A perusal of the last fifty years shows that there has been a spectacular development of Coordination chemistry and its extensive applications in laboratory, industry, medicines and in many nuclear processes, the chemistry of coordination is growing day by day and there is not least doubt that it will firmly establish itself very soon.

The present study which is related with the preparation and physico-chemical characterisation of some rare earths (Pr\(^{3+}\) and Nd\(^{3+}\)) and transition metals (Cd\(^{2+}\) and Zn\(^{2+}\)) complexes | Ternary | with formic, acetic and propionic acids as secondary ligands and glycine, \(\alpha\)-alanine, L-valine, L-leucine, L-asparagine and L-glutamine as primary ligands, has been undertaken for which no references could be traced out so far in the available literature.

The present study comprises two parts:

Part a : Rare earths (i.e. Pr\(^{3+}\) and Nd\(^{3+}\)) complexes with

1. Formic acid
2. Acetic acid
3. Propionic acid
4. Glycine
5. \(\alpha\)-Alanine
6. L-Leucine
7. L-Valine
8. L-Asparagine
9. L-Glutamine

Part b: Transition Metals (i.e. Cd$^{+2}$ and Zn$^{+2}$) complexes

x: Binary complexes with

1. Formic acid
2. Acetic acid
3. Propionic acid
4. Glycine
5. α-Alanine
6. L-Leucine
7. L-Valine
8. L-Asparagine
9. L-Glutamine

and

y: Ternary complexes

**Primary ligands:**

1. Glycine
2. α-Alanine
3. L-Leucine
4. L-Valine
5. L-Asparagine
6. L-Glutamine

**Secondary ligands:**

1. Formic acid
2. Acetic acid
3. Propionic acid

**Part a:** Generally praseodymium and neodymium form complexes in which their coordination number are six but it may be seven, and eight also. Transition metal ions are related to participation of the d electrons in the metal-ligand bond through hybridisation of metal electronic orbitals and overlap of these hybrid orbitals with appropriate ligand orbitals. The rare earth metal ions differ from each other in the number of electrons in the 4f orbitals, which orbitals are effectively shielded from interaction with ligand orbitals by electrons in the 5s and 5p orbitals. If hybridisation is to occur, it must of necessity involve normally unoccupied higher-energy orbitals (e.g., 5d, 6s, 6p), and hybridisation of this type can be expected only with the most strongly coordinating ligands.

Very few complexes of Pr$^{+3}$ and Nd$^{+3}$ with formic, acetic and propionic acids are reported in the literature by different technique. Pr$^{+3}$ and Nd$^{+3}$ form 1:1, and 1:2 complexes with all the three acids. Their values of stability constants were given in Tables 94(a) and 94(b) respectively. The trend of stability of complexes is formic acid < acetic acid < propionic acid which is expected from their $pK$ values reported in the literature.
### Table 91(a)

**RESULTS OF BINARY COMPLEXES OF PHASEOXYMUM**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Ligand</th>
<th>Composition</th>
<th>Table No.</th>
<th>Figure No.</th>
<th>Stability constants (log $\beta$) 25 ± 0.1°C</th>
<th>Stability constants (log $\beta$) 35 ± 0.1°C</th>
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<tbody>
<tr>
<td>1</td>
<td>Formic acid</td>
<td>1:1, 1:2</td>
<td>R-1</td>
<td>R-1</td>
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<td>3.68</td>
</tr>
<tr>
<td>2</td>
<td>Acetic acid</td>
<td>1:1, 1:2</td>
<td>R-2</td>
<td>R-2</td>
<td>2.25</td>
<td>3.75</td>
</tr>
<tr>
<td>3</td>
<td>Propionic acid</td>
<td>1:1, 1:2</td>
<td>R-3</td>
<td>R-3</td>
<td>2.40</td>
<td>3.82</td>
</tr>
<tr>
<td>4</td>
<td>Glycine</td>
<td>1:1</td>
<td>R-4(a to b)</td>
<td>R-4(a to b)</td>
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<td>-</td>
</tr>
<tr>
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<td>χ-Alanine</td>
<td>1:1</td>
<td>R-5(a to b)</td>
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<td>-</td>
</tr>
<tr>
<td>6</td>
<td>L-Leucine</td>
<td>1:1</td>
<td>R-6(a to b)</td>
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<td>-</td>
</tr>
<tr>
<td>7</td>
<td>L-Valine</td>
<td>1:1</td>
<td>R-7(a to b)</td>
<td>R-7(a to b)</td>
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<td>-</td>
</tr>
<tr>
<td>8</td>
<td>L-Asparagine</td>
<td>1:1</td>
<td>R-8(a to b)</td>
<td>R-8(a to b)</td>
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<td>-</td>
</tr>
<tr>
<td>9</td>
<td>L-Glutamine</td>
<td>1:1</td>
<td>R-9(a to b)</td>
<td>R-9(a to b)</td>
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</table>
## TABLE No. 91(b)

