

B. Sc. (Semester - V)
Subject: Inorganic Chemistry
Subject Code: US05CCHE22

UNIT: III Thermodynamic and Kinetic Aspects of Metal Complexes

By Dr. K. D. Patel

(A) Stability of complexes in aqueous solution:

Stability: It refers to the existence and storage of any complex and also to the action of heat or light on a compound.

Stability of complexes have been classified in to two types as under:

- 1. Thermodynamic stability: Stable (penetration) and unstable (normal) complexes:**
This type of stability deals with the properties like bond energies, stability constants and redox potentials that affect the equilibrium conditions. On the basis of thermodynamic stability of complexes in solution, **Blitz (1927)** has classified the complex compounds into stable and unstable complexes. Stable complexes are those which possess sufficient stability to retain their identity in solution while unstable complexes are those which are reversibly dissociated in solution into their components. Stable and unstable complexes have also been called **penetration** and **normal complexes** respectively.
- 2. Kinetic stability: Labile and inert complexes:** This type of stability deals with the rates of reactions (i.e., reactivity) of complexes in solution, the mechanisms of chemical reactions, formation of intermediate complexes, activation energies for the process etc. On the basis of the rate of reactions (i.e., kinetic stability) of the complex in solution, **Taube (1950)** has classified the complexes into *labile* and *inert* complexes. Labile complexes are those whose one or more ligands in the coordination sphere can be rapidly replaced by other ligands and the ability of a complex to replace its one or more ligands by other ligands is called its **lability**. Inert complexes are those whose one or more ligands can either not be replaced or can be replaced with difficulty by other ligands.

Stability of complex ions in solution:

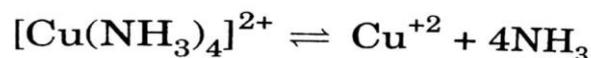
A complex ion dissociates in aqueous solution to a very small extent. Stronger is the metal-ligand bond in the complex ion, lesser is the dissociation of the complex ion and hence greater is the stability of complex ion. The stability of complex ion solution can be defined as a measure of the resistance of the replacement of a ligand by another ligand.

Dissociation of a complex ion in solution and Dissociation (or Instability) constant (K_{diss} or K_i):

In aqueous solution, a complex ion dissociates to a very small extent. When a complex ion dissociates, there lies an equilibrium between the undissociated complex ion and the species obtained by the dissociation of the complex ion. Hence the stability of the

complex ion in solution is expressed in terms of equilibrium constant of the dissociation equilibrium.

Example: The dissociation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion in solution is represented by the equilibrium:

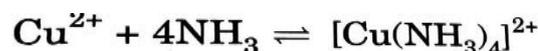


The dissociation (or instability) constant (K_{diss}) of the above equilibrium is given by:

$$\text{Instability constant } (K_{\text{dis}}) = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4]^{2+}} \quad (i)$$

Formation of a complex ion in solution and Formation (or stability) constant (K_{for} or β) :

The formation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion in solution can be represented by the equilibrium given below:



Since the above equilibrium involves the formation of complex ion, the equilibrium constant of the above formation reaction is called *formation (or stability) constant* which is represented by K_{for} . Thus, K_{for} is given by:

$$\text{Stability constant } (K_{\text{for}}) = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4} \quad (ii)$$

On comparing equations (i) and (ii) we find that

$$K_{\text{for}} \text{ (or } \beta) = \frac{1}{K_{\text{diss}} \text{ (or } K_i)}$$

Thus, the formation constant (or instability constant), K_{for} is reciprocal of dissociation constant (or instability constant), K_{diss} . K_{for} and K_{diss} are also represented as β and K_i respectively.

The values of K_{diss} and K_{for} of some complex ions in solution are given below.

Complex ion	K_{diss}	K_{for}
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	1.0×10^{-12}	1.0×10^{12}
$[\text{Co}(\text{NH}_3)_6]^{3+}$	6.2×10^{-36}	1.6×10^{35}
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$	6.1×10^{-14}	1.6×10^{13}
$[\text{Ag}(\text{CN})_2]^-$	1.8×10^{-19}	5.4×10^{18}
$[\text{Hg}(\text{CN})_4]^{2-}$	4.0×10^{-42}	2.5×10^{41}
$[\text{Fe}(\text{SCN})]^{2+}$	1.0×10^{-3}	1.0×10^3

Value of $K_1 \times K_2 \times K_3 \times \dots \times K_{n-1} \times K_n$

$$\begin{aligned}
 &= \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]} \times \dots \times \frac{[ML_{n-1}]}{[ML_{n-2}][L]} \times \frac{[ML_n]}{[ML_{n-1}][L]} \\
 &= \frac{[ML_n]}{[M][L]^n} = \beta \qquad \qquad \qquad \text{[From equation (ii)]}
 \end{aligned}$$

Here, β is called **overall stability constant** which is represented as β_n . Thus:

$$\begin{aligned}
 \beta_n &= K_1 \times K_2 \times K_3 \times \dots \times K_{n-1} \times K_n \\
 \text{or } \log \beta_n &= \log K_1 + \log K_2 + \log K_3 + \dots + \log K_{n-1} + \log K_n
 \end{aligned}$$

Kinetically labile and Kinetically inert complexes:

Depending on whether the rate of substitution reaction in complexes is slow or fast, the complexes have been classified as kinetically labile and Kinetically inert complexes by Taube (1952).

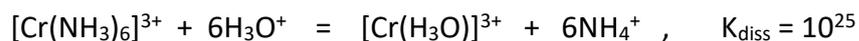
Kinetically labile complexes are those in which one or more ligands present in coordination sphere of the complex species can be replaced by other ligands *quickly* or *rapidly*. Thus, the complexes in which the ligand substitution is fast are called labile complexes. The rate of substitution of labile complex is difficult to measure and hence special techniques are used to study the kinetics of such complexes.

Kinetically inert complexes are those in which ligands present in coordination sphere of the complex species can be replaced *slowly*. Thus, the complexes in which the ligand substitution is slow are called inert complexes. The rate of substitution of inert complexes can be measured easily by conventional techniques.

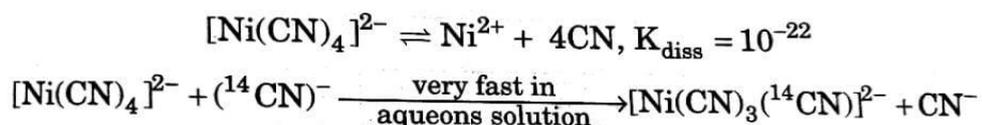
Since the terms labile and inert refer to the rate of substitution reactions, labile and inert complexes are called Kinetically labile and Kinetically inert complexes respectively.

Thermodynamically stable and thermodynamically unstable complexes: A Thermodynamically stable complex has high value of its formation constant while a thermodynamically unstable complex has low value of its formation constant. It should be understood clearly that a thermodynamically stable complex may be kinetically labile (fast reacting complex). Similarly, a thermodynamically unstable complex may be kinetically inert (slow reacting complex). The Thermodynamic stability and kinetic lability are different from each other. Thermodynamically stable complex may be labile or inert. For example: $[Fe(H_2O)_6]^{3+}$ (Bond energy = 116 Kcal mol⁻¹) and $[Cr(H_2O)_6]^{3+}$ (Bond energy = 122 Kcal mol⁻¹) have the same thermodynamic stability but $[Fe(H_2O)_6]^{3+}$ is kinetically labile (exchanges its ligands with other ligands rapidly) but $[Cr(H_2O)_6]^{3+}$ is kinetically inert (exchanges ligands slowly). $[Cr(H_2O)_6]^{3+}$ is thermodynamically unstable because of high

value of its dissociation constant, K_{diss} ($= 10^{25}$) but is kinetically inert (slow reacting complex), since it remains undecomposed in acid solution.



$[\text{Ni}(\text{CN})_4]^{2-}$ is thermodynamically stable because of low value of its dissociation constant, K_{diss} ($= 10^{-22}$) but is kinetically labile (fast reacting complex), since it exchanges CN^- ions very rapidly with added isotopically labelled cyanide ions ($^{14}\text{CN}^-$).



Activation Energy (AE):

Activation energy is defined as the energy required to convert the reacting complex into unstable or activated complex (transition state or intermediate). Thus, activation energy is the energy necessary for forming activated complex from the reacting complex. Activated complex does not represent a true molecule but represents only an imaginary molecule which cannot be isolated. It has maximum energy and has very short life. Being unstable, the activated complex finally changes to the products. Activation energy (AE) is the difference in energy between the reacting complex and activated complex, i.e.

$$A E = \text{Energy of activated complex} - \text{Energy of reacting complex}$$

Crystal Field Activation Energy (CFAE):

CFAE is defined as the change in crystal field stabilization energy (CFSE) when the reacting complex is changed into intermediate, i.e.

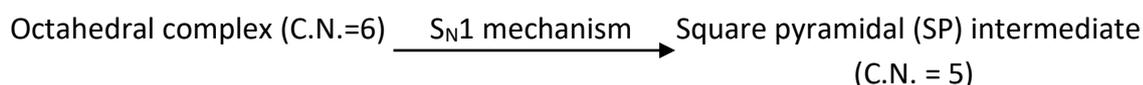
$$\text{CFAE} = \text{CFSE of intermediate} - \text{CFSE of the reacting complex}$$

If the calculated value of CFAE is negative or zero or low, the reacting complex would require less energy for its conversion into intermediate. On the other hand, calculated value of CFAE is high, the reacting complex would require more energy for its conversion into intermediate.

To explain the lability and inertness of octahedral complexes on the basis of CFT:

We know that ligand substitutions in octahedral complexes proceed either through S_N1 mechanism or through S_N2 mechanism. In order to explain the lability and inertness of octahedral complexes by CFT, we calculate the value of CFAE for various d^x ions of the complexes in both mechanisms. If the value of CFAE is negative or zero, the complex is labile (fast to react). If the value of CFAE is positive, the complex is slow to react.

(i) S_N1 mechanism: According to this mechanism, in the ligand substitution reaction of a given HS or LS octahedral complex, the octahedral complex (C.N. = 6) is converted into square pyramidal (SP) intermediate (C.N. = 5).



Thus:

CFAE value of HS or LS octahedral complex undergoing ligand substitution reaction through S_N1 mechanism

=CFSE of SP intermediate - CFSE for d^x ion in HS or LS octahedral complex (i)

If the values of CFSE of SP intermediate and for d^x ion in HS or LS octahedral complexes are put in equation (i) given above, we get CFAE value for HS or LS octahedral complexes undergoing ligand substitution reaction through S_N2 mechanism.

These values have been shown in Table :1 as under:

Table: 1 CFAE values (in Dq) of HS (weak field) and LS (strong field) octahedral complexes undergoing ligand substitution reaction through S_N1 mechanism.

d^x configuration	CFSE value for SP intermediate (C.N. = 5) (a)	CFSE value for octahedral complex (C.N. = 6) (b)	CFAE value = (a - b)
d^0	0	0	0
d^1	-4.57	-4	-0.57
d^2	-9.14	-8	-1.14
d^3	-10.00	-12	2.00
d^4 (HS)	-9.14 (HS)	-6 (HS)	-3.14 (HS)
d^4 (LS)	-14.57 (LS)	-16 (LS)	1.43 (LS)
d^5 (HS)	0 (HS)	0 (HS)	0 (HS)
d^5 (LS)	-19.4 (LS)	-20 (LS)	0.86 (LS)
d^6 (HS)	-4.57 (HS)	-4 (HS)	-0.57 (HS)
d^6 (LS)	-20.00 (LS)	-24 (LS)	4.00 (LS)
d^7 (HS)	-9.14 (HS)	-8 (HS)	-1.14 (HS)
d^7 (LS)	-19.14 (LS)	-18 (LS)	-1.14 (LS)
d^8	-10	-12	2.00
d^9	-9.14	-6	-3.14
d^{10}	0	0	0

From the value of CFAE given in Table: 1 the following points may be noted:

- Since complexes of the metal ions with d^0 , d^1 , d^2 and d^{10} configurations have negative or zero CFAE values, these complexes are labile i.e. these complexes are fast to react by S_N1 mechanism. Similarly, HS complexes of d^4 , d^5 , d^6 and d^7 ions are also labile.
- Since LS complexes of d^7 have negative value of CFAE, these complexes are labile.

(c) Complexes of d^3 and d^8 ions have positive values of CFAE, these complexes are slow to react.

Due to the decreasing order of CFAE values, the order of reactivity of the complexes of d^3 , d^8 and LS complexes of d^4 , d^5 and d^6 is as: $d^6 < d^3 \sim d^8 < d^4 < d^5$.

Above discussion can be summarised in the form of a table which is given below:

d^x ion	Sign of CFAE value	Labile or inert
d^0	0	Fast to react (Labile)
d^1	-	Fast to react
d^2	-	Fast to react
d^3	+	Slow to react (Inert)
d^4 (HS)	-	Fast to react
d^4 (LS)	+	Slow to react
d^5 (HS)	0	Fast to react
d^5 (LS)	+	Slow to react
d^6 (HS)	-	Fast to react
d^6 (LS)	+	Slow to react
d^7 (HS)	-	Fast to react
d^7 (LS)	-	Fast to react
d^8	+	Slow to react
d^9	-	Fast to react
d^{10}	0	Fast to react

(ii) **S_N2 mechanism:** According to this mechanism, in ligand substitution reaction of a given HS or LS octahedral complex, the octahedral complex may be converted into pentagonal bipyramidal (PBP) intermediate or octahedral wedge (OW) intermediate. S_N2 reaction of octahedral complexes preferably proceed through the formation of OW intermediate rather than PBP intermediate, since the formation of OW intermediate requires less energy than the formation of a PBP intermediate. Thus:

CFAE value of HS or LS octahedral complex undergoing ligand substitution reaction through S_N2 mechanism

$$= \text{CFSE of OW intermediate} - \text{CFSE of } d^x \text{ ion in HS or LS octahedral complex (ii)}$$

If the values of CFSE of OW intermediate and of d^x ions in HS or LS octahedral complexes are put into the equation (ii) given above, we get CFAE values for HS or LS octahedral complexes undergoing ligand substitution reaction through S_N2 Mechanism. These values are given in Table: 2.

