CHAPTER III

DETERMINATION OF STABILITY CONSTANTS OF Hg(II)- DIEN/ AMINE/AMINO ACID/THIOACID MIXED LIGAND COMPLEXES.
The present chapter deals with equilibrium studies of the following MA and MAL type simple and mixed ligand complexes of Hg(II).

A. (1) Hg(II)Cl-dien
B. (1) Hg(II)-dien/amine
   (ii) Hg(II)Cl-dien/amine
C. (1) Hg(II)-dien/amine acid
   (ii) Hg(II)Cl-dien/amine acid
D. (1) Hg(II)-dien/thioacid
   (ii) Hg(II)Cl-dien/thioacid
E. (1) PhHg⁺-dien/amine acid.

Diethylenetriamine was considered as the primary ligand and an amine i.e. ethylenediamine, diethylenetriamine, 2-aminoethanol; amino acid i.e. glycine, L-lysine, L-histidine DL-alanine, glutamic acid and L-cysteine, thioacid, i.e. thioglycolic acid was considered as the secondary ligand. Only three amino acids namely glycine, L-lysine and DL-alanine were taken as secondary ligands for system E. The step stability constants were evaluated.
at two different temperatures viz. 30°C and 45°C at 0.1 M ionic strength (with respect to KNO₃). With the help of stabilities at two temperatures the thermodynamic parameters namely ΔF°, ΔH° and ΔS° were calculated. The titrations have been carried out employing Bjerrum-Calvin’s pH titration technique as modified by Irving and Rossotti.

**EXPERIMENTAL**

**Materials**:- The details regarding the materials used, the method of preparation of standard solutions along with experimental set up, instrumentation have already been mentioned in the previous chapter. Some more details are described below:-

**Ligand solutions**; The ligands which have been used for these studies and the methods of preparation of their solutions are the same as mentioned in the previous chapter. However, one more ligand diethylenetriamine (dien) obtained from Plafz & Bauer, Stanford, (Conn. USA) has been used in the present studies.

**Primary complex solution**; Hg(dien)(ClO₄)₂ complex was prepared by mixing freshly prepared solution of mercuric perchlorate with 3.433 gms of dien in minimum amount of
water. The reaction mixture was shaken well and then cooled in ice bath for two hours. The crystals were filtered washed with cold water and ethanol and finally dried at 40°C in an oven. The results on analysis and i.r. of this complex are given in Chapter IV page 93, 95. (0.01 M) solution of this complex was prepared by dissolving 0.503 gms in 100 ml of redistilled water. Mercuric perchlorate solution was prepared by treating a solution of 9.50 gms of mercuric chloride with excess of 2M NaOH and decanting the supernatant liquid several times. The precipitated mercuric oxide was dissolved in minimum amount of warm 1:1 perchloric acid and solution filtered quantitatively with a few washings.

\[
\text{HgCl}_2\text{-dien solution} = 0.01 \text{M primary complex solution was prepared by mixing 50 ml each of 0.05 M diethylenetriamine and mercuric chloride solutions and raising the volume to 250 ml.}
\]

\[
\text{PhHg}^+ (\text{dien})\text{NO}_3 \text{ Solution: Phenylmercury nitrate (0.3396 gms) was weighed accurately and a paste of it made with hot water. Solution of dien (0.103 gms) in 50 ml of hot water was added slowly in small amounts with constant stirring. Phenylmercury nitrate dissolved slowly in presence of dien}
\]
and then the volume of the solution was raised to 100 ml with water.

**Instruments** including pH-meter, titration cell, thermostatic arrangement and other accessories as well as the titration techniques employed were the same as already described in the Chapter II.

**pH-titration technique and calculations:** In the present study diethylenetriamine acts as primary ligand in the metal complex formation. Following three reaction mixtures were prepared to study \( \text{Hg(II)} \)-dien/amine/amino acid/thioacid mixed ligand, as well as \( \text{Hg(II)} \)Cl-dien, simple systems.