**RESULTS OF THERMODYNAMIC PARAMETERS OF PRASEODYMIUM COMPLEXES**

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<th>Stability constants (log $\beta$)</th>
<th>Enthalpy ($\Delta H$) for the difference of 10°C</th>
<th>Free energy ($\Delta G$) Cal/mole</th>
<th>Entropy ($\Delta S$) Cal/degree/mole</th>
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<td>Acetic acid</td>
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<td>3.75</td>
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<tr>
<td>3</td>
<td>Propionic acid</td>
<td>2.40</td>
<td>3.82</td>
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</tr>
<tr>
<td>4</td>
<td>Glycine</td>
<td>4.40</td>
<td>-</td>
<td>3.70</td>
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<tr>
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<td>$\text{L}$-Valine</td>
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<td>-</td>
<td>3.20</td>
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<tr>
<td>8</td>
<td>$\text{L}$-Asparagin</td>
<td>3.50</td>
<td>-</td>
<td>3.10</td>
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<tr>
<td>9</td>
<td>$\text{L}$-Glutamine</td>
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<td>Composition</td>
<td>Table No.</td>
<td>Figure No.</td>
<td>Stability constants (log $\beta$)</td>
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<td>Acetic acid</td>
<td>1:1, 1:2</td>
<td>R-11</td>
<td>R-11</td>
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<td>3</td>
<td>Propionic acid</td>
<td>1:1, 1:2</td>
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<td>R-13(b to b)</td>
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<td>-</td>
<td>R-14(b to b)</td>
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<td>R-15(b to b)</td>
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<td>-</td>
<td>R-16(b to b)</td>
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<td>8</td>
<td>L-Asparagine</td>
<td>1:1</td>
<td>-</td>
<td>R-17(b to b)</td>
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<td>L-Glutamine</td>
<td>1:1</td>
<td>-</td>
<td>R-18(b to b)</td>
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</table>
### Table No. 92(b)

**RESULTS OF THERMODYNAMIC PARAMETERS OF NEODYMIUM COMPLEXES**

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<th>Free energy ($\Delta G$) K Cal/mole</th>
<th>Entropy ($\Delta S$) Cal/degree/mole</th>
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<td>log $\beta_{10}$</td>
<td>log $\beta_{20}$</td>
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<td>Propionic acid</td>
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<td>3.80</td>
<td>- No change -</td>
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<td>4</td>
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<table>
<thead>
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<th>S. No.</th>
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<th>Composition</th>
<th>Table No.</th>
<th>Figure No.</th>
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<th>log $\beta_{02}$</th>
<th>log $\beta_{10}$</th>
<th>log $\beta_{20}$</th>
<th>log $\beta_{30}$</th>
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<td>Figure No.</td>
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</table>
### TABLE No. 95

**RESULTS OF TERNARY COMPLEXES OF CALCIUM**

**Temperature = 25 ± 0.1°C**

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<thead>
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<th>S. No.</th>
<th>Ligand Primary</th>
<th>Secondary</th>
<th>Table No.</th>
<th>Figure No.</th>
<th>Stability constants</th>
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<td>Formic acid</td>
<td>I-19, I-20</td>
<td>T-19, T-20</td>
<td>log $\beta_{11}$</td>
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<td>Formic acid</td>
<td>I-21, I-22</td>
<td>T-21, T-22</td>
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<td>Formic acid</td>
<td>I-23, I-24</td>
<td>T-23, T-24</td>
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<th>Figure No.</th>
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</table>
### RESULTS OF TERNARY COMPLEXES OF CALCIUM