Table: 2 CFAE values (in Dq) of HS (Weak field) and LS (Strong field) octahedral complexes undergoing ligand substitution reaction through S_N^2 mechanism.

d^x configuration	CFSE value for OW intermediate (a)	CFSE value for octahedral complex (b)	CFAE value = (a - b)
d^0	0	0	0
d^1	-6.08	-4	-2.08
d^2	-8.68	-8	-0.68
d^3	-10.20	-12	1.80
d^4 (HS)	-8.79 (HS)	-6(HS)	-2.79 (HS)
d^4 (LS)	-16.26 (LS)	-16(LS)	-0.26 (LS)
d^5 (HS)	0	0(HS)	0 (HS)
d^5 (LS)	-18.86 (LS)	-20(LS)	1.14 (LS)
d^6 (HS)	-6.08 (HS)	-4(HS)	-2.08 (HS)
d^6 (LS)	-20.37 (LS)	-24(LS)	3.63 (LS)
d^7 (HS)	-8.68 (HS)	-8(HS)	-0.68 (HS)
d^7 (LS)	-18.98 (LS)	-18(LS)	-0.98 (LS)
d^8	-10.20	-12	1.80
d^9	-8.79	-6	-2.79
d^{10}	0	0	0

From the value of CFAE given in Table: 2 we get the following conclusions:

(a) Complexes of d^0 , d^1 , d^2 , d^9 and d^{10} ions are labile, since these complexes have zero or negative CFAE values. Similarly, HS complexes of d^4 , d^5 , d^6 and d^7 ions are also labile. Low spin complexes of d^4 and d^7 ions are also labile.

(b) Complexes of d^3 and d^8 ions are slow to react, since their CFAE values are positive. Similarly, LS complexes of d^5 and d^6 ions are also slow to react. The order of reactivity of the complexes of d^3 , d^3 , d^6 and d^8 ions is in the order $d^6 < d^3 \sim d^8 \sim d^5$.

Above discussion can be summarized in the form of table given below.

d^x ion	Sign of CFAE value	Labile or inert
d^0	0	Fast to react (Labile)
d^1	-	Fast to react
d^2	-	Fast to react
d^3	+	Slow to react (Inert)
d^4 (HS)	-	Fast to react
d^4 (LS)	-	Fast to react
d^5 (HS)	0	Fast to react
d^5 (LS)	+	Slow to react
d^6 (HS)	-	Fast to react
d^6 (LS)	+	Slow to react
d^7 (HS)	-	Fast to react
d^7 (LS)	-	Fast to react
d^8	+	Slow to react
d^9	-	Fast to react
d^{10}	0	Fast to react

From the combined CFAE values given in Table: 1 & 2 we get the following conclusions:

- Octahedral complexes of metal ions with d^3 and d^8 configuration and LS octahedral complexes of d^5 and d^6 ions are slow to react by S_N1 as well as by S_N2 mechanisms.
- Octahedral complexes of d^0 , d^1 , d^2 , d^9 and d^{10} and HS complexes of d^4 , d^5 , d^6 and d^7 ions would be labile whatever be the mechanism of their substitution reactions.

Factors Affecting the Stability of Metal Complexes:

The stability (or stability constants) of metal complexes depends on the following factors:

A. Properties of Central Metal Ion:

The following properties of central metal ion affect the stability of the metal complexes:

1. Size of central metal ion. For a given ligand the stability (or stability constant) of the complexes of the metallic ions having the same charge on them decreases with the increase of the size of the central metal ion. Thus, the stability of complexes given by the cations belonging to the same group and having the same charge decreases as we proceed from top to bottom in the group, since the size of the metallic cations increases in the same order.

For example:

(i) The stability of hydroxide complexes given by alkali metal ions (Li^+ , Na^+ , etc.), alkaline earth metal ion (Be^{2+} , Mg^{2+} etc.) and III B group ions (Sc^{3+} , Y^{3+} and La^{3+}) is in the order:

(a) Li^+ ($r = 0.60 \text{ \AA}$) > Na^+ ($r = 0.95 \text{ \AA}$) > K^+ ($r = 1.33 \text{ \AA}$) > Rb^+ ($r = 1.48 \text{ \AA}$) > Cs^+ ($r = 1.69 \text{ \AA}$).

(b) Be^{2+} ($r = 0.31 \text{ \AA}$) > Mg^{2+} ($r = 0.65 \text{ \AA}$) > Ca^{2+} ($r = 0.99 \text{ \AA}$) > Sr^{2+} ($r = 1.13 \text{ \AA}$) > Ba^{2+} ($r = 1.35 \text{ \AA}$) > Ra^{2+} ($r = 1.40 \text{ \AA}$).

(c) Sc^{3+} ($r = 0.81 \text{ \AA}$) > Y^{3+} ($r = 0.93 \text{ \AA}$) > La^{3+} ($r = 1.15 \text{ \AA}$)

It may be noted that EDTA complex of Mg^{2+} ($r = 0.65 \text{ \AA}$) is less than that of Ca^{2+} ($r = 0.99 \text{ \AA}$).

(ii) The inverse relation between the size of the central metal ion and the stability of the complexes formed is also confirmed when we see that the stability of the complexes of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} (These ions are *divalent ions* of the elements of 1st transition series).

Ions:	Mn^{2+}	Fe^{2+}	$Co^{2+}Ni^{2+}$	$Cu^{2+}Zn^{2+}$		
Ionic radii (Å):	0.91	0.83	0.82	0.78	0.69	0.74

Order of stability

of complexes: $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

This sequence of stability is commonly known as **Irving-William order of stability** of complexes of M^{2+} ions.

2. Charge on the central metal ion. For a given ligand, the stability of the complexes of the metallic ions having almost the same size but different charges on them decreases with the decrease of the charge on them. Thus, the stability of complexes given by: (a) La^{3+} , Sr^{2+} and K^+ ions. (b) Co^{3+} and Co^{2+} ions. (c) Fe^{3+} and Fe^{2+} ions, and (d) Th^{4+} , Y^{3+} , Ca^{2+} and Na^+ ions with the same ligand is in the order:

- (a) $La^{3+} (r = 1.15 \text{ Å}) > Sr^{2+} (= 1.13 \text{ Å}) > K^+ (= 1.33 \text{ Å})$
- (b) $Co^{3+} (r = 0.63 \text{ Å}) > Co^{2+} (= 0.74 \text{ Å})$
- (c) $Fe^{3+} (r = 0.64 \text{ Å}) > Fe^{2+} (r = 0.76 \text{ Å})$
- (d) $Th^{4+} (r = 0.95 \text{ Å}) > Y^{3+} (= 0.93 \text{ Å}) > Ca^{2+} (= 0.99 \text{ Å}) > Na^+ (= 0.95 \text{ Å})$.

If the factors 1 and 2 mentioned above are combined, then we can say that with the increase of ionic potential of the central metal ion (Ionic potential of the metal ion = charge on the metal ion/size of the ion), the stability of the complexes with the same ligand also increases. For example, the stability of hydroxide complexes of Li^+ , Ca^{2+} , Ni^{2+} , Be^{2+} ions whose ionic potential increase from Li^+ to Be^{2+} ions also increase in the same direction as shown below:

<i>Central metal ion (charge on the ion is shown in parenthesis)</i>	<i>Ionic radius (Å)</i>	<i>Ionic potential</i>	<i>Order of stability of complexes</i>
$Li^+ (+1)$	0.60	$1/0.60 = 1.6$	<div style="display: inline-block; vertical-align: middle;"> ↓ Increasing ↓ Increasing </div>
$Ca^{2+} (+2)$	0.99	$2/0.99 = 2.0$	
$Ni^{2+} (+2)$	0.72	$2/0.72 = 2.97$	
$Y^{3+} (+3)$	0.93	$3/0.93 = 3.22$	
$Th^{4+} (+4)$	0.95	$4/0.95 = 4.20$	
$Al^{3+} (+3)$	0.50	$3/0.50 = 6.0$	
$Be^{2+} (+2)$	0.31	$2/0.31 = 6.45$	

The effect of the size and charge on the central metal ion on the stability of a complex as discussed above shows that greater is the charge and smaller is the size of the metal ion, i.e. larger is the charge/radius ratio of a metal ion, greater is the stability of its complex.

Example. (i) Since Fe^{3+} ion carries higher charge ($= +3$) and has smaller size than Fe^{2+} ion, Fe^{3+} ion has larger positive charge density than Fe^{2+} ion. Hence complexes of Fe^{3+} ion are more stable than those of Fe^{2+} ion, provided that the complexes are formed with the same ligands. As a result $[\text{Fe}^{3+}(\text{CN})_6]^{3-}$ has higher value of its stability constant ($K = 10^{31}$) than $[\text{Fe}^{2+}(\text{CN})_6]^{4-}$ ($K = 10^6$). $[\text{Co}^{3+}(\text{CN})_6]^{3-}$ in aqueous medium has higher value of its stability constant ($= 10^{64}$) than $[\text{Co}^{2+}(\text{CN})_6]^{4-}$ ($= 10^{20}$). Co^{3+} ion is smaller in size than Co^{2+} .

(ii) Stability of the complexes of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} ions (all these ions have the same charge which is equal to $+2$) increases from Mn^{2+} to Cu^{2+} . This increase of stability is because of the decrease in ionic radii (size) of these ions from Mn^{2+} to Cu^{2+} .

M^{2+} ions:	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
Ionic radii (Å):	0.91	0.83	0.82	0.78	0.69
Stability of complexes					

The order of stability of the complexes shows that complexes of Mn^{2+} are the least stable and those of Cu^{2+} are the most stable.

(iii) Stability constants of the complexes of trivalent lanthanide ions in aqueous medium also increases as the atomic number of lanthanides increases.

3. Electronegativity. Electronegativity of the central ion also influences the stability of its complexes. This is because the bonding between a central ion and ligand is due to the donation of electron pairs by the ligands. Hence, a strongly electron-attracting central ion will give stable complexes. Hence, the greater the positive charge density (i.e., charge/size ratio) and the greater the electronegativity of the central ion, the greater is the stability of the complex formed by it.

4. Metal ions acting as hard acids and soft acids. Metal ions that are *hard acids* form more stable complexes with ligands containing coordinating N, O, F, etc., atoms and form comparatively less stable complexes with ligands containing coordinating P, S, Cl, etc., atoms. The metal ions that are *soft acids* form more stable complexes with ligands containing coordinating P, S, Cl, etc. atoms and comparatively less stable complexes with ligands containing coordinating N, O, F, etc., atoms.

5. Electrode potentials of metal ions. Metal ions having large negative electrode potentials ($E^0_{M^{n+}/M}$), such as Li^+ , Ba^{2+} , Mg^{2+} , Al^{3+} , etc. have a lesser tendency to attract electrons and hence have more tendency to form complexes with ligands having highly electronegative atoms such as N, O, F, etc., so that the negative charge of the ligands remains mostly centred on the ligands. On the other hand, metal ions having large positive electrode potentials ($E^0_{M^{n+}/M}$) such as Pd^{2+} , Pt^{2+} , etc., have greater tendency to accept electrons and thus form more stable complexes with ligands containing highly polarizable coordinating

atoms such as P, S, Cl, etc. In such complexes, the electron charge of the ligand is easily polarised towards the complexed metal ion having positive electrode potential.

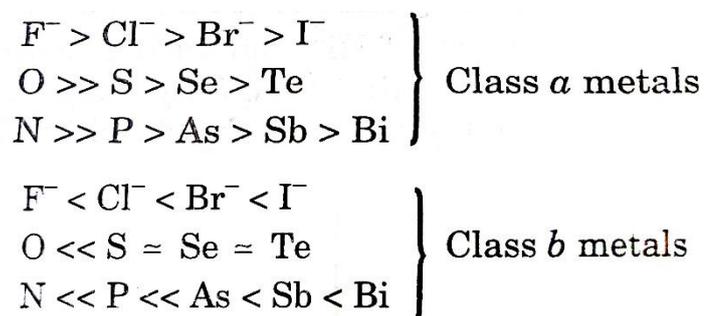
6. Class a and class b acceptor metals. *Chatt* and *Ahrland* have classified the metals into three categories: *a*, *b* and borderline, on the basis of their electron-acceptor properties. This classification is shown below (normal valence states are assumed).

(a) *Class a metals*: H, the alkali and alkaline earth metals, the element Sc → Cr, Al → Cl, Zn → Br, In, Sn, Sb and I, the lanthanides and actinides

(b) *Class b metals*: Rh, Pd, Ag, Ir, Pt, Au, Hg

(c) *Borderline metals*: The elements Mn → Cu, Ti → Po, Mo, Te, Ru, W, Re, Os, Cd.

