METAL-LIGAND EQUILIBRIA IN SOLUTION

Formation Constant:

Suppose a complex of the type MLn is formed from metal 'M' and mono-dentate ligand 'L'. The complex MLn may be formed by stepwise addition of ligand to the metal in n consecutive steps. The n consecutive steps and the correspon-ding equilibrium constants can be given as follows.

$$[M] + [L] \xrightleftharpoons{K_1} [ML] \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$[ML] + [L] \xrightleftharpoons{K_2} [ML_2] \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$[ML_2] + [L] \xrightleftharpoons{K_3} [ML_3] \qquad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$[ML_{n-1}] + [L] \xrightleftharpoons{K_n} [ML_n] \qquad K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

Where $K_1, K_2, \ldots K_n$ etc are called as stepwise formation or stability constants.

The formation of the complex ML_n may also be given by the equation

$$[M] + n[L] \xrightleftharpoons{\beta_n} [ML_n] \qquad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

Where β_n is called overall stability constant or overall formation constant

Relationship between overall stability constant and stepwise formation constant

$$M + nL \xrightleftharpoons{\beta_n} [ML_n]$$

$$\beta_n = \frac{[ML_n]}{[M][L]^n}$$

$$\Rightarrow \beta_n = \frac{[ML_n]}{[M][L]^n} \cdots\cdots \frac{[ML]}{[ML]} \cdot \frac{[ML_2]}{[ML_2]} \cdots\cdots \frac{[ML_{n-1}]}{[ML_{n-1}]}$$

$$\Rightarrow \beta_n = \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML_3]}{[ML_2][L]} \cdots\cdots \frac{[ML_{n-1}]}{[ML_{n-2}][L]} \cdot \frac{[ML_n]}{[ML_{n-1}][L]}$$

$$= K_1 \cdot K_2 \cdots\cdots\cdots K_n$$

$$\Rightarrow \beta_n = \prod_{m=1}^{n} K_m$$

from the above equations it is evident that overall stability constant β_n is equal to the product of the successive stability constants $K_1, K_2, \ldots K_{n-1}, K_n$

Trend in K values:

There is a steady decrease in K values from K_1 to K_n as number of ligands increases. The decreasing trend can be observed in the following example.

$$[Cu(H_2O)_4]^{+2} + NH_3 \overset{K_1}{\rightleftharpoons} [Cu(H_2O)_3NH_3]^{+2} + H_2O$$

$$K_1 = \frac{[Cu(H_2O)_3NH_3]^{+2}}{[Cu(H_2O)_4^{+2}]\,[NH_3]} = 1.66 \times 10^4$$

$$[Cu(H_2O)_3NH_3]^{+2} + NH_3 \overset{K_2}{\rightleftharpoons} [Cu(H_2O)_2(NH_3)_2]^{+2} + H_2O \qquad K_2 = 3.16 \times 10^3$$

$$[Cu(H_2O)_2(NH_3)_2]^{+2} + NH_3 \overset{K_3}{\rightleftharpoons} [Cu(H_2O)(NH_3)_3]^{+2} + H_2O \qquad K_3 = 8.31 \times 10^2$$

$$[Cu(H_2O)(NH_3)_3]^{+2} + NH_3 \overset{K_4}{\rightleftharpoons} [Cu(NH_3)_4]^{+2} + H_2O \qquad K_4 = 1.51 \times 10^2$$

The K values generally decrease gradually with increasing substitution of H_2O by Ligand L (i.e. NH_3). This gradual decrease in K values is attributed to Three factors, namely, the statistical factor, steric factor and the electro-static factor.

Statistical factor: As the co-ordinated water molecules are replaced by ligand molecules or ions (L), the number of water molecules in the co-ordination sphere decreases. Hence the probability of replacing water molecules also decreases. As a result K values decrease gradually.

statistical Ratio

The reaction between metal and ligand can occur in a single step or several steps for the formation of Complex (ML_n). It is almost always found that for a given M and L there is a decrease in successive formation constants $K_1, K_2 \ldots\ldots$ or $\beta_1, \beta_2 \ldots\ldots$. This is largely a 'statistical effect'. It is easier to attach L to ML'_N than to $ML'_{N-1}L$ because there are N reaction 'sites' on the former but only N-1 on the latter. Consider the equilibrium:

$$ML'_{N-n}L_n + L \rightleftharpoons ML'_{N-n-1}L_{n+1} + L'$$

The stepwise formation constant varies as n changes and the ratio between successive formation constants can be given by

$$\frac{K_{n+1}}{K_n} = \frac{n(N-n)}{(n+1)(N+1-n)}$$

Where N is the Co-ordination number and n is the number of reaction sites.

The values of this expression for N=6 and n=1 ⟶ 6 are compared with the experimental data for the Ni^{+2}/NH_3 system.

Statistical predictions and experimental ratios for the equilibrium constants in the system.

$$[Ni(H_2O)_{6-n}(NH_3)_n]^{+2} + NH_3 \rightleftharpoons [Ni(H_2O)_{5-n}(NH_3)_{n+1}]^{+2} + H_2O$$

	Experimental ratio	statistical prediction.
K_2/K_1	0.28	0.42
K_3/K_2	0.31	0.53
K_4/K_3	0.29	0.56
K_5/K_4	0.36	0.53
K_6/K_5	0.20	0.42

The experimental ratios are comparitively smaller than the statistical ratios. The reasons for this

1. Change in Co-ordination number & hybridisation.

Steric factor: This arises only when the incoming ligands are bulkier in size than the co-ordinated water molecules. As the small sized water molecules are replaced by bulkier ligands (L), the steric crowding around the central metal ion increases. As a result of these steric repulsions the subsequent steps are retarded; hence the K values gradually decrease.

Electrostatic factor: In the first step of complex formation, one ligand (L) replaces one co-ordinated water molecule to give $[M(H_2O)_{n-1}L]$. In the second step, another ligand (L) of the same charge approaches the first stage product. Now there is an electrostatic repulsion between the incoming ligand and a similar ligand already present in the complex. As a result of this electrostatic repulsion between the ligands the subsequent steps are retarded. Hence K values decrease gradually.

Therefore, the general trend in K values is $K_1 > K_2 > K_3 \ldots\ldots > K_n$.

Thermodynamic stability and kinetic stability :

The stability of complexes can be explained in two terms i.e. in Thermodynamic terms and in kinetic terms.

Thermodynamic stability deals with the bond energy, stability constants and redox potentials (properties that refer to the equilibrium conditions). Kinetic stability relates to rates, mechanism of chemical reactions, formation of intermediate complexes, activation energy for the process etc.

Thermodynamically the stability of the complex is expressed in terms of formation constant, which is an equilibrium constant of the complex, formed from its constituents

$$M + nL \rightleftharpoons [ML_n]$$

$$\beta_n = \frac{[ML_n]}{[M][L]^n}$$

Higher the value of β_n greater will be the stability of the complex. This is one of the factors which influence the behaviour of the complex. The other factor which influence the behaviour of the complex is the rate. It is often true that, a stable complex reacts slowly and unstable complex reacts rapidly. This may not be true always

For example, consider the complexes $[Ni(CN)_4]^{-2}$, $[Hg(CN)_4]^{-2}$ and $[Fe(CN)_6]^{-}$ and their corresponding stability constants.

