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Chapter

Stability Constants of Metal Complexes in Solution

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Abstract

In the formation of metal complexes in an aqueous medium, equilibrium constant or stability constant is used to determine the strength of interaction between reagents that make the final product after the formation of bonds. In general stability means that a complex may be stored for a long time under suitable conditions or this compound may be existing under suitable conditions. Regarding how much is the concentration of complexes in solution, stability constant provides this information via calculations. These calculations are very much important in many areas of science like chemistry, biology, and medicine. During the complex formation in aqueous medium, two types of stabilities are considered: one is the thermodynamic stability, and the other is kinetic stability. Stability of metal complexes may be affected by various factors like nature of central metal ion and ligand, chelating effect, etc., and some parameters like distribution coefficients, conductance, refractive index, etc. are useful for the determination of stability constants. Various modern techniques are used to determine the stability constant of simple as well as mixed ligand compounds.

Keywords: thermodynamic stability, kinetic stability, chelate effect, distribution method, ion exchange method, Bjerrum's method

1. Introduction

Stability constant of the formation of metal complexes is used to measure interaction strength of reagents. From this process, metal ion and ligand interaction formed the two types of metal complexes; one is supramolecular complexes known as host-guest complexes [1] and the other is anion-containing complexes. In the solution it provides and calculates the required information about the concentration of metal complexes.

Solubility, light, absorption conductance, partitioning behavior, conductance, and chemical reactivity are the complex characteristics which are different from their components. It is determined by various numerical and graphical methods which calculate the equilibrium constants. This is based on or related to a quantity, and this is called the complex formation function.

During the displacement process at the time of metal complex formation, some ions disappear and form a bonding between metal ions and ligands. It may be considered due to displacement of a proton from a ligand species or ions or molecules causing a drop in the pH values of the solution [2]. Irving and Rossotti

developed a technique for the calculation of stability constant, and it is called potentiometric technique.

To determine the stability constant, Bjerrum has used a very simple method, and that is metal salt solubility method. For the studies of a larger different variety of polycarboxylic acid-, oxime-, phenol-containing metal complexes, Martel and Calvin used the potentiometric technique for calculating the stability constant. Those ligands [3, 4] which are uncharged are also examined, and their stability constant calculations are determined by the limitations inherent in the ligand solubility method. The limitations of the metal salt solubility method and the result of solubility methods are compared with this. M-L, MLM, and (M3) L are some types of examples of metal-ligand bonding. One thing is common, and that is these entire types metal complexes all have one ligand.

The solubility method can only usefully be applied to studies of such complexes, and it is best applied for ML; in such types of system, only ML is formed. Jacqueline Gonzalez and his co-worker propose to explore the coordination chemistry of calcium complexes. Jacqueline and et al. followed this technique for evaluate the as partial model of the manganese-calcium cluster and spectrophotometric studies of metal complexes, i.e., they were carried calcium(II)-1,4-butanediamine in acetonitrile and calcium(II)-1,2-ethylendiamine, calcium(II)-1,3-propanediamine by them.

Spectrophotometric programming of HypSpec and received data allows the determination of the formation of solubility constants. The logarithmic values, log β_{110} = 5.25 for calcium(II)-1,3-propanediamine, log β_{110} = 4.072 for calcium(II)-1,4-butanediamine, and log β_{110} = 4.69 for calcium(II)-1,2-ethylendiamine, are obtained for the formation constants [5]. The structure of Cimetidine and histamine H2-receptor is a chelating agent. Syed Ahmad Tirmizi has examined Ni(II) cimetidine complex spectrophotometrically and found an absorption peak maximum of 622 nm with respect to different temperatures.

Syed Ahmad Tirmizi have been used to taken 1:2 ratio of metal and cimetidine compound for the formation of metal complex and this satisfied by molar ratio data. The data, 1.40–2.4 × 10^8, was calculated using the continuous variation method and stability constant at room temperature, and by using the mole ratio method, this value at 40°C was 1.24–2.4 × 10^8. In the formation of lead(II) metal complexes with 1-(aminomethyl) cyclohexene, Thanavelan et al. found the formation of their binary and ternary complexes. Glycine, L-proline, L-alanine, L-isoleucine, L-valine, and L-leucine are α-amino acids, and these are important biologically [6]. These α-amino acids are also investigated by potentiometric technique at 32°C. The mixed ligands were also studied using these methods. 50% (v/v) DMSO-water medium used for the determination of acidity constants and their stability constants these type ligands. In a stepwise manner, the ternary complexes were synthesized.

Using the stability constant method, these ternary complexes were found out, and using the parameters such as $\Delta \log K$ and $\log X$, these ternary complex data were compared with binary complex. The potentiometric technique at room temperature (25°C) was used in the investigation of some binary complex formations by Abdelatty Mohamed Radalla. These binary complexes are formed with 3D transition metal ions like Cu^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} and gallic acid's importance as a ligand and 0.10 mol dm^{-3} of $NaNO_3$. Such types of aliphatic dicarboxylic acids are very important biologically. Many acid-base characters and the nature of using metal complexes have been investigated and discussed time to time by researchers [7].

The above acids (gallic and aliphatic dicarboxylic acid) were taken to determine the acidity constants. For the purpose of determining the stability constant, binary and ternary complexes were carried in the aqueous medium using the experimental conditions as stated above. The potentiometric pH-metric titration curves are inferred for the binary complexes and ternary complexes at different ratios, and

formation of ternary metal complex formation was in a stepwise manner that provided an easy way to calculate stability constants for the formation of metal complexes.

