CHAPTER VII

SUMMARY
The physico-chemical studies on the mercury(II) mercapto carboxylate systems, preparation and determination of structures of various metal bithio- lactato-mercurates(II), metal bis(3-mercaptopropionato)-mercurates(II), Zinc(II) and mercury(II) complexes of N,N'-diphenyl-selenourea, N,N'-dibenzylselenourea, N,N'-dibenzylthiourea and analytical applications of mercapto acid complexation are the subject matter of the present thesis.

First chapter deals with the general survey of literature indicating present day knowledge in these areas and the necessity of the present study. The details of techniques involved in the present studies are also discussed in this chapter.

The Second chapter incorporates physico-chemical studies on the mercury(II) complexes of thiolactic acid and 3-mercaptopropanoic acid by potentiometric technique using mercury electrodes leading to evaluation of stability constants of mercury(II)-mercaptopropanoic acids. The results of stability constants, standard free energy enthalpy and entropy changes evaluated are
as follows.

<table>
<thead>
<tr>
<th>Complex species</th>
<th>( \frac{\Delta G^0}{K_{\text{mol}}} )</th>
<th>( \frac{\Delta G^0}{K_{\text{mol}}} )</th>
<th>( \frac{\Delta H^0}{K_{\text{mol}}} )</th>
<th>( \frac{\Delta S^0}{\text{cal.deg}^{-1}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Hg}(\text{TLA})_2])</td>
<td>39.52</td>
<td>53.89</td>
<td>38.91</td>
<td>54.84</td>
</tr>
<tr>
<td>([\text{Hg}(\text{MPA})_2])</td>
<td>38.25</td>
<td>52.16</td>
<td>37.50</td>
<td>52.85</td>
</tr>
</tbody>
</table>

It is obvious that the six membered \( \text{Hg(II)} \) chelate with 3-mercapto propanoic acid is less stable than five membered chelate of \( \text{Hg(II)} \)-thiolactonic acid.

Third chapter incorporates the preparation and determination of structures of metal bisthiolactato-mercurates(II) and metal bis(3-mercapto propionato)-mercurates(II). On the basis of elemental analysis the complexes are found to have the stoichiometries:

\[
\begin{align*}
M_2^'L & \quad \text{where } M' = K^+ \\
M^"L & \quad M" = \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Fe}^{2+}, \text{Pb}^{2+}, \text{ZrO}^{2+}, \text{UO}_2^{2+} \\
M"^'L_3 & \quad M"^' = \text{La}^{3+}, \text{Nd}^{3+}
\end{align*}
\]
The compositions of metal bis(3-mercapto-propiionate)-mercurates are:

\[ M''''L_2 \quad M''' = \text{Th}^{4+} \]

and \[ L = [\text{Hg}(\text{TLA})_2]^2^- \]

Infrared spectral data of complexes shows lowering of frequency bands due to \( \nu_{\text{as}}(\text{COO}) \), \( \nu_{\text{s}}(\text{COO}) \), \( \nu(\text{C-S}) \) and absence of a band due to \( \nu(\text{S-H}) \) at 2560 cm\(^{-1}\) and 2570 cm\(^{-1}\) (in 2-, and 3-mercapto propaneoic acids) which indicates that Hg(II) is co-ordinated to sulphur atom of \(-\text{SH}\) group and oxygen of carboxyl group and the structures of anions are as follows:

- \( M'_2L' \) where \( M' = \text{Na}^+ \) and \( \text{NH}_4^+ \)
- \( M''L' \) where \( M'' = \text{Mn}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Fe}^{2+}, \text{Zn}^{2+}, \text{Ba}^{2+}, \text{Ca}^{2+}, \text{Pb}^{2+}, \text{Cd}^{2+}, \text{ZrO}^{2+}, \text{UO}_2^{2+} \)
- \( M''''L_3 \) where \( M'''' = \text{La}^{3+}, \text{Nd}^{3+} \)
- \( M''''''L_2 \) where \( M'''''' = \text{Th}^{4+} \)

and \[ L' = [\text{Hg}(\text{MPA})_2]^2^- \]
It is obvious that Hg(II) forms four coordinate complex anions with probably tetrahedral structure.

On the basis of magnetic susceptibility studies it is concluded that first row (d^5-d^9) metal ions form four co-ordinate complexes and exist in partially spin paired states in both metal bisthiolactato-mercurates and metal bis(3-mercaptopropionato)-mercurates.

The proton magnetic resonance spectral data of sodium bis(3-mercaptopropionato)-mercurate(II) supports the above structure for the complex anion.
In the fourth chapter determination of ionic mobilities and degree of dissociation of potassium bisthiolactato-mercurate (II) and sodium bis(3-mercaptopropionato)-mercurate(II) is reported. The ionic mobility values determined by conductometric technique are 110.50 and 110.19 at 25°C and values of degree of dissociation evaluated by conductometric as well by cryoscopic method are 0.66 and 0.60 for potassium bisthiolactato-mercurate(II) and sodium bis(3-mercaptopropionato)-mercurate(II) respectively.

The solubilities of less soluble metal bisthiolactato-mercurates(II) and metal bis(3-mercaptopropionato) mercurates(II) were determined by complexometric titrations with EDTA and by conductometric technique.

The solubilities at different temperatures have the following range:

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Temperature</th>
<th>25°C</th>
<th>35°C</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal bisthiolactato-mercurates(II)</td>
<td></td>
<td>0.024-0.424</td>
<td>0.074-0.638</td>
<td>0.089-0.932</td>
</tr>
<tr>
<td>Metal bis(3-mercaptopropionato)-mercurates(II)</td>
<td></td>
<td>0.011-0.340</td>
<td>0.067-0.423</td>
<td>0.071-0.641</td>
</tr>
</tbody>
</table>
From the above data it is obvious that solubilities increase with increase in temperature. The lead derivatives of both classes of complexes show minimum solubility and nickel bisthiolactato-mercurate(II) and barium bis(3-mercaptopropionato)-mercurate(II) show maximum solubility.

Fifth chapter incorporates the studies on chelometric estimation of Mg(II) in presence of group IIB metal ions using H$_2$TLA and H$_2$MPA as masking agents. Results on masking range that 2.5 m moles of H$_2$TLA mask 0.05 m moles of Zn(II), Cd(II) and Hg(II) ions, and 2.5 m moles of H$_2$MPA mask 0.025 m moles of group IIB metal ions permitting titrations of $2.5 \times 10^2$-m.moles of Mg(II) by EDTA in presence of Eriochrome black T as indicator.

In the Sixth chapter preparation, determination of composition and structure of Zn(II) and Hg(II) complexes of DPSU, DBSU and DBTU is reported. On the basis of elemental analysis the complexes are found to have the stoichiometry - $ML_2X_2$

Where $M = \text{Zn(II), Hg(II)}$,

$L = (C_6H_{12}NH)_2$ $C = \text{Se}$,
Data on infrared spectra of complexes indicate lowering of frequencies due to $\nu$(C-S) and $\nu$(C-Se) observed at 735 cm$^{-1}$, 650 cm$^{-1}$ and 630 cm$^{-1}$ in DBTU, DPSU and DBSU respectively which indicates co-ordination of thio- and selenourea molecules to metal through sulphur or selenium atom respectively and the general structure proposed for the complexes is:

\[
\begin{align*}
\text{Cl} & \quad \xrightarrow{\text{M}} \quad \text{X} = \text{C} (\text{NHR})_2 \\
\text{Cl} & \quad \xrightarrow{\text{M}} \quad \text{X} = \text{C} (\text{NHR})_2 \\
R &= \text{C}_6\text{H}_5^- \quad \text{or} \quad \text{C}_6\text{H}_5\text{CH}_2^- \\
\text{M} &= \text{Zn(II)} \quad \text{or} \quad \text{Hg(II)} \\
\text{X} &= \text{S} \quad \text{or} \quad \text{Se}
\end{align*}
\]

On the basis of these studies it is concluded that Zn(II) and Hg(II) form four co-ordinate complexes and probably have tetrahedral geometry.