$[Ni(CN)_4]^{-2}$ $\beta_4 \sim 10^{30}$

$[Hg(CN)_4]^{-2}$ $\beta_4 \sim 10^{47}$

$[Fe(CN)_6]^{-4}$ $\beta_6 \sim 10^{37}$

All the three complexes have very large stability constants. Even though they have high stability constants, they undergo exchange reactions rapidly i.e. the bound cyanide group can be replaced by cyanide ion [containing ~~iso~~ isotopic carbon] in the solution. But the exchange is very slow incase of $[Fe(CN)_6]^{-4}$ even though it has less stability constant than $[Hg(CN)_4]^{-2}$. $[Ni(CN)_4]^{-2}$ and $[Hg(CN)_4]^{-2}$ complexes have high stability constants,

From this we can say that there is no exact correlation between stability & a complex and rate of exchange of ligands in the complex. Hence it is apt to explain the kinetic behaviour of complexes interms of lability and inertness as suggested by Taube.

Another example of a complex which is thermodynamically unstable and kinetically inert is $[Co(NH_3)_6]^{+3}$. Thus labile complexes are those complexes which undergo ligand replacement reactions rapidly.

Inorder to explain the kinetic behaviour quantitatively, Taube suggested that, those complexes which undergo ligand replacement reactions with in one minute at 25°C and 0.1 Molar reactant concentration are known as labile complexes & & so otherwise known as inert complexes.

From the above discussion, it can be inferred that stability of complex does not imply inertness and it can be concluded more precisely from the following exchange reactions. Let us consider the exchange of CN^- by $^{14}CN^-$ in the complexes $[Ni(CN)_4]^{-2}$, $[Mn(CN)_6]^{-3}$ and $[Cr(CN)_6]^{-3}$

$$[Ni(CN)_4]^{-2} + 4\,^{14}CN^- \longrightarrow [Ni(^{14}CN)_4]^{-2} + 4CN^- \quad \sim 30\,s$$

$$[Mn(CN)_6]^{-3} + 6\,^{14}CN^- \longrightarrow [Mn(^{14}CN)_6]^{-3} + 6CN^- \quad \sim 1\,h$$

$$[Cr(CN)_6]^{-3} + 6\,^{14}CN^- \longrightarrow [Cr(^{14}CN)_6]^{-3} + 6CN^- \quad \sim 24\,da$$

The exchange of CN^- by $^{14}CN^-$ in $[Ni(CN)_4]^{-2}$, $[Mn(CN)_6]^{-3}$ and $[Cr(CN)_6]^{-3}$ takes place in 30 seconds, one hour and 24 days respectively. Hence $[Ni(CN)_4]$ is a labile complex while other two complexes are inert.

The difference between the instability and lability can be explained as follows. The lability of a complex depends upon the activation energy i.e. the difference between the energy of activated complex and the reactants. A small value of activation energy results in fast reaction.

The instability of the complex depends upon the difference between free energy of products and free energy of reactants.

The substitution reactions in inert complexes can be studied by classical methods whereas in labile complexes they are studied by modern methods like flash photolysis, relaxation methods.

Factors affecting the stability of metal complexes:

The stability of metallic complexes is indeed a large and varied subject. A large number of factors affect the stability of complexes. The factors that affect the stability of metal complexes can be divided into different categories.

(i) Effect of the metal on the stability of complexes
(ii) Effect of the ligand on the stability of complexes.
(iii) Effect of solvent
(iv) Effect of temperature.

(i) Effect of metal atom & ion on the stability of a complex:

The effect of the metal atom & ion on the stability of a complex depends upon the various properties of the metal ion.

(a) charge and size of the central ion:

A metal ion with large charge and smaller size forms a stable complex generally. A smaller metal ion with large charge permits a more closer approach of the ligands and results in the formation of a stable complex. This can be understood from the following examples.

Consider the hydroxide complexes of the alkaline earth metals.

Complex ion	Size of the metal ion	Stability constant value
$[Be(OH)]^{+}$	0.31 A°	1×10^{7}
$[Mg(OH)]^{+}$	0.65 A°	1.2×10^{2}
$[Ca(OH)]^{+}$	0.99 A°	0.3×10^{2}
$[Ba(OH)]^{+}$	1.35 A°	0.04×10^{2}

In the above examples all the metal ions have same charge, but as the size of the central metal ion increases, the stability of the corresponding hydroxide complex decreases.

Consider the cyanide complexes of Fe(II) and Fe(+3) in which the metal ion has same size and ~~fe~~ different charge.

complex ion	charge	value of $\log_{10}\beta$
$[Fe(CN)_6]^{-3}$	+3	Higher
$[Fe(CN)_6]^{-4}$	+2	Lower

Thus a metal ion with larger charge forms a stable complex than a metal ion with smaller charge.

If a combination of the above two properties of the metal ion is considered, i.e. charge to radius ratio then a metal ion with large charge to radius ratio forms a more stable complex than a metal ion with small charge to radius ratio. The correlation between charge-to-radius ratio and stability of metal OH^{-} complexes ions is as shown below.

$$M^{+n} + OH^{-} \rightleftharpoons [M(OH)]^{(n-1)+}$$

Central metal ion	Ionic radius (A°)	Charge to radius ratio	Stability constant of the complex.
Li^{+}	0.60	1.7	2
Ca^{+2}	0.99	2.0	3×10^{1}
Ni^{+2}	0.69	2.9	3×10^{3} etc.

(b) The metal ions fall into three groups class a, class b and borderline basing on Ahrland-chatt-Davies emperical classification of metal ions. This classifi -cation rationalise the preference of a metal ion for one and or another of a ligan which is potentially ambidentate.

class a	Borderline	class b
H^{+}, Li^{+}, Na^{+}, K^{+}, Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2} Mn^{+2}, Al^{+3}, Sc^{+3}, Ga^{+3} In^{+3}, La^{+3}, Cr^{+3}, Co^{+3}, Fe^{+3} Ti^{+4}, Sn^{+4}	Fe^{+2}, Co^{+2}, Ni^{+2} Cu^{+2}, Zn^{+2}, Pb^{+2}	Cu^{+}, Ag^{+}, Au^{+}, Tl^{+}, Hg_2^{+2}, Hg^{+2}, Pd^{+2}, Pt^{+2}, Pt^{+4}, Tl^{+3}

This classification was made on the basis of the relative stabilities of complexes with ligands having donor atoms from groups $\overline{V}_A$, $\overline{VI}_A$ & $\overline{VII}_A$. If the stability of the complexes is greatest with the lightest element of each of these groups as the donor atom, the ions are placed in class a. Conversely, class b ions form the least stable complexes with the lightest element of each group as donor atom. class b ions form stable complexes with CO and olefins, while those of class a do not form such complexes.

The trend in complex stability with ligand donor atom type for class a metal ion

$F > Cl > Br > I$

$O >> S > Se > Te$

$N \gg P > As > Sb$

The trend in complex stability with ligand donor atom type for class b metal ions.

$F < Cl < Br < I$

$O << S \sim Se \sim Te$

$N << P > As > Sb$

Some metal ions form complexes whose stabilities donot follow any order as observed for class a or class b metal ions and these ions are placed in the borderline class. The stability of complexes of the borderline ions with a given ligand is almost invariably in the order

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

This order is known as the Irving - william series.