The values of $\Delta \log K$, percentage of relative stabilization (% R. S.), and log X were evaluated and discussed. Now it provides the outline about the various complex species for the formation of different solvents, and using the concentration distribution, these complexes were evaluated and discussed. The conductivity measurements have ascertained for the mode of ternary chelating complexes.

A study by Kathrina and Pekar suggests that pH plays an important role in the formation of metal complexes. When epigallocatechin gallate and gallic acid combine with copper(II) to form metal complexes, the pH changes its speculation. We have been able to determine its pH in frozen and fluid state with the help of multifrequency EPR spectroscopy [8]. With the help of this spectroscopy, it is able to detect that each polyphenol exhibits the formation of three different mononuclear species. If the pH ranges 4–8 for di- or polymeric complex of Cu(II), then it conjectures such metal complexes. It is only at alkaline pH values.

The line width in fluid solutions by molecular motion exhibits an incomplete average of the parameters of anisotropy spin Hamilton. If the complexes are different, then their rotational correlation times for this also vary. The analysis of the LyCEP anisotropy of the fluid solution spectra is performed using the parameters determined by the simulation of the rigid boundary spectra. Its result suggests that pH increases its value by affecting its molecular mass. It is a polyphenol ligand complex with copper, showing the coordination of an increasing number of its molecules or increasing participation of polyphenol dimers used as ligands in the copper coordination region.

The study by Vishenkova and his co-worker [8] provides the investigation of electrochemical properties of triphenylmethane dyes using a voltammetric method with constant-current potential sweep. Malachite green (MG) and basic fuchsin (BF) have been chosen as representatives of the triphenylmethane dyes [9]. The electrochemical behavior of MG and BF on the surface of a mercury film electrode depending on pH, the nature of background electrolyte, and scan rate of potential sweep has been investigated.
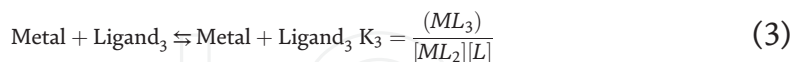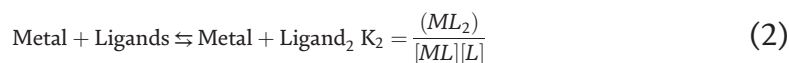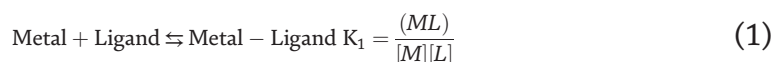
Using a voltammetric method with a constant-current potential sweep examines the electrical properties of triphenylmethane dye. In order to find out the solution of MG and BF, certain registration conditions have been prescribed for it, which have proved to be quite useful. The reduction peak for the currents of MG and BF has demonstrated that it increases linearly with respect to their concentration as 9.0×10^{-5}–7.0×10^{-3} mol/dm^3 for MG and 6.0×10^{-5}–8.0×10^{-3} mol/dm^3 for BF and correlation coefficients of these values are 0.9987 for MG and 0.9961 for BF [10].

5.0×10^{-5} and 2.0×10^{-5} mol/dm^3 are the values used as the detection limit of MG and BF, respectively. Stability constants are a very useful technique whose size is huge. Due to its usefulness, it has acquired an umbrella right in the fields of chemistry, biology, and medicine. No science subject is untouched by this. Stability constants of metal complexes are widely used in the various areas like pharmaceuticals as well as biological processes, separation techniques, analytical processes, etc. In the presented chapter, we have tried to explain this in detail by focusing our attention on the applications and solutions of stability of metal complexes in solution.
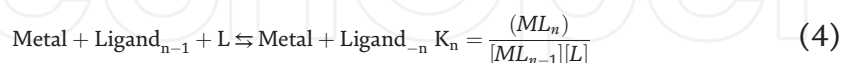
2. Stability constant of metal complexes

Stability or formation or binding constant is the type of equilibrium constant used for the formation of metal complexes in the solution. Acutely, stability
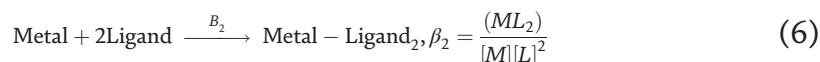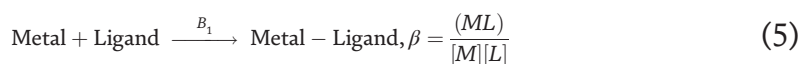
constant is applicable to measure the strength of interactions between the ligands and metal ions that are involved in complex formation in the solution [11]. A generally these 1-4 equations are expressed as the following ways:

$$\text{Metal} + \text{Ligand} \leftrightharpoons \text{Metal} - \text{Ligand} \; K_1 = \frac{(ML)}{[M][L]} \tag{1}$$

$$\text{Metal} + \text{Ligands} \leftrightharpoons \text{Metal} + \text{Ligand}_2 \; K_2 = \frac{(ML_2)}{[ML][L]} \tag{2}$$

$$\text{Metal} + \text{Ligand}_3 \leftrightharpoons \text{Metal} + \text{Ligand}_3 \; K_3 = \frac{(ML_3)}{[ML_2][L]} \tag{3}$$

Thus

$$\text{Metal} + \text{Ligand}_{n-1} + \text{L} \leftrightharpoons \text{Metal} + \text{Ligand}_{-n} \; K_n = \frac{(ML_n)}{[ML_{n-1}][L]} \tag{4}$$

