

CHAPTER 2

Metal-Ligand Equilibria in Solution:

❖ Stepwise and Overall Formation Constants and Their Interactions

The formation of a complex between a metal ion and a bunch of ligands is in fact usually a substitution reaction. However, ignoring the aquo ions, the formation of the complex can be written as:



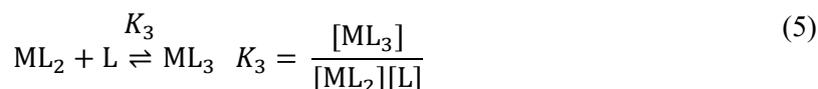
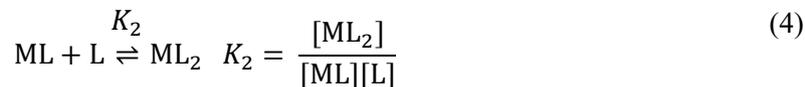
Where M represents the metal center, L is the ligand type involved, n represents the number of ligands, and β is the equilibrium constant for the whole process. The expression for β (or β_n) for the above equilibria can simply be written as:

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \quad (2)$$

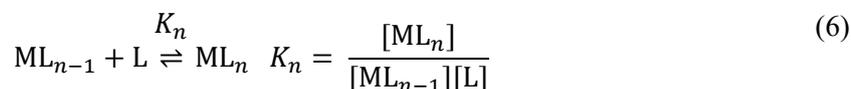
Now because the magnitude of β_n is proportional to the molar concentration of complex formed, the equilibrium constant β_n is also called formation constant of the metal complex.

The formation constant or stability constant may be defined as the equilibrium constant for the formation of a complex in solution.

The magnitude of β_n is actually a measure of the strength of the interaction between the ligands, which come in contact to form the complex, and the metal center. However, it has also been observed that the complex formation in the solution phase occurs via a step-to-step addition of the ligands to the metal center used. For instance, the chemical equation (1), which shows the formation of a complex ML_n , can also be written as a combination of many other equations representing a corresponding series of individual steps. In other words, the overall formation process of ML_n complex can be resolved into the following steps:



The equations (3–5) and corresponding equilibrium constants can further be extended for the attack of n number of ligands as given below.



Where $K_1, K_2, K_3, \dots, K_n$ are the equilibrium constants for different steps, which in turn also imparted their conventional label of stepwise stability or the stepwise formation constants. The magnitude of these individual equilibrium constants indicates the extent of the formation of different species in a particular step.

Nevertheless, the stepwise stability constant of any particular step does not include the information about the previous ones. Therefore, to include the extent of formation of a complex up to a particular step, say 3rd, the overall formation constant β_3 should be used as it indicates the extent of formation of ML_3 as a whole. Moreover, it can also be shown that the overall formation constant up to the 3rd step (β_3) can be represented as the product of K_1, K_2, K_3 .

$$\beta_3 = K_1 \times K_2 \times K_3 \quad (7)$$

$$\beta_3 = \frac{[\text{ML}]}{[\text{M}][\text{L}]} \times \frac{[\text{ML}_2]}{[\text{ML}][\text{L}]} \times \frac{[\text{ML}_3]}{[\text{ML}_2][\text{L}]} \quad (8)$$

$$\beta_3 = \frac{[\text{ML}_3]}{[\text{M}][\text{L}]^3} \quad (9)$$

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \times K_5 \times K_6 \times \dots \times K_n \quad (10)$$

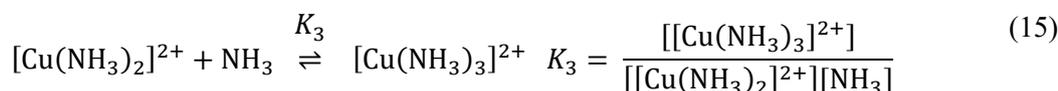
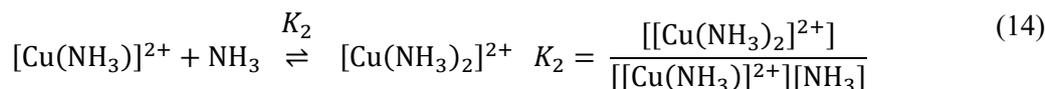
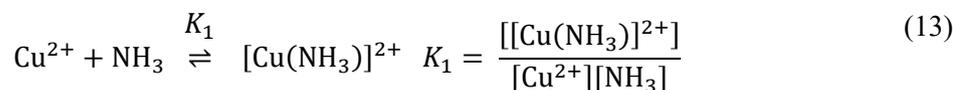
The overall stability constant is generally reported in logarithmic scale as $\log \beta$ as given below

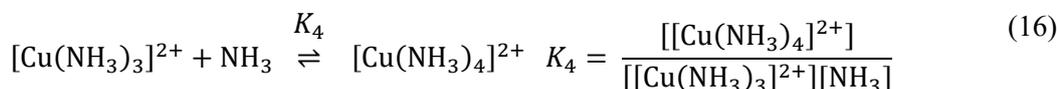
$$\log \beta_n = \log K_1 + \log K_2 + \log K_3 + \log K_4 + \log K_5 + \log K_6 + \dots + \log K_n \quad (11)$$

Or

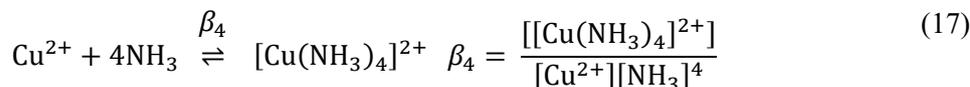
$$\log \beta_n = \sum_{i=1}^{i=n} \log K_i \quad (12)$$

The whole process of calculating the overall formation constant can be exemplified by taking the case of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex.





The overall reaction with overall formation constant can be given by the equation (17) as:



Now putting the experimental values of $\log K_1 = 4.0$, $\log K_2 = 3.2$, $\log K_3 = 2.7$ and $\log K_4 = 2.0$ in equation (12); the value of $\log \beta_4$ can be calculated as follows:

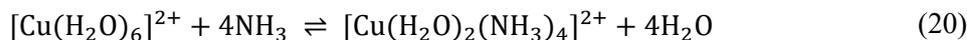
$$\log \beta_4 = 4.0 + 3.2 + 2.7 + 2.0 \quad (18)$$

$$\log \beta_4 = 11.9 \quad (19)$$

Finally, it should also be noted that the thermodynamic stability of metal complexes is calculated by the overall formation constant. If the value of $\log \beta$ is more than 8, the complex is considered as thermodynamically stable; suggesting pretty much high stability for $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex. Moreover, the term dissociation or instability constant of a metal complex may also be defined here as the reciprocal of the stability constant.

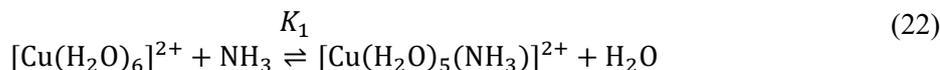
❖ Trends in Stepwise Constants

The values of stepwise equilibrium constants for the formation of a particular metal-complex decrease successively in most of the cases i.e. $K_1 > K_2 > K_3 > K_4 > K_5 > \dots > K_n$. This regular decrease in the values of stepwise formation constants may be attributed to the decrease in the number of coordinated H_2O ligands that are available for the replacement by the attacking ligands. Besides, the continuous decline in the values of successive stepwise stability constant values may also be attributed to the decreasing ability of metal ions with a progressive intake of ligands, Coulombic factors and steric hindrance. Consider the following ligand displacement reaction:



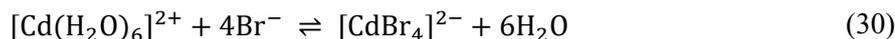
$$\beta_4 = \frac{[[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}][\text{H}_2\text{O}]^4}{[[\text{Cu}(\text{H}_2\text{O})_6]^{2+}][\text{NH}_3]^4} \quad (21)$$

The overall process can be supposed to take place through the following steps:



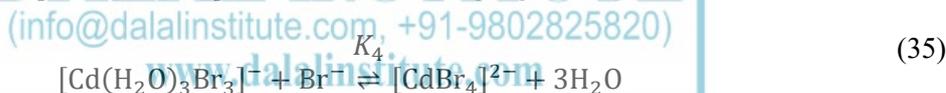
$$K_1 = \frac{[[\text{Cu}(\text{H}_2\text{O})_5(\text{NH}_3)]^{2+}][\text{H}_2\text{O}]}{[[\text{Cu}(\text{H}_2\text{O})_6]^{2+}][\text{NH}_3]} \quad (23)$$

Now although the decreasing trend in stepwise constants is pretty much common in most of the complex formation processes, still some exceptions do exist in which it is found that $K_{n+1} > K_n$. This weird behavior in stepwise equilibrium constants may be explained in terms of some unusual structural deviations and variations in the electronic structure of the metal center. The deviations in electronic configurations cause the change in crystal field stabilization energy (CFSE), and therefore, also affect the overall stability of the metal complex i.e. complex with a large magnitude of CFSE will be more stable and, consequently, will have higher value of the stepwise formation constants. Consider the following ligand displacement reaction:



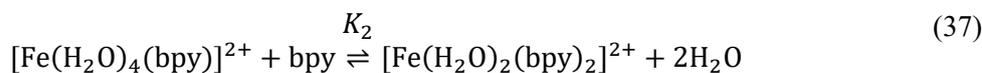
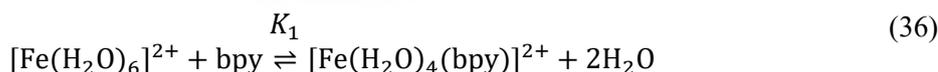
$$\beta_4 = \frac{[[\text{CdBr}_4]^{2-}][\text{H}_2\text{O}]^6}{[[\text{Cd}(\text{H}_2\text{O})_6]^{2+}][\text{Br}^-]^4} \quad (31)$$

The overall process can be supposed to take place through the following steps:



It has been observed that $\log K$ values follows the order $K_1 > K_2 > K_3 < K_4$, instead of $K_1 > K_2 > K_3 > K_4$. This unusually high value of K_4 is because the last step is actually pretty much favored by the release of three aquo ligands and some simultaneous structural and electronic changes.

Similarly, consider the formation of $[\text{Fe}(\text{bpy})_3]^{2+}$ complex:



It has been observed that $\log K$ values follow the order $K_1 > K_2 < K_3$, instead of $K_1 > K_2 > K_3$. This unusually high value of K_3 is because the complexes formed during first two steps are high spin due to weak H_2O ligands with a CFSE of $-0.4\Delta_0$ ($t_{2g}^4 e_g^2$), while the last complex $[\text{Fe}(\text{bpy})_3]^{2+}$ is low spin with a CFSE value of $-2.4\Delta_0$ ($t_{2g}^6 e_g^0$). Hence, large crystal field stabilization in the last step makes K_3 even greater than K_2 .

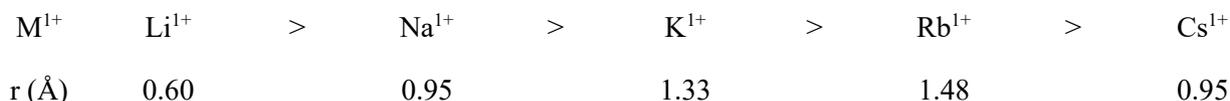
❖ Factors Affecting Stability of Metal Complexes with Reference to the Nature of Metal Ion and Ligand

The stability of transition metal complexes depends upon a number of factors but is largely governed by the nature and the coordinative environment of the ligands-attached and the nature of the central metal ion or atom itself. A detailed discussion on both is given below.

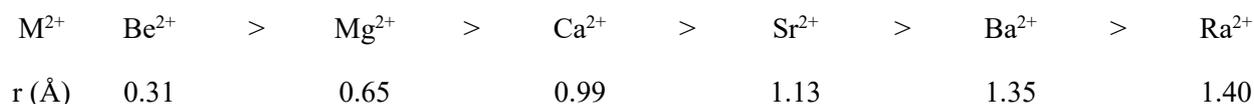
➤ Nature of the Metal Ion

The following properties of the central metal atom or ion affect the stability of the transition metal complexes to a significant extent.

1. Size of the central metal ion: The stability of metal complexes decreases with the increase in the size of central metal ion provided the valency and ligands the same. Thus, the stability of isovalent complexes decreases down the group and increases along the period as the size varies in the reverse order. Stability order of hydroxide complexes of alkali metal ions and alkaline earth metal ions is:



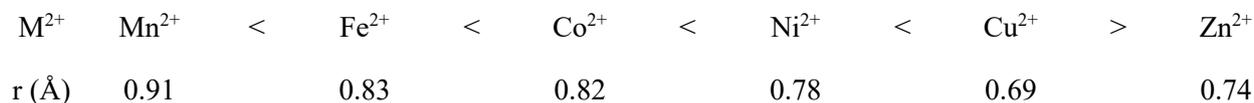
Similarly,



Similarly,



Besides the stability order of hydroxide complexes of 3rd group metal ions, there is a very popular stability order of metal complexes formed by bivalent metal ions of the first transition series, which is known as Irving-William series are given below.



The trend given by Irving-William for high spin octahedral metal complexes is actually independent of the ligand used. For instance, the variation of over first stepwise stability constant for the formation of ethylenediamine-complex on the logarithmic scale is given below. It can be clearly seen that the sequence actually starts from bivalent manganese rather Sc^{2+} , which is obviously due to the lack of data for the first two bivalent members because M(II) oxidation states are pretty much unstable.

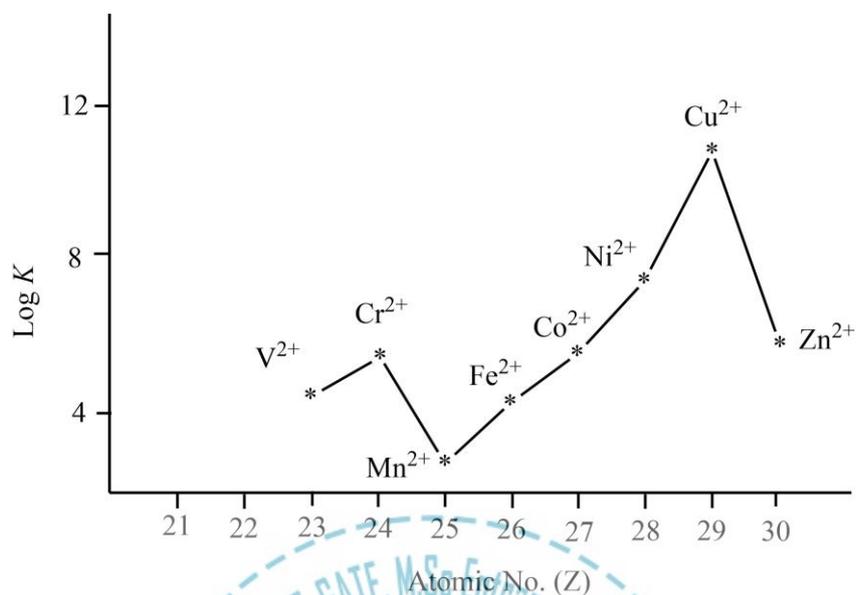


Figure 2. The first stepwise stability constants for the formation of ethylenediamine-complex.

The exceptionally special position of bivalent copper may be attributed to the formation distorted octahedral complexes Jahn-Teller effect and is discussed later in the book.

2. Charge on the central metal ion: The stability of transition metal complexes, with the same ligands and similar coordinative environment, increases with the increase of the charge on the central metal atom or ion.

M ⁿ⁺	La ³⁺	>	Sr ²⁺	>	K ¹⁺
r (Å)	1.15		1.13		1.33

Similarly,

M ⁿ⁺	Th ³⁺	>	Y ³⁺	>	Ca ²⁺	>	Na ¹⁺
r (Å)	0.95		0.93		1.14		1.16

Therefore, the greater is the charge on the central ion, the higher will be the stability of the metal complex.