(c) Inaddition to the above classification of metal ions class (a) and (b), a more useful classification of the metal ions can be done basing on the electronic configuration. Basing on this classification, the stability of the complexes can be explained conveniently.

The metal ions are classified into four categories depending upon the electronic configuration of the metal ion.

Category I: The metal ions which possess a valence shell inert gas configuration in their complexes i.e. $1s^2$ or ns^2np^6, where n has values from 2 to 6, will come under this category. These ions are spherically symmetrical with the element being in its highest possible oxidation state. The nature of the bond formed by these ions change from ionic to covalent as the charge on the ion increases. The ionic nature of the bonding decreases in the following order.

$$Na^{+} > Mg^{+2} > Al^{+3}$$

$$K^{+} > Ca^{+2} > Sc^{+3} > Ti^{+4} > V^{+5} > Cr^{+6} > Mn^{+7}$$

(Ionic) (covalent)

Category - II : The metal ions which in their complexes have pseudo-inertgas configurati i.e. $(n-1)d^{10}$ where n is 4,5,6 in their valence shell come under this category. This category includes many transition metals in formally negative oxidation states. These ions are also spherically symmetrical and these ions can either accept or donate electron pairs from or to the ligands. Thus π bonding becomes important with the increasing size as well as the oxidation number of the metal ion.

Category - III : The metal ions which in their complexes have pseudo-inertgas configuration plus two in their valence shell come under this category i.e. $(n-1)d^{10}ns^2$ where n is 4, 5, 6.

category IV: The metal ions in their complexes with incompletely filled d-orbitals $(n-1)d^{1-9}$ where n is 4, 5 & 6 come under this category. Most of the transition metals in all of their many oxidation states come under this category. No general statement can be given regarding their complexes as these ions are diverse in nature. The nature of the bond formed by these ions change from ionic to covalent.

The importance of the $M \rightarrow L$ & $L \rightarrow M$ bonding depends on the oxidation state of the metal.

In the first three categories, the central ions are spherically symmetrical these ions have completely filled non bonding level and sublevels. Thus the stability of their complexes will be primarily dependent upon their effective ionic radius and effective nuclear charge. The stability of the complexes of these ions depend upon the ionic potential φ (i.e. the ratio of effective cationic charge to effective cationic radius). The complex stability increases with increasing φ

Anomalies arise when complex stabilities of similarly charged and sized members which are in category I, II and III are compared respectively. The metal ion of category II and III form more stable complex with a given ligand. This is due to the difference in the electronic configuration of category I ions when compared with II and III. The category I ions have inert gas configuration and the other two categories have pseudo inert gas configuration and pseudo inert gas configuration plus two. The latter two categories of outer configuration are much poorer shielders of the excess positive charge located in the nucleus ~~[illegible]~~. Therefore the effective nuclear charge of Cu^+ is much larger than that of Na^+

When comparison is brought between category II and category III ions regarding the stability of their complexes then category II ions form more stable complex than category III. The category III ions have two additional s electrons to shield the nuclear charge. The complexes of category I, II and III are very less in number. Whereas complexes of category IV ions are largely known. The stability of category IV complexes depend upon the charge, size and polarizability of the ion.

(d) Ionisation Energies:

With increase in the ionisation energy of the metallic species, the stability of metal complexes increase

(ii) Effect of ligand on the stability of the complex

The following properties of the ligands effect the stability of the complexes.

(a) Basicity of the ligands:

A ligand which is a strong lewis base, will form a stable complex usually. Thus, the increase in the basicity of the ligand increases stability of the corresponding complex. This correlation between basicity and stability constant of a complex holds good for a series of closely related ligands. For a series of ligands such as NH_3, pyridine and imidazole, where the ligating atom is only nitrogen, there may be a little correlation or no correlation between basicity and stability constants. When ligands having different donor atoms are considered, the situation is even worse.

(b) Dipolemoment and Polarizability of the ligands:

As the electrostatic interaction between the metal ion and the ligands is more, polarity and polarisability of the ligand results in higher K for the complexes.

(c) π-bonding capability of the ligand:

As the π-bonding capability of the ligand increases the stability of the complex increases. The extent of π-bonding in complexes is determined from

(i) the bond length that can be determined from x-ray crystallography
(ii) infrared spectroscopy [the absorption band moves to higher region with increasing bond strength and bond order]
(iii) NMR spectroscopy

An ambidentate ligand can attach to the metal ion through any of its donor atoms. The attachement of the ambidentate ligand to the metal ion through any one of its atoms depends upon π-bonding capability of the donor atom.

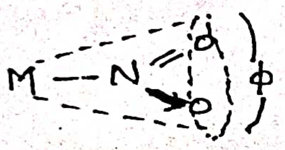
For example: In the presence of other strong π-bonding ligands like phosphine, the ambidentate ligand like SCN^- attach itself in the trans position through N atom. In the presence of ligands that cannot π-bond, the ambidentate ligand like SCN^- attach itself to the metal ion through sulphur. Therefore the N-bonded phosphine complex $[Pt(NCS)_2(PR_3)_2]$ and S-bonded $[Pt(NH_3)_2(SCN)_2]$ are more stable than the corresponding other linkage isomers.

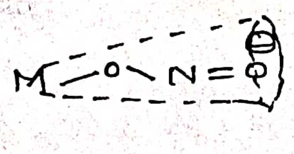
(d) Steric factors:

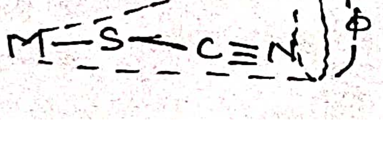
The steric factors are not much important for the proton complexes and for the monodentate ligands. The steric factors play an important role in determining the stability constant of the complexes formed from multidentate ligands.

For example, 2-methyl-8 hydroxy quinoline forms a less stable complex with metal ion than the parent compound (8 hydroxy quinoline). This is due to the steric hinderance caused by methyl group adjacent to the co-ordination site.

The stability of complexes formed by the ambidentate ligands, can also be explained using steric factors. These ambidentate ligands usually lead to the formation of linkage isomers. The isomer in which the ligand has greater angular volume (NO_2^- vs ONO^-, SCN^- vs NCS^-, OCN^- vs NCO^-) tend to give less stable complex.







M — N=C=S

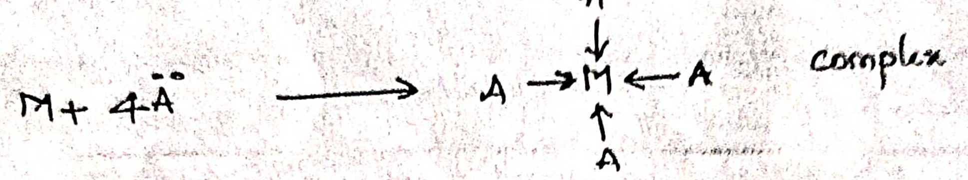
φ = 0.