K_1, K_2, K_3, ... K_n are the equilibrium constants and these are also called stepwise stability constants. The formation of the metal-ligand$_{-n}$ complex may also be expressed as equilibrium constants by the following steps:

$$\text{Metal} + \text{Ligand} \xrightarrow{\;B_1\;} \text{Metal} - \text{Ligand}, \beta = \frac{(ML)}{[M][L]} \tag{5}$$

$$\text{Metal} + 2\text{Ligand} \xrightarrow{\;B_2\;} \text{Metal} - \text{Ligand}_2, \beta_2 = \frac{(ML_2)}{[M][L]^2} \tag{6}$$

$$\text{Thus Metal} + n\text{Ligand} \xrightarrow{\;B_n\;} \text{Metal} - \text{ligandLn}, \beta_n = \frac{(MLn)}{[M][L]^n} \tag{7}$$

β_1, β_2, β_3, ... β_n are the equilibrium constants, and these equilibrium constants are known as overall stability constants or overall formation. β_n is called as the nth cumulative or overall formation constant [12]. Any metal complexes will be of greater stability if its stability constant has the higher value. Sometimes the 1/k values are alternative values of stability constant, and now this is called as instability constant. $\log_{10}K_1$, $\log_{10}K_2$ ... $\log_{10}K_n$, and $\log_{10}\beta_n$ are the ways that expressed the stepwise and cumulative stability constants.

3. Relationship or interaction between β_n and K_1, K_2, K_3, ... K_n

The parameters K and β are related together, and these are expressed in the following example:

$$\beta_3 = \frac{(ML_3)}{[M][L]3} \tag{8}$$

Now the numerator and denominator are multiplied together with the use of [metal-ligand] [metal-ligand$_2$], and after the rearranging we get the following equation:

$$\beta_3 = \frac{[ML_3]}{[M][L]^3} \times \frac{[ML][ML_2]}{[ML][ML_2]} \tag{9}$$

$$= \frac{[ML_1]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]} = K_1 \times K_2 \times K_3$$

$$\text{Thus } \beta_n = \frac{[ML_1]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} .... \frac{[ML_n]}{[ML_{n-1}][L]} = K_1 \times K_2 ... K_n \tag{10}$$

Now we expressed it as the following:

$$\beta_n = \sum_{n=1}^{n=n} K_n \qquad (11)$$

From the above relation, it is clear that the overall stability constant β_n is equal to the product of the successive (i.e., stepwise) stability constants, $K_1, K_2, K_3, \ldots K_n$. This in other words means that the value of stability constants for a given complex is actually made up of a number of stepwise stability constants. The term stability is used without qualification to mean that the complex exists under a suitable condition and that it is possible to store the complex for an appreciable amount of time. The term stability is commonly used because coordination compounds are stable in one reagent but dissociate or dissolve in the presence of another regent. It is also possible that the term stability can be referred as an action of heat or light or compound. The stability of complex [13] is expressed qualitatively in terms of thermodynamic stability and kinetic stability.

3.1 Thermodynamic stability

In a chemical reaction, chemical equilibrium is a state in which the concentration of reactants and products does not change over time. Often this condition occurs when the speed of forward reaction becomes the same as the speed of reverse reaction. It is worth noting that the velocities of the forward and backward reaction are not zero at this stage but are equal.

If hydrogen and iodine are kept together in molecular proportions in a closed process vessel at high temperature (500°C), the following action begins:

$$H_2 + I_2 \rightarrow 2HI \qquad (12)$$

In this activity, hydrogen iodide is formed by combining hydrogen and iodine, and the amount of hydrogen iodide increases with time. In contrast to this action, if the pure hydrogen iodide gas is heated to 500°C in the reaction, the compound is dissolved by reverse action, which causes hydrogen iodide to dissolve into hydrogen and iodine, and the ratio of these products increases over time. This is expressed in the following reaction:

$$2HI \rightarrow H_2 + I_2 \qquad (13)$$

For the formation of metal chelates, the thermodynamic technique provides a very significant information. Thermodynamics is a very useful technique in distinguishing between enthalpic effects and entropic effects. The bond strengths are totally effected by enthalpic effect, and this does not make any difference in the whole solution in order/disorder. Based on thermodynamics the chelate effect below can be best explained. The change of standard Gibbs free energy for equilibrium constant is response:

$$\Delta G = -2.303 \, RT \, \log_{10} \beta. \qquad (14)$$

Where:
R = gas constant
T = absolute temperature
At 25°C,

$\Delta G = (-5.708 \text{ kJ mol}^{-1}) \cdot \log \beta$.

The enthalpy term creates free energy, i.e.,

$$\Delta G = \Delta H - T\Delta S \qquad (15)$$

For metal complexes, thermodynamic stability and kinetic stability are two interpretations of the stability constant in the solution. If reaction moves from reactants to products, it refers to a change in its energy as shown in the above equation. But for the reactivity, kinetic stability is responsible for this system, and this refers to ligand species [14].

Stable and unstable are thermodynamic terms, while labile and inert are kinetic terms. As a rule of thumb, those complexes which react completely within about 1 minute at 25°C are considered labile, and those complexes which take longer time than this to react are considered inert. $[\text{Ni(CN)}_4]^{2-}$ is thermodynamically stable but kinetically inert because it rapidly exchanges ligands.

The metal complexes $[\text{Co(NH3)}_6]^{3+}$ and such types of other complexes are kinetically inert, but these are thermodynamically unstable. We may expect the complex to decompose in the presence of acid immediately because the complex is thermodynamically unstable. The rate is of the order of 10^{25} for the decomposition in acidic solution. Hence, it is thermodynamically unstable. However, nothing happens to the complex when it is kept in acidic solution for several days. While considering the stability of a complex, always the condition must be specified. Under what condition, the complex which is stable or unstable must be specified such as acidic and also basic condition, temperature, reactant, etc.