Class a metals form more stable complexes with ligands having the coordinating atoms from the second period elements (e.g., N, O, F) than those of an analogous ligand in which the donor atom is from third or later period (e.g., P, S, Cl). *Class b metals* have the relative stabilities reversed. If the ligand contains the heavier donor atoms, class *a* and *b* metals are characterised by the stability order:



Class b metals are characterised by the presence of a number of *d*-electrons beyond an inert gas core. These *d*-electrons are used to form π -bond with ligand atoms. It is believed that the stability of the complexes of *class b metals* results from covalent contribution to metal-ligand bonds and from the transfer of electron density from the metal to the ligand via π -bonding. The most stable complexes of *class b metals* are formed with ligands like PMe_3 , S^{2-} and I^- which have vacant *d*-orbitals or like CO, CN^- which have vacant molecular orbitals of low energy.

For *borderline metals* the stability constants do not display either *class a* or *class b* behaviour uniquely.

B. Properties of the Ligand:

The following properties of the ligand affect the stability of the metal complexes:

1. Size and charge of ligand. If a ligand is smaller, it can approach the metal ion more closely forming a stable bond. Similarly, a highly charged ligand would also form a strong bond with metal. Thus, the high charge and small size of a ligand leads to the formation of stable complexes. For example, the stability of the complexes of a given metal ion with halide ion used as ligands is in the order: $F^- > Cl^- > Br^- > I^-$. This order is applicable for *class a metals*. When *class b metals* (e.g. Pd, Ag, Pt, Hg etc.) are used, the above order of stability is reversed, i.e., for *class b metals* the order is: $F^- < Cl^- < Br^- < I^-$.

2. Dipole moment of ligands. For neutral ligands, the larger the magnitude of permanent dipole moment, the greater is the stability of the complexes. For example, the order of stability of complexes formed by some neutral ligands is as: ammonia > ethylamine > diethylamine > triethylamine.

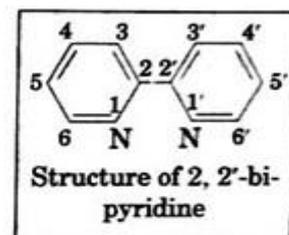
3. Basic character of ligands. The more basic is the ligand, more easily it can donate electron pairs to the central ion and hence more easily it can form complexes of greater stability. The ligand that binds H^+ firmly forms stable complexes with metal ions. Thus F^- should form more stable complexes than Cl^- , Br^- or I^- , and NH_3 , should be a better ligand than H_2O which in turn should be better than HF . ($NH_3 > H_2O > HF$). This behaviour is observed for alkali, alkaline earth and other electropositive metals like first row transition elements, lanthanides and actinides.

4. π - Bonding capacity of ligands. The ligands like CN^- , CO , PR_3 , AsR_3 , SR_2 , alkenes, alkynes which are capable of forming π -bonds with transition metal ions give more stable complexes.

5. Steric hindrance due to bulky ligands. When a bulky group is either attached to or is present near a donor atom of a ligand, repulsion between the donor atom of the ligand and the bulky group is produced and this mutual repulsion weakens the metal-ligand bonding and hence makes the complex less stable.

Examples. (i) The complex of Ni^{2+} ion with 2-methyl-8-hydroxy quinoline ($\log_{10}\beta = 17.8$) is less stable than that with 8-hydroxy quinoline ($\log_{10}\beta = 17.8$). The effect of the presence of a bulky group on the stability of a complex is commonly called *steric hindrance*.

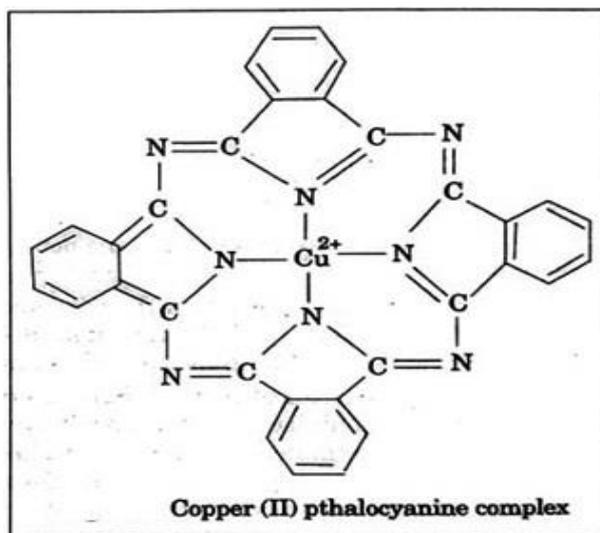
(ii) 2, 2'-bipyridine (also called 2, 2'-dipyridyl) forms complexes with metal ions which are stable but the substitution of an alkyl group in 4, 4' or 5, 5' positions gives complexes which are less stable, since the substituents crowd the metal ion. Substituents in 3, 3' positions prevent the pyridine rings from lying in the same plane and consequently the complexes formed are of lower stability.



Strain due to large ligands. The strain in the complexes with large ligands is sometimes due to the geometry of the ligand coupled with stereochemistry of the complexes. For example, triethylenetetraamine (*trien*) $H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-NH_2$ can coordinate through its four nitrogen atoms at the corners of the square, but triamino triethylamine (*tren*), $(NH_2CH_2CH_2)_3N$ cannot. Hence the former forms more stable complexes with Cu^{2+} than the latter because the former is a straight chain amine while the latter is a branched chain amine, which is unable to assume the preferred square planar geometry.

6. Forced configuration of ligands. Ligands like porphyrin and phthalocyanine which have a completely fused planar ring system, form extraordinarily stable complexes with metal ions that tend to give planar complexes e.g., Cu^{2+} complex with phthalocyanine is very stable. Similarly *trien* forms very stable complexes with $Ni(II)$ and $Cu(II)$. These ligands impose planar configurations even on metal ions that have no tendency to form planar complexes with unidentate ligands. For example, Be^{2+} and Zn^{2+} ions normally form tetrahedral complexes but when they combine with these polydentate ligands, they are forced to assume planar

configuration. Therefore, these complexes are less stable. Fig. given below shows the structure of Cu (II) pthalocyanine complex.



7. Presence of chelate rings: Chelate effect:

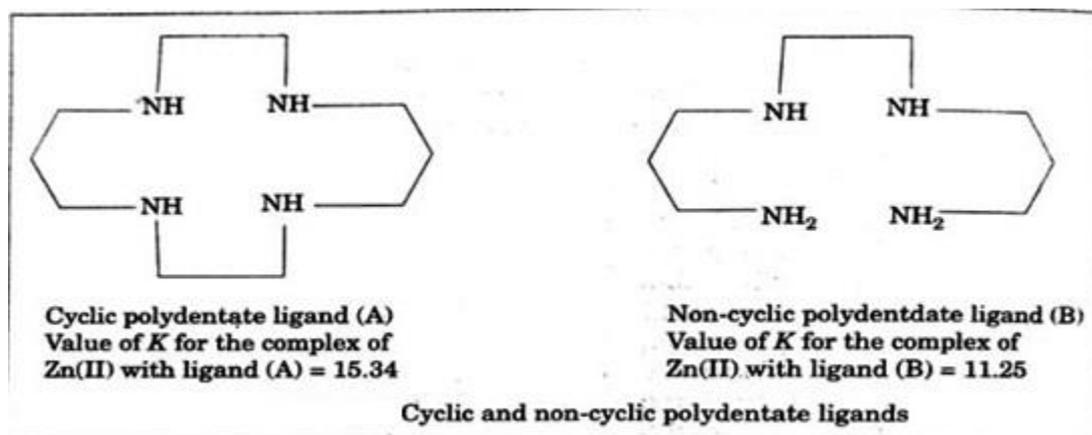
Chelated complexes (complexes containing 5- or 6-membered rings including the metal atom) are more stable than the non-chelated complexes. Greater stability of chelated complexes is called **chelate effect**. This effect is found to be maximum in complexes having 5- and 6-membered rings. With the increase in the number of rings present in the structure of the complex, the stability (or stability constant) of the complex also increases.

8. Macrocyclic ligands and macrocyclic effect: A macrocyclic ligand is a nine or more membered cyclic molecule having 3 or more potential donor atoms which can bind a metal atom inside the cavity of the macrocycle. Many synthetic macrocyclic ligands have only N donor atoms. These are also synthetic macrocyclic ligands which contain mixed (N, O), (N, S), (N, O, S), (N, O, P) etc. donor atom. Some macrocyclic ligands have conjugated π system.

It has been observed that the stability of a complex of a particular metal ion with macrocyclic ligand is several times greater than that of an open-ended multidentate ligand (chelating ligand) containing an equal number of equivalent donor atoms. *The greater stability due to a macrocyclic ligand compared to similar open-ended chelating ligand is termed as macrocyclic effect.* Thus, if ligands are multidentate and cyclic without any steric effects, the stability of the complexes is increased. *The increase in stability due to the presence of multidentate cyclic ligands is called macrocyclic effect. The enhanced stability due to macrocyclic ligand indicates greater chelate effect.*

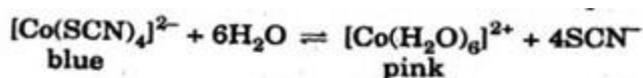
Examples (i) The cyclic crown polyether complexes are far more stable than those of their corresponding open-chain analogues.

(ii) The values of K for the complexes of Zn (II) and Ni (II) with ligand (A) are higher than those for the complexes of the same metals with ligand (B). See figure (A) and (B).

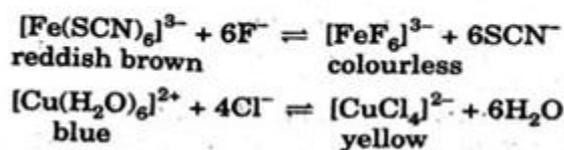


Above discussion shows that the thermodynamic stability of a complex formed by a metal with a cyclic polydentate ligand [e.g. (A)] is greater than that of the complex formed by the same metal with a non-cyclic polydentate ligand [e.g. (B)].

9. Concentration of ligand. Some complexes exist in aqueous solution only in the presence of a high concentration of the coordinating group (ligand). Otherwise in such cases, water molecules apparently show greater coordinating tendency than the groups which are originally present. For example, cobaltous ion (Co^{2+}) in presence of a high concentration of thiocyanate ions (SCN^-) forms stable blue complex ion, $[\text{Co}(\text{SCN})_4]^{2-}$. But on dilution with water, the blue complex gets destroyed and is replaced by a pink hydrated complex, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. On further addition of SCN^- ions, pink colour disappears and the original blue colour reappears. These changes indicate the competition between water molecules and thiocyanate ions to coordinate with cobaltous ion. The equilibrium reactions can be represented as follows.

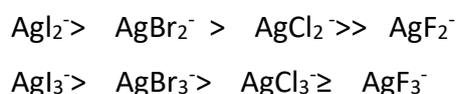


Similarly,



C. Amount of Metal-Ligand Covalent Characters Present in Complexes.

In some complexes the stability of the complex has been found to be influenced by the amount of metal-ligand covalent character present in the complex. This is more pronounced in complexes of the metals like those of copper and zinc family, Sb, Pb. For example, the stability of $[\text{AgX}_2]^-$ and $[\text{AgX}_3]^-$ are found to be in the following order



This can be due to the increase in the covalent character of Ag-X bond as we move from Ag - F to Ag - I.

Methods for the Determination of Stability Constants and Composition of a Complex:

A brief discussion of two experimental methods used for the determination of stability constants of complexes will be taken up.

1. Spectrophotometric Method:

In many cases, there is change in absorbance of a system on complex formation. This change in absorbance has been used to determine the composition and stability of metal complexes. Most of the spectrophotometric methods are not of general applicability because of various limitations.

The relationship between the absorbance (or optical density), A at a particular wavelength and concentration is given by **Beer's law**, which can be mathematically stated as

$$A = \epsilon \cdot l \cdot c.$$

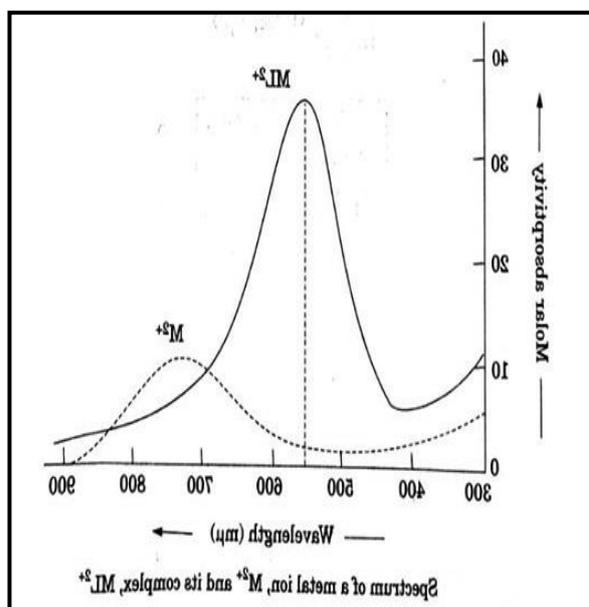
where ϵ = mole extinction coefficient

l = length of absorption cell

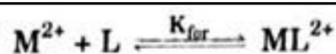
c = concentration of the complex (in moles per litre)

Thus, measuring absorbance (A) with the help of a spectrophotometer and knowing the extinction coefficient (ϵ) at that wavelength and the cell length (l), the concentration (c) can be calculated with the help of Beer's law.

