CHAPTER V
CHAPTER V
REACTION OF COPPER TARTRATE WITH BI AND TRI DENTATE LIGANDS
CONTAINING OXYGEN DONOR ATOMS.

Introduction:

As discussed in the previous chapter, copper tartrate reacts with bidentate ligands containing nitrogen and oxygen donor atoms such as glycinate and 8-hydroxy quinoline to form stable complexes. In this chapter, complexes of copper tartrate with bidentate ligands containing two oxygen donor atoms such as oxalate, salicylate, lactate, glycolate and tridentate oxygen donor ligands such as malate and l-tartrate have been described.

Oxalate, salicylate, lactate and glycolate ions as bidentate ligands.

The oxalate ion functions as a bidentate with the formation of a five membered ring (Structure-1) with a divalent metal.

mono, bis, tris and tetrakis oxalato complexes are known and have been reviewed by Krishnamurty and Harris. X-ray investigation of trans $K\left[\text{Cr(C}_2\text{O}_4\right)\_2(\text{H}_2\text{O})\_2]\text{H}_2\text{O}$ and $K\_3\left[\text{Cr(C}_2\text{O}_4\right)\_3]$ have shown that the oxalato group is bidentate and approximately planar. The oxalato group functions as bidentate to two
metal atoms simultaneously as in the gold complex (Structure-2) and in the palladium complex (Structure-3).

![Metal complexes](image)

A different bonding arrangement occurs in silver oxalate, which has a chain (Structure-4).

![Silver oxalate structure](image)

Hydroxy carboxylate such as salicylate, lactate, glycolate form a group of interesting chelating ligands. The availability of an -OH group in the hydroxycarboxylate may help to form a stronger complex than the corresponding monodentate ligands due to chelation provided the hydroxyl group is in α-position. The oxygen of the alcoholic group has two pairs of unshared electrons. Out of these at least a pair can be donated for bond formation without the liberation of proton. The more electropositive the metal is, the stronger is the bond with oxygen of the α-hydroxy group. This effect will diminish the strength of the bond between oxygen and hydrogen. Copper(II) complexes of salicylic acid \((\log{\beta_2} = 16.9)\) are more stable than those of the aliphatic
α-hydroxy carboxylic acids, such as a glycolic (log $\beta_2 3.7$) and lactic (log $\beta_2 2.7$).

The existence of negative chelates of the rare earths and the actinides with glycolic, lactic and α-hydroxy isobutyric acids have been established by the ion exchange and electrophoretic studies. The stabilities of lactate complexes are discussed in connection with α-hydroxy isobutyrate and glycolate complexes. Mohanty and Pani have investigated the solubility of antimony oxide in partially neutralised lactic acid and reported 1:2 complex. Some lactate complexes of trivalent metal ions such as Al$^{3+}$, Fe$^{3+}$, La$^{3+}$, Ce$^{3+}$, Pr$^{3+}$ and Nd$^{3+}$ and bivalent metal ions such as Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$ have been studied by pH titration method. The formation of 1:1 and 1:2 complexes have been reported.

Malate and tartrate ion as ligand:

Malate and tartrate are also very interesting ligands. Many workers have reported the formation of 1:1 complex by these ligands with metal ions. The complexes are generally very stable. In malate ion, two carboxyl groups are separated by two carbon atoms as in succinate ion but there is an alcoholic group in one of the two middle carbon atoms and hence it is in α-position to one of the two carboxylate groups and in β-position to the other carboxyl group. If only the two-COO groups in the malate ligand are assumed to be involved in complex formation, a seven membered ring would be formed and the stability of the complex would be of the
order of that formed by succinate ligand. It is reported that malate complex are more stable than succinate. The high stability has been attributed to the participation of the \(-\text{OH}\) group in the complex formation. Therefore, it is expected that malate behaves as a tridentate ligand. The chelation of the malate ligand may result in the liberation of proton of the alcoholic group. Another possibility is that the oxygen of the \(-\text{OH}\) group may donate a lone pair of electrons to the metal ion for bond formation without the liberation of proton of the \(-\text{OH}\) group which is more likely since alcoholic groups are extremely weak acids. From the study of the solubility of antimony oxide in malate solution Nanda and Pani have reported the formation of 1:2 complex. Malate complex of copper was studied by Delsal and the existence of a complex was postulated from polarimetric and electrometric measurements. The same system has also been investigated by Nanda and Pani by pH titration method within the pH range of 2 to 6. They have reported the formation of 1:1 complex. Replacement of one hydrogen atom of \(\text{CH}_2\) group in malate by alcoholic group would given tartrate ion. A similarity in the structures of tartrate complexes with malate complexes is not improbable. From steric consideration tartrate ligand cannot occupy more than three coordination positions.