1. **\( \text{Hg(II)} \)Cl-dien, simple systems**
   
   A, \( \text{KNO}_3(0.5\, \text{M}) \) 10.0 ml + \( \text{HNO}_3(0.1\, \text{M}) \) 5.0 ml
   
   B, \( \text{KNO}_3(0.5\, \text{M}) \) 10.0 ml + \( \text{HNO}_3(0.1\, \text{M}) \) 5.0 ml + primary ligand (0.01M) 10.0 ml.
   
   C, \( \text{KNO}_3(0.5\, \text{M}) \) 10.0 ml + \( \text{HNO}_3(0.1\, \text{M}) \) 5.0 ml + primary complex solution (0.01M) 10.0 ml.

2. **\( \text{Hg(II)}/\text{Hg(II)} \)Cl-dien/amine/amino acid/thioacid, mixed ligand systems**:

   A, \( \text{KNO}_3(0.5\, \text{M}) \) 10.0 ml + \( \text{HNO}_3(0.1\, \text{M}) \) 5.0 ml
   
   B, \( \text{KNO}_3(0.5\, \text{M}) \) 10.0 ml + \( \text{HNO}_3(0.1\, \text{M}) \) 5.0 ml + secondary ligand (0.01M) 10.0 ml.
The total volume in both cases was raised to 50 ml containing 10% ethanol. The solutions were titrated with a standard solution of alkali at two different temperatures i.e. 30°C and 45°C. The solutions were kept for at least thirty minutes in a thermostat in order to allow them to attain the requisite temperature and then titrated separately. The desired ionic strength was maintained by adding KNO₃ solution.

(A) \textbf{Hg(II)Cl-dien complex, simple system:}

Figure 20 deals with the pH titration curves of the Hg(II)Cl-dien complex simple system. From the titration curves it has been observed that for the same amount of alkali the ligand titration curves (B) show higher pH values as compared to acid curve designated by (A) and finally coincides with the acid curve above pH 10. The metal-ligand titration curve (C) coincides with the ligand curve (B) upto pH 3.5 and then diverges towards right indicating the release of protons due to complex formation. The horizontal distance between curve (A) and (B) was taken to evaluate
the pH values of the diethylenetriamine ligand and the horizontal distance between curves (B) and (C) was taken to evaluate the average number of ligands attached per metal ion.

pL was calculated by the same method as described in the previous chapter. Formation curves were prepared and are shown in figure 21. The results on step stability constants and other thermodynamic parameters are given in Table I.

(B) Hg(II)/Hg(II)Cl-dien/amine mixed ligand systems;

Figures 22—27 deal with the pH titration curves of above HAL type mixed ligand complexes, (where A = dien and L = en, dien and 2anath). The pH titration curves for the above systems show that for Hg(II) mixed ligand systems, the divergence of mixed ligand metal curve designated by (C) generally takes place between 3.0-4.0 pH. However, in the case of Hg(II)Cl systems the divergence of metal-ligand curve (C) from the secondary ligand curve (B) generally takes place above 6.0 pH. The formation curves of the above systems are given in figures 28, 29. Results obtained on step stability constants and other thermodynamic parameters are given in Table II.
(C) \( \text{Hg(II)/Hg(II)Cl-dien/amino acid mixed ligand systems:} \)

The pH titration curves for these mixed ligand systems are given in figures 30-41. The amino acids which have been used as secondary ligands in the above systems are, glycine, L-lysine, L-histidine, DL-alanine, glutamic acid, and L-cysteine. The formation curves of \( \text{Hg(II)/Hg(II)Cl-dien/amino acid mixed ligand complexes of the type MAL} \) are given in figures 42-45. Results obtained on stepwise stability constants and other thermodynamic parameters like entropy, enthalpy, and free energy changes are given in Tables III A and III B.