*Temperature = 25 ± 0.1°C*

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Ligands Primary / Secondary</th>
<th>Table No.</th>
<th>Figure No.</th>
<th>Stability constants (log $\beta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
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<td>log $\beta_{11}$</td>
</tr>
<tr>
<td>1</td>
<td>Glycine, Propionic acid</td>
<td>T-43, T-44</td>
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<tr>
<td>2</td>
<td>α-Alanine, Propionic acid</td>
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<td>T-45, T-46</td>
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<tr>
<td>3</td>
<td>L-Leucine, Propionic acid</td>
<td>T-47, T-48</td>
<td>T-47, T-48</td>
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<tr>
<td>4</td>
<td>L-Valine, Propionic acid</td>
<td>T-49, T-50</td>
<td>T-49, T-50</td>
<td>6.22</td>
</tr>
<tr>
<td>5</td>
<td>L-Asparagine, Propionic acid</td>
<td>T-51, T-52</td>
<td>T-51, T-52</td>
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<tr>
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<td>Figure No.</td>
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<td>L-Leucine, Formic acid</td>
<td>T-59, T-60</td>
<td>T-59, T-60</td>
<td>6.20</td>
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<tr>
<td>5</td>
<td>L-Asparagine, Formic acid</td>
<td>T-63, T-64</td>
<td>T-63, T-64</td>
<td>6.00</td>
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<tr>
<td>6</td>
<td>L-Glutamine, Formic acid</td>
<td>T-65, T-66</td>
<td>T-65, T-66</td>
<td>5.84</td>
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</table>

Temperature = 25 ± 0.1°C
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Ligands</th>
<th>Table No.</th>
<th>Figure No.</th>
<th>Stability constants</th>
<th>log $\beta_{11}$</th>
<th>log $\beta_{12}$</th>
<th>log $\beta_{21}$</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Glycine, Acetic acid</td>
<td>T-67, T-68</td>
<td>T-67, T-68</td>
<td></td>
<td>6.54</td>
<td>9.28</td>
<td>10.75</td>
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<tr>
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<td>9.06</td>
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<td>L-Leucine, Acetic acid</td>
<td>T-71, T-72</td>
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<td>6.33</td>
<td>8.79</td>
<td>10.38</td>
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<tr>
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<td>L-Valine, Acetic acid</td>
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<td>T-73, T-74</td>
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<td>6.17</td>
<td>8.57</td>
<td>10.16</td>
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<td>5</td>
<td>L-Asparagine, Acetic acid</td>
<td>T-75, T-76</td>
<td>T-75, T-76</td>
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<td>6.13</td>
<td>8.48</td>
<td>9.83</td>
</tr>
<tr>
<td>6</td>
<td>L-Glutamine, Acetic acid</td>
<td>T-77, T-78</td>
<td>T-77, T-78</td>
<td></td>
<td>5.97</td>
<td>8.26</td>
<td>9.61</td>
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</tbody>
</table>
### RESULTS OF TERNARY COMPLEXES OF ZINC