Pani et al. have investigated the tartrate complex of antimony by studying the solubility of antimony oxide in partially neutralised tartaric acid and have suggested the
1:1 complex in solution. The formation of zinc tartrate has been studied pH metrically by Patnaik and Panif. Tartrate complex of Mn(II) has been investigated by Tripathy and Patnaik and 1:1 type of complex has been reported to be formed. Carman and Kibrick and Schubort and Lindenbaum have determined the stability constant of calcium tartrate and reported the value as 63.10 and 60.26 respectively. Stability constants of tartrate complexes of yttrium have been determined by Tripathy and Patnaik by pH measurement method.

As a part of a series of investigations on copper tartrate complexes, reactions of this complex with oxalate, salicylate, lactate, glycolate, malate, and tartrate have been carried out in the present chapter.

Experimental:

Copper tartrate goes into solution in sodium malate, sodium salicylate, sodium lactate, sodium glycolate, sodium malate and sodium tartrate. These solubilities indicate complex formation. The solubilities not being in molar proportion solid compounds could not be isolated. The solubility method was therefore adopted to investigate the systems at 30 ± 0.1°.
A stock solution of 0.5 M sodium oxalate was freshly prepared and standardised by standard potassium permanganate solution. From this standard solution, seven sets of solution of different concentrations were prepared. 100 ml. of the dilute solutions were taken in different dried stoppered bottles. To each solution about 1.0 gm. of copper tartrate was added and the stoppers were tightly fixed to avoid evaporation. The bottles were placed in water heated to 35 to 40°C. Then the bottles were shaken in an electric shaker for about 6 hours and placed in a thermostat maintained at 30 ± 0.1°C. The system attained equilibrium in 48 hours. The solutions were then filtered into dry bottles and the copper content of filtrate was determined as before (Chapter-II). The pH of the solutions were also measured. The solubilities of copper tartrate in different concentrations of sodium oxalate and the pH of the solutions are recorded in Table V-(1).

**Table V-(1)**

Solubility of copper tartrate in sodium oxalate solutions at 30 ± 0.1°C.

<table>
<thead>
<tr>
<th>Starting concentration of oxalate, $\left[{{\text{C}<em>{2}\text{O}</em>{4}\text{}}}\right]_T$, mol/Litre</th>
<th>Solubility of copper tartrate in g/mole/litre</th>
<th>pH of the solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4482</td>
<td>0.7752</td>
<td>7.4</td>
</tr>
<tr>
<td>0.3532</td>
<td>0.05352</td>
<td>7.16</td>
</tr>
<tr>
<td>0.2696</td>
<td>0.03652</td>
<td>6.98</td>
</tr>
<tr>
<td>0.1854</td>
<td>0.0236</td>
<td>6.84</td>
</tr>
<tr>
<td>0.1222</td>
<td>0.01274</td>
<td>6.74</td>
</tr>
<tr>
<td>0.09656</td>
<td>0.009154</td>
<td>6.40</td>
</tr>
<tr>
<td>0.074</td>
<td>0.007382</td>
<td>6.2</td>
</tr>
</tbody>
</table>
The solubility of copper tartrate increases with increasing concentration of sodium oxalate. This may be due to the formation of a soluble oxalate complex with copper tartrate since copper oxalate which is very sparingly soluble is not precipitated. It is assumed small amount of copper tartrate present in the aqueous solution reacts with n oxalate and the complex, C is formed. The reaction may be represented by