A complex may be stable with respect to a particular condition but with respect to another. In brief, a stable complex need not be inert and similarly, and an unstable complex need not be labile. It is the measure of extent of formation or transformation of complex under a given set of conditions at equilibrium [15].

Thermodynamic stability has an important role in determining the bond strength between metal ligands. Some complexes are stable, but as soon as they are introduced into aqueous solution, it is seen that these complexes have an effect on stability and fall apart. For an example, we take the $[\text{Co (SCN)}_4]^{2+}$ complex. The ion bond of this complex is very weak and breaks down quickly to form other compounds. But when $[\text{Fe(CN)}_6]^{3-}$ is dissolved in water, it does not test Fe^{3+} by any sensitive reagent, which shows that this complex is more stable in aqueous solution. So it is indicated that thermodynamic stability deals with metal-ligand bond energy, stability constant, and other thermodynamic parameters.

This example also suggests that thermodynamic stability refers to the stability and instability of complexes. The measurement of the extent to which one type of species is converted to another species can be determined by thermodynamic stability until equilibrium is achieved. For example, tetracyanonickelate is a thermodynamically stable and kinetic labile complex. But the example of hexa-amine cobalt(III) cation is just the opposite:

$$\left[\text{Co(NH}_3)_6\right]^{3+} + 6\text{H}_3\text{O}^+ \rightarrow \left[\text{Co(H}_2\text{O)}_6\right]^{3+} + 6\text{NH}_4^{+} \qquad (16)$$
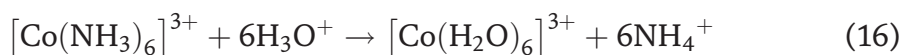
Thermodynamics is used to express the difference between stability and inertia. For the stable complex, large positive free energies have been obtained from ΔG_0 reaction. The ΔH_0, standard enthalpy change for this reaction, is related to the equilibrium constant, β_n, by the well thermodynamic equation:

$$\Delta G_0 = -RT \ln \beta \qquad (17)$$

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 \qquad (18)$$

For similar complexes of various ions of the same charge of a particular transition series and particular ligand, ΔS_0 values would not differ substantially, and hence a change in ΔH_0 value would be related to change in β_n values. So the order of values of ΔH_0 is also the order of the β_n value.

3.2 Kinetic stability

Kinetic stability is referred to the rate of reaction between the metal ions and ligand proceeds at equilibrium or used for the formation of metal complexes. To take a decision for kinetic stability of any complexes, time is a factor which plays an important role for this. It deals between the rate of reaction and what is the mechanism of this metal complex reaction.

As we discuss above in thermodynamic stability, kinetic stability is referred for the complexes at which complex is inert or labile. The term "inert" was used by Tube for the thermally stable complex and for reactive complexes the term 'labile' used [16]. The naturally occurring chlorophyll is the example of polydentate ligand. This complex is extremely inert due to exchange of Mg^{2+} ion in the aqueous media.

4. Factors affecting the stability of complexes

The nature of central atom of metal complexes, dimension, its degree of oxidation, electronic structure of these complexes, and so many other properties of complexes are affected by the stability constant. Some of the following factors described are as follows.

4.1 Nature of central metal ion

In the coordination chemistry, metal complexes are formed by the interaction between metal ions and ligands. For these type of compounds, metal ions are the coordination center, and the ligand or complexing agents are oriented surrounding it. These metal ions mostly are the transition elements. For the determination of stability constant, some important characteristics of these metal complexes may be as given below.

4.2 Ionic size

Ligands are oriented around the central metal ions in the metal complexes. The sizes of these metal ions determine the number of ligand species that will be attached or ordinated (dative covalent) in the bond formation. If the sizes of these metal ions are increased, the stability of coordination compound defiantly decreased. Zn(II) metal ions are the central atoms in their complexes, and due to their lower size (0.74A°) as compared to Cd(II) size (0.97A°), metal ions are formed more stable.
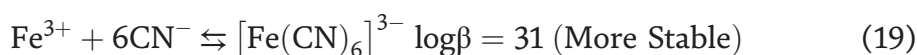
Hence, Al^{3+} ion has the greatest nuclear charge, but its size is the smallest, and the ion N^{3-} has the smallest nuclear charge, and its size is the largest [17]. Inert atoms like neon do not participate in the formation of the covalent or ionic compound, and these atoms are not included in isoelectronic series; hence, it is not easy to measure the radius of this type of atoms.

4.3 Ionic charge

The properties of stability depend on the size of the metal ion used in the complexes and the total charge thereon. If the size of these metal ions is small and the total

charge is high, then their complexes will be more stable. That is, their ratio will depend on the charge/radius. This can be demonstrated through the following reaction:

$$Fe^{3+} + 6CN^- \leftrightarrows [Fe(CN)_6]^{3-} \quad \log\beta = 31 \text{ (More Stable)} \qquad (19)$$

$$Fe^{2+} + 6CN^- \leftrightarrows [Fe(CN)_6]^{4-} \quad \log\beta = 8.3 \text{ (Less Stable)} \qquad (20)$$

An ionic charge is the electric charge of an ion which is formed by the gain (negative charge) or loss (positive charge) of one or more electrons from an atom or group of atoms. If we talk about the stability of the coordination compounds, we find that the total charge of their central metal ions affects their stability, so when we change their charge, their stability in a range of constant can be determined by propagating of error [18]. If the charge of the central metal ion is high and the size is small, the stability of the compound is high:

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+ \qquad (21)$$

$$Th^{4+} > Y^{3+} > Ca^{2+} > Na^+ \text{ and } La^{3+} > Sr^{2+} > K^+ \qquad (22)$$
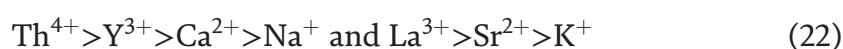
In general, the most stable coordination bonds can cause smaller and highly charged rations to form more stable coordination compounds.