Temperature $= 25 \pm 0.1{^\circ}C$

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Ligands</th>
<th>Table No.</th>
<th>Figure No.</th>
<th>Stability constants (log $\beta$)</th>
<th>log $\beta_{11}$</th>
<th>log $\beta_{12}$</th>
<th>log $\beta_{21}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$\alpha$-Alanine, Propionic acid</td>
<td>T-81, T-82</td>
<td>T-81, T-82</td>
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<td>6.51</td>
<td>9.25</td>
<td>10.71</td>
</tr>
<tr>
<td>3</td>
<td>L-Leucine, Propionic acid</td>
<td>T-83, T-84</td>
<td>T-83, T-84</td>
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<td>6.46</td>
<td>8.98</td>
<td>10.57</td>
</tr>
<tr>
<td>4</td>
<td>L-Valine, Propionic acid</td>
<td>T-85, T-86</td>
<td>T-85, T-86</td>
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<td>6.30</td>
<td>8.76</td>
<td>10.35</td>
</tr>
<tr>
<td>5</td>
<td>L-Asparagine, Propionic acid</td>
<td>T-87, T-88</td>
<td>T-87, T-88</td>
<td></td>
<td>6.26</td>
<td>8.67</td>
<td>10.02</td>
</tr>
<tr>
<td>6</td>
<td>L-Glutamine, Propionic acid</td>
<td>T-89, T-90</td>
<td>T-89, T-90</td>
<td></td>
<td>6.10</td>
<td>8.45</td>
<td>9.80</td>
</tr>
</tbody>
</table>
Some rare earth complexes of glycine, α-alanine, L-valine, L-leucine, L-asparagine and L-glutamine have also been reported in the literature by different methods. All the natural amino acids make five membered ring with complex formation. The trend of stability constant of complexes is L-glutamine < L-asparagine < L-valine < L-leucine < α-alanine < glycine. It has been observed that if size of the amino acid increases by CH₂, stability of complexes decreases i.e. L-glutamine has lower stability than L-asparagine. This effect of size on stability has also been observed in case of α-alanine and glycine (i.e. α-alanine < glycine) except in the case of L-valine and L-leucine where the order is reversed i.e. L-valine < L-leucine. This reversal order of stability is purely due to the higher basicity of L-leucine than L-valine. As the basicity of ligand increases, stability of complexes increases. The higher stability of glycine than α-alanine is due to the presence of methyl group in the α-alanine. This trend of stability of complexes with respect to ligands has confirmed the results of previous workers. The higher stabilities of glycine, α-alanine, L-leucine or L-valine complexes than those of L-glutamine and L-asparagine are due to large difference in their basic strengths. The values of stability constants and thermodynamic parameters, such as, enthalpy (ΔH), free energy (ΔG) and entropy (ΔS) have been given in table Nos. 91(a), 91(b), 92(a) and 92(b) respectively. The structures and composition
of complexes are given below in Fig. No. F-1 to F-6. Since there is no appreciable change in the stabilities of formic, acetic and propionic acids complexes or Pr$^{3+}$ and Nd$^{3+}$ at higher temperature and thereby their thermodynamic parameters were not calculated.

Structures:

M stands for Pr$^{3+}$ and Nd$^{3+}$ ions

$$
\begin{align*}
M^{3+} + 1 & \quad \text{CH}_2 \\
\text{NH}_2 & \quad \text{N}_2 \quad \text{CH}_2 \\
\text{C} = \text{O} & \quad \text{O} \quad \text{C} \\
\text{O} &
\end{align*}
$$

Glycinate ion

Fig. F-1

$$
\begin{align*}
M^{3+} + 1 & \quad \text{CH}_3 - \text{CH} \\
\text{NH}_2 & \quad \text{NH}_2 - \text{CH} \\
\text{COO}^- & \quad \text{O} \quad \text{C} = \text{O}
\end{align*}
$$

α-Alanine ion

Fig. F-2
**Fig. F-3**

L-Valinate ion

**Fig. F-4**

L-Leucinate ion
L-Glutamate ion

Fig. F-5

L-Asparagine ion

Fig. F-6
These structures confirmed the structures of amino acids complexes proposed by many authors.\textsuperscript{22,26} The remaining positions of metal ion are filled with water molecules.\textsuperscript{26}

At higher reduction potential the evolution of hydrogen occurs and its wave appeared.\textsuperscript{27} On the other hand, at -1.90 V vs SCE alkali metals (i.e. K, Na etc.) begin to reduce\textsuperscript{28} and polarography of metal complexes is not possible. Since, there is no change in $E_{1/2}$ when secondary ligand i.e. either formic acid, acetic acid or propionic acid is added to the binary system i.e. $M$ (amino acid) $|\,$, $|$ where $M = Pr^{3+}$ or $Nd^{3+}$, and amino acid = glycine, $\alpha$-alanine, $L$-valine, $L$-leucine, $L$-glutamine or $L$-asparagine $|\,$, confirms that no ternary complexes are formed.\textsuperscript{29} The order of stability of complexes with respect to metals is $Pr^{3+}$ $<$ $Nd^{3+}$ which is due to lanthanide contraction.\textsuperscript{30}

Part B : This part contains the complexation study of transition metals (i.e. Cd\textsuperscript{2+} and Zn\textsuperscript{2+}) with some carboxylic acids and amino acids. The chelating ability of transition metals has been known since long.\textsuperscript{31-37} Both Cd\textsuperscript{2+} and Zn\textsuperscript{2+} form tetrahedral and octahedral complexes\textsuperscript{38-45} in which their coordination numbers increase from 4 to 6.