\[
\text{CuT} (s) + 3\text{H}_2\text{O} \rightleftharpoons \text{CuT} (s\text{d})
\]

\[
\text{CuT} (s\text{d}) + n\text{C}_2\text{O}_4^{2-} \rightleftharpoons \text{C} \quad \ldots \quad (V-1)
\]

The equilibrium constant, K for the reaction (V-1) is given by

\[
K = \frac{[C]}{[\text{CuT} (\text{sol}) \times [\text{C}_2\text{O}_4^{2-}]^n} \quad \ldots \quad (V-2)
\]

The square bracket, [ ] represent molar concentration.

So long as the solid, CuT is in equilibrium with the solution, \( \text{CuT} (s\text{d}) \) is constant and hence

\[
K = \frac{[C]}{[\text{C}_2\text{O}_4^{2-}]^n} \quad \ldots \quad (V-3)
\]

or \( \log [C] = n \log [\text{C}_2\text{O}_4^{2-}] + \log K \quad \ldots \quad (V-4) \)

This equation (V-4) is of the form, \( y = mx + c \) which represents a straight line. Thus, the plot of \( \log [C] \) against \( \log [\text{C}_2\text{O}_4^{2-}] \) would give a straight line. The value of \( n \) and \( \log K \) would be equal to the slope and intercept of the straight line respectively.

\( [C] \) is obtained by subtracting the solubility of copper tartrate in water \( (3.405 \times 10^{-3} \text{ g.mole/litre}) \) from the total copper in solution. The total oxalate, \( [\text{C}_2\text{O}_4^{2-}]_T \) is
equal to the sum of the concentration of oxalic acid $H_2C_2O_4$, bioxalate $HC_2O_4^-$. Oxalate ion $C_2O_4^{2-}$ and oxalate present in the complex, $n [C]$. 

$$[C_2O_4^{2-}] = n [C] = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}] \ldots (V-6)$$

It can be shown that

$$[C_2O_4^{2-}] = \frac{K_2}{[H^+]} [HC_2O_4^-] = \frac{K_1K_2}{[H^+]^2} [H_2C_2O_4] \ldots (V-7)$$

Where, $K_1$ and $K_2$ are respectively first and second dissociation constant of oxalic acid ($K_1 = 5.7 \times 10^{-2}$ and $K_2 = 6.9 \times 10^{-4}$) Hence

$$[C_2O_4^{2-}] = n [C] = \text{unreacted oxalate} = \left(1 + \frac{[H^+]}{K_2}\right) + \frac{[H^+]^2}{K_1K_2} [C_2O_4^{2-}] \times a \ldots (V-7)$$

Where, $a = 1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2}$

As the pH of the system lies above 6, the value of $a$ can be taken as one since most of the oxalate will be present as oxalate ion. Since the solubility is small compared to the oxalate concentration, Equation (V-4) can be written as

$$\log [C] = \log K + n \log \left[\frac{C_2O_4^{2-}}{[C_2O_4^{2-}]_T}\right] \ldots (V-8)$$

By plotting $\log [C]$ against $\log \left[\frac{C_2O_4^{2-}}{[C_2O_4^{2-}]_T}\right]$ very nearly straight line is obtained and the value of $n$ is nearly 2. The value of $n$ is taken as 2 and from equation (V-7), the value of $\left[\frac{C_2O_4^{2-}}{[C_2O_4^{2-}]_T}\right]$ is calculated. When $\log [C]$ is plotted against $\log \left[\frac{C_2O_4^{2-}}{[C_2O_4^{2-}]_T}\right]$, a straight line is obtained and the value of $n$ is again 2. (Fig V-1)
The value of $K$ for equation (V-2) calculated from the intercept is 0.04786.