3. Charge to size ratio of the metal ion: Now although we have already studied the effect of size and charge of the metal center on the overall stability of the complex, the more precise parameter, however, to do so is the ratio of the two. The charge to size ratio can be used to rationalize all the orders discussed previously on the charge or the size factor only.

M ⁿ⁺	Co ³⁺	>	Co ²⁺
Charge/size	4.76		2.70

Hence, the greater is the charge and smaller the size i.e. large charge/size ratio increases the stability of these complexes quite significantly. A more illustrative presentation using different metal ions from different groups or periods is given below.

Table 1. The variation of charge-to-size ratio for different types of the metal ion.

Metal ion	Charge	Ionic radius	Charge/size
Li ⁺	+1	0.6	1.6
Ca ²⁺	+2	0.99	2.0
Ni ²⁺	+2	0.72	2.97
Y ³⁺	+3	0.93	3.22
Th ⁴⁺	+4	0.95	4.20
Al ²⁺	+2	0.50	6.0
Ba ²⁺	+2	0.31	6.45

The data listed above infers that the charge-to-size ratio is increasing 1.6 to 6.45 as we move from Li⁺ to Ba²⁺; and remarkably the stability of complexes also follows the same order, confirming our initial statement.

Furthermore, the charge-to-size ratio can also be used to rationalize the effect of electronegativity of the metal ion. As the bonding between metal ion and ligands is considered in the electron donation ability of the ligand, the electronegativity of the central metal ion also plays a key role in the stability of metal complexes. Conclusively, the greater is the positive charge density on the central metal ion, greater will be the electronegativity and consequently greater stability of the complexes.

4. Class of the metal ion: It has been observed that class *a* metals e.g. alkali metal ion, alkaline earth metal ions and metals from first transition series are shown to form stable complexes with ligands having N, O or F as the donor site. On the other hand, class *b* metals e.g. metals from second and third transition series are shown to form stable complexes ligands having P, S or Cl like donor atoms. However, borderline metals do not show unique behavior towards complex formation as far as stability is concerned.

This trend is explainable by the hard-soft acid-base principle which states that hard acid prefers hard base while soft acid prefers soft base for binding to yield stable systems. Metals such as Li¹⁺, Ba²⁺, Mg²⁺ and Al³⁺, which have large negative reduction potential have a lesser tendency to attract electrons, and hence, form stable complexes with highly electronegative groups like N, F or O so that they become unable to draw the unwanted electron density due to polarization. However, Metals like Pd²⁺ or Pt²⁺ which have large positive reduction potential have a greater tendency to accept electron and hence form stable complexes with less electronegative groups like P so that they can easily grab the electron density by polarizing the surrounding.

Table 2. The class *a*, class *b* and borderline metals.

Class <i>a</i> metals	Class <i>b</i> metals	Borderline metals
H ⁺ , Li ⁺ , Na ⁺ , K ⁺	Cu ⁺ , Ag ⁺ , Au ⁺ , Tl ⁺	
Be ²⁺ , Mg ²⁺ , Ca ²⁺ , Sr ²⁺	Hg ²⁺ , Pd ²⁺ , Pt ²⁺	Mn ²⁺ , Fe ²⁺ , Co ²⁺ , Sr ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺
Al ³⁺ , Ga ³⁺ , In ³⁺ , Cr ³⁺ , Mn ³⁺ , Fe ³⁺ , Co ³⁺ , La ³⁺ , Ce ³⁺ , Gd ³⁺	Tl ³⁺	
In ⁴⁺ , Zr ⁴⁺ , Hf ⁴⁺ , Th ⁴⁺ , U ⁴⁺ , Pu ⁴⁺	Pt ⁴⁺	

For class *a* metals, the stability of different metal complexes with different ligands follows the order:



For class *b* metals, the stability of different metal complexes with different ligands follows the order:



For borderline metals, the stability of different metal complexes is pretty much independent of the nature of the ligand and follows the order given by the Irving-William series.

➤ Nature of the Ligand

The following properties of ligands-attached affect the stability of the transition metal complexes to a significant extent.

1. Charge and size of the ligand: Just like the metal, the charge and size of the ligand also play a significant role in deciding the stability of the transition metal complexes. Smaller size ligands are expected to form more stable complexes as they can approach the metal ion more closely and ligands with higher charges are expected with the same trend as they would form a strong bond with the central metal ion. However, this is true only for class *a* metal ions and this order gets a reverse sweep for class *b* metal ion. This can be illustrated as follows:

The stability order of halide complexes with class *a* metal ion is:



The stability order of halide complexes with class *b* metal ion is:



2. Basicity of the ligand: Stability of the metal complexes increases with the increase in the basic nature of the ligands as the donation of electron pair becomes more favorable. Thus, NH_3 should be a better ligand than H_2O which in turn should form more stable complexes than HF . This trend is quite robust for alkali metals, alkaline earth metals, $3d$ transition series, lanthanides and actinides. For instance, the stability order for metal complexes of a bivalent transition metal is:



3. Back-bonding capacity of ligand: The ligands such as CO , CN^- , PR_3 , NO , alkenes and alkynes have special ability to form π -bonding with the central metal ion usually form more stable complexes than the others.

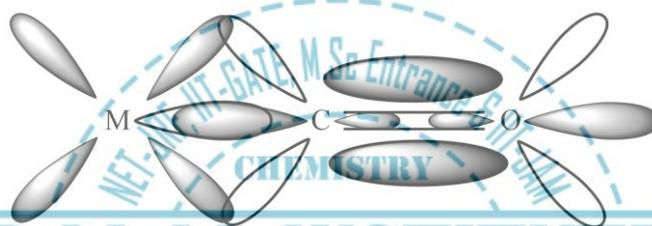


Figure 3. The back bonding mode in metal carbonyl complexes enhances stability.

4. Steric effects of the ligand: Metal complexes with bulky groups are usually less stable due to the weakening of the metal–ligand bond arising from the steric hindrances. For instance, consider the case of bivalent nickel complexes with 8-hydroxy quinoline and 2-methyle-8-hydroxy quinoline; the former is more stable in comparison to the other due to less steric hindrance.

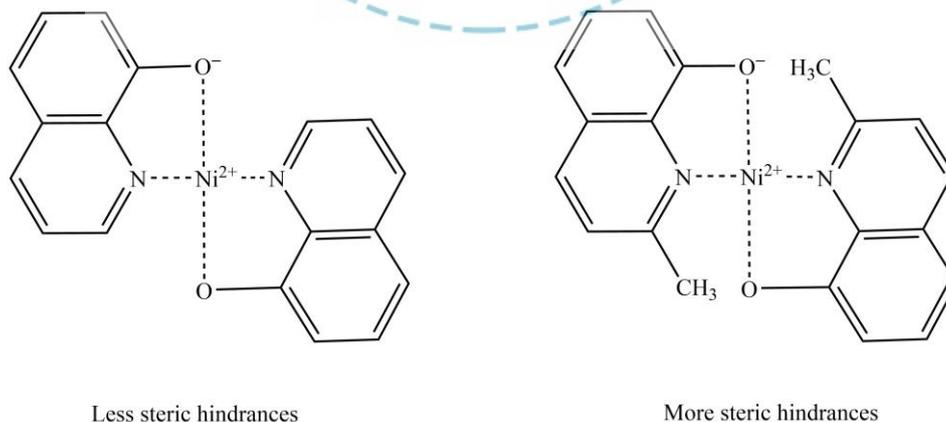


Figure 4. Bivalent nickel complexes with 8-hydroxy quinoline and 2-methyle-8-hydroxy quinoline.

5. Dipole moment of the ligand: Neutral ligands are shown to produce more stable complexes as their permanent dipole moment increases. For example, consider the stability order for amine complexes:



6. Special configuration of the ligand: The ligands like porphyrin and their derivatives usually form very stable organometallic complex as they are stabilized by the aromatic character which extends over its entire structure due to exclusive planarity.