In Fig. a graph is drawn between the wavelength and molar absorptivity of a representative metal in $[M^{2+}]$ which is shown by broken lines and its complex ion $[ML]^{2+}$ which is shown by dark lines. From the graph it is quite clear that the absorption by the complex occurs over the entire region of the metal ion absorption but at $550 \text{ m}\mu$ only the complex absorbs.



The formation constant (K_{for}) for the reaction:



is given by:

$$K_{\text{for}} = \frac{[ML^{2+}]}{[M^{2+}][L]} \quad (A)$$

If the values of $[ML^{2+}]$, $[M^{2+}]$ and $[L]$ are put in the above equation, we can get the value of K_{for} . The values of $[ML^{2+}]$, $[M^{2+}]$ and $[L]$ can be determined as follows:

If C_M and C_L are the total concentration of the metal ion and ligand respectively, then:

$$C_M = [M^{2+}] + [ML^{2+}] \quad (i)$$

$$C_L = [L] + [ML^{2+}] \quad (ii)$$

We know that:

$$A = \sum_{ML^{2+}} \epsilon \times l \times [ML^{2+}]$$

or $[ML^{2+}] = \frac{A}{\sum_{ML^{2+}} \epsilon \times l} \quad (iii)$

With the help of equation (iii) equation (i) becomes

$$C_M = [M^{2+}] + \frac{A}{\sum_{ML^{2+}} \epsilon \times l}$$

or $[M^{2+}] = C_M - \frac{A}{\sum_{ML^{2+}} \epsilon \times l} \quad (iv)$

With the help of equation (iii) equation (ii) becomes

$$C_L = [L] + [ML^{2+}]$$

$$= [L] + \frac{A}{\sum_{ML^{2+}} \epsilon \times l}$$

or $[L] = C_L - \frac{A}{\sum_{ML^{2+}} \epsilon \times l} \quad (v)$

Put the values of $[ML^{2+}]$, $[M^{2+}]$ and $[L]$ from equations (iii), (iv) and (v) in equation (A) to get the value of K_{for} . The experiment can be repeated at different C_M and C_L values to check the value of K_{for} .

2. Method of Continuous Variation (Job's Method)

This method is a variation of the spectrophotometric method and is used to determine the composition of a complex. This is mainly used for solution where only one complex is formed.

Different steps of the procedure are:

(i) Make 10 solutions of the complex containing metal ion and ligand in such proportions that the total volume of each solution is 10 ml as shown below:

<i>Solutions No. (10 solutions):</i>	1	2	3	4	5	6	7	8	9	10
<i>Volume of the metal ion (ml):</i>	0	1	2	3	4	5	6	7	8	9
<i>Volume of the ligand (ml):</i>	10	9	8	7	6	5	4	3	2	1

Thus, we see that the sum of the concentration of the ligand, C_L and that of the metal ion, C_M is constant. Only their ratios, $C_L : C_M$ are changed. Thus:

$$C_L + C_M = C \quad \dots \quad \dots \quad (i)$$

where C is a constant.

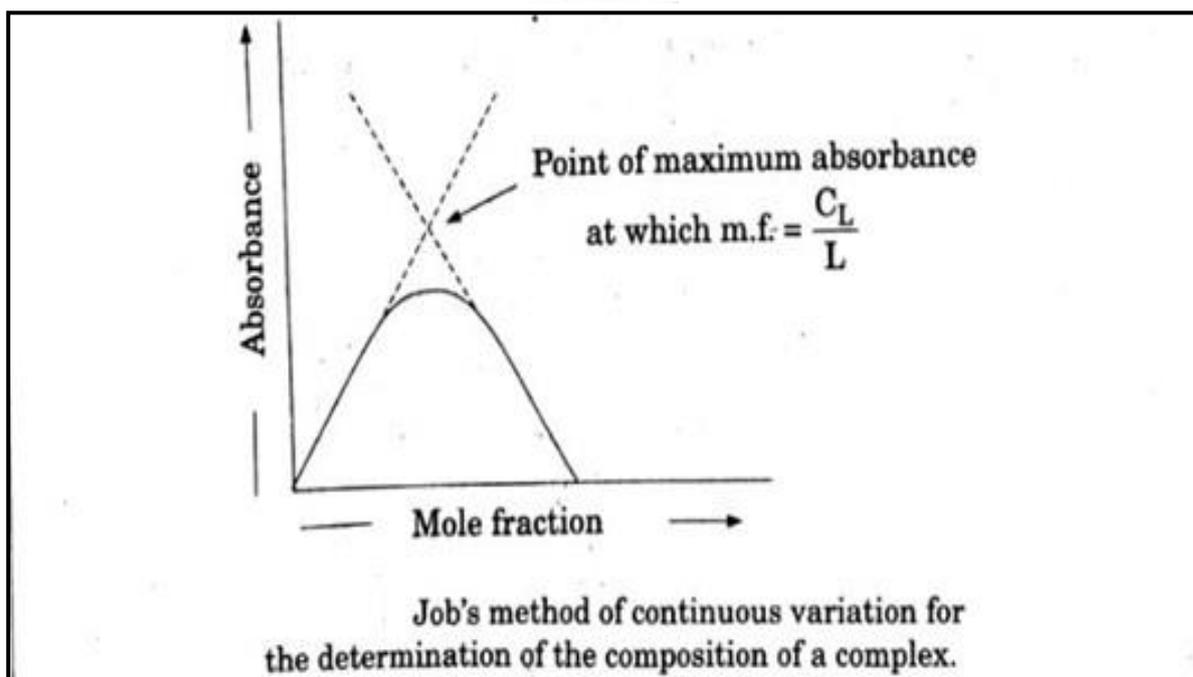
(ii) Determine the optical densities of the solutions as prepared in step (i) with the help of a spectrophotometer at such a wave length of light that the complex absorbs strongly and the metal ion and the ligand do not.

(iii) Draw a graph between the mole fraction of the ligand, $m.f. \left(m.f. = \frac{C_L}{C} \right)$ and optical density (or absorbance).

The graph obtained is of the type as shown in Fig. below.

When the legs of the curve are extrapolated, they cross each other at a point at which the absorbance is maximum.

If the formula of the complex is ML_n , then $n = \frac{C_L}{C_M}$ (ii)



Equation (i) can also be written as:

$$\frac{C_L}{C} + \frac{C_M}{C} = \frac{C}{C} = 1 \quad (iii)$$

With the help of equation viz.,

$$m.f. = \frac{C_L}{C} \quad (iv)$$

or $\frac{C_L}{C} = mf$

equation (iii) reduces to:

$$m.f. + \frac{C_M}{C} = 1$$

or $\frac{C_M}{C} = 1 - m.f.$ (v)

Dividing equation (iv) by equation (v), we get

$$\frac{C_L}{C} \times \frac{C}{C_M} = \frac{m.f.}{1 - m.f.}$$

or $\frac{C_L}{C_M} = \frac{m.f.}{1 - m.f.}$

or $n = \frac{m.f.}{1 - m.f.}$ [See equ. (ii)] (vi)

From the value of n as given by equation (vi) we can determine the composition of the complex, ML_n .

Limitations:

- (i) This method can be used when only one complex is formed under the experimental conditions.
- (ii) This method is used when there is no change in the total volume of the solutions containing metal ions and ligand.

(B) Ligand Substitution Reactions in Octahedral Complexes

What are Substitution Reactions in Coordination Compounds?

Substitution reactions in coordination compounds are the reactions in which a ligand present in the coordination sphere of the complex compound is replaced (substituted) by another ligand (nucleophile) or the metal in a complex compound is replaced of another metal (electrophile). Substitution reactions are also called **exchange reactions** or **replacement reactions** or **displacement reactions**.

Classification of Substitution Reactions in Complexes:

Depending on whether a ligand is exchanged by another ligand or a metal is replaced by another metal, substitution reactions of coordination compounds have been classified into the following categories.

1. Nucleophile (or ligand) substitution reactions (S_N reactions): In these reactions a ligand present in the coordination sphere is replaced by another ligand (nucleophile).

For example:



Nucleophile

In this reaction the ligand, L (leaving group) present in complex (MA_5L) is replaced by another ligand E (entering group). E is called nucleophile, since it is electron pair donor (Lewis base). Coordination numbers of the new complex (MA_5E) and the original complex (MA_5L) are the same (= 6). In this reaction L is the leaving (outgoing) group.

2. Electrophile (or metal) substitution reaction (S_E reaction): In these reactions the metal present in a complex is replaced by another metal (electrophile).

For example:



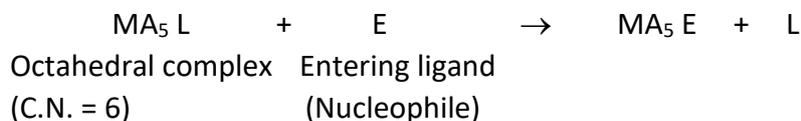
Electrophile

In this reaction the metal (M) present in the complex, M^1A_5L is replaced by another metal M^2 . M^2 metal is called **electrophile**, since it is **electron pair acceptor (Lewis acid)**. Coordination numbers of the two complexes (M^1A_5L) and M^2A_5L) are the same (=6). In this reaction M^1 is the leaving (outgoing) metal and M^2 is the entering metal.

Nucleophilic (Ligand) Substitution Reactions in Octahedral Complexes:

Nucleophilic substitution reaction in an octahedral complex is a reaction in which one of the ligands present in an octahedral complex is replaced by another ligand.

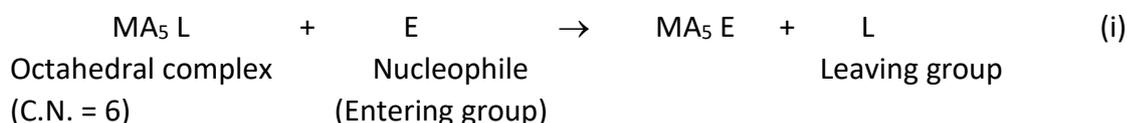
For example, the reaction,



is a nucleophilic substitution reaction in which the ligand L present in octahedral complex (MA_5L) is replaced by another ligand E. Thus, E is the entering ligand and L is the leaving ligand. Since all the ligands are nucleophiles (electron pair donors or Lewis bases), these reactions are called nucleophilic substitution reactions.

Mechanism to Explain the Nucleophilic (Ligand) Substitution Reactions in Octahedral Complexes:

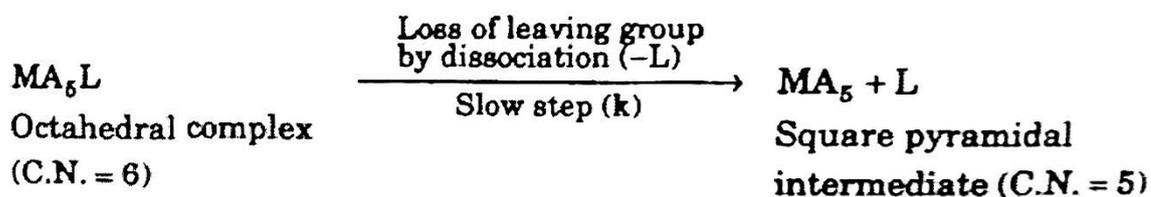
Let us consider the following nucleophilic (ligand) substitution reaction in octahedral complex, MA_5L



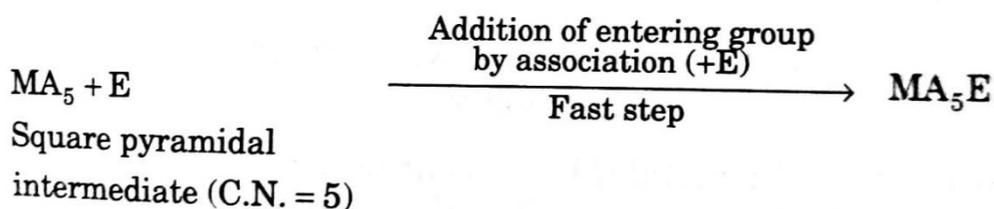
Here, MA_5L is an octahedral complex in which L is the leaving group, i.e. L is replaced by E. Thus, E is the entering group (nucleophile). There are two mechanisms to explain the occurrence of the above ligand substitution reaction (i).

1. Unimolecular nucleophilic substitution or dissociative $\text{S}_{\text{N}}1$ mechanism. According to this mechanism the ligand substitution reaction (i) proceeds through the following steps:

(a) *Dissociative step (D): Loss of leaving group*



(b) *Associative step: Addition of entering group*



In *dissociative step (a)* the octahedral complex (MA_5L) dissociates to lose the leaving group (L) and forms square pyramidal intermediate (MA_5) with C.N. = 5. Thus, in this step M-X bond present in MA_5L molecule is *broken*. Hence step (a) can also be called **bond breaking step**. In *associative step (b)*, the square pyramidal intermediate formed in step (a) adds the entering group E (nucleophile) by association and forms the octahedral complex, MA_5E .