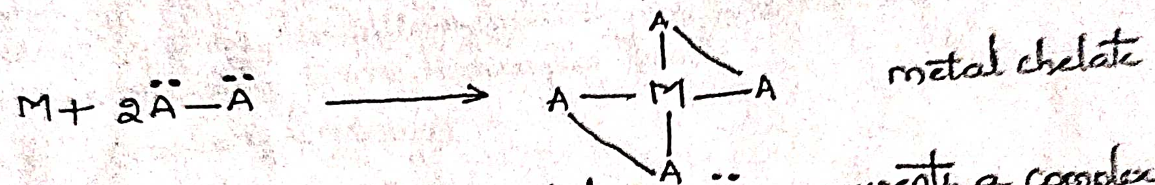
Chelate and chelate effect:

The term 'chelate' was first introduced by Morgan and Drew. The term chelate was introduced to describe the cyclic structure which arise due to the combination of metallic atom with organic or inorganic molecules or ions. The rings in such compounds are termed as chelate rings and the phenomenon as the chelation.

The chelate compounds can also be defined as the complexes in which the donor atoms are attached to each other as well as to the metal so that the metal becomes part of a heterocyclic ring

A simple chelate ring and a complex can be schematically represented as follows.





where M represents the metal ion, Ä represents a complexing reagent and Ä—Ä represents a chelating agent. The basic difference between metal chelate and metal complex is that the metal chelate has cyclic ring and metal complex has no cyclic ring

Characteristics of chelates:

1. Chelates possess the following properties different from the salts
   (a) Chelates have low melting points.
   (b) They are quite stable.
   (c) They dissolve easily in organic solvents.
2. The donor groups of the chelating ligand are firmly linked to the metal ion present in the ring. The linkage is either covalent or co-ordinate covalent, which holds the metal ion into ~~the chl~~ chelating ring.
3. The presence of heterocyclic ring is essential for the formation of chelates
4. The metal ion must be of appropriate size to fit in the ring.
5. The charge on the metal ion is generally large which is responsible for attracting the lone pairs of the electrons of the donor atoms.

6. In most of the chelates, the number of atoms forming the ring of the chelate is five or six. But the former is more stable.

The word 'chelate' is derived from the Greek word 'chelos' meaning crab's claws. This is because both the claws and ligand may hold an object (i.e. metal ion) through more than one point of attachment.

The chelate ring forming groups:

The rings may be closed by the formation of covalent linkages or co-ordinate linkages or by a combination of both.

(a) Covalent linkage:

This linkage is generally produced by the replacement of a proton in an organic group. Functional groups of this type are sometimes called acidic groups. They are called acidic groups because hydrogen atom from them are replaced. Some examples are

(i) —COOH (carboxyl group)
(ii) —SO_3H (Sulphonic group)
(iii) —OH (Enolic hydroxyl group)

(b) Co-ordinate linkage: This linkage occurs without the replacement of hydrogen and by the donation of an electron pair. The most common examples are

(i) —NH_2 (Primary, secondary & tertiary amine)
(ii) =NOH (oxime)
(iii) —OH (alcoholic hydroxyl group)
(iv) —CO (carbonyl group)
(v) —S— (thioether)

Classification of chelates:

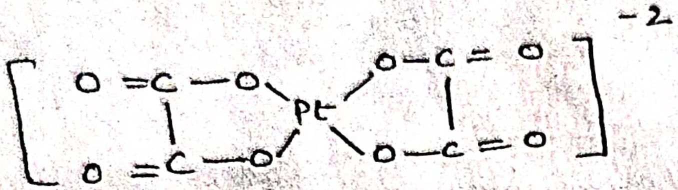
The chelates can be classified on the basis of

(i) the total number of donor groups in the complexing agent i.e. monodentate, bidentate etc
(ii) the relative number of acidic and co-ordinating groups involved in ring formation

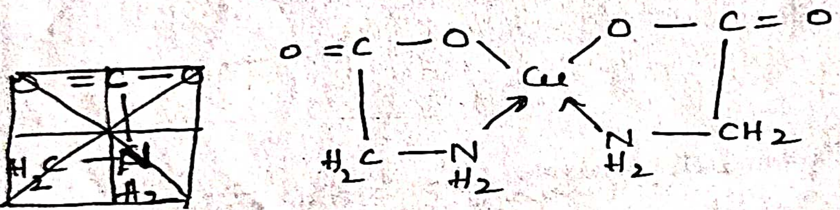
I Bidentate groups: Examples are oxalates, glycine, phenanthroline etc

(a) Two acidic groups: Rings of this type are formed by the replacement of two hydrogen atoms by the metallic cation

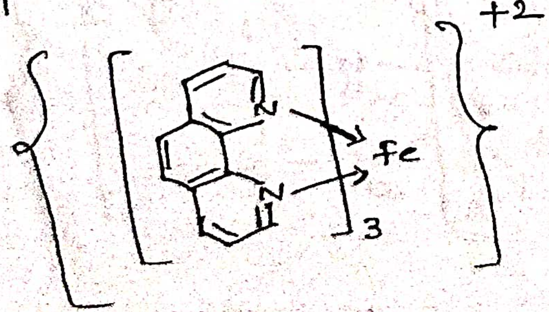
Platinum ions react with oxalate ions to form platinum oxalate.



(b) One acidic group and one co-ordinating group: The Cu^{+2} ion reacts with glycine to produce copper glycinate in which each glycine molecule is attached to the copper ~~atom~~ ion by one covalent bond and one co-ordinate covalent bond.

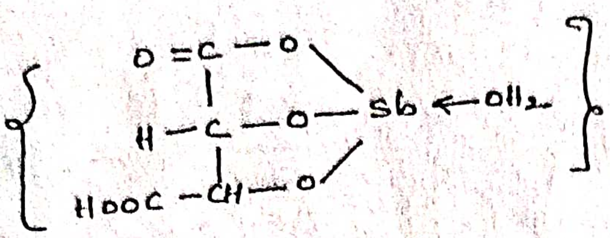


(C) Two Co-ordinating groups: Orthophenanthroline is a heterocyclic organic compound having two co-ordinating nitrogens. This organic compound forms a complex with ferrous ion.

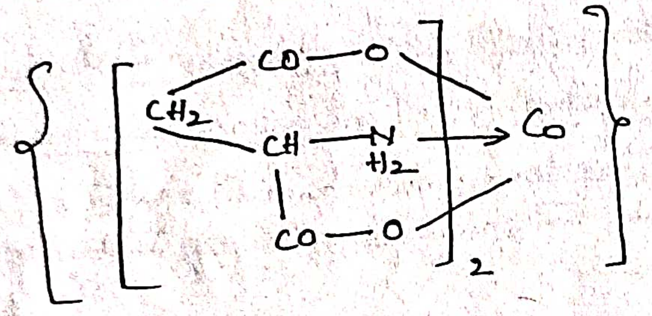


Tridentate Groups:

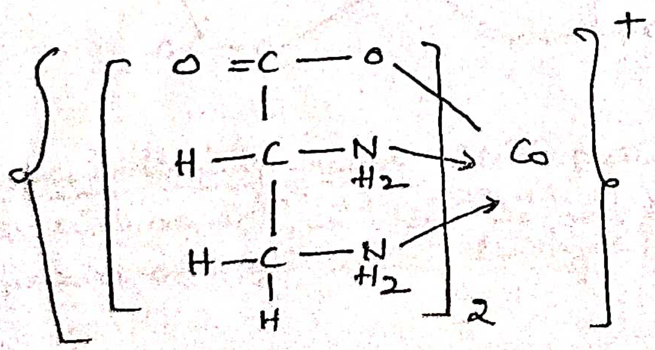
(a) Three acidic groups: Antimony can attach to the tartarate ion by the removal of three hydrogen atoms to form three covalent bonds.



