CHAPTER II

COMPOSITION OF METAL CHELATE COMPOUNDS
Ley\textsuperscript{1} during the investigation on copper glycinate complex assigned cyclic structure in order to account for its unusual colour and very low electrical conductance. He further studied the compounds formed by other metals and aminoacids. The special properties of these chelates were studied by employing several methods to show the formation of the cyclic structure. The experimental work of Werner,\textsuperscript{2} Ley (loc. cit) and Tschugaeff\textsuperscript{3} clearly showed the formation of covalent ring.

Ortho hydroxy aromatic aldehydes and ketones alone formed strong complexes with metal ions. In the case of m- and p- compounds complex formation did not take place. The formation of stable complexes, when the functional groups are present in ortho position, strongly supports the formation of a six membered ring.

The methods available for the determination of composition of chelates are briefly discussed in the following pages:

\textbf{Spectrophotometric Methods}

Ley (loc. cit) observed that characteristic colour is one of the important and distinguishing features of chelate compounds. He employed absorption spectra to distinguish free metal ion and the chelate compound. Pfeiffer\textsuperscript{4} investigated the coloured lakes of alizarin and its derivatives, and 6-,8\textsuperscript{1} -dihydroxy azo compounds and found that highly coloured lakes were formed only with dyes having acidic groups ortho to the chromophoric group.
Job's Method of Continuous Variations: The most common and familiar method of continuous variations was introduced by Job for the determination of the composition of the complexes. The principle of the method lies in the determination of optical densities of solutions containing different ratios of metal ion solution and the ligand solution, the total molar volume being kept constant.

The formation of a single and successive complexes on the addition of a reagent to metal ions in solution is discussed below.

Let a metal M react with n moles of ligand to form a complex MAₙ.

\[ M + nA \rightleftharpoons MAₙ; \quad K_{MAₙ} = \frac{[MAₙ]}{[M][A]^n} \quad \ldots \ (1) \]

where K is the formation constant and square brackets represent concentrations.

The optical density of the solution will have maximum or minimum value, when the complex formation was maximum or complete. A solution of the metal ion is mixed with a solution of the ligand (A) keeping the total molar concentration constant in each case. The following equations can be written:

\[ [M] = M_t - [MAₙ] \quad \ldots \ (2) \]
\[ [A] = A_t - n [MA_n] \]  \hspace{1cm} (3)

\( M_t \) and \( A_t \) are the total molarities of species containing \( M \) and \( A \). The optical density of the solution, \( D \), at a given wavelength represents the total absorption of all species in the solution.

\[ D = I \left( \epsilon_1[M] + \epsilon_2[A] + \epsilon_3[MA_n] \right) \]  \hspace{1cm} (4)

where \( I \) is the path length of the light through the solution and \( \epsilon_1, \epsilon_2 \) and \( \epsilon_3 \) are extinction coefficients of \( M, A \) and \( MA_n \) respectively. Let \( Y \) be a function which represents the differences in optical density \( D \) (Eq. 4) and the corresponding optical densities for no reaction.

\[ Y = I \left( \epsilon_1[M] + \epsilon_2[A] + \epsilon_3[MA_n] \right) - I \left( \epsilon_1 M_t + \epsilon_2 A_t \right) \]  \hspace{1cm} (5)

When the chelating agent is optically transparent Eq. 5 may be simplified by assuming \( \epsilon_2 = 0 \). If the length of the cell is 1 cm. the function \( Y \) is defined as

\[ Y = \epsilon_1[M] + \epsilon_3[MA_n] - \epsilon_1 M_t \]  \hspace{1cm} (6)

Differentiation of above equation with respect to \( A_t \) and combination with the differentiated form of Eq. 2 gives

\[ \frac{dY}{dA_t} = (\epsilon_3 - \epsilon_1) \frac{d[MA_n]}{dA_t} \]  \hspace{1cm} (7)

This equation is the basis for the Job's method of continuous variations, since \( \epsilon_1, \epsilon_2 \) and \( \epsilon_3 \) are finite quantities, a maximum or minimum in \( Y \) corresponds to a maximum in \( MA_n \).