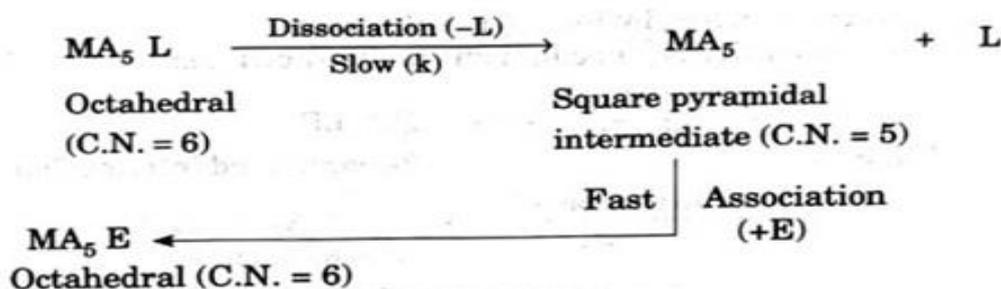
Since the dissociation step (step (a)) is a slow step, it is the rate determining step. The reaction of this slow step is unimolecular, since it involves only one reacting species viz MA_5L . The rate of this reaction depends on the concentration of MA_5L only, i.e. the rate law of this reaction is represented as:

$$\begin{aligned} \text{Rate (r)} &= k[MA_5 L] \\ &= k[\text{Initial complex}] \end{aligned}$$

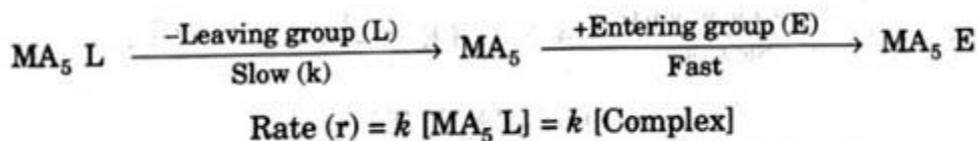
Since the rate of reaction (r) depends on the concentration of one species only viz complex ($MA_5 L$), S_N1 mechanism is also called **unimolecular S_N mechanism** or **S_N1 mechanism**.

In this mechanism, since the octahedral complex MA_5L dissociates in rate determining step (slow step), the mechanism is called **dissociative S_N1 mechanism**. Above discussion shows that the rate of reaction (i) is directly proportional to concentration of MA_5L and is independent of the concentration of the entering group E .

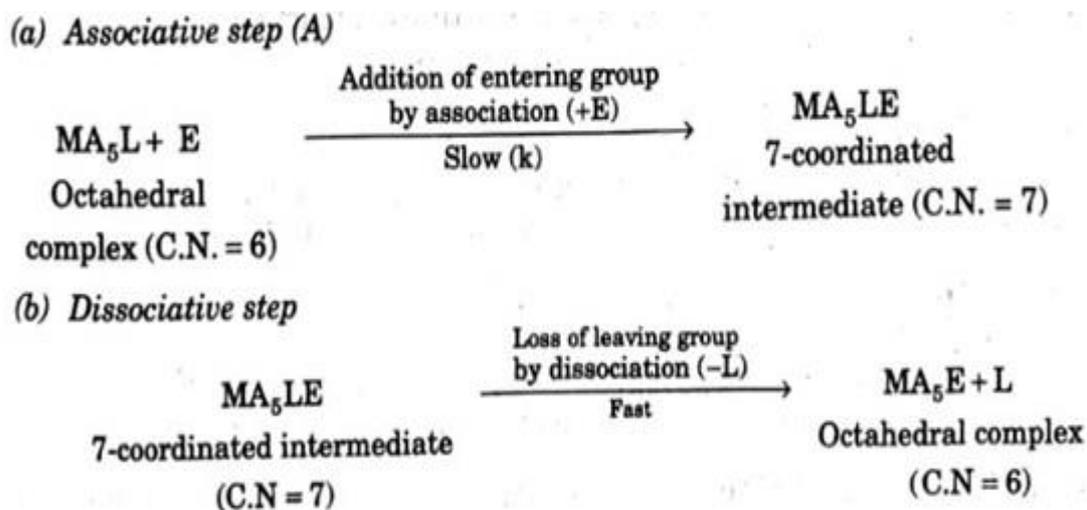
Both the steps of dissociative S_N1 mechanism can be combined together and can be represented as:



In a simplified way the above steps of dissociative S_N1 mechanism can also be shown as: -



2. Bimolecular nucleophilic substitution or associative S_N2 mechanism. According to this mechanism the ligand substitution reaction (i) proceeds through the following steps:



In associative step (a) the nucleophile (entering group), E attacks the octahedral complex (MA₅L) and gets associated with it to form a 7- coordinated intermediate (MA₅LE). Thus, in this step a new bond (M-E bond) is formed to produce MA₅LE. Hence this step can also be called **bond making step**. In dissociative step (b), 7-coordinated intermediate (MA₅LE) formed in step (a) breaks up and the leaving ligand (L) is ejected.

Since step (a) is slow step, it is the rate determining step. The reaction of this step is bimolecular, since it involves two species viz MA₅L and E. The rate of this reaction depends on the concentration of the complex (MA₅L) as well as on the concentration of the entering ligand (E) i.e. the rate law for this reaction is represented as:

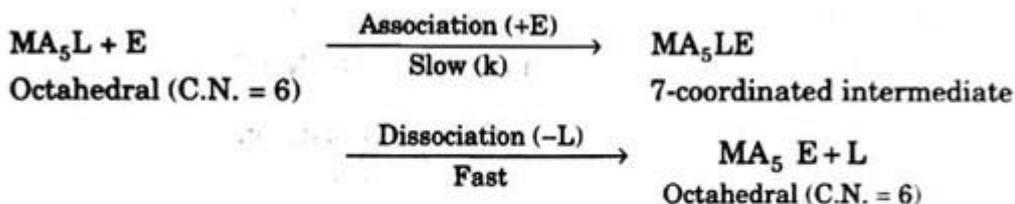
$$\text{Rate (r)} = k[\text{MA}_5\text{L}][\text{E}]$$

$$= k [\text{Complex}][\text{Entering group}]$$

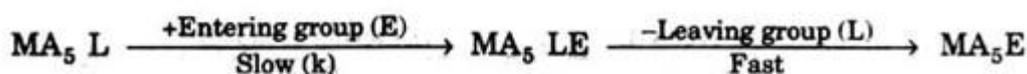
Since the rate of reaction depends on the concentration of the complex (MA₅L) and the entering group or nucleophile (E), this mechanism is also called **bimolecular S_N mechanism** or **S_N2 mechanism**.

In this mechanism, since the entering group (E) gets associated with the complex (MA₅L) in rate determining step (slow step) to form 7- coordinated intermediate, this mechanism is also called **associative mechanism**.

Both the steps of associative S_N2 mechanism can be shown as:



In a simplified way both the above steps of associative S_N2 mechanism can also be shown as:

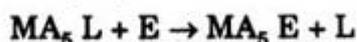


$$\text{Rate (r)} = k[\text{MA}_5\text{L}][\text{E}]$$

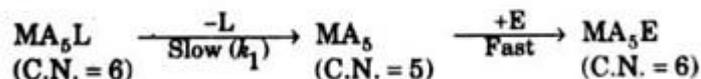
$$= k[\text{Complex}][\text{Entering group}]$$

Comparison Between S_N1 and S_N2 Mechanisms.

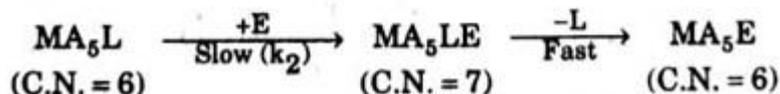
Let us consider the following ligand substitution reaction



S_N1 mechanism



S_N2 mechanism



(i) In S_N1 mechanism the rate determining step (slow step) is metal-ligand bond (M-L bond) breaking step, since in this step MA₅L (C.N.= 6) is changed into MA₅(C.N. = 5). In S_N2 mechanism the rate determining step (slow step) is a metal - ligand bond (M-E bond) forming step, since in this step MA₅L (C.N. = 6) is converted into MA₅LE (C.N. = 7).

(ii) S_N1 mechanism follows first order rate law. Thus, rate determining step is unimolecular, i.e. rate of reaction is first order w.r.t. MA₅L Hence:

$$\text{Rate (r) of S}_{\text{N}}^1 \text{ mechanism} = k_1[\text{MA}_5\text{L}]$$

$$= k_2[\text{Complex}]$$

S_N2 mechanism follows second order rate law. Thus, the rate determining step is bimolecular and the rate of reaction is first order w.r.t to MA₅L and first order w.r.t E. Hence:

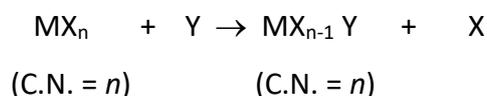
$$\text{Rate (r) S}_{\text{N}}^2 \text{ of mechanism} = k_1 [\text{MA}_5\text{L}][\text{E}]$$

$$= k_2[\text{Complex}][\text{Entering group}]$$

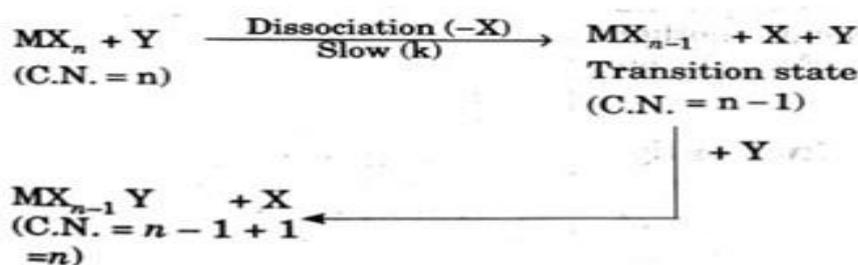
Reaction Profile of Dissociative (D) Mechanism:

Reaction profile is a graphic representation of the energy as a function of the reaction coordinate. Reaction coordinate represents the progress of a reaction from reactants to products.

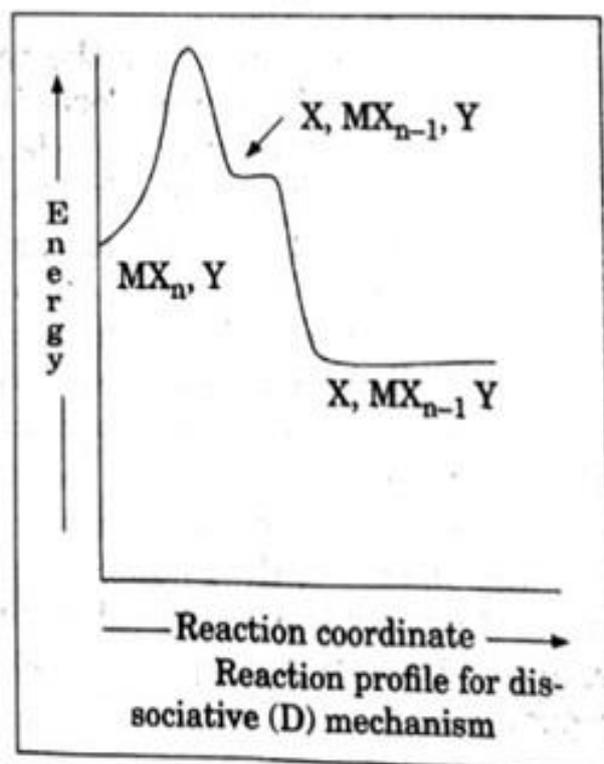
Let us consider the following ligand substitution reaction:



Here, X is the leaving group and Y is the entering group. The coordination number of the reacting complex, MX_n and the formed complex, MX_{n-1}Y is the same ($= n$). If the above reaction proceeds through dissociative mechanism, then the conversion of MX_n into MX_{n-1}Y can be shown by the following steps:



Above mechanism shows that in the first step M-X bond is broken and transition state, MX_{n-1} (intermediate) is obtained. Thus, the complex MX_n should have activation energy required for the transition state before M-X bond is broken to form MX_{n-1} which has lower C.N. than MX_n . Once M-X bond is broken, the leaving group (X) leaves the coordination sphere of MX_n to form the intermediate (MX_{n-1}) which has a plateau as is evident from the reaction profile shown in Fig. Since the leaving group (X) leaves the coordination sphere of MX_n a vacancy is created in the coordination sphere. This vacancy is then filled up by the entering group (Y) to form the products MX_{n-1}Y and X. The products, MX_{n-1}Y and X have lower energy than the reactants MX_n and Y. The reaction profile has one hill and one plateau.

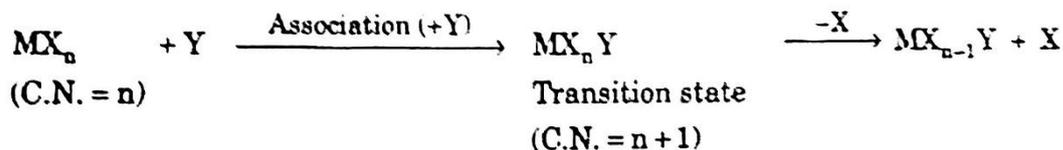


Reaction Profile for Associative (A) Mechanism

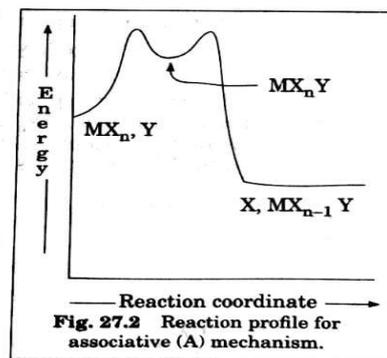
Let us consider the following ligand substitution reaction:



If this reaction proceeds through associative mechanism ($\text{S}_{\text{N}}2$ mechanism), then the conversion of MX_n into MX_{n-1}Y can be shown by the following steps:



In associative mechanism, the energy of the reactant (MX_n) and entering group (Y) keeps on increasing till the activation energy for the transition state (intermediate), MX_nY is reached. Transition state has higher C.N. (= $n + 1$) than the original complex, MX_n (C.N. = n). Now the bond between M and X in transition state is broken and M-Y bond is formed in MX_{n-1}Y . So, the intermediate passes through another smaller hill to stable products, MX_{n-1}Y and X. (See figure).