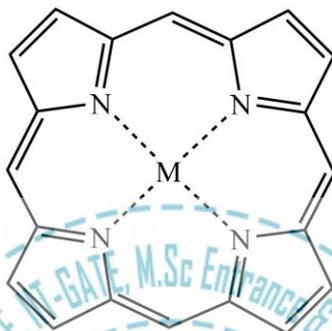


Figure 5. Structure the simplest porphyrin complex.

7. Chelating effect of ligand: The ligands which can form five or six-membered ring structure with the metal center usually form more stable complexes than the others. This effect is called as the chelation and the ligands are called as chelating ligands.

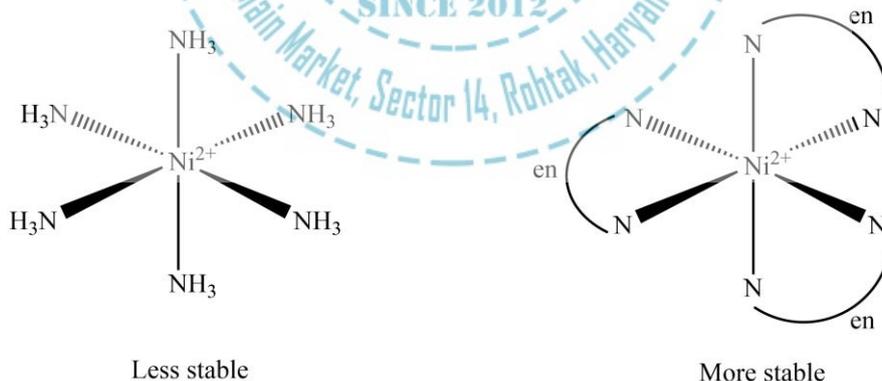


Figure 6. Complexes of bivalent nickel with monodentate amine and bidentate ethylene diamine ligands to form the chelate in the latter case.

The $\log \beta$ values for $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{Ni}(\text{en})_3]^{2+}$ complexes are 8.6 and 18.6, respectively; which in turn confirms the higher stability of the chelate one.

8. Macrocyclic effect of ligand: It has been observed that nine or more membered cyclic ring systems with three or more donor atoms form extensively more stable metal complexes than their acyclic analogues. This effect is called as macrocyclic effect and these types of ligands are called as macrocyclic ligands. The very strong affinity of macrocyclic groups can be considered as a combination of the entropic effect like in the chelation, joined with an extra energetic contribution which comes from the pre-organized nature of the ligating groups that is, no additional strains are introduced to the ligand on coordination.

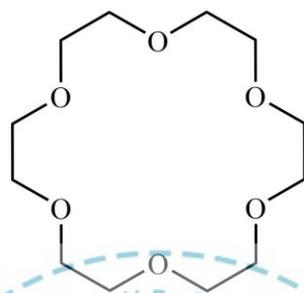


Figure 7. Structure of 18-Crown-6.

9. Concentration of ligand: It has been observed that sometimes complexation occurs only at a high concentration of the ligands otherwise solvent molecules tend to bind the metal ion more preferably. For example, $[\text{Co}(\text{SCN})_4]^{2-}$ exists only at a high concentration of thiocyanate ions and as we dilute the aqueous solution, the blue color complex starts disappearing and pink colored $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ become dominant.

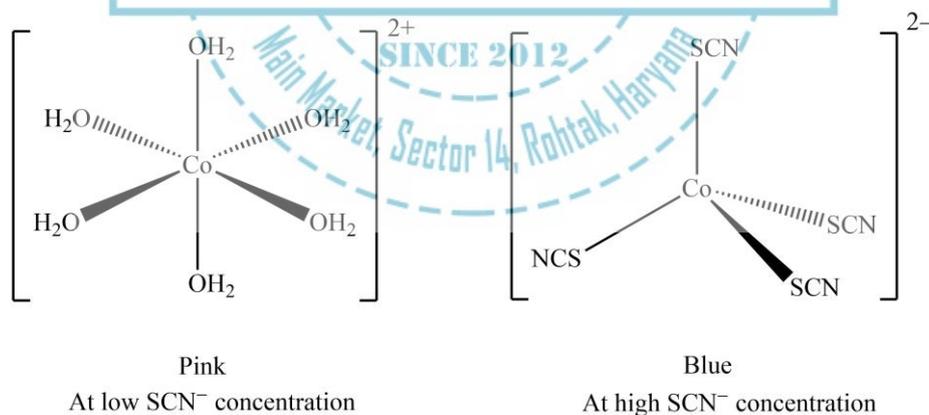


Figure 8. Structure of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{SCN})_4]^{2-}$.

As the octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex transform into T_d -symmetry $[\text{Co}(\text{SCN})_4]^{2-}$ at high ligand concentration, the huge shift in the intensity and the color from pale pink to very deep blue is obviously due to the removal center of symmetry, making $d-d$ transitions as Laporte selection allowed in nature.

❖ Chelate Effect and Its Thermodynamic Origin

The chelate effect or chelation may simply be defined as an equilibrium reaction between the complexing agent and a metal ion, characterized by the formation of two or more bonds between metal and the complexing agent, resulting in the formation of a ring structure including the metal ion.

The term ‘chelates’ was first proposed by Morgan and Drew in 1920 for the cyclic structure arising from the assembly of metals with organic ligands. The chelate effect results in the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar non-chelating monodentate ligands for the same metal. This, in turn, results in the larger values of overall formation constants for the chelate complexes than their monodentate counterparts.



Figure 9. Popular chelating ligands; (a) ethylenediamine (symmetrical) and (b) glycinate (unsymmetrical).

➤ Characteristic Features of Chelates

The Chelate complexes generally have low melting points and are soluble in the organic solvents. Now though the phenomenon of chelation follows pretty much all rules of metal-ligand bonding as followed by simple complexes; two characteristic features of the chelate complexes are unique and can be given as:

1. Ligand-type: One of the most obvious features of the chelates is that only polydentate ligands are capable of forming chelate complexes. The ligand can be bidentate, tridentate or even hexa-dentate; but it must have more than one donor sites to form the chelate.

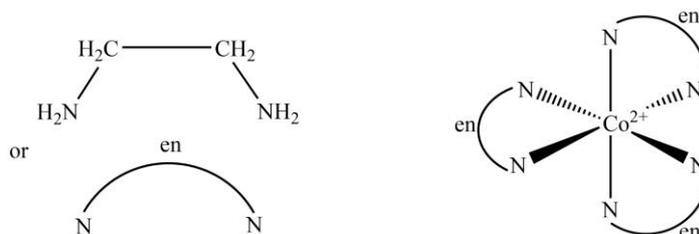


Figure 10. Structure of chelate complex of Co^{2+} with the bidentate ligand.

