

Stability of Metal Complexes

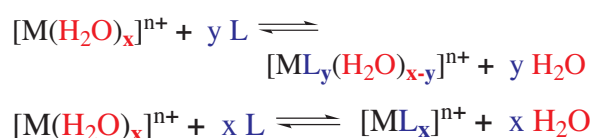
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A coordination complex of the type $[ML_x]^{n+}$ is formed when each neutral ligand (L) donates a lone pair of electrons to a metal centre (M^{n+}). Here, x is the coordination number and $n+$ is the oxidation number of M . We know that the spectral and magnetic properties of complexes depend on the oxidation number, coordination number, and the geometry of the complex. For example, depending on the conditions (temperature and concentration), the Co(II) centre is known to form both $[Co(H_2O)_4]^{2+}$ and $[Co(H_2O)_6]^{2+}$ with tetrahedral and octahedral geometries, respectively.

Aqua Complexes

A metal cation dissolves in water to form an aqua complex, $[M(H_2O)_x]^{n+}$. Water is not a strong ligand, and the Crystal Field Stabilization Energy (CFSE) is less. Thus, other strong ligands can easily substitute water molecules in the aqua complex to form a series of complexes. Substitution of water by a neutral ligand(s) L can be represented as shown below ($x > y$).



Aqua complexes of the first transition series undergo substitution reactions spontaneously when $L = NH_3$, pyridine (py), ethylenediamine (en), CN^- , etc, because the CFSE produced by those L ligands are higher than those produced with water molecules.

Stability Constants

The thermodynamic stability of a species (product) is a measure of the extent to which it forms from the reactants under equilibrium conditions. The equilibrium constant K is related to changes in Gibbs free energy (ΔG), enthalpy (ΔH), entropy (ΔS) and temperature (T) as given below.

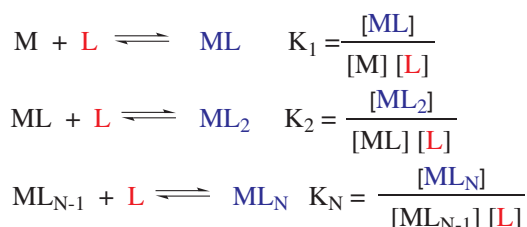
$$\Delta G = \Delta H - T\Delta S = -RT \ln K$$

Stable complexes are formed when K is significantly high and ΔG is more negative.

The kinetic stability of a species deals with the rate of the reaction, i.e. how fast the transformation is taking place. Kinetic products are labile and prone to undergo substitution reactions readily. Kinetically inert products are less reactive and are not always thermodynamically stable.

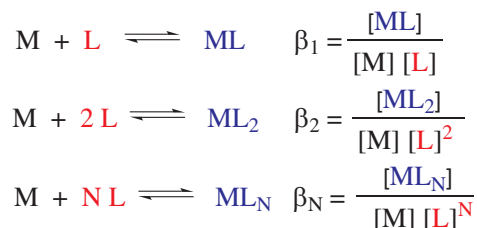
Let us consider a solution containing metal centre M and monodentate ligands (L) where the maximum coordination number of M is N . Therefore, the system can have N equilibria due to the stepwise addition of ligands to M forming intermediates such as ML , ML_2 , and ML_N .

The system can be described by the following equations and equilibrium constants K_1 , K_2 , K_N . Square brackets indicate the concentrations of the enclosed species.



The equilibrium constants K_1 , K_2 ... K_N are called the stepwise formation constants (or stepwise stability constants). With a few exceptions, the values of successive stability constants decrease regularly from K_1 to K_N . i.e. $K_1 > K_2 > \dots > K_{N-1} > K_N$.

An alternative method of forming ML_N is given below.



β_i Values are called overall formation or stability constants and the relationship between K_i and β is given

below.

$$\beta = \prod_{i=1}^{i=N} K_i$$

Stability constants are usually given in $\log_{10}\beta$ values, thus, higher the $\log_{10}\beta$ value higher thermodynamic stability of the complex.