Acid Hydrolysis (Aquation)

What is Acid Hydrolysis?

The ligand substitution reaction occurring in aqueous medium in which a ligand present in the coordination sphere of a complex species is replaced by H_2O molecule is called **acid hydrolysis** (or **aquation**) of the complex. For example, the reaction



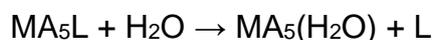
is an acid hydrolysis reaction. In this reaction L is the leaving ligand and H_2O is the entering group. The ligand A is called inert ligand, since this ligand remains attached in the product, $\text{MA}_5(\text{H}_2\text{O})$ also.

Mechanism of Acid Hydrolysis (Aquation) of Different Types of Octahedral Complexes:

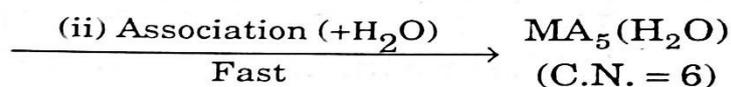
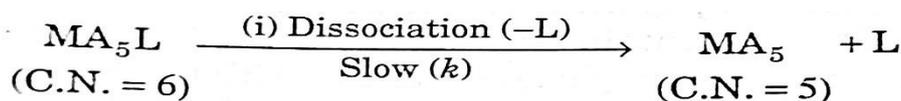
The mechanism of acid hydrolysis occurring in the following types of octahedral complexes:

1. Octahedral Complexes in Which None of the Inert Ligands is a π - Donor or a π -acceptor.

Let us consider the acid hydrolysis of MA_5L complex in which A_5 are inert ligands. None of these ligands is a π -donor or a π - accepter. The hydrolysis of MA_5L can be represented as:

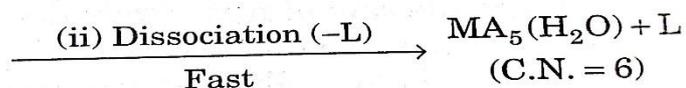
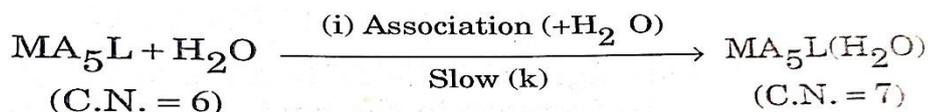


S_N1 mechanism: As a matter of fact, this reaction proceeds through the following two steps which are based on S_N1mechanism.



$$\begin{aligned} \text{Rate of reaction} &= k [\text{Complex}] \\ &= k [MA_5 L] \end{aligned}$$

S_N2 mechanism: Hydrolysis reaction (i) may also proceed through the following two steps which are based on S_N2mechanism.



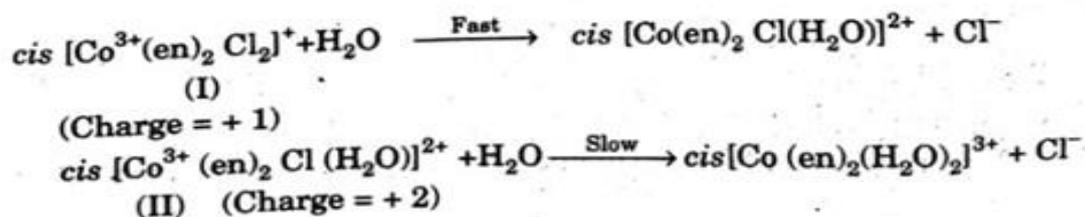
$$\begin{aligned} \text{Rate of reaction} &= k [\text{Complex}] [H_2O] \\ &= k [\text{Complex}] \\ &= k [MA_5L] \end{aligned}$$

It is clear from the above discussion that both the mechanisms predict that rate of hydrolysis reaction (i) is dependent only on the concentration of the complex, MA_5L . Thus, the measurement of the rate of hydrolysis reaction is not able to decide whether the hydrolysis reaction (i) proceeds through S_N1 mechanism or through S_N2 mechanism. Consequently, we will have to look to some other factors to decide the type of mechanism.

The factors to decide the type of mechanism are given below:

1. Charge on the complex: It has been observed during the hydrolysis of several octahedral complexes of Co(III) and other metal ions that the rate of hydrolysis of a complex decreases with the increase in the charge on the complex.

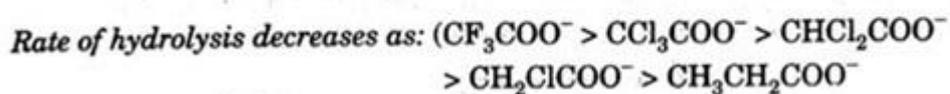
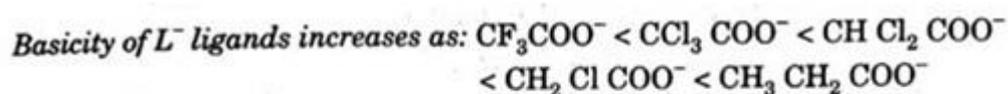
Example. The rate of hydrolysis of $\text{cis} [\text{Co}(\text{en})_2\text{Cl}_2]^+(\text{I})$ is some hundred times faster than that of $\text{cis} [\text{Co}(\text{en})_2\text{Cl}(\text{H}_2\text{O})]^{2+}(\text{II})$. Thus, the hydrolysis of (I) is fast and that of (II) is slow as shown below.



Explanation. The above observation can be explained by $\text{S}_{\text{N}}1$ mechanism of hydrolysis reaction, since the increase in the positive charge on the complex makes the dissociation of the leaving group (Cl^- ion) from the metal ion (Co^{3+}) more difficult and hence the rate of hydrolysis becomes slow.

If the hydrolysis is supposed to proceed through $\text{S}_{\text{N}}2$ mechanism, the rate of hydrolysis would remain unchanged with the increase or decrease in the charge on the complex.

2. Basicity of leaving group, L: If we study the rate of hydrolysis of complexes, $[\text{Co}(\text{NH}_3)_5\text{L}]^{2+}$ which contain different L Ligands (leaving groups), we find that the rate of hydrolysis of these complexes decreases with the increase of the basicity of L^- ligands. For example, the rate of hydrolysis of the complexes, $[\text{Co}(\text{NH}_3)_5\text{L}]^{2+}$ containing $\text{L}^- = \text{CF}_3\text{COO}^-$, CCl_3COO^- , $\text{CHCl}_2\text{COO}^-$, CHClCOO^- , $\text{CH}_2\text{ClCOO}^-$, $\text{CH}_3\text{CH}_2\text{COO}^-$ decreases from CF_3COO^- to $\text{CH}_3\text{CH}_2\text{COO}^-$, since the basicity of these ligands increases in the same direction.



Explanation. Since the strength of $\text{Co}^{3+}\text{-L}^-$ bond is directly proportional to the basicity of L^- ligand, with the increase in the basicity of L^- ligands $\text{Co}^{3+}\text{-L}^-$ bond becomes stronger and hence the rate of hydrolysis decreases. Now since the rate determining step in the hydrolysis reaction involves dissociation of $\text{Co}^{3+}\text{-L}^-$ bond, the hydrolysis reaction proceeds through $\text{S}_{\text{N}}1$ mechanism.

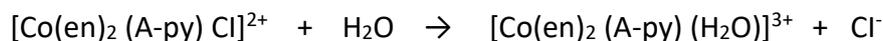
3. Inductive effect of the inert group: It has been seen that the rate constants of acid hydrolysis reaction:



increase with the CH_3 substitution in pyridine. In this reaction A-py stands for various derivatives of pyridine which are obtained by removing one of the H-atoms of pyridine by CH_3 group. A-py is an inert ligand, since it remains coordinated to the metal in the product, $[\text{Co}(\text{en})_2(\text{A-py})(\text{H}_2\text{O})]^{3+}$. The increase in rate constants is due to the inductive effect caused by the increasing CH_3 substitution which results in distorting electron density towards

Co-atom and thus helps the dissociation of Cl⁻ ion (leaving group). This again confirms the fact that the acid hydrolysis reaction given above occurs through dissociative S_N¹ mechanism.

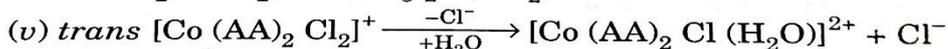
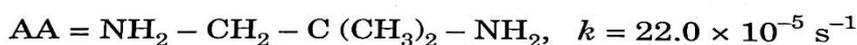
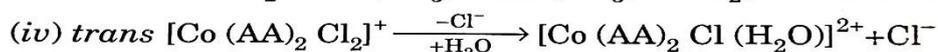
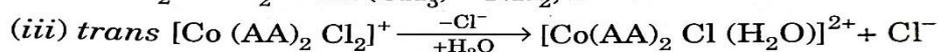
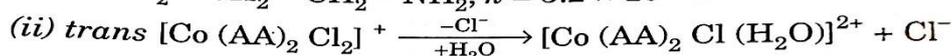
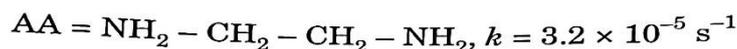
The values of rate constants (in sec⁻¹) for the acid hydrolysis reaction:



in which A-py is pyridine, 3-methyl pyridine and 4-methyl pyridine are 1.1×10^{-5} , 1.3×10^{-5} and 1.4×10^{-5} respectively.

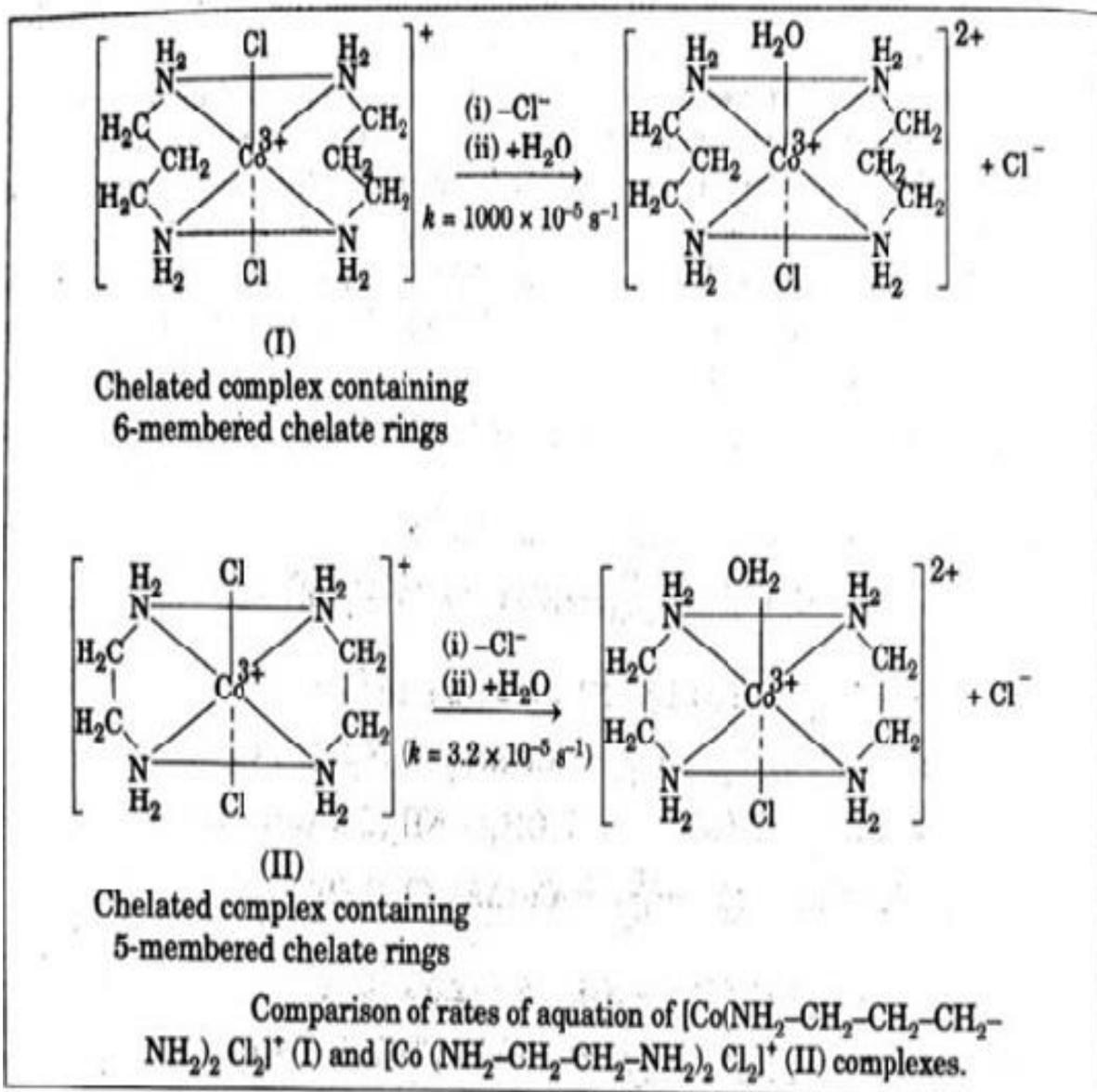
4. Steric effects: In the complexes of *trans* (Co (AA)₂ Cl₂)⁺ type, if the bidentate ligand AA is NH₂ – CH₂ – CH₂ – NH₂, NH₂ – CH₂ – CH(CH₃) – NH₂, *dl* H₂N – CH (CH₃) – CH(CH₃) – NH₂, NH₂ – CH₂ – C (CH₃)₂ and *meso* H₂N – CH (CH₃) – CH(CH₃) – NH₂, then the bulk of the ligand, (AA) increase, i.e. the ligand (AA) becomes more bulky. Due to the increase in the bulk of the ligand the steric overcrowding (hindrance) of the ligand round the central metal ion (Co³⁺) also increases. Due to the increase in the overcrowding of the ligand round the central metal in (Co³⁺) another ligand cannot be taken up by the complex. i.e. there is no possibility of S_N2 mechanism. On the contrary the removal of a ligand will reduce the overcrowding of the ligand round the central metal ion. This gives the evidence of S_N2 mechanism.