4.4 Electronegativity

When an electron pair attracts a central ion toward itself, a strong stability complex is formed, and this is due to electron donation from ligand → metal ion. This donation process is increasing the bond stability of metal complexes exerted the polarizing effect on certain metal ions. Li^+, Na^+, Mg^{2+}, Ca^{2+}, Al^{3+}, etc. are such type of metal cation which is not able to attract so strongly from a highly electronegative containing stable complexes, and these atoms are O, N, F, Au, Hg, Ag, Pd, Pt, and Pb. Such type of ligands that contains P, S, As, Br and I atom are formed stable complex because these accepts electron from M → π-bonding. Hg^{2+}, Pb^{2+}, Cd^{2+}, and Bi^{3+} metal ions are also electronegative ions which form insoluble salts of metal sulfide which are insoluble in aqueous medium.

4.5 Temperature and pressure

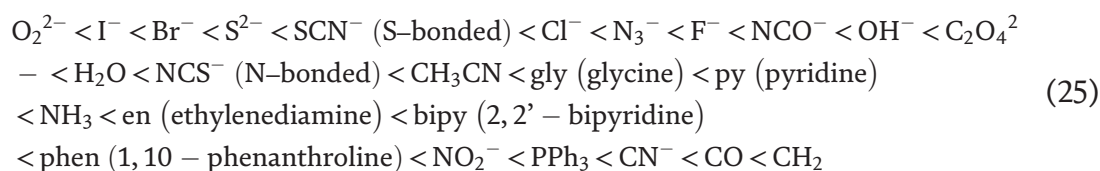Volatile ligands may be lost at higher temperature. This is exemplified by the loss of water by hydrates and ammonia:

$$[Co(NH_3)_6]Cl_3 \ (\Delta 175 - 180°C) \rightarrow [Co(NH_3)_5Cl]Cl_2 + NH_3 \qquad (23)$$

The transformation of certain coordination compounds from one to another is shown as follows:

$$AgHg[AgI_4] \ (red)(45°C) \leftrightarrows Ag_2[HgI_4] \ (yellow) \qquad (24)$$

4.6 Ligand nature

A ligand is an ion or small molecule that binds to a metal atom (in chemistry) or to a biomolecule (in biochemistry) to form a complex, such as the iron-cyanide coordination complex Prussian blue or the iron-containing blood-protein hemoglobin. The ligands are arranged in spectrochemical series which are based on the order of their field strength. It is not possible to form the entire series by studying

complexes with a single metal ion; the series has been developed by overlapping different sequences obtained from spectroscopic studies [19]. The order of common ligands according to their increasing ligand field strength is

$$O_2^{2-} < I^- < Br^- < S^{2-} < SCN^- \text{ (S–bonded)} < Cl^- < N_3^- < F^- < NCO^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- \text{ (N–bonded)} < CH_3CN < \text{gly (glycine)} < \text{py (pyridine)} < NH_3 < \text{en (ethylenediamine)} < \text{bipy (2, 2' – bipyridine)} < \text{phen (1, 10 – phenanthroline)} < NO_2^- < PPh_3 < CN^- < CO < CH_2 \tag{25}$$

The above spectrochemical series help us to for determination of strength of ligands. The left last ligand is as weaker ligand. These weaker ligand cannot forcible binding the 3d electron and resultant outer octahedral complexes formed. It is as- $Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+}$. For the given ligand, it is not possible to say about the exerted strong or weaker field on the central metal ion. The values of Δ are observed as:

1. Increasing the oxidation number the value of Δ increased.

2. Δ increases from top to bottom.

However, when we consider the metal ion, the following two useful trends are observed:

1. Δ increases with increasing oxidation number.

2. Δ increases down a group. For the determination of stability constant, the nature of the ligand plays an important role.

The following factors described the nature of ligands.

4.7 Size and charge

The size and charge are two factors that affect the production of metal complexes. The less charges and small sizes of ligands are more favorable for less stable bond formation with metal and ligand. But if this condition just opposite the product of metal and ligand will be a more stable compound. So, less nuclear charge and more size= less stable complex whereas if more nuclear charge and small in size= less stable complex. We take fluoride as an example because due to their smaller size than other halide and their highest electro negativity than the other halides formed more stable complexes. So, fluoride ion complexes are more stable than the other halides:

$$FeF_2^+ \ \log \beta = 6.0 \tag{26}$$

$$FeCl_2^+ \ \log \beta = 1.3 \tag{27}$$

As compared to S^{2-} ion, O_2^{2-} ions formed more stable complexes.

4.8 Basic character

It is suggested by Calvin and Wilson that the metal complexes will be more stable if the basic character or strength of ligands is higher. It means that the donating power of ligands to central metal ions is high [20].

It means that the donating power of ligands to central metal ions is high. In the case of complex formation of aliphatic diamines and aromatic diamines, the stable complex is formed by aliphatic diamines, while an unstable coordination complex is formed with aromatic diamines. So, from the above discussion, we find that the stability will be grater if the e-donation power is greater.
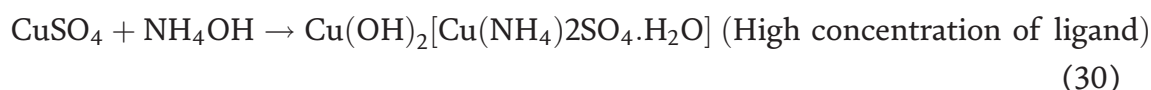
Thus it is clear that greater basic power of electron-donating species will form always a stable complex. NH_3, CN^-, and F^- behaved as ligands and formed stable complexes; on the other hand, these are more basic in nature.