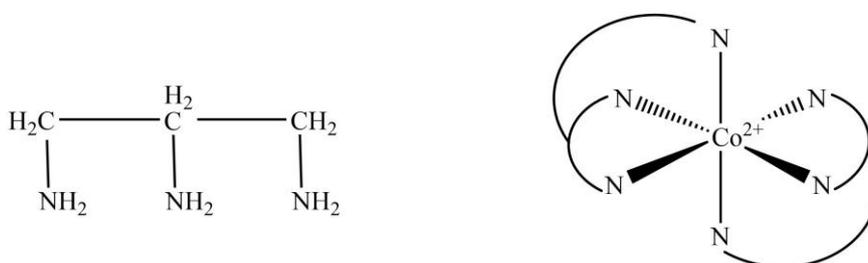
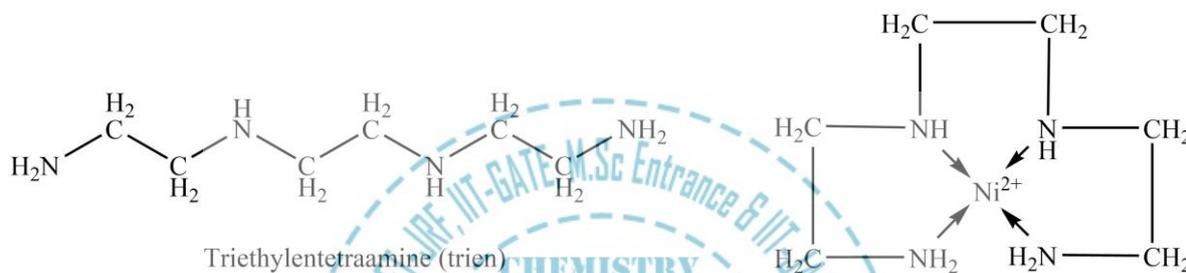
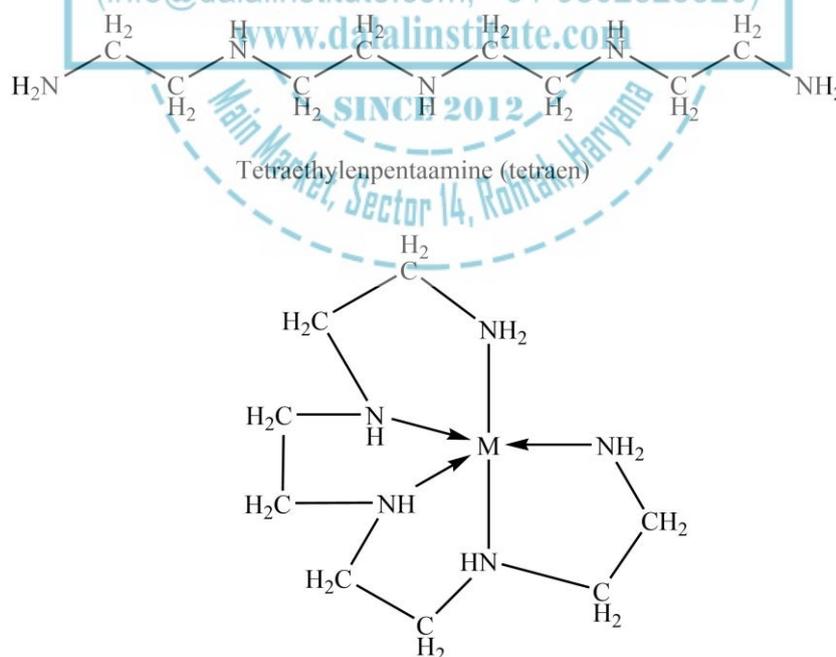
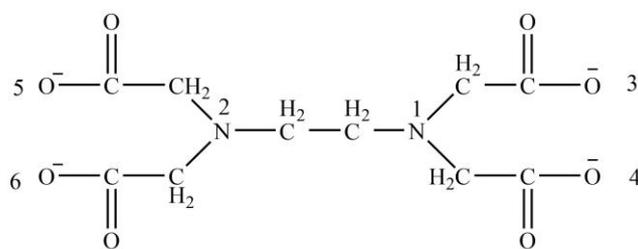
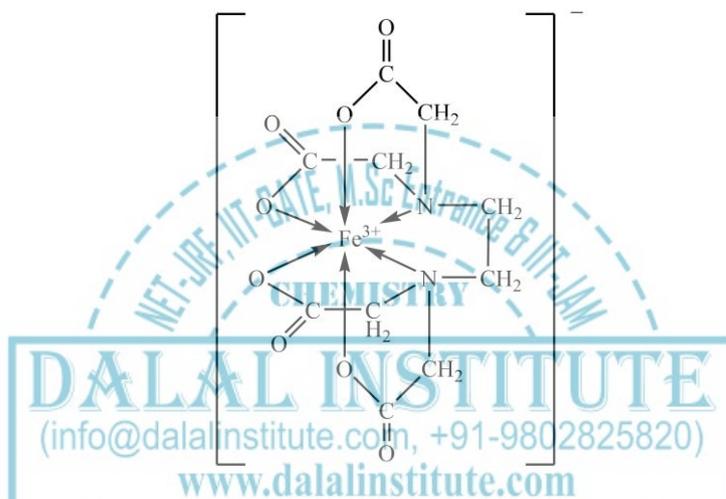
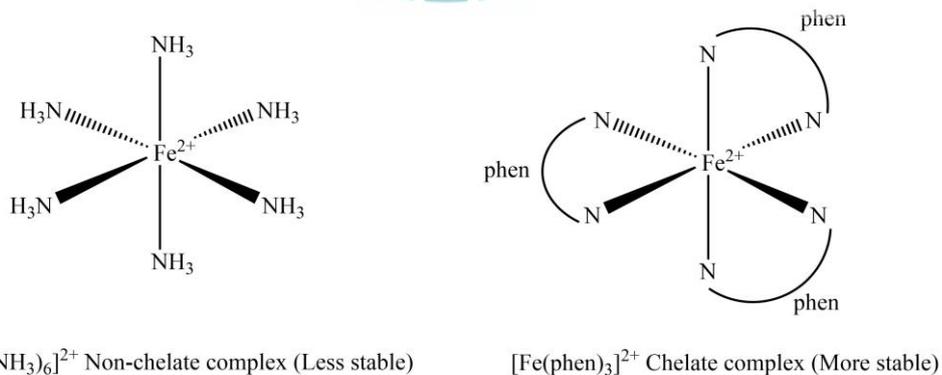
Figure 11. Structure of chelate complex of Co^{2+} with a tridentate ligand.Figure 12. Structure of chelate-complex of Ni^{2+} with a tetradentate ligand.

Figure 13. Structure of metal chelate-complex with a pentadentate ligand.

Ethylenediaminetetraacetate (EDTA⁴⁻)Figure 14. Structure of chelate complex of Fe³⁺ with hexadentate ligand.

2. Stability: The chelating agent binds with the metal-center of suitable size firmly and the bond can be covalent or coordinate. This makes the chelate complexes as more stable than their non-chelating counterparts.

Figure 15. Structure of chelate complex of Fe²⁺ with a bidentate ligand.

Also, it has also been observed that five and six-membered ring chelate complexes are more stable than the other due less steric strain. The chelating ligands like ethylenediamine, which do not have multiple bonds, prefer to form five-membered rings complexes; while the chelating ligands like acetylacetonate, which do have double bonds, prefer form six-membered rings complexes.

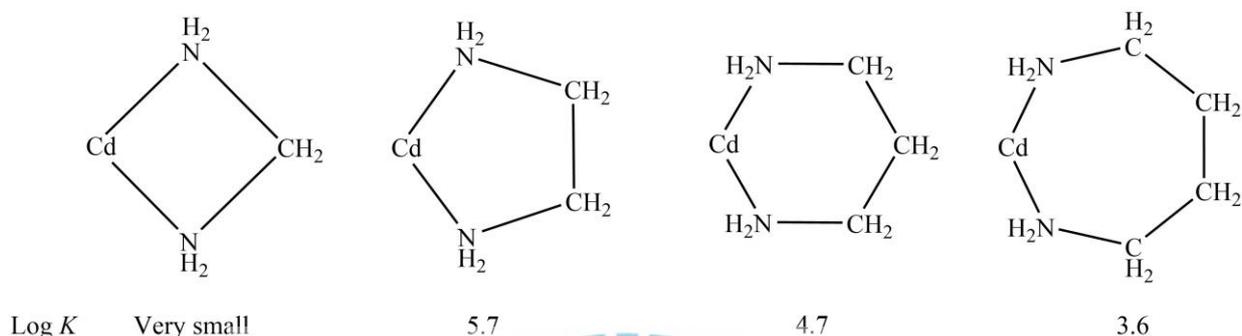


Figure 16. Stability order for the bivalent cadmium complexes of bidentate amines.

Furthermore, the chelating ligands with bulky groups usually form less stable complexes due to the weakening of the metal–ligand bond arising from the steric hindrances. For instance, consider the case of metal complexes involving 2,2-bipyridyl and its derivatives as the chelating ligand. The structures of bivalent iron complexes with normal 2,2-bipyridyl and 4,4'-Dimethyl-2,2'-bipyridyl as the chelating ligand clearly shows that the former has less steric hindrance, and therefore, is more stable.