The $pK$ values of selected amino acids were determined by titration methods and given in research paper.\textsuperscript{29} All
natural amino acids are dipolar \( \text{H}_3\text{NCHR-COO}^- \) ion. Its \( K_a \) refers the acidity of an ammonium ion, \( \text{R NH}_3^+ \),

\[
\text{H}_3\text{NCHR-COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O}^+ + \text{H}_2\text{N CHRCOO}^- \\
\text{Acid} \quad \text{H}_2\text{O}^+ \quad \text{H}_2\text{N CHRCOO}^- \\
K_a = \frac{\text{H}_2\text{O}^+ \text{H}_2\text{N CHRCOO}^-}{\text{H}_3\text{N CHRCOO}^-}
\]

and \( K_b \) actually refers to the basicity of a carboxylic ion, \( \text{RCOO}^- \).

\[
\text{H}_3\text{N CHRCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{N CHRCOOH} + \text{OH}^- \\
\text{Base} \quad \text{H}_3\text{N CHRCOOH} \quad \text{OH}^- \\
K_b = \frac{\text{H}_3\text{N CHRCOOH} \text{OH}^-}{\text{H}_3\text{N CHRCOO}^-}
\]

When the solution of an amino acid is made alkaline, the dipolar ion is converted into the anion as

\[
\text{H}_3\text{N CHRCOO}^- + \text{OH}^- \rightleftharpoons \text{H}_2\text{N CHRCOO}^- + \text{H}_2\text{O} \\
\text{Stronger acid} \quad \text{Stronger base} \quad \text{Weaker base} \quad \text{Weaker acid}
\]

The free ligand concentrations of amino acid were determined as suggested. The metal and ligand were taken in the ratio (1:40) and \( E_{1/2} \) shift was observed at different pH values, it was seen that the maximum shift of \( E_{1/2} \) was observed at pH = 8.50 ± 0.1 and hence this pH was selected for the present study. The ionic strength (\( \mu \)) was adjusted at 1 = 0 with potassium nitrate. The values of stability constants for binary and ternary complexes of Cd\(^{+2} \) and Zn\(^{+2} \).
were given in tables No. 93 to 100. The trends of stabilities of complexes for binary and ternary complexes are: (see page No. 263)

Here it has also been observed that if side chain in amino acid | glycine, \(\alpha\)-alanine, L-valine, L-leucine, L-asparagine and L-glutamine | increases by \(\text{CH}_2\), stability of complexes decreases^{18-20} i.e. \(\mathcal{M}(\alpha\text{-alan.})\) | system has lower stability than \(\mathcal{M}\) (gly.) |. This effect of side chain has also been seen in case of L-asparagine and L-glutamine excepting in the case of L-valine, and L-leucine, where the order is reversed i.e. L-valine \(<\) L-leucine. This reversal order of stability in case of L-valine and L-leucine is due to the higher basicity of L-leucine than L-valine.^{21}