(b) Solubility of copper tartrate in sodium salicylate solution:

This system was also similarly studied. The solubility of copper tartrate in different concentrations of sodium salicylate and the pH of the solutions are recorded in Table V-(2). The value of $n$ obtained from the curve (Fig. V-2) is $1$ and $K$ is 0.08511. The probable structure of the complex in solution is given by

![Complex Structure]

There is no evidence of two salicylate ligands coordinating with copper tartrate probably due to steric effect. Tartrate ligand being very strong chelating ligand specially with copper(II) salicylate ligand is not capable to displace it to form the bis-complex.

(c) Solubility of copper tartrate in sodium lactate:

This system was also similarly studied. The solubility and pH data are recorded in Table V-(3). The plot of log $[\text{Cu}]$ against log $[\text{lactate}]$ is shown in Fig. V-3. The value of
'n' found is 1 and that of K is 0.07943. The probable structure in solution is given by

![Chemical Structure](image)

It is of interest to note that two lactate ligands do not coordinate with copper tartrate. This means that lactate ligand is a weaker ligand compared to oxalate. It is therefore, not capable to displace one of the three coordination positions occupied by tartrate ligand. Two lactate ligands coordinated to copper(II) probably do not give square planar configuration round copper atom.

(d) Solubility of copper tartrate in sodium glycolate solution:

This system was similarly studied. The solubility of copper tartrate in different concentrations of sodium glycolate and the pH of the solutions are recorded in Table V-(4). The plot of log $[C]$ against log $[glycolate]$ is shown in Fig. V-4. The value of $n$ found is 1 and that of K is 0.0708. The probable structure in solution is given by

![Chemical Structure](image)
In this case, also two glycolate ligands like lactate ligand do not coordinate with copper tartrate.

\((e)\) Solubility of copper tartrate in sodium malate solution:

The system was also similarly studied. The solubility data and pH of the solutions are recorded in Table V-5. The plot of log \([C]\) against log \([\text{malate}]\) is shown in Fig.V-5. The value of \(n\) found is 1 and that of \(K\) is 0.03802. The probable structure in solution is given by

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{C} \\
\text{Cu} \\
\text{O} \\
\text{C} \\
\text{O}
\end{array}
\]

\(2^-\)

\((f)\) Solubility of copper tartrate in sodium tartrate:

As discussed earlier, the sparingly soluble copper tartrate with chain structure in which the ligand forms bridge between two copper atoms is formed with d- or l-tartrate and the copper has a distorted octahedral coordination sphere of six oxygen atoms. Such a structure indicates the possibility of the formation of a soluble complex \([\text{CuT}_2]^2^-\). The structure of such a complex if formed would be
Sodium 1-tartrate was used in this investigation. The solubility of copper tartrate increases with increasing concentration of sodium tartrate. This suggests copper tartrate is not a simple salt like copper sulphate. The results obtained (solubility and pH) are recorded in Table V-6. The value of \( n \) is one and \( K \) is 0.0488. The results are consistent with above conclusion.
**TABLE V-(2)**
Solubility of copper tartrate in sodium salicylate solution
30 ± 0.1°

<table>
<thead>
<tr>
<th>Starting concentration of salicylate, M/Litre.</th>
<th>Solubility of copper tartrate in mole/litre</th>
<th>pH of the solution.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3812</td>
<td>0.08468</td>
<td>6.42</td>
</tr>
<tr>
<td>0.3160</td>
<td>0.06948</td>
<td>6.36</td>
</tr>
<tr>
<td>0.2524</td>
<td>0.05588</td>
<td>6.28</td>
</tr>
<tr>
<td>0.1908</td>
<td>0.04414</td>
<td>6.18</td>
</tr>
<tr>
<td>0.1276</td>
<td>0.03094</td>
<td>6.10</td>
</tr>
<tr>
<td>0.1014</td>
<td>0.02478</td>
<td>6.06</td>
</tr>
<tr>
<td>0.0758</td>
<td>0.01926</td>
<td>6.02</td>
</tr>
</tbody>
</table>