(D) \( \text{Hg(II)/Hg(II)Cl-dien/thioacid mixed ligand systems:} \)

Figures 46, 47 deal with the pH titration curves of the above MAL type mixed ligand systems. Diethylenetriamine was considered as the primary ligand and thio glycolic acid as the secondary ligand. The formation curves of the above systems are given in figure 48. Results obtained on step stability constants and other thermodynamic parameters namely \( \Delta H^0 \), \( \Delta S^0 \), and \( \Delta F^0 \) at 30°C and 45°C are given in Table IV.
(E) **PhHg⁺ : dien : amino acid mixed ligand systems:**

The pH titration curves of the PhHg⁺ : dien : amino acid mixed ligand systems are given in Figures 49-51. Amino acids which have been considered as secondary ligands are glycine, L-lysine, DL-alanine. The formation curves of these systems are given in Figure 52. From the formation curves, the stability constants were evaluated by Bjerrum's half n method. Results on stability constants and other thermodynamic parameters, \( \Delta H^0 \), \( \Delta S^0 \), and \( \Delta F^0 \) are given in Table V.

**RESULTS AND DISCUSSION**

(A) **Hg(II)Cl-dien complex, MACl type, simple system.**

Diethyleneetriamine is completely protonated in the reaction mixture in presence of strong acid and on titrating with alkali, the deprotonation takes place according to the following equation:

\[
\begin{align*}
\text{[dien H\textsubscript{3}}^+] \quad & \stackrel{k_1}{\longrightarrow} \quad \text{[dien H\textsubscript{2}}^2+] + \text{H}^+ \\
\text{[dien H\textsubscript{2}}^2+] \quad & \stackrel{k_2}{\longrightarrow} \quad \text{[dien H}^+] + \text{H}^+ \\
\text{[dien H}^+] \quad & \stackrel{k_3}{\longrightarrow} \quad \text{[dien]} + \text{H}^+
\end{align*}
\]
The protonation constant values of dien have already been reported by Smith and Martell.\(^{(1)}\) The \(pK_1\), \(pK_2\) and \(pK_3\) values of dien at \(25^\circ C\) are 9.84, 9.02 and 4.23 respectively. When the reaction mixture containing mercuric chloride and primary ligand (dien) is titrated with standard alkali the deprotonation of protonated ligand (dien) starts and with the increase of pH the concentration of free ligand increases which then combines with the metal salt to form MACl primary complex according to the equation given below:

\[
\text{HgCl}_2 + \text{dien} \rightleftharpoons \text{Hg(dien)Cl} + \text{Cl}^-
\]

A perusal of the table (1) indicates that with the increase of temperature the free energy has more negative value at higher temperature. The entropy term is positive and overrides the unfavourable enthalpy term. Therefore the entropy term favours the complex formation.

(B) \(\text{Hg(II)/Hg(II)Cl-dien/en,dien,2amath mixed ligand systems}\):

The sequence of deprotonation of protonated amines and the values of \(pK_1\), \(pK_2\) and \(pK_3\) as reported by Smith and Martell\(^{(2)}\) have already been mentioned. When the
TABLE - I

METAL LIGAND STABILITY CONSTANTS OF 1:1:1 TERNARY Hg(II)Cl COMPLEX, IONIC STRENGTH \( \mu = 0.1 \text{M} (\text{KNO}_3) \)

| MAL system  | \(30^\circ\text{C}\) | | \(45^\circ\text{C}\) | | \(30^\circ\text{C}\) | |
|-------------|-----------------|-----------|-----------------|-----------|-----------------|
|              | \(-\Delta F^o\) | LogK kcal/mole | \(-\Delta F^o\) | LogK kcal/mole | \(\Delta H^o\) Kcal/mole | \(\Delta S^o\) cal/deg/mole |
| Hg(II)Cl-dien | 11.0 | 15.25 | 11.47 | 16.69 | 13.82 | 95.94 |
reaction mixture containing MA/MACl complex and secondary ligand in the ratio of 1:1 is titrated with standard alkali the deprotonation of amines takes place and concentration of free amines increases which then combines with the MA/MACl complex to form mixed ligand complex according to the equation.

\[
\begin{align*}
&\text{[Hg(II) - dien]} \\
\rightarrow^+ \text{[Hg(II) - dien - L]} \\
\text{[Cl-Hg-dien]^+} \rightarrow
\end{align*}
\]

Where L is the secondary ligand. A perusal of the table II indicates: \( \log K_{MAL}^{MA} \) values are generally higher than the \( \log K_{MACl}^{MAL} \) values. The reason for this may be that in the former case a five or six coordinate species is formed from three coordinate species while in the latter case the five or six coordinate species is derived from a four coordinate species.
### Metal Ligand Stability Constants of 1:1:1 Ternary Hg(II) Complexes

**Ionic Strength \( \mu = 0.1 \text{M} \) (KNO\(_3\))

<table>
<thead>
<tr>
<th>MAL system</th>
<th>30°0 Log(^{MAL})</th>
<th>-Δ(F^0) kcal/mole</th>
<th>45°0 Log(^{MAL})</th>
<th>-Δ(F^0) kcal/mole</th>
<th>ΔH(^0) kcal/mole</th>
<th>30°0 ΔS(^0) cal/deg/mole</th>
<th>45°0 ΔS(^0) cal/deg/mole</th>
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<tbody>
<tr>
<td>Hg(II)(dien)(en)</td>
<td>8.80</td>
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<td>-90.76</td>
<td>-90.75</td>
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<td>Hg(II)(dien)(dien)</td>
<td>7.35</td>
<td>10.19</td>
<td>7.63</td>
<td>11.10</td>
<td>8.24</td>
<td>60.83</td>
<td>60.82</td>
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<tr>
<td>Hg(II)(dien)(2 amath)</td>
<td>5.00</td>
<td>6.93</td>
<td>3.30</td>
<td>4.80</td>
<td>-50.0</td>
<td>-142.15</td>
<td>-142.14</td>
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<table>
<thead>
<tr>
<th></th>
<th>30°0 Log(^{MAL})</th>
<th>-Δ(F^0) kcal/mole</th>
<th>45°0 Log(^{MAL})</th>
<th>-Δ(F^0) kcal/mole</th>
<th>ΔH(^0) kcal/mole</th>
<th>30°0 ΔS(^0) cal/deg/mole</th>
<th>45°0 ΔS(^0) cal/deg/mole</th>
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<tr>
<td>Hg(II)(dien)(en)</td>
<td>6.51</td>
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<td>6.50</td>
<td>9.46</td>
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<td>Hg(II)(dien)(dien)</td>
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<td>6.95</td>
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<td>4.55</td>
<td>6.31</td>
<td>4.82</td>
<td>7.01</td>
<td>7.94</td>
<td>47.03</td>
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</table>
The negative enthalpy change values for the systems Hg(II)(dien)(en) and Hg(II)(dien)(2amath) $\log_{MA}^{MAL}$ are favourable for the complex formation whereas in all other systems the entropy term is favourable for complex formation.

(C) Hg(II)/Hg(II)Cl-dien/amino acid mixed ligand systems:

The sequence of protonation of various amino acids and the protonation constant values as reported by Smith and Martell have already been mentioned in the previous Chapter. A perusal of the tables IIIA and B indicate that $\log_{MA}^{MAL}$ values are generally higher than the corresponding values of $\log_{MACl}^{MAL}$. However, Table III B reveals that for the mixed ligand systems of L-histidine and L-cysteine the $\log_{MACl}^{MAL}$ values are higher as compared to the values of $\log_{MA}^{MAL}$ for the same systems as shown in Table III A. It may be attributed to the formation of MAClL species through an additional equilibrium. For the mixed ligand systems of glycine, L-lysine, and glutamic acid (Table III A) and L-cysteine (Table III B) the negative enthalpy term which is higher in magnitude as compared to the unfavourable entropy term, strongly favours the complex formation. Therefore the overall change in
# TABLE III A