The increase in the bulk of the ligand (AA) also increases the value of rate constant for the acid hydrolysis reaction of the complexes as is evident from the following acid hydrolysis reactions.



Let us compare the rates of aquation of [Co³⁺(NH₂-CH₂-CH₂-CH₂-NH₂)₂Cl₂]⁺ (I) and [Co³⁺(NH₂-CH₂-CH₂-NH₂)₂Cl₂]⁺ (II). In complex (I), NH₂-CH₂-CH₂-CH₂-NH₂ is propylenediamine and in complex (II), NH₂-CH₂-CH₂-NH₂ is ethylenediamine.

Both the complexes are chelated octahedral complexes. Complex (I) contains 6-membered chelate rings while complex (II) has 5-membered chelated rings. Now since 6-membered chelate ring present in (I) produces greater steric strain round the central Co³⁺ ion than 5-membered chelates ring present in (II), the aquation of (I) will be fast than that of (II) through dissociative S_N1 mechanism.

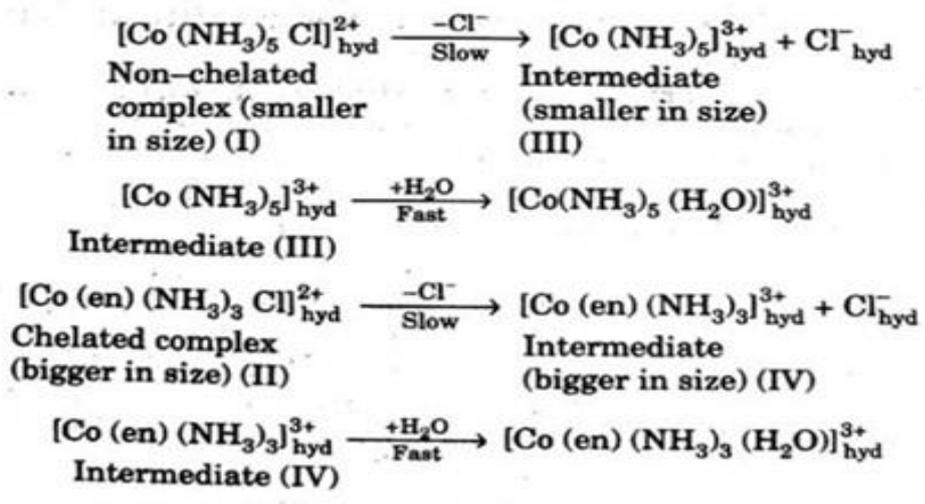


The value of k for the aquation of complex (I) is much higher than that of complex (II). Experimentally this prediction has been found true.

5. Solvation effects: According to solvation theory in aqueous medium, the reacting complexes, the intermediates formed and the products obtained are all in the hydrated state. The hydrated state of a species is represented by putting a subscript, *hyd* in the species.

On comparing the rate of aquation of the complexes $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ (I) and $[\text{Co}(\text{en})(\text{NH}_3)_3\text{Cl}]^{2+}$ (II). Complex (I) is smaller in size than complex (II), since complex (I) has only monodentate ligands while complex (II) has chelated as well as monodentate ligands.

If the aquation of the complexes is proceed through dissociative $\text{S}_{\text{N}}1$ mechanism, then the aquation of these complexes can be represented as:

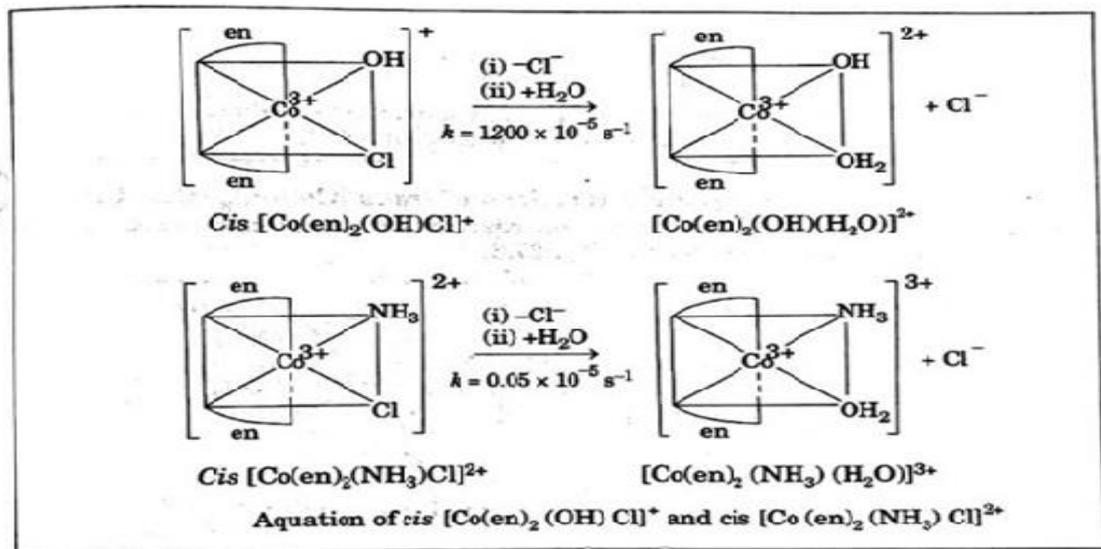


Now since intermediate (IV) is obtained from bigger complex (II) and intermediate (III) is obtained from smaller complex (I), (IV) is bigger in size than (III). Being bigger in size, the intermediate (IV) is stabilised by hydration to a lesser extent and hence requires more energy for its formation than the intermediate (III). As a result, complex (II) would be aquated at a slower rate than complex (I).

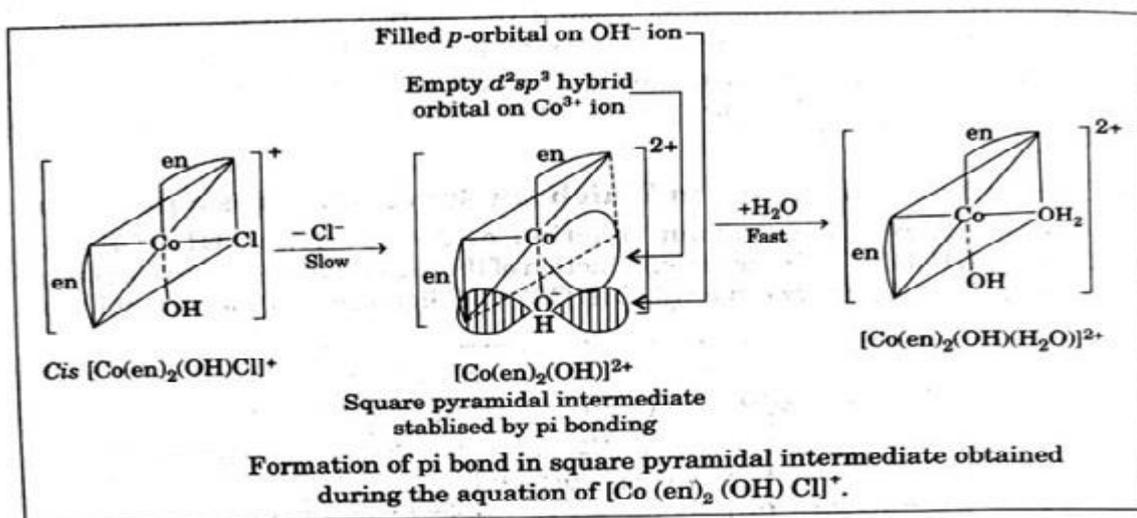
Since the steric overcrowding around the central metal ion in complexes $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ and $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ is almost the same, the difference in the rate of aquation of these complexes can be interpreted on the basis of solvation effect. The rate of aquation of these complexes are as: $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ = 180 \times 10^{-3} \text{S}^{-1}$, $(\text{Co}(\text{en})_2\text{Cl}_2)^+ = 3.2 \times 10^{-5} \text{S}^{-1}$

II. Octahedral Complexes in which the Inert Ligand is a π- Donor:

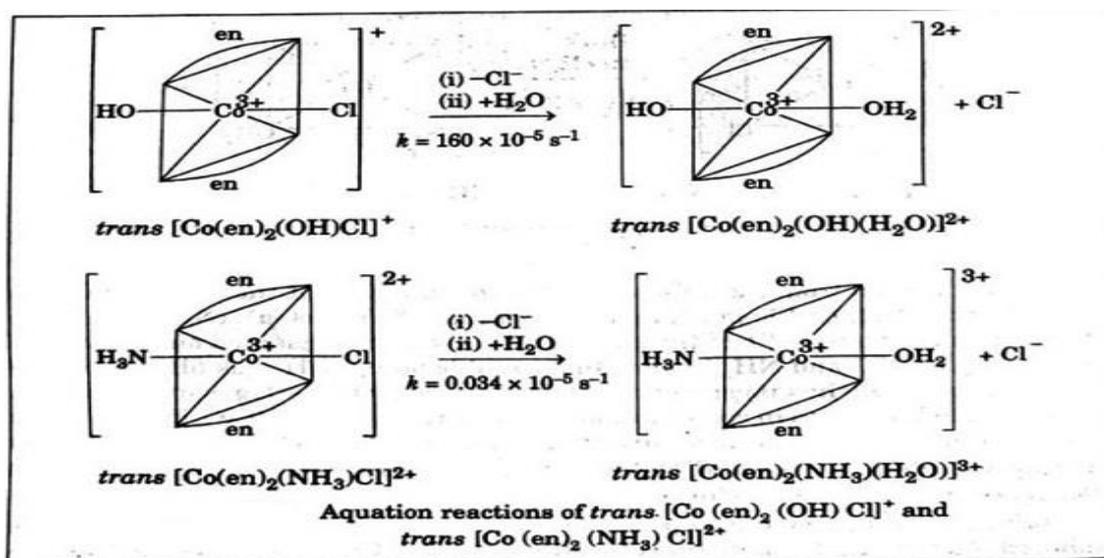
Let us consider the aquation reaction of *cis* $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$ and *cis* $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$. The aquation reaction of these complexes can be represented as shown in figure below. In *cis* $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$, OH⁻ ligand is a π- donor inert ligand.



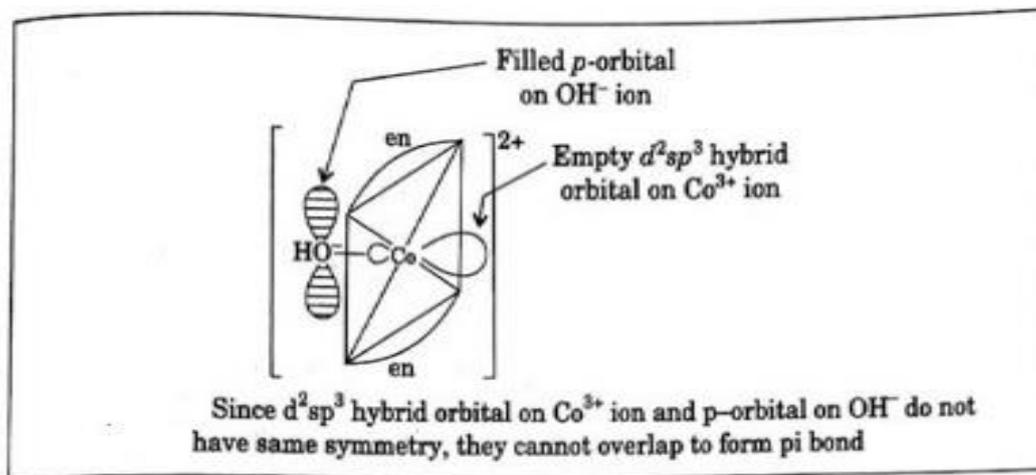
It may be seen from the values of rate constant (k) that the rate of aquation of *cis* $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$ is much higher than that of *cis* $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$. The difference in the values of k of the two complexes can be explained on the basis of the capacity of OH^- and NH_3 ligands to form π -bonding. OH^- has filled p -orbital while NH_3 molecule has no such orbital. The lone pair of electrons on N-atom in NH_3 molecule is used up in coordination. The central metal ion (Co^{3+} ion) of square pyramidal intermediate formed during the aquation of *cis* $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$ has one empty $d^2 sp^3$ hybrid orbital. This empty $d^2 sp^3$ hybrid orbital overlaps with the filled p -orbital on OH^- ion to form a π -bond as shown in fig. below.