Factors Affecting the Stability of Metal Complexes

Stable complexes do not undergo oxidation, hydrolysis, disproportionation, or decomposition at room temperature. The stability of a complex depends upon the nature and the properties of the metal and the surrounding ligands.

1. Properties of metal centres

Stability of complexes derived from Group 1 and 2 metals, and lanthanides are less stable when compared to those derived from transition metals. Metal ions of Groups 1 and 2 elements possess a noble gas structure. Metal ions with smaller radii and higher charge produce more stable complexes due to electrostatic interactions.

The stability of complexes of Group 1 metal ions decreases in the following order.



Group 1 cations form stable complexes with macrocyclic ligands (*e.g.*, crown ethers) with O or/and N donor atoms. For example, Li^+ , Na^+ and K^+ form relatively stable cations (1), (2) and (3) with 12-crown-4, 15-crown-5, and 18-crown-6, respectively.

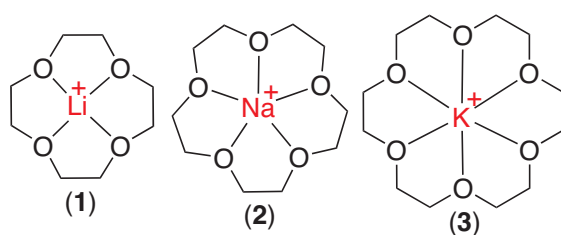
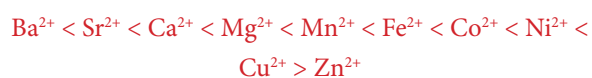


Figure 1. Complexes of crown ethers

Given below is the order of stability of some divalent cations in Irving-William's series.



The stability constants for the formation of $\text{Be}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ are 10^7 , 120, 30 and 4 respectively.

The stability increases from left to right across the Periodic Table. Stable divalent cations of the first transition series form a wider range of complexes. Metal ions with d^{10} configuration (Cu^+ , Zn^{2+} , Hg^+ , Ag^+ , Au^+) form stable complexes with electro-negative ligands such as Cl^- and CN^- .

Transition metal cation in a coordination complex can have several oxidation states. A metal ion with a higher oxidation state forms more stable complexes than its less positive ions. The higher oxidation states provide a higher charge on the metal, which increases the electrostatic attraction with ligands, *e.g.*, $[\text{Fe}(\text{CN})_6]^{3-}$ is more stable than $[\text{Fe}(\text{CN})_6]^{4-}$.

The stability of a metal complex depends on the d-electron configuration and hybridization of the metal centre, and its geometry. $[\text{CoF}_6]^{3-}$ is a high-spin, outer-orbital complex and it is more labile than $[\text{Co}(\text{NH}_3)_6]^{3+}$, which is a low-spin, inner-orbital complex.

Square planar complexes with d^8 configuration are more labile, less sterically hindered, and prone to undergo ligand substitution reactions.

2. Effect of ligands on stability of complexes

Stability of metal complexes depends on the size (steric effect), charge, basicity and denticity of the ligands.

(a) Size and charge of ligands

Charged ligands such as halides form more stable complexes when the charge to size ratio is larger. For example, F^- forms more stable complexes than Cl^- as the size of F^- is smaller than that of Cl^- . The stability constants of $[\text{FeF}]^{2+}$ and $[\text{FeCl}]^{2+}$ are 1×10^6 and 20 respectively.

(b) Basicity of ligands

The stability of a complex depends on the strength of the metal-ligand (M-L) bond(s), which is determined by the σ -donor and π -acceptor ability of the ligand L. Strong bases are good σ -donors and form strong M-L bonds. The basicity of some amines and phosphines is as follows.



(c) Chelate effect

A ligand having more than one donor atom can form more than one attachment to the metal. Multidentate **chelating** ligands form more stable complexes, and this stable ring formation is known as the **chelate effect**. The thermodynamic stability of chelate complexes relates to the increase in the entropy parameter (*i.e.*, ΔS is positive).