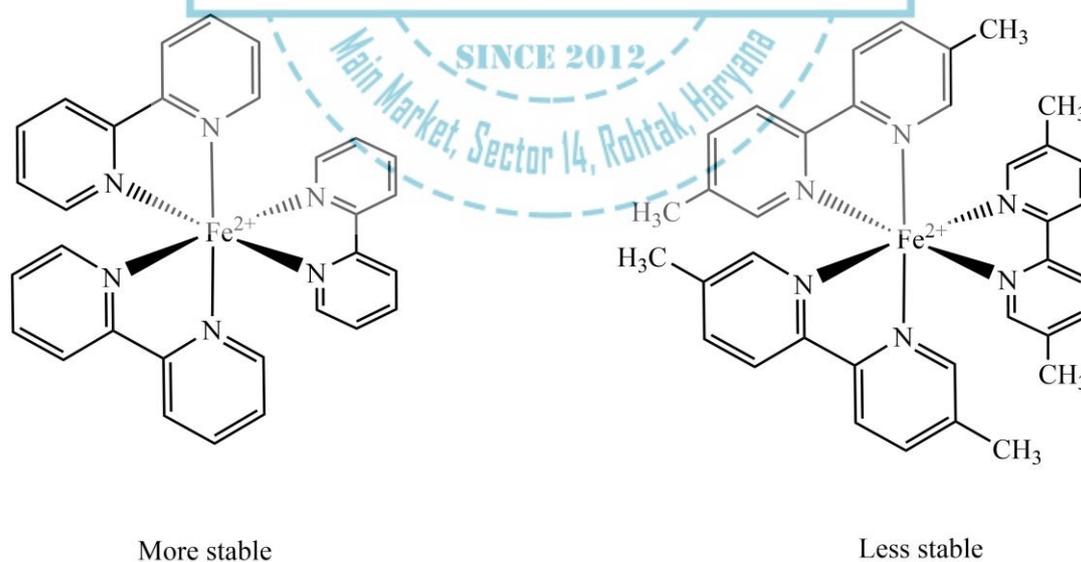


Figure 17. Structures of bivalent iron complexes with normal 2,2-bipyridyl and 4,4'-Dimethyl-2,2'-bipyridyl as the chelating ligand.

➤ **Thermodynamic Explanation of Chelation**

The principal driving force for the chelation phenomena is the stability gain arising from the increasing entropy during the complexation. The free energy change for a general reaction is given by:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{or} \quad \Delta G^\circ = -RT \ln K \quad (39)$$

Now, as the enthalpy change between non-chelate and chelates is almost negligible because of the similar metal–ligand donor type, the free energy change is primarily governed by the value of ΔS° . Furthermore, it follows from the equation (39) that ΔG° will become more negative with a more positive value of ΔS° , which in turn would increase the value of stability constant K . Hence, the stability of metal complexes increases with chelation as it occurs through an increment in the entropy of the system.



$$1 + 4 = 5 \qquad \qquad \qquad 1 + 4 = 5$$



$$1 + 2 = 3 \qquad \qquad \qquad 1 + 4 = 5$$

Thus, chelation is a thermodynamically favorable process as the number of species in the product are higher than that of what it was in the starting materials leading to enhanced randomness.



$$1 + 1 = 2 \qquad \qquad \qquad 1 + 4 = 5$$

It is obvious that entropy increase in case of trien is higher than ethylenediamine ligand making the trien chelate complex as more stable. The stability of chelate complexes increases with the denticity of the chelating agent.

➤ **Factors Affecting the Stability of Chelate Complexes**

1. The size of the chelate ring: Five or six membered chelate rings are more stable than the four, seven, eight or higher membered chelate rings due to less steric strain.

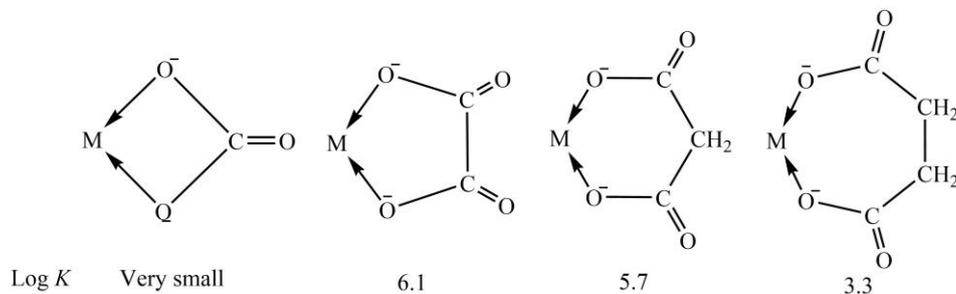


Figure 18. Stability order for the Cu^{2+} complexes with chelating ligands.

2. Number of chelate rings and nature of the metal ion: it has been observed that as the number of donor sites increase, the stability of metal chelates also increases. Furthermore, the stability of chelate complexes was also found in accordance with the Irving-William series.

Table 3. The values of overall formation constants ($\log \beta$) for different types of metal ions as a function of the number of chelate rings.

Metal complex	No. of chelate rings	Values of overall formation constants ($\log \beta$)						
		Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺
M(NH ₃) ₄	0	–	3.7	5.31	7.79	12.59	9.06	6.92
M(en) ₂	2	4.9	7.7	10.9	14.5	20.2	11.2	10.3
M(trien)	3	4.9	7.8	11.0	14.1	20.2	12.1	10.0
M(tren)	3	5.8	8.8	12.8	14.0	18.8	14.6	12.3
M(dien) ₂	4	7.0	10.4	14.1	18.9	21.3	14.4	13.8
M(penten)	5	9.4	11.2	15.8	19.3	22.4	16.2	16.2

In addition to stability prediction by Irving Williams series, transition metal ions usually form more stable chelate complexes and follow the order given by Maley and Mellor.



3. Resonance effect: The resonance stabilization of the chelate ring also enhances complex stability. For example, the exceptionally high $\log \beta$ for [Fe(acac)₃] is due to resonance stabilization in the chelating ligand.

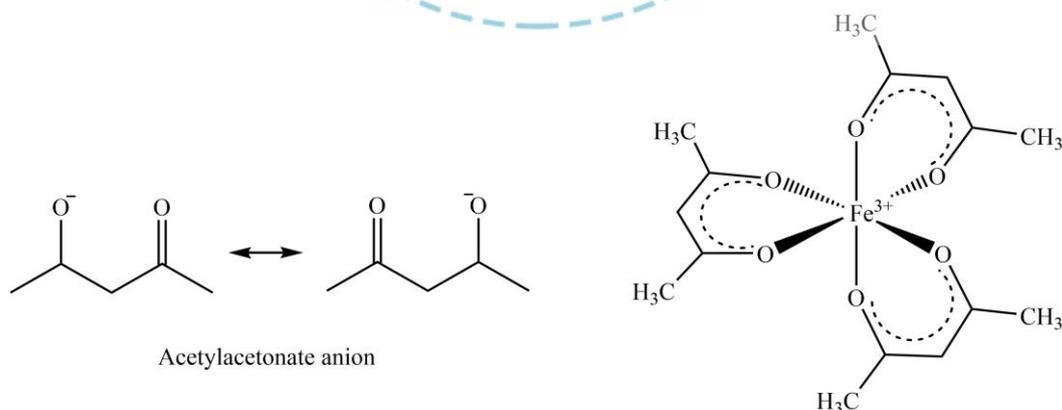


Figure 19. The resonance stabilization in tris(acetylacetonato) iron(III) or [Fe(acac)₃].

4. Lewis base strength and charge of ligand: Calvin and Wilson studied the Cu^{2+} chelate complexes and proved that the stability of the chelate complexes increases with the increase of the basic character of the ligand. Moreover, it has also been observed that the uncharged ligands like ethylenediamine or triethylenetetraamine form more stable complexes than the anionic ligands like oxalato or glycinate.