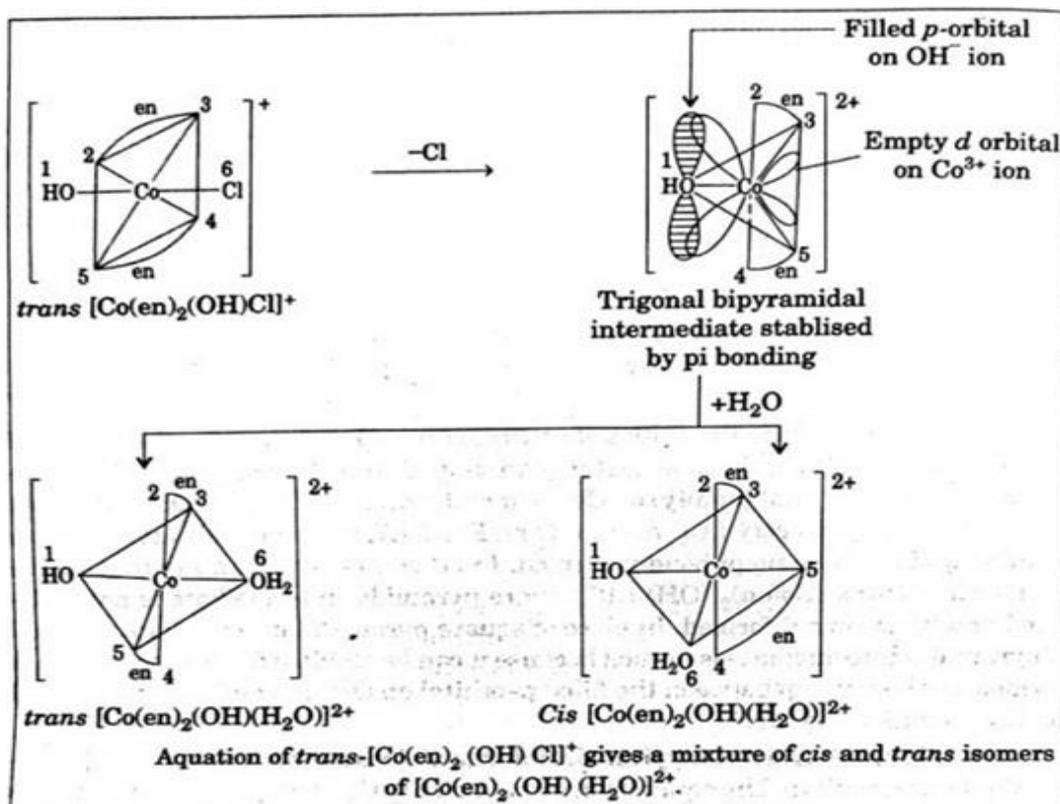
It is due to the formation of π -bond that the square pyramidal intermediate is stabilised. As a result, the aquation of *cis* $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$ becomes easier than the aquation of *cis* $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ whose square pyramidal intermediate cannot be stabilised by π -bonding. Let us consider the aquation reactions of *trans* $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$ and *trans* $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$. The aquation reactions of these complexes proceed through $\text{S}_{\text{N}}1$ mechanism as shown in Fig. below.



It may be seen from the values of rate constant (k) that the rate of aquation of *trans* $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$ is much faster than that of *trans* $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^{2+}$. Since the d^2sp^3 hybrid orbital (empty) on Co^{3+} ion and p -orbital (filled) on OH^- ion do not have the same symmetry as is evident from below fig., these orbitals are incapable of overlapping.



Thus, no π - bond is formed. In other words we can say that in the aquation of *trans* $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$ square pyramidal intermediate is not stabilised and hence is not formed. In place of square pyramidal intermediate, trigonal bipyramidal intermediate is formed because it can be stabilised by π - bond which is formed by the overlap between the filled p -orbital on OH^- ion and empty d -orbital on Co^{3+} ion. (See figure given below).



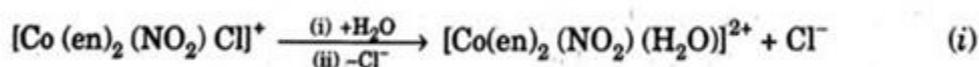
The π -bonded trigonal bipyramidal intermediate is more stable than square pyramidal intermediate. The aquation of *trans* $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]^+$ gives a mixture of *cis* and *trans* isomers of $[\text{Co}(\text{en})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$ as shown in Fig. It may be noted that the aquation of *trans* $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$ gives only *trans* $[\text{Co}(\text{en})_2(\text{NH}_3)(\text{H}_2\text{O})]^{3+}$.

From the above discussion the following points may be noted:

- (i) The aquation reactions discussed above proceed through dissociative S_N1 mechanism.
- (ii) Like OH^- , NH_2^- , Cl^- , Br^- etc are also π -bonding inert ligands (π -donors). Thus, the mechanism of aquation of the complexes containing these π -bonding inert ligands (NH_2^- , Cl^- , Br^- etc) is the same as that of the complexes containing OH^- .
- (iii) The aquation of a *cis* isomer containing a π inert ligand gives square pyramidal intermediate while the aquation of a *trans* isomer gives trigonal bipyramidal intermediate.
- (iv) When square pyramidal intermediate is formed, the aquation reaction gives complex of the same geometry. On the other hand, when trigonal bipyramidal is formed, the aquation reaction gives a mixture of *cis* and *trans* isomers.

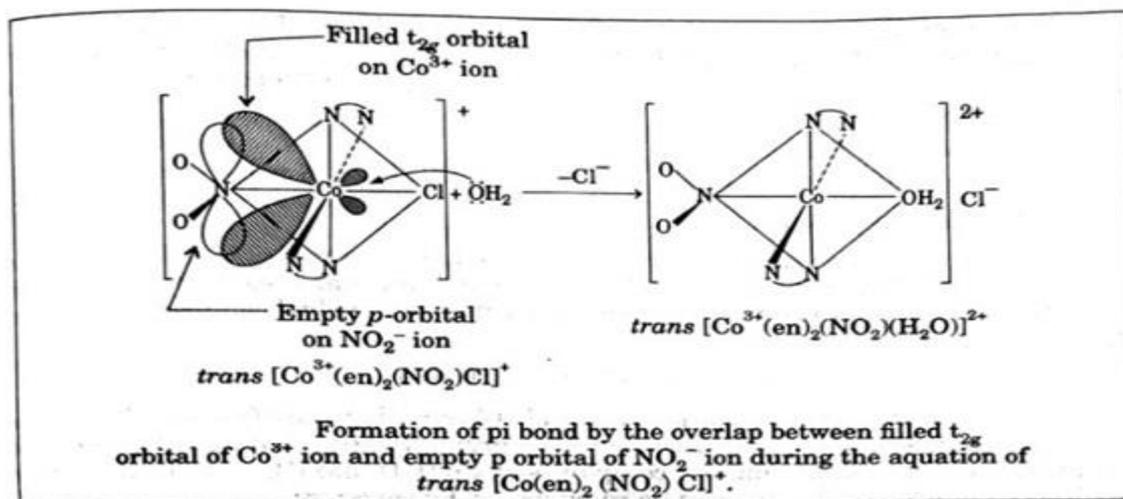
III. Octahedral Complexes in which the Inert Ligand is a π - Acceptor:

Aquation of octahedral complexes in which the inert ligand is π -acceptor proceeds through associative S_N2 mechanism. Thus, the aquation of $[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]^+$ in which the ligand, NO_2^- is an inert π -acceptor and the ligand, Cl^- is the leaving group proceeds through associative S_N2 mechanism as shown below:



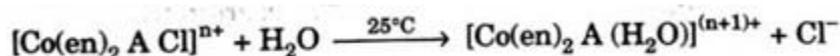
The inert π acceptor ligand, NO_2^- is called **spectator ligand**. Depending on whether the inert π acceptor ligand (NO_2^-) is placed *trans* or *cis* to the leaving group (Cl^-) in the octahedral complex, the following two cases may be studied.

(a) Aquation of *trans* $[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]^+$ complex: In this complex NO_2^- and Cl^- are placed *trans* to each other. In this complex one of the filled t_{2g} orbitals of Co^{3+} ion can overlap with the empty p -orbital of NO_2^- ligand to form a π -bond (See fig. given below). The formation of π -bond strengthens the Co-Cl bond and hence the dissociation of Co-Cl bond to release the leaving group (Cl^-) becomes difficult. Thus, the aquation of *trans* $[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]^+$ cannot proceed through dissociation S_N1 mechanism. Due to the presence of π -acceptor ligand (NO_2^-) in *trans* complex, the formation of Co- OH_2 bond is easier and hence the aquation of the complex proceeds through associative S_N2 mechanism as represented by reaction (i).



(b) Aquation of $\text{cis} [\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]^+$ complex. In this complex NO_2^- and Cl^- are placed *cis* to each other. In this complex, since NO_2^- ion is *cis* to Cl^- ion, the extent of overlap between one of the filled t_{2g} orbitals of Co^{3+} ion and empty p -orbital of NO_2^- ion is less than when NO_2^- ion is placed *trans* to Cl^- ion. Hence the formation of $\text{Cu}-\text{OH}_2$ bond would not be easy in *cis* complex. This proves that the aquation of *cis* complex also proceeds through associative $\text{S}_{\text{N}}2$ mechanism and not through dissociative $\text{S}_{\text{N}}1$ mechanism.

The values of rate constants and % *cis* product obtained by the aquation of *cis* and *trans* isomers of $[\text{Co}(\text{en})_2 \text{A Cl}]^{n+}$ represented as:



are given in Table as under. A is the π -acceptor ligand and Cl^- ion is the leaving group.

Table: Rate constant and % *cis* product obtained in aquation of $[\text{Co}(\text{en})_2\text{A Cl}]^{n+}$ represented as:



Isomer	Pi acceptor ligand (A)	$10^7 k, \text{s}^{-1}$	% <i>cis</i> product
<i>cis</i>	OH^-	1,30,000	100
<i>cis</i>	N_3^-	2,400	100
<i>cis</i>	Cl^-	2,400	100
<i>cis</i>	NCS^-	110	100
<i>trans</i>	OH^-	14,000	75
<i>trans</i>	N_3^-	2,500	20
<i>trans</i>	Cl^-	350	35
<i>trans</i>	NCS^-	0.5	50-70

It may be seen from this table that when the π -acceptor ligand, A is OH^- , Cl^- and NCS^- , the hydrolysis of *cis* $[\text{Co}(\text{en})_2 \text{A Cl}]^{n+}$ proceeds faster than the *trans* $[\text{Co}(\text{en})_2 \text{A Cl}]^{n+}$. *cis*-isomers, unlike *trans* isomers, react with retention with their configuration.

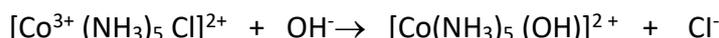
Base Hydrolysis

What is Base Hydrolysis?

The substitution reaction in which the anion of water (i.e. OH⁻ ion) replaces the coordinated ligand from a complex species is known as **base hydrolysis** of the complex species. For example, base hydrolysis of an octahedral complex, MA₅L can be represented by the equation.

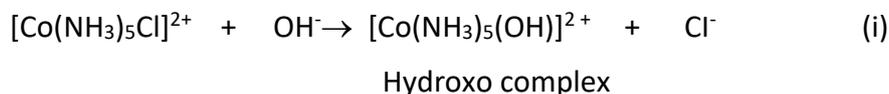


In this reaction the coordinated ligand (L) is replaced by OH⁻ ion. Thus, L is the leaving group and OH⁻ ion is the entering group. Here we shall discuss the base hydrolysis of octahedral ammine complexes of Co (III) like [Co(NH₃)₅Cl]²⁺. Base hydrolysis of [Co(NH₃)₅Cl]²⁺ can be represented by reaction:

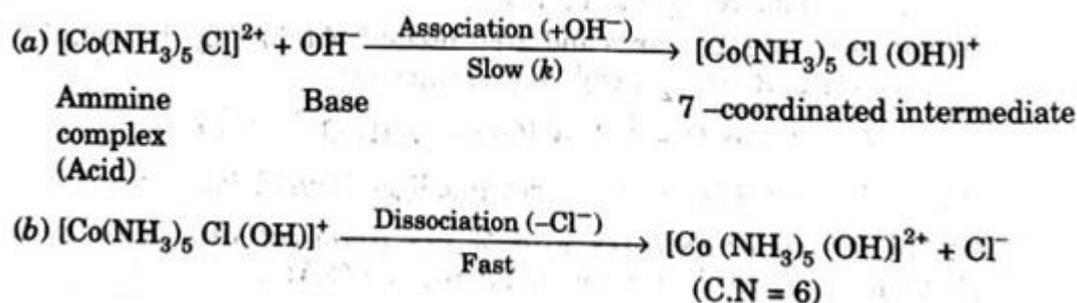


Mechanism to Explain the Base Hydrolysis of [Co³⁺(NH₃)₅Cl]²⁺ :

Following two mechanisms have been proposed to explain the base hydrolysis of [Co(NH₃)₅Cl]²⁺ represented by the following equation:



1. Associative S_N2 mechanism. This mechanism proceeds through the following steps:



Rate of base hydrolysis reaction (i): Since step (a) is a slow step, it is the rate determining step. Thus, the rate law for reaction (i) is given by:

$$\begin{array}{l}
 \text{Rate } (r) = k \times (\text{Conc. of complex ion}) \times (\text{Conc. of } OH^- \text{ ion}) \\
 \text{or } r = k \times \text{Conc. of } [Co(NH_3)_5Cl]^{2+} \times [OH^-] \quad (ii) \\
 = k \times [\text{Complex}] [\text{Base}]
 \end{array}$$

The steps given at (a) and (b) can be combined together as shown below.