The stability of copper(II) complexes (4)-(6) increases as the number of chelating donor atoms increases (see Table 1).

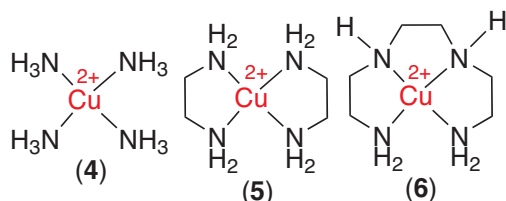


Figure 2. Tetrahedral Cu(II) complexes

NH_3 is a monodentate ligand and it donates a pair of electrons to the tetrahedral Cu(II) centre. Each **en** ligand has two N donor atoms which enable it to form two stable 5-member rings. The **trien** ligand in complex cation (6) with three 5-membered chelate rings, holds the Cu(II) centre with four attachments, making (6) more stable than (4) and (5) as shown by their $\log \beta$ values in Table 1.

Table 1. $\log \beta$ values of Cu(II) complexes

Complex	$\log \beta$
$[\text{Cu}(\text{NH}_3)_4]^{2+}$ (4)	12.7
$[\text{Cu}(\text{en})_2]^{2+}$ (5)	19.7
$[\text{Cu}(\text{trien})]^{2+}$ (6)	20.5

(d) Size of the chelate ring

Generally, the 5-membered chelate rings are more stable than the smaller 4- and 3-membered rings. The 5-membered chelate rings have the optimal angle of attachment. The 3-membered chelate are very strained and are unstable. The 6-Membered chelate rings are slightly less stable than the 5-membered chelate rings but more stable than the larger 7, 8 and 9-membered rings.

(e) Steric effects

The presence of bulky groups either attached to

or near a donor atom can weaken the metal-ligand bond due to **steric hindrance**. The stability constants of complexes based on 8-hydroxyquinoline ligands (7) - (9) with divalent ions of Mn, Co, Ni and Cu are given in Table 2 for comparison.

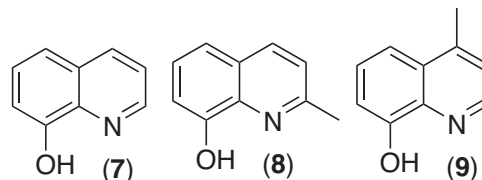


Figure 3. Derivatives of 8-hydroxyquinoline

Table 2. $\log \beta$ values for complexes (7)-(9) with various metal centers

Metal	$\log \beta$		
	(7)	(8)	(9)
Mn	15.5	14.0	15.5
Co	19.7	18.5	20.0
Ni	21.4	17.8	22.3
Cu	26.2	23.8	-

(f) Macrocyclic effect

Macrocyclic effect is an extension of the chelate effect. Macrocyclic ligand should have at least 3 donor atoms in a macrocycle (or cyclic molecule) containing at least 9 atoms including donor atoms, *e.g.*, crown ethers, cyclams, porphyrins, *etc.* Donor atoms are arranged in fixed positions in a more rigid environment. Macrocyclic effect enhances the **complexation affinity** of the multidentate cyclic ligand when compared its analogous acyclic ligand. The K^+ -18-crown-6 complex cation (3) is more stable than the potassium complex cation (10) formed with the acyclic pentaglyme molecule (11). The binding free energies of K^+ for (3) and (10) are -8.4 and -3.0 kcal mol^{-1} , respectively.

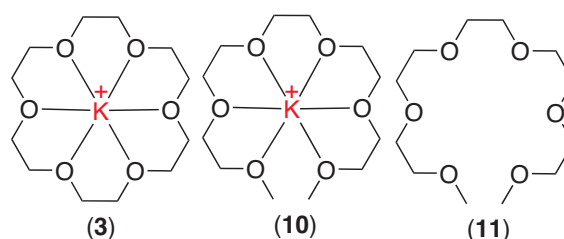


Figure 4. Potassium salts of 18-crown-6 and pentaglyme

Three-dimensional analogues of crown ethers are

called **cryptands** which form very stable complexes with selective guest ions.