4.9 Ligand concentration

We know that if the concentration of coordination group is higher, these coordination compounds will exist in the water as solution. It is noted that greater coordinating tendency show the water molecules than the coordinating group which is originally present. SCN^- (thiocynate) ions are present in higher concentration; with the Co^{2+} metal ion, it formed a blue-colored complex which is stable in state, but on dilution of water medium, a pink color is generated in place of blue, or blue color complex is destroyed by $[Co(H_2O)_6]^{2+}$, and now if we added further SCN^-, the pink color will not appear:

$$[Co(SCN)_4]^2 - + H_2O \leftrightarrows [Co(H_2O)_6]^{2+} + 4SCN^-$$

Blue   Pink   (28)
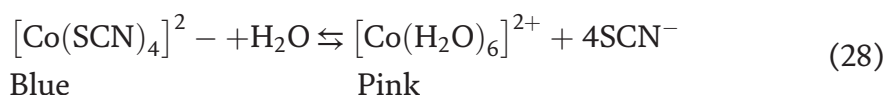
Now it is clear that H_2O and SCN^- are in competition for the formation of Co(II) metal-containing complex compound. In the case of tetra-amine cupric sulfate metal complex, ammonia acts as a donor atom or ligand. If the concentration of NH_3 is lower in the reaction, copper hydroxide is formed but at higher concentration formed tetra-amine cupric sulfate as in the following reaction:

$$CuSO_4 + NH_4OH \rightarrow Cu(OH)_2 \text{ (Small quantity of ligand)} \tag{29}$$

$$CuSO_4 + NH_4OH \rightarrow Cu(OH)_2[Cu(NH_4)2SO_4.H_2O] \text{ (High concentration of ligand)} \tag{30}$$

4.10 Chelating effect

For a metal ion, chelating ligand is enhanced and affinity it and this is known as chelate effect and compared it with non-chelating and monodentate ligand or the multidentate ligand is acts as chelating agent. Ethylenediamine is a simple chelating agent (**Figure 1**).

Due to the bidentate nature of ethylenediamine, it forms two bonds with metal ion or central atom. Water forms a complex with Ni(II) metal ion, but due to its monodentate nature, it is not a chelating ligand (**Figures 2** and **3**).

The dentate cheater of ligand provides bonding strength to the metal ion or central atom, and as the number of dentate increased, the tightness also increased. This phenomenon is known as chelating effect, whereas the formation of metal complexes with these chelating ligands is called chelation:
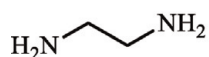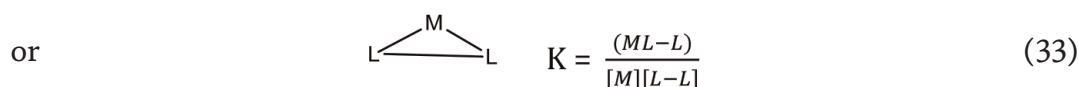

Figure 1.
Structure of ethylenediamine.
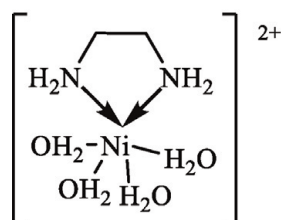
Figure 2.
Structure of chelating configuration of ethylenediamine ligand.
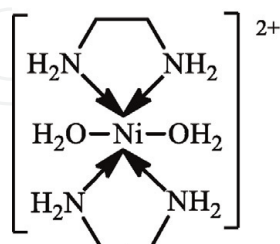
Figure 3.
Structure of chelate with three ethylenediamine ligands.

$$\text{Metal} + 2\,\text{Ligand} \leftrightarrow \text{MetalLigand}_2 \quad K = \frac{(ML2)}{[M][L]2} \tag{31}$$

$$\text{Metal} + \text{Ligand–Ligand} \leftrightarrow \text{MetalLigand} - \text{Ligand} \tag{32}$$

or $\quad K = \dfrac{(ML-L)}{[M][L-L]} \tag{33}$

Some factors are of much importance for chelation as follows.

4.11 Ring size

The sizes of the chelating ring are increased as well as the stability of metal complex decreased. According to Schwarzenbach, connecting bridges form the chelating rings. The elongated ring predominates when long bridges connect to the ligand to form a long ring. It is usually observed that an increased a chelate ring size leads to a decrease in complex stability.

He interpreted this statement. The entropy of complex will be change if the size of chelating ring is increased, i.e., second donor atom is allowed by the chelating ring. As the size of chelating ring increased, the stability should be increased with entropy effect. Four-membered ring compounds are unstable, whereas five-membered are more stable. So the chelating ring increased its size and the stability of the formed metal complexes.

4.12 Number of rings

The number of chelating rings also decides the stability of complexes. Non-chelating metal compounds are less stable than chelating compounds. These numbers increase the thermodynamic volume, and this is also known as an entropy term. In recent years ligands capable of occupying as many as six coordination positions on a single metal ion have been described. The studies on the formation constants of coordination compounds with these ligands have been reported.

The numbers of ligand or chelating agents are affecting the stability of metal complexes so as these numbers go up and down, the stability will also vary with it.

For the Ni(II) complexes with ethylenediamine as chelating agent, its log K_1 value is 7.9 and if chelating agents are trine and penten, then the log K_1 values are 7.9 and 19.3, respectively. If the metal ion change Zn is used in place of Ni (II), then the values of log K_1 for ethylenediamine, trine, and penten are 6.0, 12.1, and 16.2, respectively. The log βMY values of metal ions are given in **Table 1**.