If the total concentration of metal and chelating agent is maintained a constant, the maximum (or minimum) value of \( Y \), the
absorption intensity increment, will correspond to the maximum concentration of metal chelate, when the metal-ligand ratio used for the measurement corresponds to the actual interacting ratio. A plot of $Y$ versus the concentration of the experimental solution, generally expressed in terms of $X$, the mole fraction of chelating agent ($A$) will have a maximum (or minimum) at value of $X$ which corresponds to the composition of the metal chelate.

When a chelating agent interacts with a metal ion forming more than one complex, for example, the metal chelate $MA_n$ (Eq. 1) may further interact with $P$ moles of $A$ to form a species $MA_{n+p}$:

$$MA_n + pA \leftrightarrow MA_{n+p}; \quad K_{MA_{n+p}} = \frac{[MA_{n+p}]}{[MA_n][A]^P} \quad (8)$$

equations 2 and 3 now become

$$[M] = M_t - [MA_n] [MA_{n+p}] \quad \ldots \quad (9)$$

$$[A] = A_t - n[MA_n] - n+p [MA_{n+p}] \quad \ldots \quad (10)$$

Assuming $\varepsilon_A$ for $A$ is zero and $l = 1$ cm., the $Y$ function has the form

$$Y = \varepsilon_1 [M] + \varepsilon_3 [MA_n] + \varepsilon_4 [MA_{n+p}] - \varepsilon_1 M_t \quad \ldots \quad (11)$$

Differentiation of equation 11 and combination with differentiated form of (Eq. 9) give

$$\frac{dY}{dA_t} = (\varepsilon_3 - \varepsilon_1) \frac{d[MA_n]}{dA_t} + (\varepsilon_4 - \varepsilon_1) \frac{d[MA_{n+p}]}{dA_t} \quad \ldots \quad (12)$$

It is evident that the maximum value of $Y$ need not coincide with
maximum in $[MA_n]$ or $[MA_{n+p}]$ since it is not necessary that both $d[MA_n]/dA_t$ and $d[MA_{n+p}]/dA_t$ be zero simultaneously when $dY/dA_t$ is zero. Also, the value of $X$ at which $dY/dA_t$ is zero usually varies with the value of the extinction coefficient and therefore with the wavelength used.

If $\varepsilon_3$ coefficient of the lower chelate is greater than $\varepsilon_4$, the extinction coefficient of the higher chelate increases the likelihood of establishing the existence of the lower chelate in the equilibrium mixture. For many systems there is very little difference in the absorption intensities of the two chelate systems present. Vosburg and Cooper\textsuperscript{6} pointed out that combining ratios of metal and chelating agents may be determined, when stepwise chelate formation occurs, by the proper choice of wavelength. If a suitable wavelength can be found so that $\varepsilon_4 = \varepsilon_3$ and $\varepsilon_3 \neq \varepsilon_1$, the Eq. 11 is simplified. Equation 12 reduces to equation 7 and the maximum in $Y$ corresponds to the maximum in $MA_n$.

When the absorption intensities of the higher and lower chelates are equivalent ($\varepsilon_3 = \varepsilon_4$), Equation 12 becomes

$$\frac{dY}{dA_t} = (\varepsilon_3 - \varepsilon_1) \frac{d[MA_n]}{dA_t} + \frac{d[MA_{n+p}]}{dA_t} \quad \ldots \quad (13)$$

If the lower chelate $MA_n$ is more stable both $[MA_{n+p}]$ and $d[MA_{n+p}]/dA_t$ must be relatively small, and the maximum in $Y$ corresponds approximately to a maximum $MA_n$. 
Vosburg and Cooper (loc. cit.) used a different function \( Y^1 \) to determine the composition of the \( \text{MA}_{n+p} \) species. The \( Y^1 \) function has been defined as the difference between the measured optical density and the density calculated on the assumption that all of \( M \) has been converted to \( \text{MA}_n \).

\[
Y^1 = \epsilon_3 [\text{MA}_n] + \epsilon_4 [\text{MA}_{n+p}] - \epsilon_3 M_t \quad \ldots \quad (14)
\]

The assumption of the presence of a negligible concentration of free metal ion is generally valid, if the complexes are sufficiently stable. Under these conditions

\[
\frac{dY^1}{dA} = (\epsilon_4 - \epsilon_3) \frac{d[\text{MA}_{n+p}]}{dA} \quad \ldots \quad (15)
\]

If a wavelength is found where \( \epsilon_4 > \epsilon_3 \), a maximum in \( Y^1 \) corresponds to a maximum in \( \text{MA}_{n+p} \).

Similar treatment holds good in the case of three or more stable complexes.

**Slope Ratio Method:** This method was first proposed by Harvey and Manning for the determination of composition of complexes in solution. Consider the equation

\[
mA + nB \rightleftharpoons A_mB_n \quad \ldots \quad (1)
\]

If the concentration of \( B \) in equation 1 is constant and in sufficient excess to make dissociation negligible, the equilibrium concentration of the complex \( A_mB_n \) will be proportional to the concentration of \( A \) used in the reaction and hence

\[
[\text{A}_mB_n] = \frac{C_A}{n} \quad \ldots \quad (2)
\]
the brackets refer to equilibrium concentration and $C_A$ to the total concentration, from Beer's Law $E = \varepsilon L \left[ A_m B_n \right]$ .. (3)

where $E$ is the measured extinction, the molar extinction coefficient and $L$ the thickness of the cell in centimeters. Substituting the value $A_m B_n$ of Equation 2 into Equation 3.

$$E = \varepsilon L \frac{C_A}{m} \quad ...$$ (4)

$E$ is plotted against different concentrations of $A$, keeping the concentration of $B$ constant and in excess. Equation 4 is valid over the straight line portion of the curve and this will have a slope given by

$$\text{Slope}_1 = \varepsilon \frac{L}{m} \quad ...$$ (5)

Similarly if $A$ is the component in constant excess and the concentration of $B$ varied

$$[A_m B_n] = C_B/n \quad ...$$ (6)

If $E$ is plotted against $C_B$, the slope of straight line portion of the curve will be

$$\text{Slope}_2 = \varepsilon \frac{L}{n} \quad ...$$ (7)

The ratio of $n$ to $m$ in the complex may be determined by taking the ratio of the two slopes

$$\frac{\text{Slope}_1}{\text{Slope}_2} = \frac{n}{m} \quad ...$$ (8)

This method enables to establish the ratios of colour forming radicles to the metal ions.

**Molar Ratio Method**: Yoe and Jones in 1944 introduced molar ratio method for the determination of composition of complexes. For a stable complex, they observed, that a plot of optical density against molar ratio of component $B$ to
component A, with A constant, rose from the origin as a straight line and broke sharply to constant optical density at the molar ratio of the components of the complex. A complex which was slightly dissociated gave a continuous curve which became approximately parallel to the molar ratio axis only when an excess of the variable component was added. Results obtained by extrapolating this curve are uncertain. Harvey and Manning (loc. cit.) found that in some cases such curve may be made to break sharply at the correct molar ratio, if the ionic strength of the solution is adjusted by the addition of an unreacting electrolyte. Thus the molar ratio method may be extended by carefully controlling the ionic strength of the solution.

Polarographic Methods

The reduction (oxidation) potential of metal ion at the dropping mercury electrode (D.M.E) provides data for the detection of chelates in certain non-aqueous and aqueous solutions. In general, complex formation results in a shift of the reduction potential of a metal at the D.M.E to more negative values.

The correlation of this shifting of the potentials with both the concentration and with solution pH provides an excellent method for determining the composition of metal chelates.

The two important considerations for the use of half wave potential data for the elucidation of composition of complex are:
(1) the electrode reaction should be thermodynamically reversible
this is a necessary prerequisite to the analysis of data and
(2) the rate controlling step of the electrode reaction should
be the diffusion of the reducible species to the D.M.E. Since
the chelating agent is liberated in many systems at the surface
of the mercury drop, measurement of $E_1$ is made generally in the
presence of relatively large excess of ligand with respect to
metal ion.

Lingane$^9$ has summarised and classified the various elec-
trode reactions that involve chelated metal ions. The two types
that are frequently encountered in the analysis are: (1) reduc-
tion of the metal ion to the metallic state, accompanied by
the formation of amalgam, and (ii) reduction of metal chelate
from one oxidation state to another.

(1) The reduction of a chelated metal ion to the corre-
sponding amalgam proceeds as follows:

$$M^{n-pb}_p + ne + Hg \rightleftharpoons p^{A-b} + M(\text{Hg})$$

where $M(\text{Hg})$ represents the amalgam of the metal in its reduced
state. The corresponding simplified equation for the polaro-
graphic wave may be written thus:

$$E = E_\frac{1}{2} - \frac{0.0591}{n} \log \frac{i}{i_{d-1}} \cdots \quad (1)$$

where $E =$ applied potential at any point on the curve
$i =$ current flowing at potential $E$
\[ i_d = \text{limiting diffusion current} \]

\[ E_{1/2} = \text{half wave potential} \]

\[ n = \text{number of electrons involved in reduction} \]

The above equation may be used to determine the \( E_{1/2} \) as well as the reversibility of the electrode process. A plot of \( E \) vs. \( 1/(i_d - i) \) should be linear, the slope of which is equal to \(-0.0591/n\) for one electron reaction, \( n \) is equal to unity, and \( \Delta E/ \Delta \log i/(i_d - i) \) equals to \(-0.0591 \text{ volt}\). An integral value of 'n' is one of the requirements for reversibility. Furthermore the intercept along the \( E \) axis when \( \log i/i_d - 1 = 0 \), is equal to \( E_{1/2} \), the half wave potential.

(ii) The electrode reaction for a system in which a metal complex is reduced to a lower oxidation state is represented by the reaction:

\[
\begin{align*}
\text{MA}_p^{n^b} + n^e & \rightarrow \text{MA}_q^{n-a-q^b} + (p - q)^A^{-b} \\
\end{align*}
\]

The polarographic wave, in this case may be entirely cathodic, entirely anodic or cathodic-anodic, depending on whether the solution contains solely ions of the one oxidation state or a mixture of oxidation states. If the electrode process is reversible, the cathodic, the anodic and composite cathodic-anodic wave have identical \( E_{1/2} \) values. This behaviour may be used to establish further the reversibility of the reduction. The potential \( E \) at any point on the curve is defined by the relationship:
\[ E = E^o - \frac{0.0591}{n} \log \frac{1 - (i_d)}{(i_d)^c - 1} \] ...

where the subscripts of \( i_d \) denote cathodic (c) or anodic (a) current and the \( E^o \) is given by

\[ E^o = E^c - \frac{(n-a)(0.0591)}{n} \log A^{-b} \]

where \( E^c \) is the standard reduction potential corresponding to the transformation

\[ \text{MA}^{n-pb} (a=1) \quad \text{MA}^{n-s-qb} (s=1) + (p-q) A (s=1) \]

From the equation

\[ E = E^o - \frac{0.0591}{n} \log K_c - p \frac{0.0591}{n} \log A^{-b} \]

it follows that (i) the \( E \) should vary linearly with the logarithm of the free ligand concentration and (ii) the slope of the linear plot is given by the equation

\[ \frac{E}{\log A^{-b}} = -p \frac{0.0591}{n} \]

Since \( n \) for a reversible reaction may be obtained from equation 1, the 'Coordination number' \( p \) and thus the formula of metal chelate may be determined. By measuring \( E \) values at various known concentrations of the chelating agent, the coordination number and hence the composition of the chelate can be determined.

Many other methods based on electrical conductance, potentiometric, optical activity, solubility, reaction rates, X-ray measurements and oxidation potentials are also used for the determination of the composition of chelates.
REFERENCES