METAL LIGAND STABILITY CONSTANTS OF $1:1:1$ Hg(II) COMPLEXES  
IONIC STRENGTH $\mu = 0.1$ M (KNO$_3$)

<table>
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<tr>
<th>MAL system</th>
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<td></td>
<td>MAL</td>
<td>$\Delta F^0$</td>
<td>MAL</td>
<td>$\Delta F^0$</td>
<td>$\Delta H^0$</td>
<td>$\Delta S^0$</td>
<td>$\Delta H^0$</td>
<td>$\Delta S^0$</td>
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<tr>
<td></td>
<td>$\log_{\text{MAL}}$</td>
<td>kcal/mole</td>
<td>$\log_{\text{MAL}}$</td>
<td>kcal/mole</td>
<td>kcal/mole</td>
<td>cal/deg/mole</td>
<td>cal/deg/mole</td>
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<tr>
<td>Hg(II)(dien)(gly)</td>
<td>6.35</td>
<td>8.80</td>
<td>6.00</td>
<td>8.73</td>
<td>-10.29</td>
<td>-4.92</td>
<td>-4.91</td>
<td></td>
</tr>
<tr>
<td>Hg(II)(dien)(lys)</td>
<td>5.95</td>
<td>8.25</td>
<td>5.50</td>
<td>8.80</td>
<td>-13.24</td>
<td>-16.47</td>
<td>-13.96</td>
<td></td>
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<tr>
<td>Hg(II)(dien)(alan)</td>
<td>6.37</td>
<td>8.83</td>
<td>6.73</td>
<td>9.75</td>
<td>10.59</td>
<td>64.09</td>
<td>64.09</td>
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<tr>
<td>Hg(II)(dien)(glu)</td>
<td>6.31</td>
<td>8.75</td>
<td>6.02</td>
<td>8.76</td>
<td>-8.53</td>
<td>0.73</td>
<td>0.72</td>
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<tr>
<td>Hg(II)(dien)(cyst)</td>
<td>4.47</td>
<td>6.20</td>
<td>4.92</td>
<td>7.16</td>
<td>13.24</td>
<td>64.16</td>
<td>64.16</td>
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<tr>
<td>MAL system</td>
<td>30°C</td>
<td>45°C</td>
<td>30°C</td>
<td>45°C</td>
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<tr>
<td></td>
<td>Log\textsubscript{MAL}</td>
<td>$-\Delta F^0$ kcal/mole</td>
<td>Log\textsubscript{MAL}</td>
<td>$-\Delta F^0$ kcal/mole</td>
<td>$\Delta H^0$ kcal/mole</td>
<td>$\Delta S^0$ cal/deg/mole</td>
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<td>Hg(II)(dien)(gly)</td>
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<td>Hg(II)(dien)(lys)</td>
<td>5.50</td>
<td>7.63</td>
<td>6.75</td>
<td>9.82</td>
<td>36.76</td>
<td>146.50</td>
<td>146.48</td>
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<td>Hg(II)(dien)(hist)</td>
<td>4.30</td>
<td>5.96</td>
<td>4.85</td>
<td>7.06</td>
<td>16.18</td>
<td>73.07</td>
<td>73.08</td>
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<tr>
<td>Hg(II)(dien)(alan)</td>
<td>5.35</td>
<td>7.42</td>
<td>5.45</td>
<td>7.93</td>
<td>2.94</td>
<td>34.19</td>
<td>34.18</td>
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<tr>
<td>Hg(II)(dien)(glu)</td>
<td>5.84</td>
<td>8.10</td>
<td>6.33</td>
<td>9.21</td>
<td>14.41</td>
<td>74.29</td>
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<tr>
<td>Hg(II)(dien)(cyst)</td>
<td>5.70</td>
<td>7.90</td>
<td>5.45</td>
<td>7.93</td>
<td>-7.35</td>
<td>1.82</td>
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</table>
free energy is due to favourable enthalpy term. Tables III A and III B also reveal that for all other mixed ligand systems the entropy term is positive and over weighs the unfavourable enthalpy term. Therefore the overall change in free energy is due to favourable entropy term.