As the basicity of ligand increases, stability of complex increases.^{22} Similar trends of stabilities have also been observed in ternary complexes i.e. \(\mathcal{M}(\lambda)(Y)\) |, \(\mathcal{M}(\lambda)_2(Y)\) | and \(\mathcal{M}(\lambda)(Y)_2\) | systems have lower stabilities than \(\mathcal{M}(\lambda^1)(Y)\) |, \(\mathcal{M}(\lambda^2)(Y)\) | and \(\mathcal{M}(\lambda^1)(Y)_2\) |. Where \(\lambda = \text{L-glutamine or } \alpha\text{-alanine } \lambda^1 = \text{L-asparagine or glycine} \) and \(Y = \text{formic, acid or acetic acid or propionic acid }\). The systems \(\mathcal{M}(\text{amino acid})(\text{formic acid})\) | \(\mathcal{M}(\text{amino acid})-(\text{propionic acid})\) | \(\mathcal{M}(\text{amino acid})-(\text{acetic acid})\) | and \(\mathcal{M}(\text{amino acid})\) | have the following order of their stabilities \(\mathcal{M}(\text{amino acid})-(\text{formic acid}) \cdots\mathcal{M}(\text{amino acid})-(\text{acetic acid})\) |. Where \(M = \text{Ca}^{+2} \) or \(\text{Zn}^{+2}\), amino acids = glycine
\[ M (\text{L-glut.}) \quad \land \quad M (L-\text{asp.}) \quad \land \quad M (\text{L-val.}) \quad \land \quad M (\text{L-leu.}) \quad \land \quad M (\text{L-ala.}) \quad \land \quad M (\text{gly.}) \]

\[ M(\text{L-glut.}) \quad (\text{for.}) \quad \land \quad M(\text{L-asp.}) \quad (\text{for.}) \quad \land \quad M(\text{L-val.}) \quad (\text{for.}) \quad \land \quad M(\text{L-leu.}) \quad (\text{for.}) \quad \land \quad M(\text{L-ala.}) \quad (\text{for.}) \quad \land \quad M(\text{gly.}) \quad (\text{for.}) \]

\[ M(\text{L-glut.}) \quad \land \quad M(\text{L-asp.}) \quad \land \quad M(\text{L-val.}) \quad \land \quad M(\text{L-leu.}) \quad \land \quad M(\text{L-ala.}) \quad \land \quad M(\text{gly.}) \]

\[ M(\text{L-glut.}) \quad \land \quad M(\text{L-asp.}) \quad \land \quad M(\text{L-val.}) \quad \land \quad M(\text{L-leu.}) \quad \land \quad M(\text{L-ala.}) \quad \land \quad M(\text{gly.}) \]

\[ M(\text{L-glut.}) \quad (\text{prop.}) \quad \land \quad M(\text{L-asp.}) \quad (\text{prop.}) \quad \land \quad M(\text{L-val.}) \quad (\text{prop.}) \quad \land \quad M(\text{L-leu.}) \quad (\text{prop.}) \quad \land \quad M(\text{L-ala.}) \quad (\text{prop.}) \quad \land \quad M(\text{gly.}) \quad (\text{prop.}) \]

Where $M$ stands for $\text{Cd}^{2+}$ or $\text{Zn}^{2+}$ ions.
or ω-alanine, or L-valine, or L-leucine, or L-asparagine or L-glutamine which can be explained on the basis of increased sizes, steric hindrance and basicities of amino acids and also the pH values of formic acid, acetic acid and propionic acid respectively. The order of stabilities of complexes with respect to metal ions is Cd$^{2+} <$ Zn$^{2+}$, which can be explained on the basis of their ionic sizes. Cd$^{2+}$ ion has ionic radii 0.97 Å$^0$ and Zn$^{2+}$ ion has 0.72 Å$^0$.

As the ionic size of metal increases, stability of complexes decreases.$^{49}$ The structures of binary and ternary complexes of Cd$^{2+}$ and Zn$^{2+}$ are given below in figure No. F-7 to F-28 respectively. The remaining positions of metal ions are satisfied by water molecules.$^{50}$ Since there is no appreciable change in $E_{1/2}$ of metal complexes at higher temperature confirms that these complexes have the same stability at higher temperature and hence their thermodynamic parameters were not calculated.

**Structures:**

$M$ stands for Zn$^{2+}$ and Cd$^{2+}$ ions.