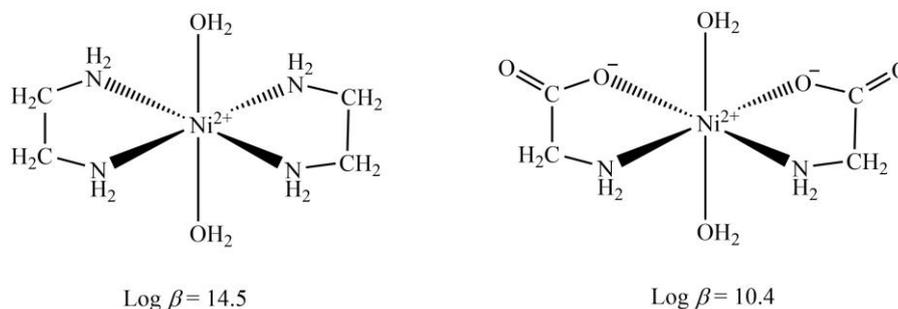


Figure 20. Stability order for the Ni^{2+} complexes with neutral and anionic chelating ligands.

5. Steric hindrance and strain due to large ligands: The chelating ligands with large groups usually form less stable complexes due to the weakening of the metal–ligand bond arising from the steric hindrances. For example, ethylenediamine form more stable complexes with bivalent metal ions than N-tetramethylethylenediamine, which obviously due to greater steric hindrance in the later one. Moreover, the overall stability can also be affected by the strain in metal–chelates arising from the particular geometry of the chelating ligand. For instance, trien-complexes of bivalent copper are more stable than their tren-complexes due to less steric strain as trien-ligand can adapt square planar coordination much easily.

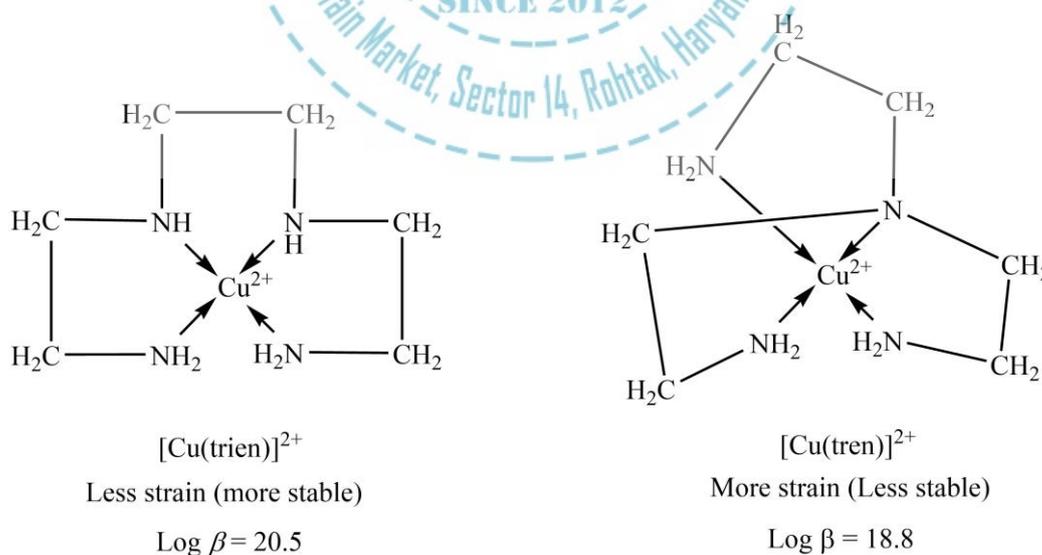


Figure 21. Stability order for the Cu^{2+} complexes with chelating ligands.

➤ **Main Applications of Chelates**

1. The colored chelate complex formation with Al^{3+} , Ni^{2+} , Mg^{2+} can be used to quantify these metals from their solutions.
2. The hardness of water can be removed by synthesizing the water-soluble chelate complexes of Mg^{2+} and Ca^{2+} ion which otherwise undergoes precipitations reaction.
3. Some neutral chelate complexes are sparingly soluble in water but have high solubility in an organic solvent that can be used to purify metal in the organic phase.
4. The chelating agents like EDTA can be used to eliminate harmful radioactive metal from the body forming their water-soluble complexes.
5. Chelating agents can also act food preservatives by binding or sequestering metal ions like iron or copper in certain foods in order to prevent the metals from oxidizing and speeding up spoilage.

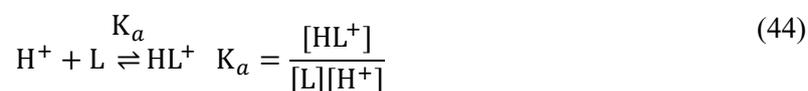
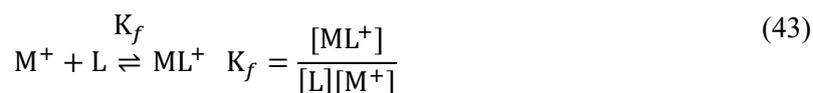
❖ **Determination of Binary Formation Constants by pH-metry and Spectrophotometry**

The stability constants for metal complexes can be calculated using various techniques but the two of most popular experimental methods are pH-metry and spectrophotometric analysis owing to their simple setup and good accuracy.

➤ **pH-metric Method**

The alteration of hydronium ion concentration during the complex formation can be used to calculate the stability constant. Actually, H^+ ions are in direct competition with metal ions for the association with ligand species present in the solution.

Consider the ligand displacement reaction in which a metal ion along with some weak acid is added to ligand solution.



Where K_f and K_a are formation constants for the metal complex and acid association constant, respectively. Now let C_M , C_L and C_H as the molar concentration for metal ion, ligand and acid, we have

$$C_H = [\text{H}^+] + [\text{HL}^+] \quad (45)$$

$$C_L = [\text{L}] + [\text{ML}^+] + [\text{HL}^+] \quad (46)$$

$$C_M = [M^+] + [ML^+] \quad (47)$$

The above three equations can be solved as follows, From equation (47):

$$[M^+] = C_M - [ML^+] \quad (48)$$

The total ligand concentration can be calculated by using equation (44) and putting the value of $[HL^+]$ from equation (45) as:

$$[L] = \frac{C_H - [H^+]}{K_a[H^+]} \quad (49)$$

Now subtracting equation (45) from equation (46) and putting the value of $[L]$ from equation (49), we get:

$$[ML^+] = C_L - C_H + [H^+] - \frac{C_H - [H^+]}{K_a[H^+]} \quad (50)$$

Thus, using the values of $[M]$, $[L]$ and $[ML^+]$ from equation (48), (49) and (50) in equation (43); we would be to calculate the formation constant by knowing C_M , C_L , C_H , K_a and the concentration of $[H^+]$ ion which is generally given by the pH-meter. It has also been observed that the accuracy of the formation constant is high if the value to K_f is within the range of 10^5 times than that of K_a .

➤ Spectrophotometric Method

1. Conventional Spectrophotometric Method: The change in the absorbance during the complex formation can be used to find out the stability constant very easily. According to Beer-Lambert law:

$$A = \epsilon \cdot c \cdot l \quad (51)$$

where A is the absorbance, l is the optical path length, ϵ is a molar extinction coefficient and c is a concentration of the solution. Thus, by measuring the absorbance at a particular wavelength for a metal complex solution of known path length and known concentration, the value of the molar extinction coefficient can be calculated. Consider the general metal-ligand equilibria:



Now let C_M and C_L as the molar concentration for metal ion and ligand, respectively. We have

$$C_M = [M] + [ML] \quad (53)$$

$$C_L = [L] + [ML] \quad (54)$$

Now if we measure the absorbance of ML complex at a known path length and molar absorption coefficient; its concentration can be given by using equation (51) as:

$$[\text{ML}] = c = \frac{A}{\epsilon l} \quad (55)$$

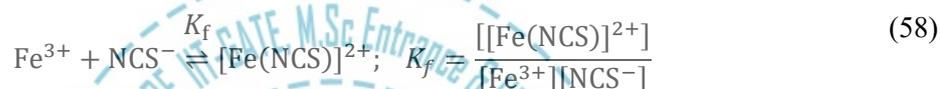
Putting the value of equation (55) in equation (53) and (54), we get:

$$[\text{M}] = M_L - [\text{ML}] = M_L - \frac{A}{\epsilon l} \quad (56)$$

$$[\text{L}] = C_L - [\text{ML}] = C_L - \frac{A}{\epsilon l} \quad (57)$$

Here and now, we can calculate the value of formation constant (K_f) by put the values of $[\text{ML}]$, $[\text{M}]$ and $[\text{L}]$ from equation (55), (56) and (57) in equation (52).