(D) $\text{Hg(II)/Hg(II)Cl-dien/thioacid mixed ligand systems}$

The protonation constants of thioglycolic acid as reported by Smith and Martell$^4$ and the order of protonation has been discussed in previous chapter. It is evident from Table IV that $\text{Log}^{\text{MAL}}_{\text{MACl}}$ values are higher than $\text{Log}^{\text{MAL}}_{\text{MA}}$ values. The free energy change has more negative value at higher temperature and the entropy change accompanying the complex formation is positive and higher in magnitude as compared to the unfavourable enthalpy term and as a result of this the entropy term favours the complex formation.

(E) $\text{PhHg}^+$ - dien / amino acid systems:

A perusal of the Table V shows that the stability constant values of $\text{PhHg}^+$ - dien : amino acid systems are
very low as compared to similar Hg(II) complexes. The negative enthalpy term for PhHg⁺(dien) alanine system is responsible for the overall free energy changes whereas in the other two systems the more positive entropy favours the complex formation.
### Table IV

**Metal Ligand Stability Constants of 1:1:1 Ternary Hg(II) Complexes**

Ionic Strength \( \mu = 0.1M (KNO_3) \)

<table>
<thead>
<tr>
<th>MAL System</th>
<th>Log ( K^{MAL} )</th>
<th>( \Delta F^{0} ) kcal/mole</th>
<th>Log ( K^{MAL} )</th>
<th>( \Delta F^{0} ) kcal/mole</th>
<th>( \Delta H^{0} ) kcal/mole</th>
<th>( \Delta S^{0} ) cal/deg/mole</th>
<th>( \Delta S^{0} ) cal/deg/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(II)(dien)(TGA)</td>
<td>4.73</td>
<td>6.56</td>
<td>5.10</td>
<td>7.42</td>
<td>10.88</td>
<td>57.56</td>
<td>57.55</td>
</tr>
<tr>
<td>Hg(II)(dien)(TGA)</td>
<td>5.77</td>
<td>8.00</td>
<td>6.34</td>
<td>9.23</td>
<td>16.76</td>
<td>81.72</td>
<td>81.72</td>
</tr>
</tbody>
</table>
### TABLE V

Metal Ligand Stability Constants of 1:1:1 Ternary PhHg⁺ Complexes

Ionic Strength 0.1M (KNO₃)

<table>
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<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PhHg(dien)glycine</td>
<td>3.02</td>
<td>4.19</td>
<td>3.05</td>
<td>4.44</td>
<td>0.88</td>
<td>16.73</td>
<td>16.73</td>
</tr>
<tr>
<td>PhHg(dien)lysine</td>
<td>3.25</td>
<td>4.51</td>
<td>3.80</td>
<td>5.53</td>
<td>16.18</td>
<td>68.28</td>
<td>68.27</td>
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<tr>
<td>PhHg(dien)alanine</td>
<td>3.32</td>
<td>4.61</td>
<td>3.04</td>
<td>4.42</td>
<td>-8.24</td>
<td>-11.98</td>
<td>-12.01</td>
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</table>
### REFERENCES

1. **Smith, R.M. and Martell, A.E.**  
   "Critical stability constants"  
   Vol. 2: Amines Plenum Press,  
   New York and London (1975)  
   P. 101.

2. **Ibid**  

3. **Martell, A.E. and Smith, R.M.**  
   Ibid, Vol. 1 (1974), PP. 1, 4,  
   27, 47, 58, 61.

4. **Martell, A.E. and Smith, R.M.**  