**TABLE V-(3)**
Solubility of copper tartrate in sodium lactate solution at 30 ± 0.1°

<table>
<thead>
<tr>
<th>Starting concentration of lactate, M/Litre.</th>
<th>Solubility of copper tartrate in mole/litre</th>
<th>pH of the solution.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3758</td>
<td>0.07926</td>
<td>6.6</td>
</tr>
<tr>
<td>0.3132</td>
<td>0.0665</td>
<td>6.4</td>
</tr>
<tr>
<td>0.2501</td>
<td>0.05352</td>
<td>6.26</td>
</tr>
<tr>
<td>0.1880</td>
<td>0.04142</td>
<td>6.12</td>
</tr>
<tr>
<td>0.1250</td>
<td>0.02852</td>
<td>6.08</td>
</tr>
<tr>
<td>0.09996</td>
<td>0.02335</td>
<td>6.06</td>
</tr>
<tr>
<td>0.07514</td>
<td>0.01854</td>
<td>6.04</td>
</tr>
</tbody>
</table>
### Table V-(4)

**Solubility of copper tartrate in sodium glycolate at 30 ± 0.1°C**

<table>
<thead>
<tr>
<th>Starting concentration of glycolate, M/Litre</th>
<th>Solubility of copper tartrate in Mole/litre</th>
<th>pH of the solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3630</td>
<td>0.0665</td>
<td>6.80</td>
</tr>
<tr>
<td>0.3024</td>
<td>0.05588</td>
<td>6.78</td>
</tr>
<tr>
<td>0.2416</td>
<td>0.04509</td>
<td>6.76</td>
</tr>
<tr>
<td>0.1816</td>
<td>0.03502</td>
<td>6.72</td>
</tr>
<tr>
<td>0.1214</td>
<td>0.02478</td>
<td>6.70</td>
</tr>
<tr>
<td>0.0958</td>
<td>0.01925</td>
<td>6.68</td>
</tr>
<tr>
<td>0.0726</td>
<td>0.0160</td>
<td>6.66</td>
</tr>
</tbody>
</table>

### Table V-(5)

**Solubility of copper tartrate in sodium malate at 30 ± 0.1°C**

<table>
<thead>
<tr>
<th>Starting concentration of malate, M/Litre</th>
<th>Solubility of copper tartrate in Mole/litre</th>
<th>pH of the solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2023</td>
<td>0.0264</td>
<td>7.2</td>
</tr>
<tr>
<td>0.1670</td>
<td>0.0204</td>
<td>6.96</td>
</tr>
<tr>
<td>0.11096</td>
<td>0.01436</td>
<td>6.82</td>
</tr>
<tr>
<td>0.08852</td>
<td>0.01192</td>
<td>6.66</td>
</tr>
<tr>
<td>0.0671</td>
<td>0.01048</td>
<td>6.54</td>
</tr>
</tbody>
</table>
### TABLE V(6)

Solubility of copper tartrate in sodium l-tartrate at 30 ± 0.1°

<table>
<thead>
<tr>
<th>Starting concentration of tartrate, $\text{M/Litre.}$</th>
<th>Solubility of copper tartrate in $\text{mole/litre.}$</th>
<th>pH of the solution.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2316</td>
<td>0.03502</td>
<td>7.96</td>
</tr>
<tr>
<td>0.1751</td>
<td>0.02852</td>
<td>7.78</td>
</tr>
<tr>
<td>0.1170</td>
<td>0.02038</td>
<td>7.54</td>
</tr>
<tr>
<td>0.0938</td>
<td>0.0172</td>
<td>7.32</td>
</tr>
<tr>
<td>0.0712</td>
<td>0.01462</td>
<td>7.18</td>
</tr>
</tbody>
</table>
REFERENCES