For example, the above method can successfully be used to calculate the stability constant for the following reaction:



Ferric ion and thiocyanate ions are colorless in aqueous solution but their metal-ligand equilibria generate instance blood-red color and its λ_{max} is at 450 nm. In order to find the value of ϵ , we will have to measure the absorbance of $[\text{Fe}(\text{H}_2\text{O})_5(\text{NCS})]^{2+}$ complex prepared by dissolving Fe^{3+} ions in excess of NCS^- ligand so that all the ferric ions convert into the complex. Once the value of ϵ for $[\text{Fe}(\text{H}_2\text{O})_5(\text{NCS})]^{2+}$ is known, its equilibrium concentrations can easily be obtained by recording the absorption spectra. Then, using these equilibrium concentrations in equation (58) will give you the value of formation constant.

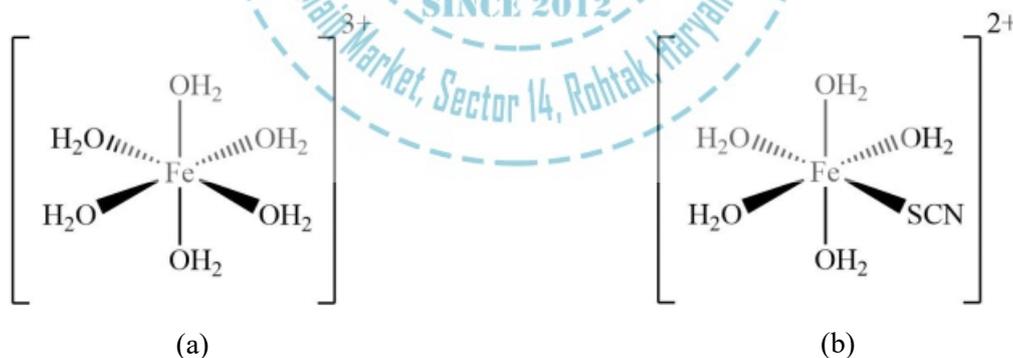
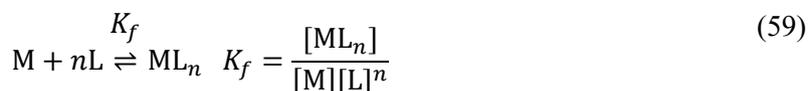


Figure 22. (a) Fe^{3+} ion in water (b) $[\text{Fe}(\text{SCN})]^{2+}$ ion in water.

2. Method of continuous variation or Job's method: This method is the variation of the spectroscopic method and is very useful in determining the composition of the metal complexes. This method is used when only one complex is formed under the given experimental conditions and the volume of the solution remains constant. Consider the metal-ligand equilibria:



Prepare ten metal-ligand solutions with varying concentrations as given below.

Metal ion (<i>ml</i>)	0	1	2	3	4	5	6	7	8	9
Ligand (<i>ml</i>)	10	9	8	7	6	5	3	2	1	0

Now, let C_M and C_L as the molar concentration for metal ion and ligand, respectively. we have:

$$C_M + C_L = C \quad (60)$$

$$x = \frac{C_L}{C} \quad (61)$$

$$1 - x = \frac{C_M}{C} \quad (62)$$

Where C is a constant; while x and $(1-x)$ are the mole fractions for ligand and metal ion, respectively. Now by assuming that the complex absorbs much stronger than that of metal ion or ligand in the visible region, spectrophotometry can be used to determine the relative quantities of all three-species present at equilibrium. Thus, the maximum amount of complex and consequently maximum absorbance will be observed when the metal ion and the ligands are present in the stoichiometric ratio yielding the value of n for ML_n .

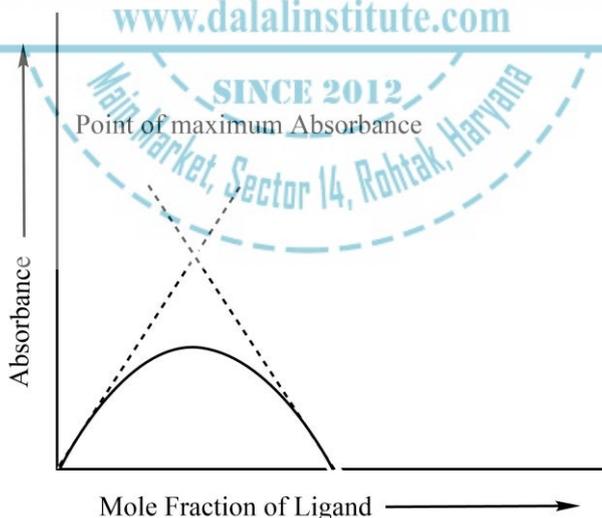


Figure 23. Continuous method of variation (Job's Plot).

$$\text{For complex } ML_n \quad n = \frac{C_L}{C_M} \quad (63)$$

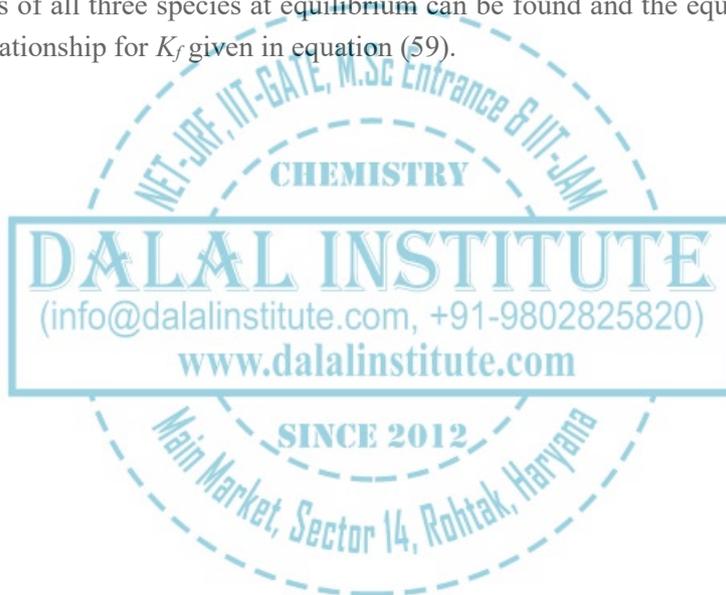
Dividing equation (61) by (62) we get:

$$n = \frac{C_L}{C_M} = \frac{C_L}{C} \times \frac{C}{C_M} = \frac{x}{1-x} \quad (64)$$

Thus, the composition of the complex is obtained by knowing the value of n . The absorbance calculated at the crossover point is the theoretical maximum amount of the complex formed that would occur if the equilibrium constant is very large. Here and now, as the absorbance is proportional to concentration, the extrapolated absorbance gives the maximum concentration of the complex while observed absorbance at the same mole fraction gives the concentration of the complex actually formed. Hence, we have:

$$\frac{[ML_n]_{\text{actual}}}{[ML_n]_{\text{maximum}}} = \frac{A_{\text{observed}}}{A_{\text{maximum}}} \quad (65)$$

Now the concentrations of all three species at equilibrium can be found and the equilibrium constant can be calculated using the relationship for K_f given in equation (59).



❖ Problems

- Q 1. Discuss the thermodynamic stability of a complex and correlate stepwise constant with overall stability constant.
- Q 2. How chelation and nature of donor atom affect the stability of metal complexes.
- Q 3. Discuss the determination of formation constant by pH-metry.
- Q 4. What is $\log \beta$? How is it related to the stability of complexes?
- Q 5. Illustrate with suitable example the trends in stepwise formation constant.
- Q 6. Discuss a spectrophotometric method for the determination of stability constants of complexes.
- Q 7. How does the nature of the central metal ion affect the stability of the complexes?

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