(b) Two acidic groups and one co-ordinating group: Aspartic acid combines with trivalent cobalt to form a water soluble tridentate compound.

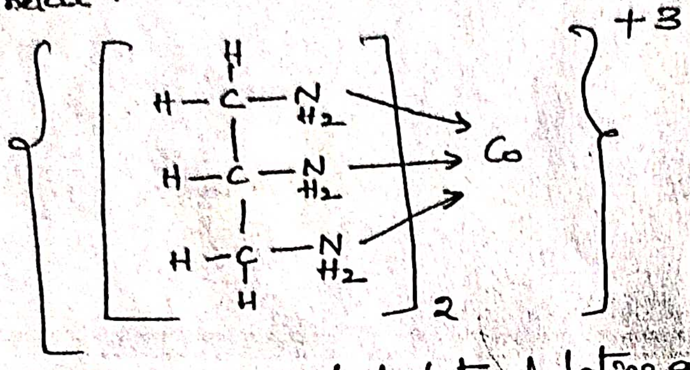


(c) one acidic group and two co-ordinating groups: The cobalt ion interacts with diaminopropionic acid to give a tridentate compound in which each molecule of the acid is attached to the cobalt atom by two co-ordinating linkages and one covalent linkage.



(d) Three Co-ordinating groups:

Triaminopropane combines with cobalt (III) to produce a chelate, in which one molecule of the triaminopropane occupies three co-ordination positions about the metal.

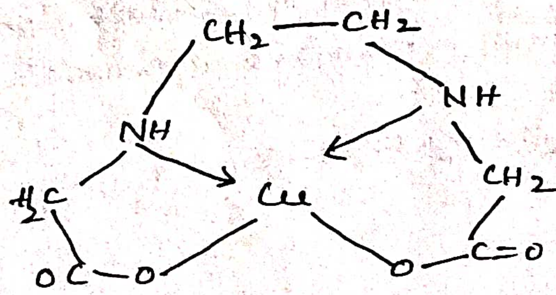


Very few polydentate chelating agents beyond tridentate ligands are known.

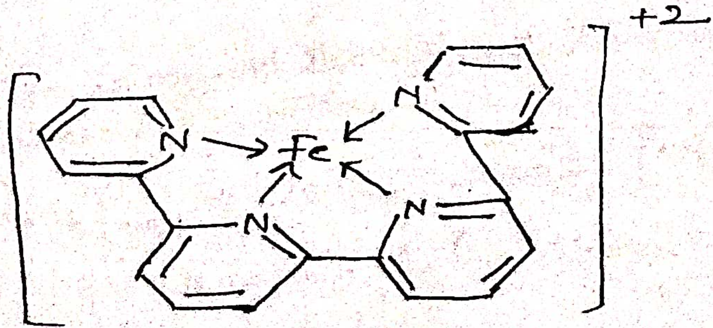
Quadridentate ligands: Two of the possible five classes are known.

(a) Two acidic groups and two co-ordinating groups:

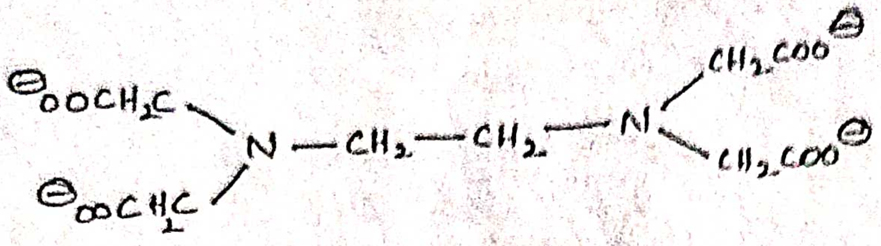
Ethylene diamine acetic acid reacts with the cupric ion to produce a quadridentate grouping containing Two Covalent bonds and two co-ordinate linkages



(b) Four co-ordinating groups: Tetra pyridyl reacts with certain bivalent transition metals such as Fe^{+2}, Co^{+2}, Ni^{+2} Cu^{+2} and Zn^{+2}, to form a quadridentate compoun by four co-ordinate covalent linkages.



Ethylene diamine tetraacetato is a hexadentate ligand:



Chelate Effect:

The extra stability attained by the complex due to the presence of chelate ring is known as chelate effect.

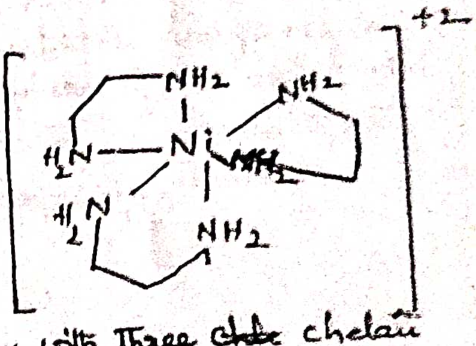
The extra stability attained by chelates can be inferred from the following example.

The overall stability constant of hexamine nickel complex is $\beta_6 = 10^{8.6}$

$$Ni^{+2}_{(aq)} + 6NH_{3(aq)} \rightleftharpoons [Ni(NH_3)_6]^{+2}$$

and the overall stability of the chelates Tris (ethylene diamine) nickel complex is $\beta_n = 10^{18.3}$

$$Ni^{+2}_{(aq)} + 3\ NH_2-CH_2-CH_2-NH_2 \rightleftharpoons$$



From the above β_n values it is clear that, the complex with three ~~chde~~ chelate ring is about 10^{10} times more stable than its monodentate complex analogue. The thermodynamic stability of the chelates can be explained in terms of free energy changes (ΔG°)

The free energy and stability constant can be compared more easily by combining the above two reactions.

$$[Ni(NH_3)_6]^{+2}_{(aq)} + 3(en)_{aq} \rightleftharpoons [Ni(en)_3]^{+2}_{aq} + 6NH_{3\,aq}$$

Where en is ethylene diamine

For the above reaction $K = 10^{7.7}$

$$\Delta G^\circ = -RT\ln K = -67\ \mathrm{kJ/mol} \quad \text{--- ①}$$

$$\Delta H^\circ = -12\ \mathrm{kJ/mol}$$

$$-T\Delta S = -55\ \mathrm{kJ/mol}$$

We also know that $\Delta G^\circ = \Delta H^\circ - T\Delta S$ ——— ②

∴ from ① and ② $-RT\ln K = \Delta H^\circ - T\Delta S$

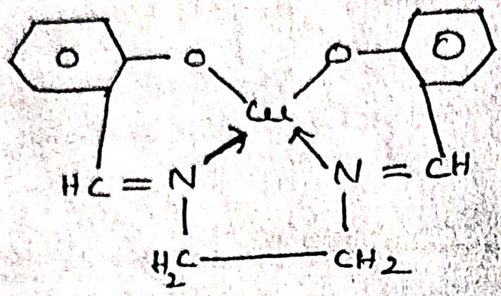
From the above relation It can be conclude that, the stability of the complex inturn depends upon enthalpy and entropy of the reaction. The enthalpy and entropy values of the above reaction are in favour of the chelate complex. The entropy contribution is far more important than enthalpy contribution. For a large number of such reactions, with different metal ions and ligands, the enthalpy contribution is relatively small. Hence a general conclusion can be made, that the chelate effect is essentially an entropy effect.

The extra stability of the chelate ring is due to the entropy change involved in the process of chelation. The entropy change can be viewed statistically or as probability factor. Suppose that the donor atom is same in both monodentate and bidentate ligands. The dissociation of M-L bond in monodentate complexes will release the ligand completely from the co-ordination sphere of the metal and these ligands are present in the solvent. The dissociation of M-L bond of the bidentate ligand complex, does not release the ligand completely. Hence the stability of chelate is very large.

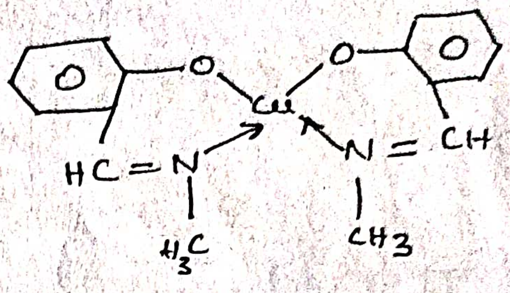
Factors influencing the stability of metal chelates:

1. Size of the chelate ring: The stability will be maximum for a chelate with strainless sized ring of a size, in which the metal ion can be just accomodated. The five and six membered rings are most stable. Generally, the chelates with saturated compound tend to form five membered structure and those ligands with double bonds ~~tend~~ tend to form six membered rings.

(2) Number of rings with in the chelate:
As the number of rings with in the chelate ~~for~~ increase, the stability of chelate complex increases.



(a)



(b)

In the above two chelates, chelate(a) is more stable than chelate (b) because complex (a) has three interlocked rings and complex(b) has two interlocked rings

(3) Resonance effect: The stability of chelate complex increases with unhindered resonance of the chelate ring. on the other hand, resonance in the attached benzene rings may interfere with resonance of the chelate ring and in such cases, the stability of the chelate is lowered.

(4) Steric effect: The substitution at 3rd position of acetylacetone by isopropyl group & secondary butyl group does not give usual coloured chelates with cupric and ferric ion. This strange behaviour is due to steric effect of ~~isopry~~ isopropyl and secondary butyl groups.

(5) Basic strength and chelate stability: As the basicity of the donor group increases, the strength of ML bond increases

(6) Effect of substitution on the ligand: The substitution of a group on the chelating agent may influence the process of chelation in two ways.

(a) The substituted group may influence the acidity of the donor group; or may ~~infer~~ interfere with or enhance the resonance of chelate ring.

(b) The substitution of bulky groups on chelating agents causes steric hinderance and prevents the ligand ions or molecules from acquiring the orientation about the central metal ion.

(7) Effect of metal ion:

Transition metals usually form covalent bonds with electron donors. Where as in the chelates of alkaline earths and alkali metals the bond is an ionic bond. The stability of transition metal chelates decreases with increasing basicity of the metal. Hence transition metals which form the strongest covalent bond with ligand molecules produce stablest chelates.

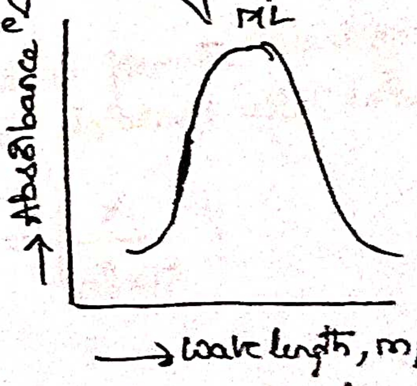
In the ionic type chelates, a metal ion with large ionic charge and small ionic radius form stable compounds.

Determination of Stability constant:

The stability constant can be determined by spectrophotometric method, by pH method, by e.m.f method, by ion exchange method etc.

1. Spectrophotometric method:

This method is developed basing on the simple point that the , is complex absorbs light differently than the metal ion from which it formed. In this method, the wavelength at which the absorption of the complex would be maximum is determined. This can be done by measuring absorban at different wavelengths for the complex. Commonly wavelength corresponding to the maximum absorbance is the suitable wavelength. The graph between the absorbance and wavelength is shown in figure



Continuous variation method:

In this continuous variation method, the total analytical concentration of metal and ligand is kept constant and the ratio of metal ion and ligand is varied.

Let the ~~tot~~ total concentration be c and concentration of ligand be C_L and that of metal ion be C_M

$$\Rightarrow C_L + C_M = C.$$

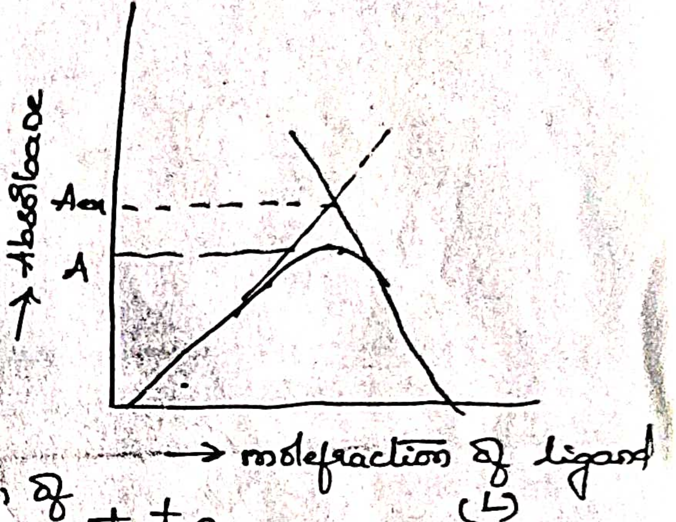
For the solutions with varying concentrations of ligand and metal, absorbances are noted at suitable wavelength. After knowing the absorbances a graph is drawn between the molefraction of the ligand (L) in the mixture vs absorbance

Molefraction of the ligand (L) = $\frac{C_L}{C}$

$$\frac{C_L}{C} + \frac{C_M}{C} = \frac{C}{C}$$

$$\Rightarrow L + \frac{C_M}{C} = 1$$

$$\Rightarrow \frac{C_M}{C} = 1 - L$$



The curve drawn between mole fraction of ligand (L) and absorbance is extrapolated to meet at a point.

The molefraction corresponding to the point of intersection gives the formula of the complex.

$$\therefore n = \frac{C_L}{C_M} = \frac{L}{1-L}$$

The stability constant can also be calculated from the absorbance corresponding to the curve and point of intersection obtained after extrapolati

Molefraction of the Complex $\frac{[ML]}{C} = \left(\frac{A}{A_{ext}}\right)$

$$\Rightarrow [ML] = \left(\frac{A}{A_{ext}}\right)C$$

$$[M] = C_M - [ML]$$

$$= C_M - \left(\frac{A}{A_{ext}}\right)C$$

$$[L] = C_L - [ML]$$

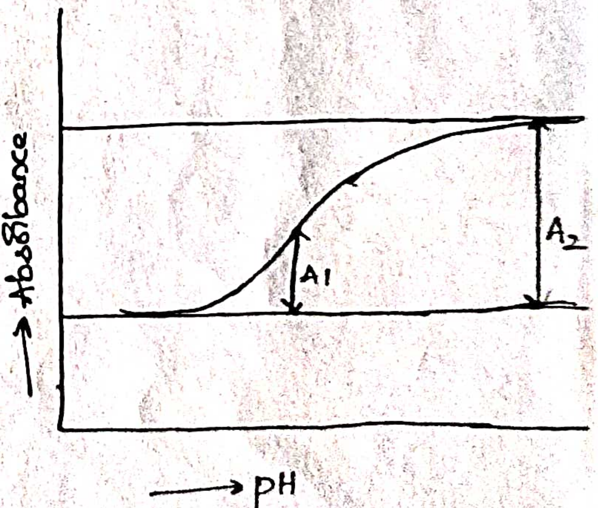
$$= C_L - \left(\frac{A}{A_{ext}}\right)C$$

$$\therefore K = \frac{[ML]}{[M][L]}$$

$$= \frac{\left(\frac{A}{A_{ext}}\right)C}{\left[C_M - \left(\frac{A}{A_{ext}}\right)C\right]\left[C_L - \left(\frac{A}{A_{ext}}\right)C\right]}$$

(2) pH Method:

This method is applied when the ligand is either an acid or a base with known ionisation constant & when two different equilibria compete for the metal & ligand and when one of these equilibrium constants is known. In the case of acid ligand, protons compete with the metal ion for the ligand. The absorbance of the complex in presence of large concentration of metal ion is measured in the pH range. Then a graph is drawn between absorbance and pH.



Where A_1 is the absorbance of the complex at low pH and A_2 is the absorbance when metal is completely complexed at higher pH.

The ratio of metal complex to acid ligand concentration is

$$\frac{[ML]}{H_nL} = \frac{A_1}{A_2 - A_1}$$

The competing equilibrium is

$$M^{+a} + H_nL \overset{K'}{\rightleftharpoons} ML + nH^{+}$$

$$\therefore K' = \frac{[ML][H^+]^n}{[M^{+a}][H_nL]}$$

$$\rightarrow -\log K' = -\log \frac{[ML][H^+]^n}{[M^{+a}][H_nL]}$$

$$\rightarrow pK' = -\log \frac{[ML]}{[H_nL]} - \log [H^+]^n + \log [M^{a+}]$$

$$= -\log \left(\frac{A_1}{A_2 - A_1}\right) + n\,pH + \log [M^{a+}]$$

A graph is drawn between $\frac{[ML]}{[H_nL]}$ and pH, which is a straight line whose slope is n, since both K' and $[M^{a+}]$ are both constant. Hence stability constant value can be determined from the above equation.

HARD AND SOFT ACID-BASE THEORY

The most widely acceptable definition about acid and bases was given by G.N.Lewis. According to Lewis, theory, a base is any species that is capable of donating a pair of electrons to the formation of a covalent bond and an acid is any species that is capable of accepting of a pair of electrons to form a covalent bond. Neutralisation can then be attributed to the formation of the covalent bond.

for example;

$$H^{+} + :\underset{..}{\ddot{O}}:H^{\ominus} \longrightarrow H:\underset{..}{\ddot{O}}:H$$

In the above reaction, the H^+ is capable of accepting a pair of electrons to form a covalent bond and is therefore an acid, whereas, the OH^- has an electron pair to donate to the formation of the covalent bond and is, therefore, a base.

Though Lewis theory has some weaknesses, because of its generality and usefulness in discussing and predicting the course of many chemical reactions it is wid acc. Basing on Lewis theory Luder and Zuffanti classified chemical reactions into three categories acid-base, oxidation-reduction and free radicals. Recently, Pearson generalised these chemical reactions simply as acid-base and redox type. Basing on Lewis theory it is not possible to arrange acids and bases in an order according to their strengths. However, relative strengths can be obtained as per their reactions.

$$A' + A:B \longrightarrow A':B + A$$

and $$B' + A:B \longrightarrow A:B' + B$$

If the reaction proceeds towards right then it is possible to conclude that A' is stronger acid than A and B' as a stronger base than B. The relative strengths could then be expressed in terms of relative stabilities of acid-base complexes.

The relationship between the acid-base strengths and the stability of the complex can be expressed by the equilibrium equation

$$\log K = S_A S_B$$

Where S_A and S_B are quantities related to the relative acid and base strengths. In addition to these strengths, some other factors pertaining to acid and base may effect the stability of the complex. This implies that some other terms must occur in the equilibrium expression.

Even though it is not possible to define a quantitative acid-base scale, a qualitative correlation can be observed. One such qualitative approach is the Ahaland-Chatt-Davies emperical classification. According to this classification the metal ions fall into three classes; class (a), class(b) and Border line. The class(a) (acceptor) metal ions form their most stable complexes with the ~~heavier~~ first members of each of the non-metal groups in the periodic table; whereas class(b) metal ions form their most stable complexes with the heavier members of the given group.

class(a) $N >> P > As > Sb > Bi$

$O >> S > Se > Te$

$F > Cl > Br > I$

class(b) $N << P > As > Sb > Bi$

$O << S \sim Se \sim Te$

$F < Cl < Br < I$

From the above tendencies it is possible to conclude that the class (a) metal ions are small in size and not very easily polarised, whereas the class(b) metal ions are essentially opposite in character. The small, non polarisable class(a) ions tend to combine with a non-metal having quite similar properties and the large polarisable class(b) ions tend to combine with non metals having the same general characteristics as they.

The above observations ~~are~~ were expanded and were much generalised by R.G. Pearson in terms of hard and soft acids and bases. Pearson defined soft base as one in which the donor atom is of high polarizability and of low electronegativity and is associated with empty lowlying orbitals.

A hard base is one in which the donor atom is of low polarizability and high electronegativity and is associated with empty orbitals of high energy.

Soft acid is one in which the acceptor atom has low or zero positive charge, large size and several easily excitable outer electrons.

Hard acid is one in which the acceptor atom has small size, high positive oxidation state, and the absence of any ~~other~~ outer electrons which are easily excited to higher states.

The correlating principle on which acid-base reactions depend is simply that, hard acids prefer to co-ordinate with hard bases and soft acids prefer to co-ordinate with soft bases.

The following is the list of Hard and soft acids & bases.

TABLE 9–3. Classification of Lewis Acids.[a]

Hard	Soft
H^+, Li^+, Na^+, K^+ Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+} Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+} N^{3+}, Gd^{3+}, Lu^{3+} Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+} Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, U^{4+} Pu^{4+}, Ce^{3+}, Hf^{4+} UO_2^{2+}, $(CH_3)_2Sn^{2+}$, VO^{2+}, MoO^{3+} $BeMe_2$, BF_3, $B(OR)_3$ $Al(CH_3)_3$, $AlCl_3$, AlH_3 RPO_2^+, $ROPO_2^+$ RSO_2^+, $ROSO_2^+$, SO_3 I^{7+}, I^{5+}, Cl^{7+}, Cr^{6+} RCO^+, CO_2, NC^+ HX (hydrogen bonding molecules)	Cu^+, Ag^+, Au^+, Tl^+, Hg^+ Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+, $Co(CN)_5^{2-}$, Pt^{4+}, Te^{4+} Tl^{3+}, $Tl(CH_3)_3$, BH_3, $Ga(CH_3)_3$, $GaCl_3$, GaI_3, $InCl_3$ RS^+, RSe^+, RTe^+ I^+, Br^+, HO^+, RO^+ I_2, Br_2, ICN, etc. Trinitrobenzene, etc. Chloranil, quinones, etc. Tetracyanoethylene, etc. O, Cl, Br, I, N M^0 (metal atoms) Bulk metals CH_2, carbenes

Borderline
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Rh^{3+},
Ir^{3+}, $B(CH_3)_3$, SO_2, NO^+, Ru^{2+}, Os^{2+}, R_3C^+, $C_6H_5^+$, GaH_3

[a] From R.G. Pearson, *Chem. in Britain*, 3, 103 (1967).

TABLE 9–4. Classification of Bases.[a]
The symbol R stands for an alkyl group such as CH_3 or C_2H_5.

Hard	Soft
H_2O, OH^-, F^- $CH_3CO_2^-$, PO_4^{3-}, SO_4^{2-} Cl^-, CO_3^{2-}, ClO_4^-, NO_3^- ROH, RO^-, R_2O NH_3, RNH_2, N_2H_4	R_2S, RSH, RS^- I^-, SCN^-, $S_2O_3^{2-}$ R_3P, R_3As, $(RO)_3P$ CN^-, RNC, CO C_2H_4, C_6H_6 H^-, R^-

Borderline
$C_6H_5NH_2$, C_5H_5N; N_3^-, Br^-, NO_2^-, SO_3^{2-}

The above correlating principle of hard acid co-ordinates to hard base and soft acid co-ordinates to soft base can be explained using π-bonding theory.

The bonding between a hard-acid and hard base is primarily ionic, whereas the bonding between a soft acid and soft base is primarily covalent. However in π bond formation, hard acids have vacant orbitals and therefore they can accept π electrons and hard bases have filled outer orbitals and can donate π electrons. The reverse situation exists for soft acids and soft base complexes. Therefore soft acid - soft base complexes are quite stable, the complexes of hard acid-soft b and soft acid-hard base are least stable.

In addition to ionic and π bonding, the operation of vanderwaals forces can also be considered to contribute to the stabilisation of the acid-base comple

Irving-Williams Series:

According to Ahaland-Chatt-Davies, the metal ions are emperically classified into three classes class(a), class(b) and Border line. This classification was done basing on the relative stabilities of the complexes formed by the metal ions with ligands having donor atoms from VA, VIA and VIIA groups.

class(a) metal ions form stable complexes with the lightest element of each of these groups as the donor atom

class(a) metal ions

Li^+, Na^+ K^+
Be^{+2} Mg^{+2} Ca^{+2} Sr^{+2}
Al^{+3} Ga^{+3} Ca^{+3} Fe^{+3} Co^{+3} etc.

class(b) metal ions form least stable complexes with the lightest elements of each group as donor atom.

class(b) metal ions:

Cu^+ Ag^+ Au^+ Tl^+
Hg^{+2} Pd^{+2} Pt^{+2} Tl^{+3}

Some metal ions do not follow any of these orders as observed for class(a) & class(b) metal ions. Such metals ions are classified as border line type.

Ex: Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2} etc.

For these metal ions, the stability of complexes with a given ligand is almost in the order

$$Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$$

This order is known as the Irving-William series.

With a given ligand, the stability order of these border line metal ion complexes can be graphically represented as follows.

Although the figure shows the trend in K_1 values, the Irving - Williams series generally holds good for K_2 and K_3 also.

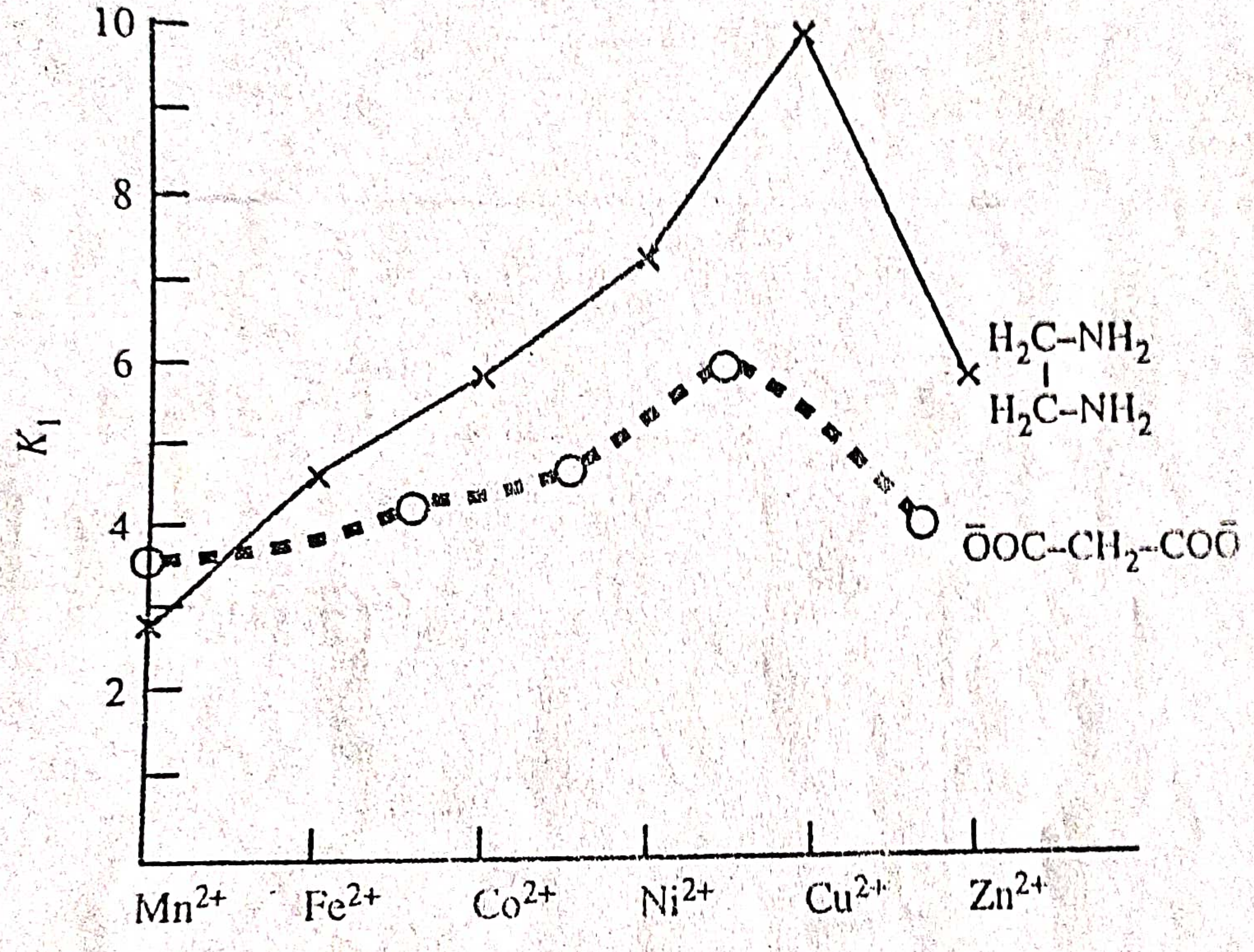


Fig. [illegible] *Trend in* K_1 *values as* M^{2+} *is altered, illustrating the Irving-Williams series*