

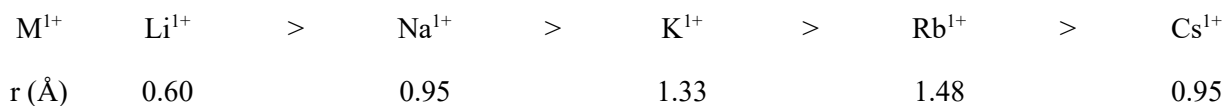
❖ Factors Affecting Stability of Metal Complexes with Reference to the Nature of Metal Ion and Ligand

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

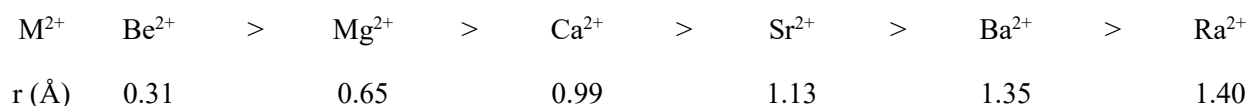
➤ Nature of the Metal Ion

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

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



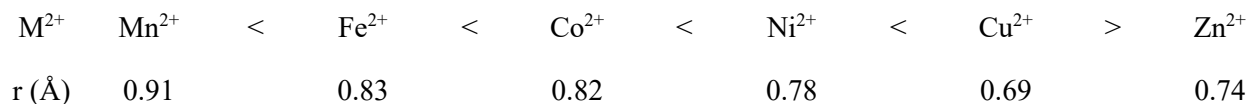
Similarly,



Similarly,



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



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

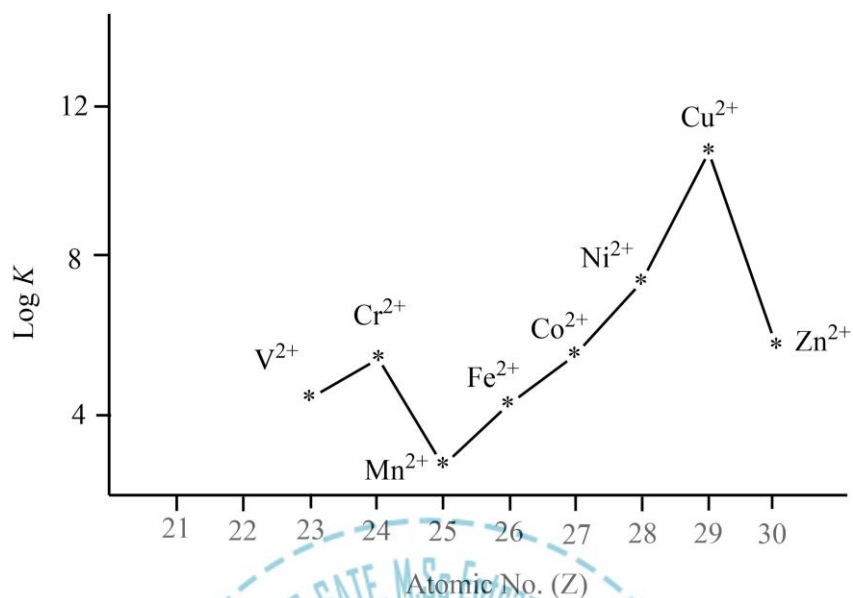


Figure 2. The first stepwise stability constants for the formation of ethylenediamine-complex.

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

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

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

Similarly,

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

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

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

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

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

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

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

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

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

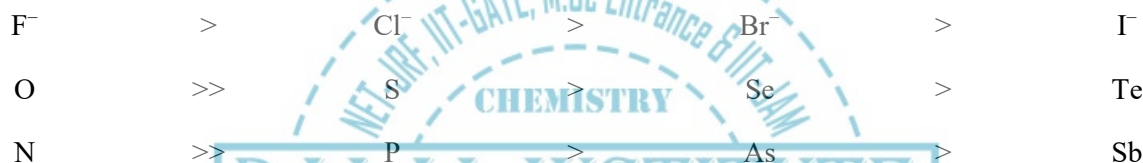
4. Class of the metal ion: It has been observed that class *a* metals e.g. alkali metal ion, alkaline earth metal ions and metals from first transition series are shown to form stable complexes with ligands having N, O or F as the donor site. On the other hand, class *b* metals e.g. metals from second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

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

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

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

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



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



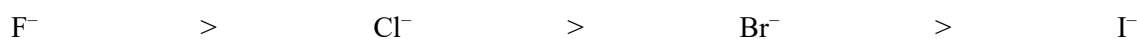
For borderline metals, the stability of different metal complexes is pretty much independent of the nature of the ligand and follows the order given by the Irving-William series.

➤ Nature of the Ligand

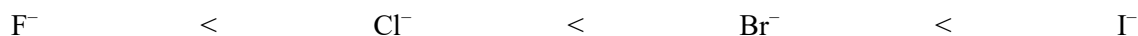
The following properties of ligands-attached affect the stability of the transition metal complexes to a significant extent.

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

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



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



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



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

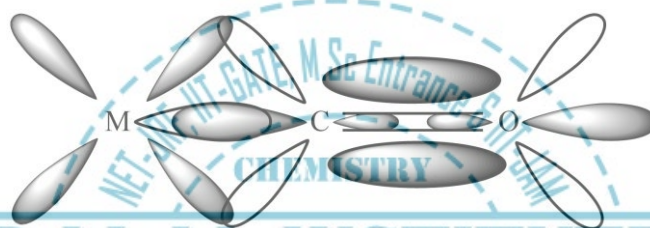


Figure 3. The back bonding mode in metal carbonyl complexes enhances stability.