Hard and Soft Acids and Bases

Pearson proposed a method of identifying the overall stability of a metal complex. He classified metals and ligands into hard and soft acids and bases (HSAB), see Table 3.

Table 3. Some selected examples of hard and soft acids and bases

Bases	
Hard	H ₂ O, ROH, R ₂ O, OH ⁻ , OR ⁻ , NO ₃ ⁻ , RCO ₂ ⁻ , SO ₄ ²⁻ , CO ₃ ²⁻ , C ₂ O ₄ ²⁻ , PO ₄ ³⁻ , NH ₃ , NR ₃ , NR ₂ H, NH ₂ R, F ⁻ , O ²⁻
Soft	R ₂ S, RSH, SCN ⁻ , CNR, P(OR) ₃ , AsR ₃ , R ₃ P, I ⁻ , CN ⁻ , H ⁻ , R ⁻ , S ₂ O ₃ ²⁻
Border line	Py, Br ⁻ , NO ₂ ⁻ , S ₂ O ₃ ²⁻
Acids	
Hard	Mn ²⁺ , Cr ³⁺ , Fe ³⁺ , Co ³⁺ , Ti ⁴⁺ , H ⁺
Soft	Cu ⁺ , Ag ⁺ , Au ⁺ , Pd ²⁺ , Pd ⁰ , Pt ⁰
Border line	Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Rh ³⁺ , Ir ³⁺

According to HSAB theory, a metal ion is a **hard acid** if it has a **higher charge** and a **smaller size**. That means it has a higher **polarizing power**. A **ligand** is a **hard base** if the **polarizability** is **less** and a soft base if the polarizability is high. Most ligands with donor atoms such as N, O, F are hard bases whilst with S and P are soft bases. The HSAB Theory is summarized as follows.

Stable complexes are formed when (i) soft metals combine with soft ligands and (ii) hard metals combine with hard ligands.

Less stable complexes are formed when (i) soft metals combine with hard ligands and (ii) hard metals combine with soft ligands.

Problems

- Show that $\beta_2 = K_1 K_2$ for the equilibrium

$$M + 2 L \rightleftharpoons ML_2$$
 - If β_2 is $10^{6.0}$ and $\log K_2$ is 2.0. Calculate the stepwise formation constant K_1 .
 - Calculate ΔG for this reaction at 25 °C.
- Calculate β_4 for the following reaction.

$$Cd^{2+} + 4 CN^- \rightleftharpoons [Cd(CN)_4]^{2-}$$
 if K_1, K_2, K_3 and K_4 are $10^{5.48}, 10^{5.12}, 10^{4.63}$, and $10^{3.65}$, respectively.
- The $\log \beta_4$ value for the formation of $[Cd(NH_3)_4]^{2+}$ by the reaction between Cd^{2+} and NH_3 is equal to 7.12. If the $\log \beta_4$ value of $[Cd(CN)_4]^{2-}$ is 18.8, which ion is more stable than the other?
- Consider the following **log β** values.

$Ni^{2+} + 2 NH_3$	5.00
$Ni^{2+} + 4 NH_3$	7.87
$Ni^{2+} + 6 NH_3$	8.61
$Ni^{2+} + 1 en$	7.51
$Ni^{2+} + 2 en$	13.86
$Ni^{2+} + 3 en$	18.28

 - Calculate K_2 for the formation of $[Ni(en)_2]^{2+}$.
 - Calculate K_3 for the formation of $[Ni(en)_3]^{2+}$.
 - Show that $[Ni(en)_3]^{2+}$ is more stable than $[Ni(NH_3)_6]^{2+}$.
 - Calculate $K_5 \cdot K_6$ for the formation of $[Ni(NH_3)_6]^{2+}$.
- Explain the entropy effect associated with the following conversions.
 - $[Cu(H_2O)_6]^{2+} \rightarrow [Cu(C_2O_4)_3]^{4-}$
 - $[Cu(H_2O)_6]^{2+} \rightarrow [Cu(EDTA)]^{2-}$