(II) ternary systems show that the enhancement in the stability of the Schiff base complexes follow the Irving - Williams order of stability.

8. The species distribution diagrams have been obtained for all the thirty two Schiff base complex systems. The diagrams indicate that the Schiff base complex MAB is predominant in 1:1 systems, while M(AB)$_2$ is a major species in 1:2 systems. From the distribution diagrams, it is revealed that the MAB species is formed comparatively at lower pH for all the systems and MAB$_2$/MA$_2$B$_2$ species is formed in predominant amount as the pH increases.

9. Schiff base ligands, thiophenal-val ($L^1$)/ thiophenal-phe ($L^2$)/ thiophenal-his ($L^3$) were prepared by refluxing thiophene-2-carboxaldehyde and valine/phenylalanine/histidine in 1:1 molar ratio in methanol. All the Schiff bases are air sensitive in nature and soluble in common organic solvents like MeOH, EtOH, DMF, DMSO and CH$_3$CN.

10. Co(II), Ni(II), Cu(II) and Zn(II) complexes of these Schiff base ligand were synthesized and characterized. The infrared spectral data show that Schiff base ligand AB is tridentate, binding through imino nitrogen, thiophene ring sulphur and carboxylato oxygen. The Electronic spectral studies coupled with
magnetic moment values predict tetrahedral structure for Co(II)/Ni(II)/Zn(II) complexes and square planar structure for Cu(II) complexes.

11. Co(II) and Cu(II) have been found to be stabilized in the unusual oxidation states of the metal during electrolysis, whereas Ni(II) and Zn(II) complexes do not show any peak in this potential range under similar conditions indicating the complexes are electrochemically inactive.

12. The results of thermal studies of the complexes indicate the absence of lattice as well as coordinated water molecules. The complexes decompose in two steps *viz.* step in which there is loss of chloride ion and partial decomposition of ligand and step in which there is loss of remaining portion of the ligand leading to the final product as metallic oxide. The studies reveal that the complexes are thermally quite stable to varying degree of temperature.

13. Antimicrobial studies reveal that the activities of metal complexes are higher than those of the corresponding free ligands. The increase in the antimicrobial activity of the complexes can be explained on the basis of Overtone’s concept and Tweedy’s theory. However, the bioactivity of the compound varies with respect to metal ions and microorganisms.

14. Gel electrophoresis experiments using pUC19 DNA were performed with M(II) Schiff base complexes in the presence of H₂O₂ as oxidant. The free ligands exhibit no significant cleavage activity in the presence of H₂O₂. All the metal complexes have more cleavage activity with different cleaving ability due to the formation of hydroxyl free radicals.

15. In computational studies, the numbering pattern, 3-D structure and electrostatic potential diagram of Schiff base ligands were presented. The
electronegative hetero atoms through which the Schiff base ligands coordinate were identified as the thiophene ring sulphur, azomethine nitrogen and carboxylato oxygen by the studies. The non planar nature of the Schiff base ligands and solubility were also established.

16. The 3D-structure of the Ni(II)-thiophenal-val/phe/trp/thr/gln/glu/asp/his systems have been included. For the selected Ni(II)-thiophenal-val, the effective coordination and the stability of the complexes have been discussed from the Huckel charges. The bond length values determined in the computational studies substantiate the strength of the bond. The geometry with minimum steric energy and distortion in the geometry has been discussed.