$Ni(NH_3)_6{}^{2+}$ is an octahedral metal complex, and at 25 °C its log β_6 value is 8.3, but $Ni(ethylenediamine)_3{}^{2+}$ complex is also octahedral in geometry, with 18.4 as the value of log β_6. The calculated stability value of $Ni(ethylenediamine)_3{}^{2+}$ 10^{10} times is more stable because three rings are formed as chelating rings by ethylenediamine as compared to no such ring is formed. Ethylenediaminetetraacetate (EDTA) is a hexadentate ligand that usually formed stable metal complexes due to its chelating power.

4.13 Steric effect

A special effect in molecules is when the atoms occupy space. This is called steric effect. Energy is needed to bring these atoms closer to each other. These electrons run away from near atoms. There can be many ways of generating it. We know the repulsion between valence electrons as the steric effect which increases the energy of the current system [21]. Favorable or unfavorable any response is created.

For example, if the static effect is greater than that of a product in a metal complex formation process, then the static increase would favor this reaction. But if the case is opposite, the skepticism will be toward retardation.

This effect will mainly depend on the conformational states, and the minimum steric interaction theory can also be considered. The effect of secondary steric is seen on receptor binding produced by an alternative such as:

1. Reduced access to a critical group.

2. Stick barrier.

3. Electronic resonance substitution bond by repulsion.

4. Population of a conformer changes due to active shielding effect.

4.14 Macrocyclic effect

The macrocyclic effect is exactly like the image of the chelate effect. It means the principle of both is the same. But the macrocyclic effect suggests cyclic deformation of the ligand. Macrocyclic ligands are more tainted than chelating agents. Rather, their compounds are more stable due to their cyclically constrained constriction. It requires some entropy in the body to react with the metal ion. For example, for a

Metal ion	log βMY (25°C, I = 0.1 M)
Ca^{2+}	11.2
Cu^{2+}	19.8
Fe^{3+}	24.9

Table 1.
Metal ion vs. log βMY values.
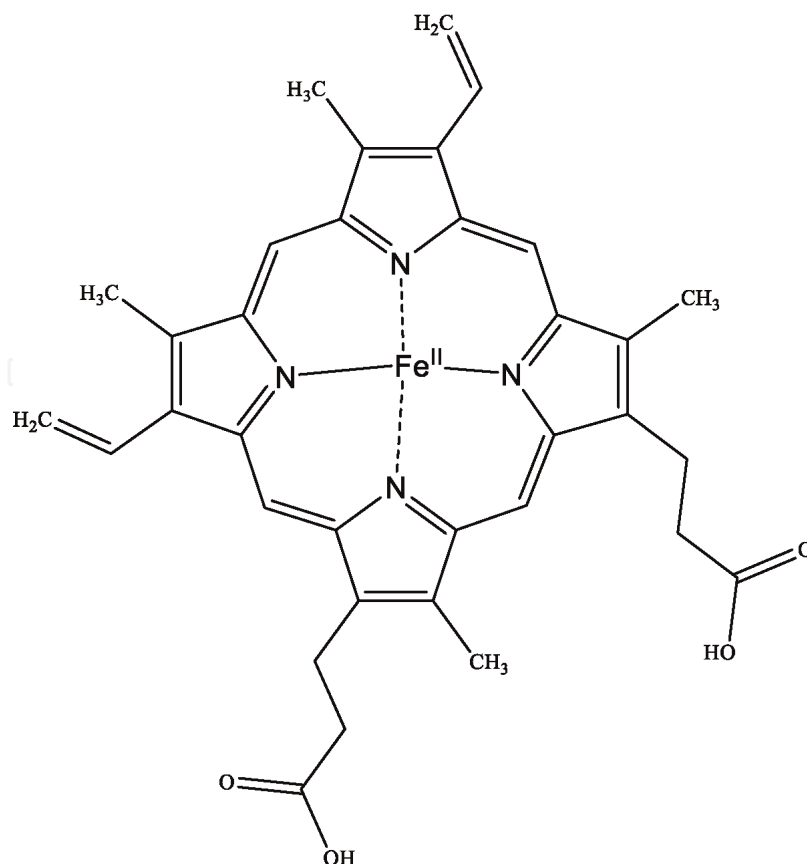
Figure 4.
Structure of hemoglobin is the biological complex compound which contains Fe(II) metal ion.

tetradentate cyclic ligand, we can use heme-B which forms a metal complex using Fe^{+2} ions in biological systems (**Figure 4**).

The n-dentate chelating agents play an important role for the formation of more stable metal complexes as compared to n-unidentate ligands. But the n-dentate macrocyclic ligand gives more stable environment in the metal complexes as compared to open-chain ligands. This change is very favorable for entropy (ΔS) and enthalpy (ΔH) change.

5. Determination of stability constants of complexes in solution

There are so many parameters to determination of formation constants or stability constant in solution for all types of chelating agents. These numerous parameters or techniques are refractive index, conductance, temperature, distribution coefficients, refractive index, nuclear magnetic resonance volume changes, and optical activity.

5.1 Methods based on study of heterogeneous equilibrium

5.1.1 Solubility methods

Solubility products are helpful and used for the insoluble salt that metal ions formed and complexes which are also formed by metal ions and are more soluble. The formation constant is observed in presence of donor atoms by measuring increased solubility.

5.1.2 Distribution method

To determine the solubility constant, it involves the distribution of the ligands or any complex species; metal ions are present in two immiscible solvents like water and carbon tetrachloride, benzene, etc.

5.1.3 Ion exchange method

In this method metal ions or ligands are present in solution and on exchanger. A solid polymers containing with positive and negative ions are ion exchange resins. These are insoluble in nature. This technique is helpful to determine the metal ions in resin phase, liquid phase, or even in radioactive metal. This method is also helpful to determine the polarizing effect of metal ions on the stability of ligands like Cu(II) and Zn(II) with amino acid complex formation.

5.1.4 Electrometric techniques

At the equilibrium free metal and ions are present in the solution, and using the different electrometric techniques as described determines its stability constant.

5.1.5 Potentiometric methods

This method is based upon the titration method or follows its principle. A stranded acid-base solution used as titrate and which is titrated, it may be strong base or strong acid follows as potentiometrically. The concentration of solution using 10^{3-} M does not decomposed during the reaction process, and this method is useful for protonated and nonprotonated ligands.

5.1.6 Polarographic method

This is the graphic method used to determine the stability constant in producing metal complex formation by plotting a polarograph between the absences of substances and the presence of substances. During the complex formation, the presence of metal ions produced a shift in the half-wave potential in the solution.

5.2 Other methods

5.2.1 Rate method

If a complex is relatively slow to form and also decomposes at measurable rate, it is possible, in favorable situations, to determine the equilibrium constant.

5.2.2 Freezing technique

This involves the study of the equilibrium constant of slow complex formation reactions. The use of tracer technique is extremely useful for determining the concentrations of dissociation products of the coordination compound.

5.2.3 Biological method

This method is based on the study of the effect of an equilibrium concentration of some ions on the function at a definite organ of a living organism. The

equilibrium concentration of the ion studied may be determined by the action of this organ in systems with complex formation.

5.2.4 Spectrophotometric method

The solution of 25 ml is adopted by preparing at the 1.0×10^{-5} M ligand or 1.0×10^{-5} M concentration and 1.0×10^{-5} M for the metal ion: $\log K = \dfrac{[HL]}{[l]} + pH$

The solutions containing the metal ions were considered both at a pH sufficiently high to give almost complete complexation and at a pH value selected in order to obtain an equilibrium system of ligand and complexes.

In order to avoid modification of the spectral behavior of the ligand due to pH variations, it has been verified that the range of pH considered in all cases does not affect absorbance values. Use the collected pH values adopted for the determinations as well as selected wavelengths. The ionic strengths calculated from the composition of solutions allowed activity coefficient corrections. Absorbance values were determined at wavelengths in the range 430–700 nm, every 2 nm.

5.2.5 Bjerrum's method

For a successive metal complex formation, use this method. If ligand is protonate and the produced complex has maximum number of donate atoms of ligands, a selective light is absorbed by this complex, while for determination of stability constant, it is just known about the composition of formed species.
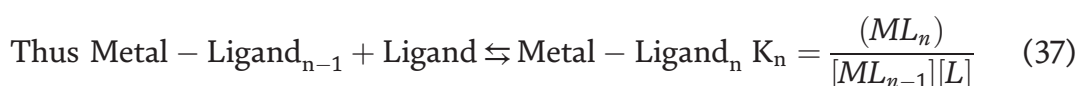
Bjerrum (1941) used the method stepwise addition of the ligands to coordination sphere for the formation of complex. So, complex metal–ligand$_n$ forms as the following steps [22]. The equilibrium constants, K_1, K_2, K_3, ... K_n are called stepwise stability constants. The formation of the complex metal-ligand$_n$ may also be expressed by the following steps and equilibrium constants.

Where:

M = central metal cation

L = monodentate ligand

N = maximum coordination number for the metal ion M for the ligand

$$\text{Metal} + \text{Ligand} \leftrightarrows \text{Metal} - \text{Ligand} \quad K_1 = \frac{(ML)}{[M][L]} \tag{34}$$

$$\text{Metal} - \text{Ligand} \leftrightarrows \text{Metal} - \text{Ligand}_2 \quad K_2 = \frac{(ML_2)}{[ML][L]} \tag{35}$$

$$\text{Metal} - \text{Ligand}_2 \leftrightarrows \text{Metal} - \text{Ligand}_3 \quad K_3 = \frac{(ML_3)}{[ML_2][L]} \tag{36}$$

$$\text{Thus Metal} - \text{Ligand}_{n-1} + \text{Ligand} \leftrightarrows \text{Metal} - \text{Ligand}_n \quad K_n = \frac{(ML_n)}{[ML_{n-1}][L]} \tag{37}$$

5.2.6 Isotopic dilution method

If a complex ion is slow to reach equilibrium, it is often possible to apply the method of isotopic dilution to determine the equilibrium concentration of one or more of the species. Most often radioactive isotopes are used.

5.2.7 Conductance measurement method

This method was extensively used by Werner and others to study metal complexes. In the case of a series of complexes of Co(III) and Pt(IV), Werner assigned the correct formulae on the basis of their molar conductance values measured in freshly prepared dilute solutions. In some cases, the conductance of the solution increased with time due to a chemical change, e.g.,

$$[Co(NH_3)_4 Br_2]^+ + 2H_2O \; [Co(NH_3)_4(H_2O)_2]^{3+} + 2Br^- \qquad (38)$$

6. Conclusion

It is concluded that the information presented is very important to determine the stability constant of the ligand metal complexes. Some methods like spectrophotometric method, Bjerrum's method, distribution method, ion exchange method, electrometric techniques, and potentiometric method have a huge contribution in quantitative analysis by easily finding the stability constants of metal complexes in aqueous solutions.

Acknowledgements

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