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

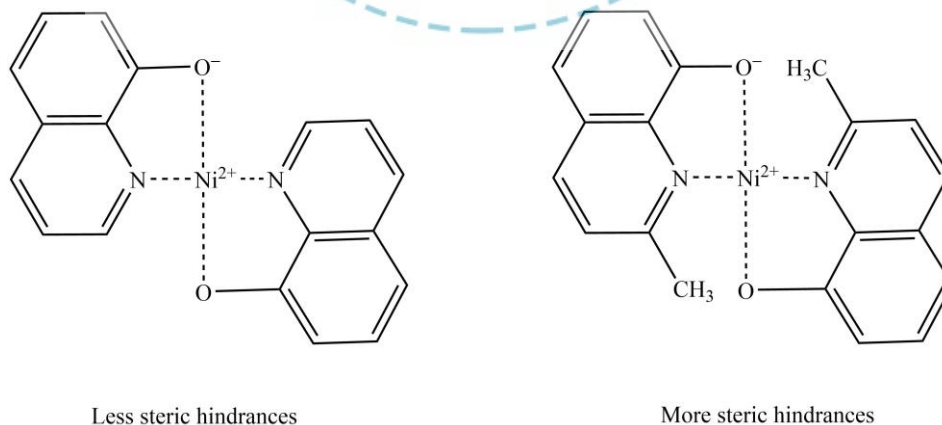
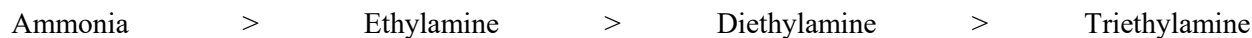


Figure 4. Bivalent nickel complexes with 8-hydroxy quinoline and 2-methyle-8-hydroxy quinoline.

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



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

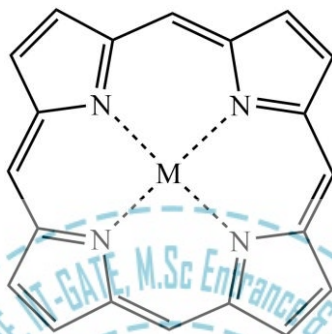


Figure 5. Structure the simplest porphyrin complex.

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

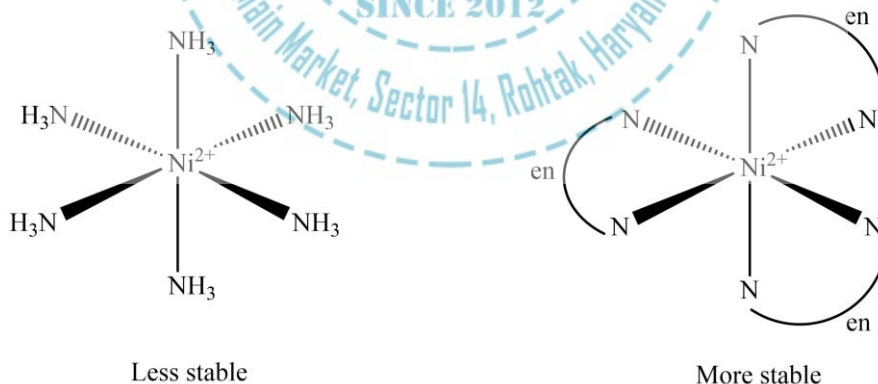


Figure 6. Complexes of bivalent nickel with monodentate amine and bidentate ethylene diamine ligands to form the chelate in the latter case.

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

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

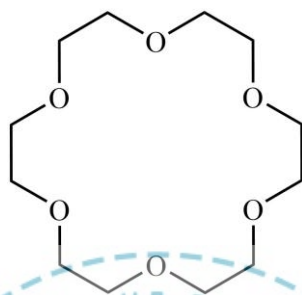


Figure 7. Structure of 18-Crown-6.

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

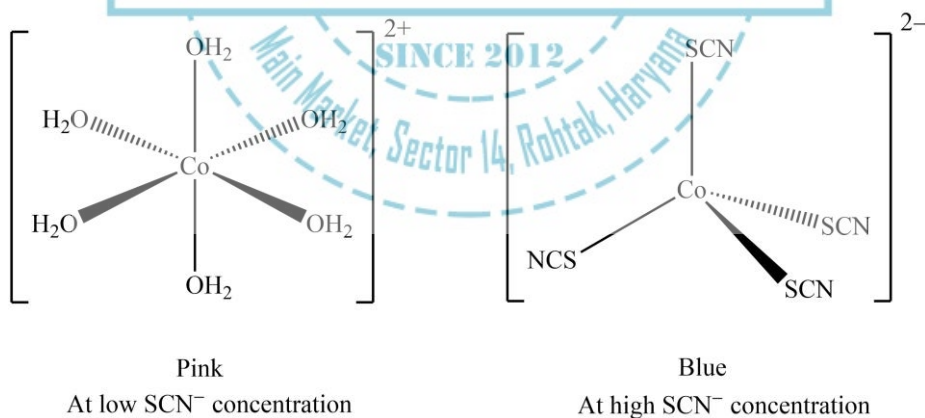


Figure 8. Structure of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{SCN})_4]^{2-}$.

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

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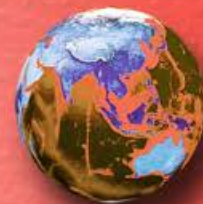
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