(a) **Binary Complexes**:

\[
\text{M}^{+2} + 1 \quad \xrightarrow{\text{CH}_2} \quad \text{H}_2 \quad \text{N} \quad \text{CH}_2
\]

\[
\text{NH}_2 \quad \text{0} \quad \text{C} \quad \text{0}
\]

Glycinate ion 1:1

Fig. F-7
\[ M^{+2} + 2 \quad \text{CH}_2 \quad \text{NH}_2 \quad \text{BC} = 0 \]

Glycinate ion

Fig. F-8

\[ M^{+2} + 3 \quad \text{CH}_2 \quad \text{NH}_2 \quad \text{BC} = 0 \]

Glycinate ion

Fig. F-9

\[ M^{+2} + 1 \quad \text{CH}_3 \quad \text{CH} \quad \text{NH}_2 \quad \text{BC} = 0 \]

\(-\text{Alanyl} \text{ate ion}\)

Fig. F-10
$M^{+2} + 2\quad \begin{array}{c}
\text{CH}_3 - \text{CH} \\
\text{NH}_2 \\
\text{O} - \text{C} = \text{O}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{CH}_3 \\
\text{H}_2 \\
\text{N} - \text{M} \\
\text{C} - \text{O} \\
\text{O} - \text{C} = \text{O}
\end{array}
$

$\alpha\text{-Alaninate ion}$

$1:2$

Fig. F-11

$M^{+2} + 3\quad \begin{array}{c}
\text{CH}_3 - \text{CH} \\
\text{NH}_2 \\
\text{O} - \text{C} = \text{O}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{HC} \\
\text{N} - \text{M} \\
\text{O} - \text{C} = \text{O}
\end{array}
$

$\alpha\text{-Alaninate ion}$

$1:3$

Fig. F-12

$L$-Valinate ion

$M^{+2} + 1\quad \begin{array}{c}
\text{H}_3\text{C} \\
\text{H} - \text{C} - \text{CH} \\
\text{H}_3\text{C} \\
\text{NH}_2
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{H}_2 \\
\text{N} - \text{M} \\
\text{O} - \text{C} = \text{O}
\end{array}
$

$1:1$

Fig. F-13
Fig. F-14

Fig. F-15
\[ \text{L-Leucinate ion} \quad \text{1:1} \]

\[ \text{L-Valinate ion} \quad \text{1:2} \]
Fig. F-18

Fig. 19
Fig. F-20

Fig. F-21
L-Asparaginate ion

Fig. F-22

L-Asparaginate ion

Fig. F-23
\[ M + 3n + 2 \rightarrow \text{L-Asparagine ion} \]

\[ H_2N - C = O \]

\[ CH_2 \]

\[ CH \]

\[ O = C \]

\[ NH_2 \]

\[ NH_2 \]

\[ CH - CH_2 - C \]

\[ 1:3 \]

**Fig. F-24**

\((b)\) **Ternary complexes:**

\[ M + 1X + 1Y \rightleftharpoons | M(X) - (Y) | \]

\[ M + 2X + 1Y \rightleftharpoons | M(X)_2 - (Y) |^{-1} \]

\[ 1:1:1:1 \]

**Fig. F-25**

\[ 1:2:1:1 \]

**Fig. F-26**
\[ M + 1X + 2Y \rightleftharpoons M(X) - (Y)_2 \quad ^{-1} \]

*Fig. F-27*

where \( M \) stands for \( \text{Cd}^{2+} \) or \( \text{Zn}^{2+} \) ions.

\[ X = \text{glycine, or } \alpha-\text{Alanine, or } \text{L-Valine or L-Leucine,} \]

or \( \text{L-Glutamine or L-Asparagine} \),

and

\[ Y = \text{Formic or Acetic or Propionic acids.} \]

These structures confirm the structures suggested by many workers. 45, 48

**Thermodynamic Parameters**: Thermodynamic parameters such as enthalpy change (\( \Delta H \)), free energy change (\( \Delta G \)) and entropy change have been calculated by the following equations. 51

\[
\Delta H = \frac{2.303 \text{ RT}_1 \infty T_2 \log K_2/K_1}{(T_2 - T_1)} \tag{1}
\]

\[
\Delta G = -2.303 \text{ RT log } K \tag{2}
\]

and

\[
\Delta S = \Delta H - T \Delta S \tag{3}
\]

where \( R \) is solution constant and \( K_1 \) and \( K_2 \) are the values of stability constants of complexes at temperatures \( T_1 \) and \( T_2 \) respectively. It is clear from the values of \( \Delta S \) and \( \Delta G \) (Tables No. 91(b) and 92(b)) that complexes of rare earths are not stable at higher temperature. 52-53
Factors affecting on stability constants:

There are many factors affecting the stability of complexes. Some main factors are as follows:

(a) Nature of metal ion:

1. Size and charge: Because of the strong electrostatic field round the cation, the smaller the size and the larger the charge of a metal ion, the more stable are the metal complexes. The order of stability of complexes formed by the stable dispositive ion of the first transition series, irrespective of the ligand, is found to be related to the ionic radius:

<table>
<thead>
<tr>
<th>Order of stability</th>
<th>Mn^{2+}</th>
<th>Fe^{2+}</th>
<th>Co^{2+}</th>
<th>Ni^{2+}</th>
<th>Cu^{2+}</th>
<th>Zn^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic radius (Å)</td>
<td>0.91</td>
<td>0.83</td>
<td>0.82</td>
<td>0.78</td>
<td>0.69</td>
<td>0.74</td>
</tr>
</tbody>
</table>

2. Crystal field effect:

The crystal field stabilization energy (CFSE) plays an important role in the stability of transition metal complexes and appears to be responsible for the natural order of stability of complexes of the first row transition metals. In an octahedral field electrons in three t_{2g} orbitals have a lower energy than electrons in two e.g. d orbitals. When an electron is placed in a t_{2g} orbital rather than in one of the five degenerate d orbitals, the stabilization of the magnitude of 0.4 Å 0 is obtained. This is why the stabilities of high spin octahedral complexes of Mn^{2+} ions
between Mn$^{+2}$ and Zn$^{+2}$ with a given ligand frequently vary in the natural order of stability. The d$^3$ and d$^8$ will be most stable since they have the greatest CFSE.

(b) **Properties of Ligands**:

1. **Basic strength of ligand**: It is well known that more available the electron pair of the group, the stronger is the covalent bond which it may form with a metal.$^{55}$

2. **Chelate formation**:

   The formation of a chelate ring increases the stability of a complex over$^{56}$ that of comparable complexes where chelation is not possible, for example, $\text{Ni(en)}_3^{+2}$ $\text{Ni(NH}_3)_6^{+2}$. The more extensive the chelation, the more extensive the chelation, the more stable the complex. The stability of complexes depends upon the number of rings. The greater the number of rings, the higher is the stability. Pfeiffer observed that in general the five numbered ring is more stable when the ring is entirely saturated, but the six numbered rings$^{56}$ also favoured when one or more double bonds are present.

3. **Resonance effect**:

   The importance of resonance effects on the stability of metal chelates has been investigated by Calvin and Wilson (1943)$^{55}$ They came to the conclusion that unhindered resonance of the chelate came to the conclusion that
unhindered resonance of the chelate ring enhances the 
stability. On the other hand, resonance in the attached 
benzene rings may interfere with resonance of the chelate 
is lowered down.

(c) Steric effect:

These are associated with the presence of bulky 
groups either attached to or near enough to a donor atom to 
cause mutual repulsion between the ligands and the acid, therefore 
a weakening of metal-ligand bonds.\textsuperscript{57,58} In amino acids, 
the stability has been observed in the order L-glutamine \textless 
L-asparagine \textless L-valine \textless L-leucine \textless α-alanine \textless glycine 
which is purely due to steric hindrance and basicities of 
amino acids.

Conclusion:

In the present study the stability of complexes has 
been observed in the following orders

1. \( | M(\text{fer.}) | \textless | M(\text{acet.}) | \textless | M(\text{prop.}) | \)

2. \( | M(L\text{-glut.}) | \textless | M(L\text{-asp.}) | \textless | M(L\text{-val.}) | \textless 
    | M(L\text{-leu.}) | \textless | M(α\text{-ala.}) | \textless | M(\text{gly.}) | \)

and for ternary complexes, the order of stabilities is same 
as in binary complexes. The reasons have already been given 
in the previously pages. Besides these, pH, of the solution, 
ionic strength (\( \mu \)) and variation of temperature also affect 
the stability of complexes.
References:


