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**KARAIKUDI - 630 003**

**DIRECTORATE OF DISTANCE EDUCATION**

**M.Sc.,**

**III-SEMESTER**

**34431**

**ADVANCED INORGANIC CHEMISTRY**

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# SYLLABI-BOOK MAPPING TABLE

## ADVANCED INORGANIC CHEMISTRY

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Syllabi	Mapping in Book
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Kinetics and mechanisms of reactions in solution Labile and inert complexes Ligand displacement reactions Hydrolysis, anation, aquation in octahedral complexes Substitution reactions in square planar complexes Trans effect – Electron transfer reactions	
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<b>Unit -5 : Spinels</b>	<b>Pages 64 -75</b>
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<b>Unit -7: Boranes</b>	<b>Pages 83-98</b>
Boranes: Structure and bonding in polyhedral boranes Carboranes, Styx notation	

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Wade's rule;  
Electron count in polyhedral boranes, isolobal analogy.

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### **BLOCK-3 ORGANOMETALLIC CHEMISTRY**

#### **Unit-8: Definition of Organometallics**

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#### **Unit-9: Metallocenes**

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#### **Unit-10: Metal carbonyl**

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# BLOCK- 1 COORDINATION CHEMISTRY

## UNIT-1 STABILITY OF COORDINATION COMPOUNDS

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NOTES

### 1.0 Introduction

When the term stability is applied to coordination compounds (metal complexes), there can be two interpretations w.r.t thermodynamic and kinetics. Thermodynamic stability refers to the change in free energy on going from reactants to products, i.e.,  $\Delta G$  for the reaction. Recall that  $\Delta G = \Delta H - T\Delta S = -RT \ln K$ , where  $\Delta H$  is the enthalpy,  $\Delta S$  the entropy  $T$  the absolute temperature and  $K$  is the equilibrium constant for the reaction. Kinetic stability refers to reactivity, generally ligand substitution. When assessing chemical reactions we need to consider both thermodynamic and kinetic aspects because although a reaction may be thermodynamically feasible, there might be kinetic constraints. In this section we are going to focus on the formation constants, stepwise formation constants with their methods of determination and chelate effect.

### 1.1 Objectives

After going through this unit, you will be able to:

- Understand about the stability constants
- Understand the methods of determining the stability constants
- Appreciate the chelation effect

### 1.2 Stability Constants

When a metal ion in aqueous solutions interacts with a neutral and monodentate ligand, the system at the equilibrium may be described by the equation



Where  $x$  is the number of water molecules in the aqua complexes and  $n$  is the oxidation number of the metal ion. When  $L$  is an anionic ligand, the ligand binding equilibrium would be :



## NOTES

We may write the equilibrium reaction in a simplified and generalized form without referring to the number of coordinated water molecules as follows:



The equilibrium constant of the reaction is given by the equation given below

$$K_f = \frac{[ML]}{[M][L]}$$

$K_f$  is called **formation constant** of the complex.

Note that here we assume that the concentration of  $H_2O$  is constant in a dilute solution of the metal complex and it is incorporated into the above  $K_f$  equation. If a large amount of the complex is formed then the equilibrium concentrations  $[ML]$  is larger than the product of  $[M][L]$ , then  $K_f$  is more than 1.0. Such a situation would arise when the ligand L binds to the metal more tightly than  $H_2O$ . Thus a large value of  $K_f$  merely indicates that L is a stronger ligand than  $H_2O$ . Similarly, when  $K_f$  is less than 1.0, the L is a weaker ligand than  $H_2O$ . The magnitude of the formation constant is the measure of stability of a coordination complex. In a thermodynamic sense, the formation constants are also called **Stability constants**. In studying the formation of complexes in solution, two types of stability of complexes are found

### 1. Thermodynamic Stability

It is a measure of the extent of which the complex will form or will be transformed into another species under certain conditions, when the system has reached in equilibrium. This type of stabilities are dealt with metal-ligand bond energies, stability constant etc.,

### 2. Kinetic Stability

IT refers to the rate with which transformation leading to the attainment of equilibrium will occur. When we are interested in kinetic stability for complex ions in solutions are dealt with rates and mechanism of chemical reactions. These reactions may be substitution, isomerisation, recemisation and electron or group transfer reactions. In the kinetic sense, it is more proper to call the complexes inert or labile complex rather than stable or unstable complex. The complexes in which the ligands are rapidly replaced by others are called labile complexes, while those in which substitution occurs slowly are called inert complexes.

### 1.3 Stepwise and Overall Formation Constants

According to J. Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex  $ML_n$  may be supposed to take place by the following n consecutive steps.

where M = central metal cation

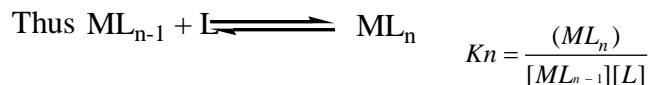
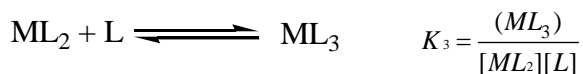
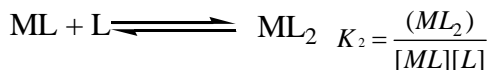
L = monodentate ligand

n = maximum co-ordination number for the metal ion M for

the ligand



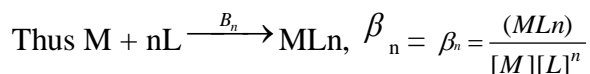
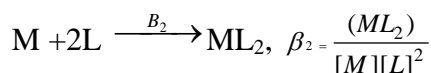
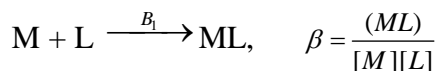
$$K_1 = \frac{(ML)}{[M][L]}$$



NOTES

The equilibrium constants,  $K_1, K_2, K_3, \dots, K_n$  are called **stepwise stability constants**.

The formation of the complex  $ML_n$  may also be expressed by the following steps and equilibrium constants.



The equilibrium constants,  $\beta_1, \beta_2, \beta_3, \dots$  are called stepwise formation constants.  $\beta_n$  is called as  $n^{\text{th}}$  overall (or cumulative) formation constant or **overall stability constants**. The higher the value of stability constant ( $k$ ) for a complex ion, the greater will be its stability. Alternatively  $1/k$  values sometimes are called instability constant.

Stepwise and cumulative stability constants are also expressed as  $\log_{10}K_1, \log_{10}K_2, \dots, \log_{10}K_n$  and  $\log_{10}\beta_n$  respectively.

**Relationship between  $\beta_n$  and  $K_1, K_2, K_3, \dots, K_n$**

$K$ 's and  $\beta$ 's are related to one another as said

Consider for example, the expression for  $\beta_3$  is:-

$$\beta_3 = \frac{[ML_3]}{[M][L]^3}$$

On multiplying both numerator and denominator by  $[ML][ML_2]$  and on rearranging we get:

$$\begin{aligned} \beta_3 &= \frac{[ML_3]}{[M][L]^3} \times \frac{[ML][ML_2]}{[ML][ML_2]} \\ &= \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \times \frac{[ML_3]}{[ML_2][L]} \end{aligned}$$

$$= K_1 \times K_2 \times K_3$$

$$\text{Thus } \beta_n = \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[ML][L]} \dots \frac{[ML_n]}{[ML_{n-1}][L]}$$

$$= K_1 \times K_2 \dots K_n$$

Or

$$\beta_n = \sum_{n=1}^{n=n} K_n$$

NOTES

From above relation, it is clear that the overall stability constant  $\beta_n$  is equal to the product of the successive (i.e. stepwise) stability constants,  $K_1, K_2, K_3, \dots, K_n$ . This in other words means that the value of stability constants for a given complex is actually made up of a number of stepwise stability constants.

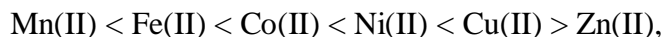
**Factors Affecting Stability Constant (K)**

**Metal:** The nature of the metal ions influences the stability of the complex as follows

- Stability (or stability constant) increases with decreasing size of metal ion. K generally varies with radius of metal ion  $r$  as  $1/r$ .
- Stability constants for a complex increase with the charge of the central ion. The K for the Fe(II) complexes will be less than the K for the corresponding Fe(III) complexes.
- The ions with high polarizability give complexes with higher stability constants. Thus Cu(I) complexes have higher K values than the similar sized Na(I) complexes, similarly of Ca(II) and Cd(II) or Al (III) and Ga(III) the former have low K values for the complex formation.
- Electronegativity increases the polarizing power and the ions with higher electronegativity give stable complexes.
- Ionization Energies: The electronegativity, covalent nature and ionic radii can be related to the ionization energies of the atoms. It is found that the stability constants for the metal complexes with a ligand increases with the ionization energies of the metallic species.

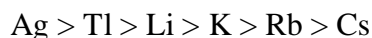
Observations of Bjerrum-Nielsen and others show that although most of the metals of the periodic table form complexes, this tendency is the most with transition metals. The reason being that the chelate effect is almost an entropy effect for the metal ions of nontransitional group, while for the transition metals it is partly an enthalpy effect which increases the crystal field strength. The increase in crystal field strength increases the points of attachment of the ligand to the metal ion imparting greater chelating tendency to the latter.

Mellor and Maley have shown that the stabilities of the complexes of bivalent metal ions follow the order:  $\text{Pd} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Co} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn} > \text{Mg}$  irrespective of the nature of the ligand. Irving and Williams from the analysis of the data on stability constants of transition metal ions, found that the order holds good.



This order according to them follows logically from a consideration of the reciprocal of ionic radius and second ionization potential of the metal, and is known as 'Natural Order of Stability'.

Univalent ions have not been extensively studied but data on the complexes of the univalent ions with dibenzol methanate ion shows the order of the stability as:



**Factors Related With Ligands**

The properties of the ligands which affect the stability of the metal complexes are as under:

**Basicity of the ligands:** The greater is the Lewis base strength, higher is expected to be the stability constant of the complex.

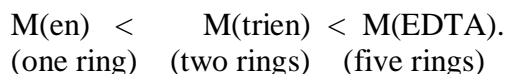
**Dipole moment and polarizability of the ligands:** Due to the greater electrostatic interactions between the metal ion and the ligands, polarity and polarizability of ligand results in higher K for the complexes.

**(M→L) π- back bonding** always increases the stability of the complex.

**Steric factor:** It plays an important role in determining the stability constants for the complexes.

**Ring Formation and Size of the Ring**

Ring complexes or chelates are very stable due to reduced strain. The number of ring formed the size of the rings and stabilizing or interfering resonance interactions are determined by the structure of the chelating agent. Schwarzenbach and Co-workers have observed that there is a decrease in chelate stability with the increase in ring size. The stability of a five membered ring is not mainly due to entropy but rather to the enthalpy of formation; Further the stability increases with the increase in the number of rings in the molecule:



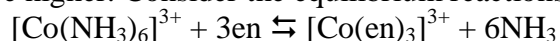
**Steric Effect:** Steric hindrance can influence stability in many ways, e.g.

- (i) Metal-ligand bonds are weakened due to the presence of bulky group near the coordinating site.
- (ii) The substituting group prevents the ligand from assuming the planar configuration and hence introduce strain in the metal-donor bond.
- (iii) Steric hinderance is also due to strained structure of the chelated ring, since it breaks the usual linear configuration of the complexes.

From the study of the copper complexes of substituted malonic acids Riley concluded that ethyl and propyl groups had a larger effect than methyl in reducing the stability.

**Chelate Effect**

The chief factor responsible for the stability of the chelate ring is the entropy change which can be viewed statistically or as probability factor. Considering the electronic effect of the donor atom to be the same in the monodentate and the bidentate ligands, it can be seen that the dissociation of a monodentate from a complex will be higher than that in the chelating bidentate. The dissociation of the M-L bond in monodentate will release the ligand completely from the coordination sphere of the metal, so that it can be easily swept off by the solvent. But the dissociation of one M-L bond for the bidentate ligand does not release the ligand completely (for which simultaneous dissociation at both ends is required). Hence the stability constant for metal chelate must be higher. Consider the equilibrium reactions



Assuming that (i) Co-N bond strength in the two complexes is same (the f value of ammonia and ethylenediamine are within 3%), and (ii) the entropy

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changes due to structure making and structure breaking are negligible due to the similar size of the complexes, it can be seen that the  $\Delta S^\circ$  will increase for the reaction as the number of moles of the products are more than those for the reactants. This will help the reaction to go to the right.

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### 1.4 Determining Stability Constants

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In order to determine the values of  $n$  formation constants,  $n + 2$  independent concentration measurements are needed. These can be used to obtain the concentration of the  $n$  species,  $ML_1$   $ML_2$  ----  $ML_n$  and also those of  $M$  &  $L$ . We should know the quantities of  $M$  and  $L$  used in the experiment. This means that  $n$  additional pieces of information are needed. If it is certain that only one complex of known empirical formula is formed, then a measurement of the concentration of the uncomplexed  $M$  or  $L$  is sufficient to determine the formation constant. This measurement can be made in many ways, by polarographic or emf measurements (if a suitable reversible electrode exists), by pH measurements (if the acid dissociation constant of  $HL$  is known) and by many other techniques. Various experimental methods are used to determine the composition and stability constants of the complexes.

1. Measurement of colligative properties
2. Optical methods (spectrophotometric study of systems with two & three or more components)
3. NMR & ESR methods
4. Calorimetry
5. Determination of equilibrium constants via kinetic measurements
6. Extraction methods
7. Solubility studies
8. Study of ion exchange Equilibria
9. Potentiometry & pH-metric equilibrium studies
10. Polarography and

Other methods such as measurement of conductivity, polarimetry, Infrared spectrophotometry, Raman spectrophotometry, equilibrium study of metal complexes of anionic ligands, polarographic diffusion current, chronopotentiometry, cyclic voltammetry, gas chromatography, density measurement, magnetic susceptibility measurement, emission titration, measurement of self-diffusion coefficient, positronium annihilation and pressure measurement in the case of gaseous ligands are also employed. The possibilities for the application of other methods are limited as they each relate only to a well-defined group of equilibrium systems.

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#### 1.4.1 pHMetric Method

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##### Bjerrum's Method

It is a potentiometric method for determining the stability constant of a complex. Although Bjerrum applied the method primarily to the binding of simple molecules or negative ions to positive metal ions. It may be used with equal success with chelating agents. The theoretical relationship outlined by Bjerrum are not restricted to complex formation but may be applied to any equilibrium process regardless of the nature of the interacting substances. Thus, it has been used with success on acid base, and redox equilibria. Although the



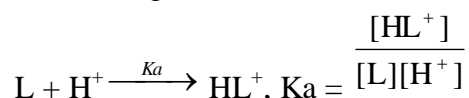
reactions to be considered involve ions that are more or less completely hydrated, rather than the simple ions, but this fact does not affect the validity of the conclusions, provided the activity of the water is maintained constant.

Formation or dissociation of a complex ion for molecule in the solution always takes place in several steps, which can be easily determined by measuring pH in this method.

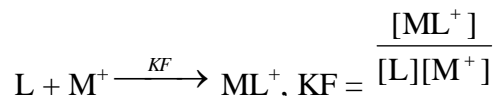
### Experimental Determination of Stability Constant by Bjerrum's Method

This is a potentiometric method. When the ligand is a weak base or acid, competition between hydrogen ion and metal ions for ligand can be used to the determination of the formation constant.

Let us consider the equilibrium in which an acid and metal ions are added to a basic ligand in solution. Thus the following equation are obtained:



Basic Ligand Acid



Basic Ligand Metal ion

Here  $K_a$  and  $K_f$  are the acid association constant of the ligand and formation constant respectively.

Now if  $C_H$ ,  $C_M$  and  $C_L$  are the total amounts in moles/litre of acid ( $H^+$ ), metal ( $m^+$ ) and basic ligand (L), we have

$$\begin{aligned} C_H &= [H^+] + [HL^+] \\ C_L &= [L] + [ML^+] + [HL^+] \\ C_M &= [M^+] + [ML^+] \end{aligned}$$

Solving the last three equations given above and using the acid association constant of the ligand,  $K_a$ . Then we get

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

$$[M^+] = C_m - [ML^+]$$

$$L = \frac{C_H - [H^+]}{K_a[H^+]}$$

Thus on putting the values of  $[ML^+]$ ,  $[M^+]$  and  $[L]$  from the above equation in

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

The value of  $K_1$  can be calculated. For the determination of  $[ML^+]$ ,  $[M^+]$  and  $[L]$ , the values of  $C_H$ ,  $C_L$ ,  $C_m$ ,  $K_a$  and  $[H^+]$ , is generally determined potentiometrically using a pH meter.

In order to get better results, the ligand must be a medium weak acid or base and the formation constant,  $K_1$ , should be within a factor of  $10^5$  of the value of the acid association constant of the ligand,  $K_a$ .

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## 1.4.2 Spectrophotometry Measurements

The basic principle of the spectrophotometric technique is the measurement of interactions between radiation energy and electrons of the substance. This is used in estimation of the concentration of metal ion in liquid solution. One of the most spectacular effects of complex formation is the change of spectral properties. Complexes absorb the light due to

- (1) The excitation of electrons of both the metal ion and the ligand is influenced by their interaction.
- (2) The electrons of transition metal ions are easily excited and absorb in the visible region.
- (3) The electron system of non-transition metal ions and ligands are stable requiring greater amount of energy, so absorb in the ultraviolet region.
- (4) A charge transfer from ligand to metal ion may occur on irradiation due to interaction of central ion and ligand. This causes in the charge transfer spectra to occur in the visible and near ultraviolet region. The following points are to be noted during measurements.

**Beer's Law:** If a given species in solution absorbs light and obeys Beer's law, then it is possible to find out its concentration. This law can be regarded as idealized behaviour of the species towards strictly monochromatic radiation. The formation constant of a complex can be calculated by taking known amount of metal and ligand and measuring the optical density of the metal, ligand and the metal-ligand mixture separately.

**Selection of Wavelength:** Firstly, it is necessary to select the wavelength at which complex species has a greater absorption to that of free metal ion or free ligand. For this, spectra of metal-ligand mixture is compared with the spectra of free metal ion and free ligand. It is also important that at a wavelength selected, only one complex species should predominantly absorb light. As nitrate ions have no absorbance in the spectral range of 250 nm to 1800 nm, metal nitrate solution will show absorption of light by metal ions alone.

**Selection of pH:** For selecting the optimum pH for studying complex formation, a preliminary study of spectra of (i) The metal ion (ii) The ligand ion and (iii) Metal ion + ligand, has to be made over a large range of pH up to the pH of hydrolysis. If more than one complex is formed at different pH conditions, their existence can be decided by this type of study. The pH at which absorption due to complex is far greater than that of metal ion or the ligand alone, is selected for the study of that species. As the complex formation is the function of pH; it should be kept constant for that system. Similarly, by adding appropriate volume of potassium nitrate, ionic strength is maintained constant throughout. pH can be maintained constant by using a proper buffer, but buffer should not interfere with the complex formation and should not absorb itself at the maximum wavelength of absorption of complex species. For complexes which show different colour with a change in pH, a plot of optical density against wavelength over a wide range of pH gives a number of curves representing absorption spectra. The points at which the curves corresponding to a number of solutions having equal formal concentration of metal and ligand intercept are called the isobestic points.

### The Composition of the Complexes

Before determining the stability constants of a given complex; it is necessary to ascertain the number of ligand groups attached to the metal ion. The composition of the complex can be determined by *Job's method of continuous variation*.

#### Job's Method of Continuous Variation

It consists of mixing equinormal solutions of metal and ligand in varying proportion but keeping the total concentration of the metal plus the ligand constant in the mixtures. The absorbance of these mixtures is measured at a suitable wavelength. If  $x$  mole/litre of L are added to  $(1-x)$  mole/litre of M and if  $C_1$ ,  $C_2$  and  $C_3$  are the equilibrium concentrations in mole/litre of M, L and  $ML_n$  respectively, then,

$$C_1 = (1-x) - C_3$$

$$C_2 = (x - nC_3)$$

$$C_3 = C_1 C_2^n$$

'n' is the number of ligands attached to a metal ion which can be easily determined from the position of the maximum or minimum in the graph. If the metal ion and the ligand are colourless, but the complex species is coloured, then there will be maximum at the composition of the complex in the plots of absorbance versus composition. Job's method is ordinarily applicable to systems in which only one complex is present.

#### **Calculations of Stability Constants**

The stability constant of a complex can be determined from Job's curve by the following two methods:

##### **From extinction coefficient data**

Optical density of solution (M : L = 1 : 25) can be considered to be due to the complex. The concentration of complex may be taken equal to that of the metal ions as all the metal ions are utilized in forming the complex. From optical density, one may determine the extinction coefficient of the complex by using Beer's law. From this value, the concentration and stability constants of the complex in various mixtures can be calculated.

##### **Method of Corresponding Solutions**

A solution (M : L = 1 : 1) can be diluted at constant ionic strength, until solutions are obtained having the same optical densities. In this way, pairs of solutions may be prepared which have the same optical density [equal concentration of the complex] but different total concentration of the metal and ligand.

Suppose  $D_1$  and  $D_2$  are the concentrations of  $[ML_1]$  and  $[ML_2]$  respectively obtained from the observed solutions (i) and (ii). Now; as  $D_1 = D_2$ , we can write  $[ML_1] = [ML_2]$  and the formation constant  $k'$  is given by

$$k' = \frac{[ML_1]}{[M]_1[L]_1} = \frac{[ML_2]}{[M]_2[L]_2}$$

Since,  $[ML_1] = [ML_2] = [ML]$

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## NOTES

$$k' = \frac{[\text{ML}]}{T_{\text{M1}} - [\text{ML}] T_{\text{L1}} - [\text{ML}]} = \frac{[\text{ML}]}{T_{\text{M2}} - [\text{ML}] T_{\text{L2}} - [\text{ML}]}$$

Where,  $T_{\text{M1}}$  and  $T_{\text{L1}}$  are the concentrations of total metal and total ligand respectively in solution (i) and  $T_{\text{M2}}$  and  $T_{\text{L2}}$  are the concentrations of total metal and total ligand respectively in solution (ii). As the values of  $T_{\text{M}}$  and  $T_{\text{L}}$  are known, the value of  $k'$  can be calculated.

The extent of complex formation is characterised by the ligand number  $n$ , given as

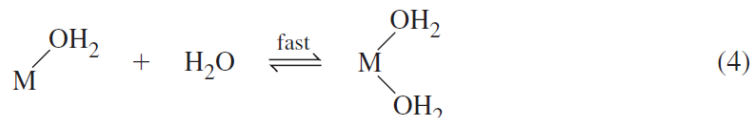
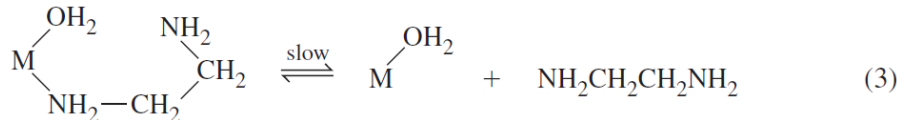
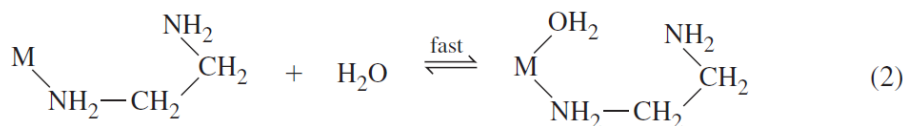
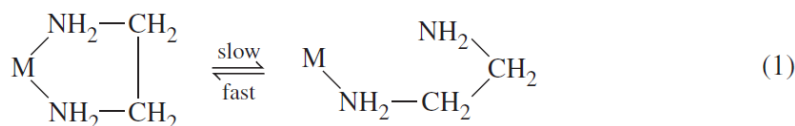
$$n = \frac{T_{\text{L}} - [\text{L}]}{T_{\text{M}}}$$

Where  $T_{\text{L}}$  is the concentration of ligand in all forms,  $[\text{L}]$  is the concentration of free chelating species and  $T_{\text{M}}$  is the total concentration of metal ion (bound or free).

### 1.5 Chelate Effect

The chelate effect causes polydentate complexes to be thermodynamically more stable than their monodentate counterparts. Substitution for a chelated ligand is generally a slower reaction than that for a similar monodentate ligand. Explanations for this effect centre on two factors. First, the  $\Delta H$  associated with removal of the first bound atom is larger than for a related monodentate ligand. If this atom does separate from the metal centre, its kinetic barrier for subsequent reattachment is lower than for a related monodentate ligand since the former remains in close proximity to the metal centre.

Consider the general scheme below:



The first dissociation (1) is expected to be slower than a similar dissociation of ammonia, because the ethylenediamine ligand must bend and rotate to move the free amine away from the metal. The reverse reaction associated with the first dissociation is fast. Indeed, the uncoordinated nitrogen

is held near the metal by the rest of the ligand, making reattachment more likely. This kinetic chelate effect dramatically reduces aquation reaction rates.

### 1.6 Check Your Progress

1. What is meant by stepwise formation constant?
2. What are the different methods used to determine stability constants?
3. Explain chelate effect.
4. Give the expression of the real stability constant?

### 1.7 Answers To Check Your Progress Questions

1. When more than one coordinated water molecule of  $[M(H_2O)_x]^{n+}$  is replaced by the ligand L, then we have to consider several steps. At each step we need to consider an equilibrium constant called the **stepwise formation constant** (or stepwise stability constant).
2. Various experimental methods are used to determine the composition and stability constants of the complexes; these are
  - Measurement of colligative properties
  - Optical methods (spectrophotometric study of systems with two & three or more components)
  - NMR & ESR methods
  - Calorimetry
  - Determination of equilibrium constants via kinetic measurements
  - Extraction methods
  - Solubility studies
  - Study of ion exchange Equilibria
  - Potentiometry & pH-metric equilibrium studies
  - Polarography and
  - Other methods
3. When a ligand attaches to the metal ion in a manner that forms a ring, then the metal- ligand association is found to be more stable. In other words, we can say that complexes containing chelate rings are more stable than complexes without rings. This is known as the chelate effect.

### 1.8 Summary

- Inorganic chemists frequently use stability constants, sometimes called formation constants, as indicators of bonding strength. These are equilibrium constants for reactions that form coordination complexes.
- When more than one coordinated water molecule of  $[M(H_2O)_x]^{n+}$  is replaced by the ligand L, then we have to consider several steps. At each step we need to consider an equilibrium constant called the **stepwise formation constant** (or stepwise stability constant).
- Various experimental methods are used to determine the composition and stability constants of the complexes; these are pH metric, spectrophotometric, polarographic, etc.
- For determining the stability constants of a given complex through spectrophotometric method; it is necessary to ascertain the number of ligand groups attached to the metal ion. The composition of the complex can be determined by *Job's method of continuous variation*.

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- The chelate effect causes polydentate complexes to be thermodynamically more stable than their monodentate counterparts. Complexes containing chelate rings are more stable than complexes without rings.

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### 1.9 Keywords

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**Chelate Effect:** Complexes containing chelate rings are more stable than complexes without rings and is known as chelate effect.

**Bjerrum's Method:** It is a potentiometric method for determining the stability constant for complex formation.

**Job's method of continuous variation:** The composition of the complex can be determined by **Job's method of continuous variation.**

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### 1.10 Self-assessment questions and exercises

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1. Explain in detail about the formation constants.
  2. Discuss in detail about stepwise formation constants.
  3. Give the detailed picture of spectrophotometric method for determining stability constants
  4. Explain about chelate effect with an example.
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### 1.11 Further readings

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1. Huheey, J.E., E.A. Keiter and R.L. Keiter. 2002. Inorganic Chemistry: Principles of Structure and Reactivity, 4<sup>th</sup> Edition. New York: HarperCollins Publishers.
2. Gary L. Miessler., Paul J. Fischer., Donald A. Tarr. Inorganic Chemistry, 5<sup>th</sup> ed : Pearson
3. Shriver and Atkins., Inorganic Chemistry, 5<sup>th</sup> ed : W. H. Freeman and Company New York.

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# UNIT-II KINETICS AND MECHANISMS OF COORDINATION COMPOUNDS

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Complementary and Non-  
Complementary Reactions

## Structure

- 2.0 Introduction
  - 2.1 Objectives
  - 2.2 Kinetics and mechanisms of reactions in solution
    - 2.2.1 Labile complex & inert complex
    - 2.2.2 Factors affecting the labile/inert nature of complexes
  - 2.3 Ligand displacement reactions
    - 2.3.1 Hydrolysis in octahedral complexes
    - 2.3.2 Anation in octahedral complexes
    - 2.3.3 Aquation in octahedral complexes
  - 2.4 Substitution in square planar complexes
    - 2.4.1 Trans effect
  - 2.5 Electron transfer reactions
  - 2.6 Check Your Progress
  - 2.7 Answers to check your progress questions
  - 2.8 Summary
  - 2.9 Keywords
  - 2.10 Self-assessment questions and exercises
  - 2.11 Further readings
- 

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## 2.0 Introduction

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Reactions of coordination compounds are understood using the same fundamental concepts applied to all reactions. The chemistry of coordination compounds is distinctive because (1) the complexes have a relatively large diversity of geometries and more possibilities for rearrangement, and (2) metal atoms impose significant variability on the reactivity of their complexes. Reactions of coordination complexes can be divided into (1) substitution at the metal centre, (2) oxidation–reduction, and (3) reactions of the ligands that do not change the attachments to the metal centre. In this context, we discuss in detail about the labile and inert complexes, different types of ligand displacement reactions in octahedral complexes, mechanisms behind the substitution reactions in square planar complexes, Trans effect and the electron transfer reactions.

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## 2.1 Objectives

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After going through this unit, you will be able to:

- Understand the concept behind the kinetics and mechanisms of reactions in solution.
- Explain the different types of ligand displacement reactions in octahedral complexes.
- Understand the mechanisms behind substitution reactions in square planar complexes and the importance of Trans effect.
- Learn about the electron transfer reactions.

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## 2.2 Kinetics and Mechanisms of Reactions in Solution

**Thermodynamics:** When examining thermodynamics of a reaction we are entirely interested in the start and finish of a reaction. What is the extent of reaction? Where does the equilibrium lie? How do we investigate this?

**Kinetics:** How fast does a reaction reach equilibrium? This relates directly to the mechanism.

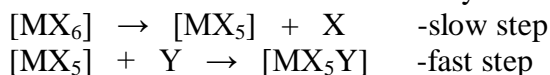
Substitution reactions involve either replacement of ligands by other ligands- nucleophilic substitution ( $S_N$ ) or replacement of central metal ion by other metal ions- electrophilic substitution ( $S_E$ ) which is rare.

Two main types of nucleophilic substitution mechanisms are,

- 1) Unimolecular nucleophilic substitution ( $S_N1$ ) or Dissociative mechanism
- 2) Bimolecular nucleophilic substitution ( $S_N2$ ) or Associative or Displacement mechanism

### Unimolecular Nucleophilic Substitution ( $S_N1$ ) or Dissociative mechanism

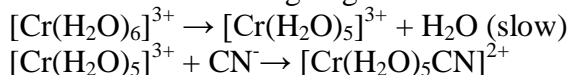
According to this mechanism, the complex first undergoes dissociation losing the ligand to be replaced, X and changes into a five coordinated intermediate which then readily adds the new ligand, Y.



The characteristics of this reaction are,

1. Only one species,  $[MX_6]$  is involved in the formation of the activated species in the slow step.
2. In the second step, the activated species undergoes fast reaction with incoming ligand, Y.
3. The activation energy for the first step is high and that for the second step is low.
4. The rate of the overall reaction depends on  $[MX_6]$  and not on  $[Y]$ .
5. The reaction is first order with respect to  $MX_6$  and is zero order with respect to Y.
6. In the formation of the activated complex, the coordination number of the metal ion is decreased by one.
7. The rate law for the substitution is  $v = k_1[MX_6]$

Example for a reaction undergoing this mechanism is,



### Types of intermediates formed during $S_N1$ reaction

Consider an octahedral complex  $MA_5X$  being attacked by a nucleophile, Y. If the reaction proceeds through a dissociative  $S_N1$  mechanism, two types of intermediates can be formed.

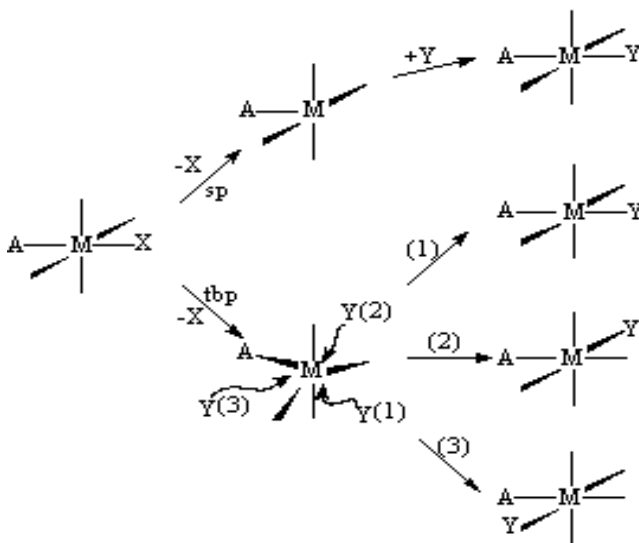
- 1) The bond M-X dissociates causing least disturbance to the remaining  $MA_5$  intermediate which has a square pyramidal



geometry. The intermediate  $MA_5$  is then attacked by  $Y$  to produce  $MA_5Y$ .

- The bond  $M-X$  dissociates and the remaining  $MA_5$  species immediately adjust the bond angles to produce a trigonal bipyramidal intermediate which is then attacked by  $Y$  to produce  $MA_5Y$ .

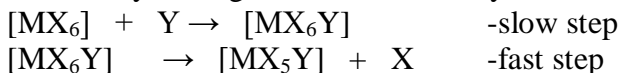
It is evident that the formation of a trigonal bipyramidal



intermediate involves the movement of at least two metal ligand bonds whereas no such movement is required during the formation of a square pyramidal intermediate.  $S_N1$  reactions thus proceed generally through the more stable square pyramidal intermediate unless the trigonal bipyramidal intermediate is stabilized by  $\pi$  bonding.

### Bimolecular Nucleophilic Substitution ( $S_N2$ ) or Associative or Displacement mechanism

According to this mechanism, the new ligand first adds on to the complex to form a seven coordinated activated or intermediate complex which then readily undergoes dissociation to yield the final product.



In this case, the reaction rate depends upon the first step. i.e upon the concentration of the complex as well as the concentration of the incoming ligand  $Y$ .

The characteristics of this reaction are,

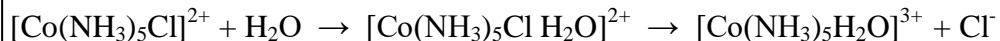
- In this reaction, two species ( $MX_6$  and  $Y$ ) are involved in the formation of the activated species;  $Y$  is added to the reactant complex to form the activated species.
- In the second fast step, the activated complex loses a ligand and the new ligand  $Y$  becomes a permanent part of the molecule.
- The rate of the overall reaction depends on both  $[MX_6]$  and  $[Y]$ .

### NOTES

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4. The reaction is first order with respect to  $\text{MX}_6$  and first order with respect to  $\text{Y}$ ; the overall order is 2.
5. In the formation of the activated species, the coordination number of the metal is increased.
6. The general rate law for the substitution is  $v = k_1[\text{MX}_6][\text{Y}]$ .

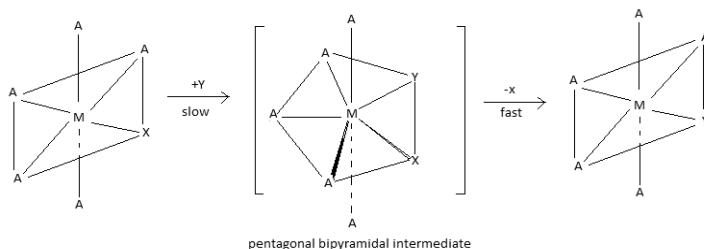
Example for a reaction undergoing this mechanism is,



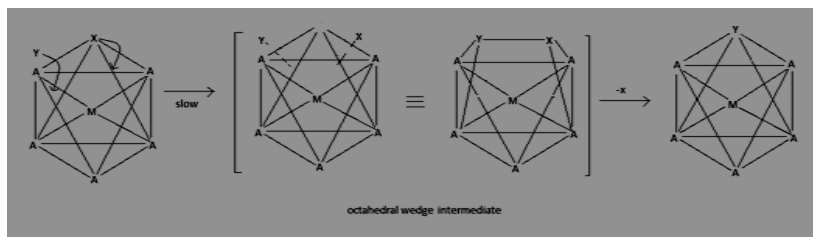
**Types of intermediates formed during  $\text{S}_{\text{N}}2$  reaction**

If the reaction proceeds through an associative  $\text{S}_{\text{N}}2$  mechanism, there are two types of intermediates.

If the nucleophile  $\text{Y}$  attacks through one of the edges of the octahedron, a pentagonal bipyramidal intermediate is formed. The formation of pentagonal bipyramidal intermediate requires the movement of at least four ligands to adjust the nucleophile  $\text{Y}$ . The ligand- ligand repulsions also increase the energy of pentagonal bipyramidal intermediate because the decrease in  $\text{A-M-A}$  bond angles brings the electron pairs of metal bonds nearer to one another in this intermediate.



The second type of intermediate is formed if the nucleophile  $\text{Y}$  attacks through the middle of one of the triangular faces of the octahedron. As soon as  $\text{Y}$  starts approaching  $\text{M}$ , the outgoing ligand  $\text{X}$  starts moving towards the middle of another triangular face so that the octahedral wedge intermediate formed has both  $\text{X}$  and  $\text{Y}$  ligands in equivalent positions. The formation of an octahedral wedge intermediate requires minimum movement of ligands and the ligand- ligand repulsions are less than the repulsions in pentagonal bipyramidal intermediate. i.e it requires less energy than pentagonal bipyramidal intermediate. Therefore  $\text{S}_{\text{N}}2$  reactions generally proceed through an octahedral wedge intermediate.



**S<sub>N</sub>1 Vs S<sub>N</sub>2 mechanisms**

S<sub>N</sub>1 and S<sub>N</sub>2 mechanisms can be differentiated from each other by the following points.

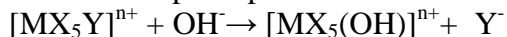
- 1) In S<sub>N</sub>1 process, the rate determining slow step is a metal ligand bond breaking step, and the coordination number of the complex is reduced from 6 to 5. In S<sub>N</sub>2 process, the rate determining step involves a metal ligand bond making step and the coordination number is increased to 7.
- 2) The rate of S<sub>N</sub>1 mechanism is first order with respect to MX<sub>6</sub>. i.e rate determining is unimolecular. On the other hand, the rate determining step for S<sub>N</sub>2 mechanism is bimolecular. i.e its reaction rate is second order: first order with respect to MX<sub>6</sub> and first order with respect to Y.

**SOLVOLYTIC REACTIONS**

Consider a substitution reaction of octahedral complex [MX<sub>6</sub>]<sup>n+</sup> in presence of a ligand Y<sup>-</sup> in aqueous medium. Since water also acts as a ligand and is much more abundant than Y<sup>-</sup>, aquation occurs called as solvolytic reaction.



The reaction in aqueous medium in which a water molecule replaces a coordinated ligand from the complex species is termed as aquation reaction or acid hydrolysis. The reaction in aqueous medium in which the anion of water molecule i.e OH<sup>-</sup> ion replaces a coordinated ligand from the complex species is termed as base hydrolysis.



Since some OH<sup>-</sup> ions are always present due to auto ionization of H<sub>2</sub>O, some [MX<sub>5</sub>(OH)]<sup>n+</sup> is always formed along with [MX<sub>5</sub>(H<sub>2</sub>O)]<sup>(n+1)+</sup> during the hydrolysis of [MX<sub>5</sub>Y]<sup>n+</sup> even in neutral aqueous medium.

**2.2.1 Labile & Inert Complex**

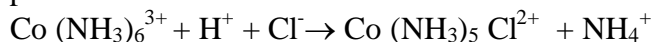
Many reactions require substitution, replacing one ligand by another. In the kinetic sense, it is more proper to call the complexes inert or labile rather than stable or unstable ones. The term labile is applied to very reactive complexes whereas less reactive complexes are called inert. Taube has defined labile as systems which undergo substitution reactions within 1 minute at room temperature and in 0.1 solutions. Labile Complexes are those undergoing substitution with t<sub>1/2</sub> < 1 minute. For eg. Cu(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> is a labile or fast reacting complex. When a solution containing this blue species is added to concentrated hydrochloric acid, the solution turns green rapidly as the solutions are mixed



NOTES

NOTES

The term inert is used for reactions that are either too slow to measure or slow enough to follow at ordinary conditions by conventional techniques. Eg : The complex  $\text{Co}(\text{NH}_3)_6^{3+}$  is an example of a relatively inert or slow – reacting complex. The complex must be heated in 6M hydrochloric acid for many hours to obtain any perceptible amount of the chloro complex.



Inert complexes undergoing substitution with  $t_{1/2} > 1$  minute. Inert doesn't mean unreactive and Inert doesn't mean thermodynamically stable. Inert does mean slow to react (also known as Robust). For example

$[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2+}$  = labile, but it is very thermodynamically stable

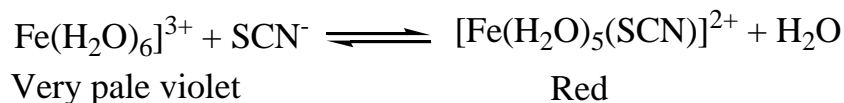
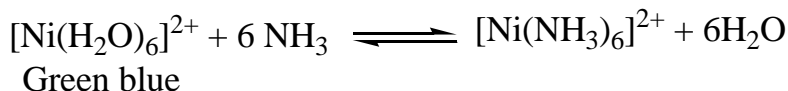
$[\text{Co}(\text{NH}_3)_6]^{3+}$  = inert, but thermodynamically unstable.

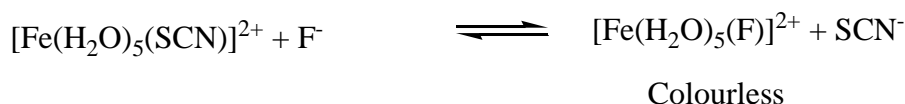
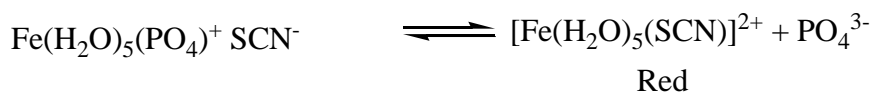
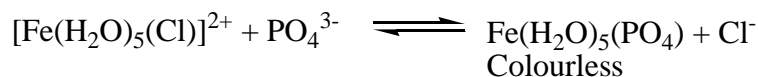
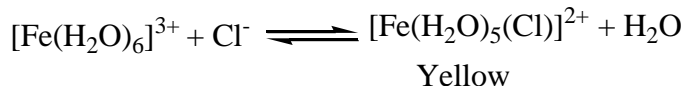
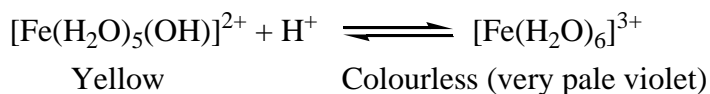
Inert complexes react slowly, so their products can be isolated and studied. Those with large LFSE,  $d^3$ , low spin  $d^4$ - $d^6$  are inert metal ions.

### 2.2.2 Factors affecting the labile/inert nature of complexes

1. The size of the central atom affects the ease with which ligands can be replaced. The smaller the central atom, more tightly the ligands are held and the more inert the complex is formed.
2. The higher the charge of the central ion, more inert the complex is.
3. The degree of lability or inertness of a transition – metal complex can be correlated with the d-electron configuration of the metal ion. If a complex contains electron in the antibonding  $e_g^*$  orbitals, the ligands are expected to be relatively weakly bound and are to be easily displaced. If a complex contains an empty  $t_{2g}$  orbital, the four lobes of that orbital correspond to directions from which an incoming ligand can approach the complex with little electrostatic repulsion. Therefore one concludes that a complex of a central ion with one or more  $e_g^*$  electrons or with fewer 3d electrons should be labile and that a complex with any other electronic configuration should be relatively inert.

A well-studied class of substitution reactions involves aqueous metal ions ( $[\text{M}(\text{H}_2\text{O})_m]^{n+}$ ) as reactants. These reactions can produce coloured products used to identify metal ions:





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Ligand substitution reactions involving  $[\text{M}(\text{H}_2\text{O})_m]^{n+}$  are rapid and generally form species that also undergo fast reactions. Addition of  $\text{HNO}_3$ ,  $\text{NaCl}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{KSCN}$ , and  $\text{NaF}$  successively to a solution of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  provides a classic example. The initial solution is yellow because of the presence of  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  and other Fe(III) complexes containing water and hydroxide ligands derived from the hydrolysis of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . Although the exact complexes formed and their equilibrium concentrations depend on the concentrations of the ions involved, these products are representative:

While the fate of these reactions is partially governed by the relative bond strengths between Fe(III) and the incoming and departing ligands, the examination of water exchange reactions, is insightful since the bonds broken and made during the substitution have essentially identical strengths. Water exchange rate constants vary widely as a function of the metal ion.

Rate constants like those in are known for many substitution reactions, and general trends in the speeds of these reactions have been correlated to the electronic configuration of the starting complex. The rate constants for water exchange differ by more than 13 orders of magnitude for  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ . It is also intriguing that  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  undergoes water exchange roughly 6 times faster than does  $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ ,



## NOTES

Complex	colour	electron config.	water exchange rate ( $s^{-1}$ , 25 °C)
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	violet	$(t_{2g})^1$	$1.8 \times 10^5$
$[\text{V}(\text{H}_2\text{O})_6]^{2+}$	violet	$(t_{2g})^3$	$8.7 \times 10^1$
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	yellow	$(t_{2g})^2$	$5.0 \times 10^2$
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	blue	$(t_{2g})^3(e_g)^1$	$1.2 \times 10^8$
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	violet	$(t_{2g})^3$	$2.4 \times 10^{-6}$
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	pale pink	$(t_{2g})^3(e_g)^2$	$2.1 \times 10^7$
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	blue-green	$(t_{2g})^4(e_g)^2$	$4.4 \times 10^6$
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	pale violet	$(t_{2g})^3(e_g)^2$	$1.6 \times 10^2$
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	pink	$(t_{2g})^5(e_g)^2$	$3.2 \times 10^6$
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	green	$(t_{2g})^6(e_g)^2$	$3.2 \times 10^4$
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	blue	$(t_{2g})^6(e_g)^3$	$4.4 \times 10^9$
$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$		$(t_{2g})^6(e_g)^4$	$>10^7$

Rate Constants for Water Exchange in  $[\text{M}(\text{H}_2\text{O})_6]^{n+}$ 

The reactions of Coordination Complexes may be divided into three classes:

- i) Substitution at the metal center
- ii) Reactions of the coordinated ligands
- iii) Oxidation and Reduction reactions at the metal center.

For the purposes of our discussion we will confine our discussion to (i) for substitution reactions on **Octahedral** and **Square Planar** complexes. We will only briefly discuss one specific reaction involving a coordinated ligand.

### 2.3 Ligand Displacement Reactions in Octahedral Complexes

#### 2.3.1 Hydrolysis in Octahedral Complexes:

These are the substitution reactions in which a ligand is replaced by a water molecule or by  $\text{OH}^-$  groups. The reactions in which an aqua complex is formed by the replacement of a ligand by  $\text{H}_2\text{O}$  molecule are called acidhydrolysis or aquation. The reactions in which a hydroxo complex is formed by the replacement of a ligand by  $\text{OH}^-$  group are called basehydrolysis.

#### Substitution in octahedral complexes

##### Intimate and stoichiometric mechanisms

Let us consider the following reaction:



where X is the leaving group and Y is the entering

These reactions can be explained in two ways: (i) intimate mechanism and (ii) stoichiometric mechanism

Dissociative and associative activations are known as intimate mechanism. In dissociative activation, breaking of the bond between the metal and the leaving group is important and in associative activation, bond formation between the metal and the entering ligand is important. The sequence of elementary steps from reactants to products is called stoichiometric mechanism.

#### Dissociative Reaction mechanism

- formation of an intermediate
- coordination number of the intermediate is lower than that in the starting complex
- corresponds to  $S_N^1$  mechanism for organic compounds

#### Associative Reaction Mechanism

- two-step pathway
- formation of an intermediate
- coordination number of the intermediate is higher than that in the starting complex.

#### Interchange Reaction Mechanism

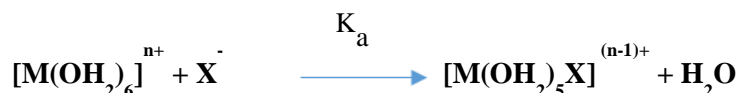
- Bond formation between the metal and entering group is concurrent with bond cleavage between the metal and the leaving group.
- corresponds to  $S_N^2$  reaction in organic chemistry
- no intermediate

Dissociative and associative mechanisms involve two-step pathways and an intermediate. An interchange mechanism is a concerted process where there is no intermediate.

### Intimate mechanism

#### 2.3.2 Anation in Octahedral Complexes

These are the reactions in which an aquo ligand ( $H_2O$  molecule) from an aquo complex is replaced from the co-ordination shell by some anion. It appears that the ligand displacement reaction like,



This type of reaction is important as its behavior indicates not only how new complexes are formed but also where coordinated water is replaced by  $X^-$ .



Generally two observations can be drawn:

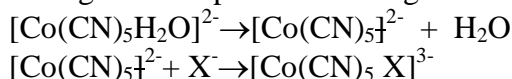
NOTES

NOTES

- For a given aqua ion, the rate of aquation show little dependence on the nature of “L”.
- The rate constant for aquation of a given aqua complex is almost the same as for H<sub>2</sub>O exchange.

An aquation reaction is the reverse of acid hydrolysis reaction (aquation). Kinetic studies of these reactions in aqueous solution show that these are bimolecular reactions with rate depends on the concentrations of the complex and Y. It always goes via the aquo complex, i.e. in two steps, the replacement of one ligand with water, then water is replaced with another ligand.

The following reaction proceeds through an intermediate Co(CN)<sub>5</sub><sup>2-</sup>

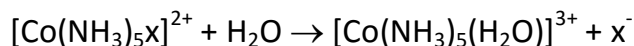


### 2.3.3 Aquation In Octahedral Complexes (AcidHydrolysis)

The replacement of ligand X by H<sub>2</sub>O is called aquation, where X is the labile ligand.



Occurs in neutral and acid solutions (pH < 3). Rate is independent of water molecule



The rate of such reactions are pH dependent and generally follow the rate law

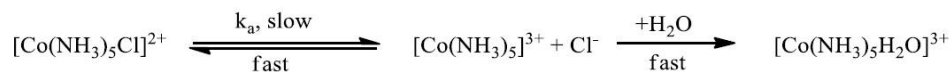
$$v = K_A[\text{L}_5\text{CoX}] + K_B[\text{L}_5\text{CoX}][\text{OH}^-]$$

In general, K<sub>B</sub> (for base hydrolysis) is some 10<sup>4</sup> times K<sub>A</sub> (for acid hydrolysis)

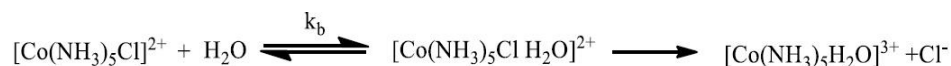
Thus the rate law does not tell us whether H<sub>2</sub>O is involved in the rate – determining step.

#### MECHANISMS OF ACID HYDROLYSIS

##### *Dissociative Mechanism*



##### *Associative Mechanism*



#### Factors affecting these reactions

##### Nature of the entering or leaving group



Let us consider the complex,  $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$ . The rates of aquation for this complex very much depends on the nature of the leaving group, X. As an example, for the complex,  $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]^{2+}$ ,  $k$  is of the order of  $10^{-5} \text{ s}^{-1}$ . When  $\text{I}^-$  is present instead of  $\text{NO}_3^-$ , the rate decreases and is of the order of  $10^{-6} \text{ s}^{-1}$  for the complex,  $[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$ . Both  $\text{NO}_3^-$  and  $\text{I}^-$  are leaving groups. The reaction slows down when the leaving group is  $\text{I}^-$ . In the case of the complex,  $[\text{Co}(\text{NH}_3)_5\text{F}]$ , the rate is the order of  $10^{-8}$ . That is, the reaction further slows down. Thus it is proved that M-X bond breaking is very much important in aquation reactions than bond formation.

Anation reactions do not depend very much on the nature of the entering group, Y-. Instead, it is very much dependent on the nature of the bond being broken. Experimental data show that the rate is of the order  $10^{-6}$  for the different entering groups (Y-),  $\text{N}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  or  $\text{NCS}^-$  clearly indicating that the rate is independent of the nature of the entering group.

### **Steric effects of inert (non-leaving) ligands**

When the non-leaving ligands are bulky, they will be crowding the central metal ion and hence, the incoming ligand will find it difficult to approach the central metal ion slowing down the rate of reaction taking place by associative mechanism. Instead, if the reaction takes place by dissociative mechanism, (that is, one ligand breaks first and then a new ligand approaches), the rate of the reaction will increase because the crowding around the metal ion is reduced.

### **Electronic effects of inert ligands**

If the existing ligand is capable of  $\pi$ -donation to the metal and stabilize the transition state, the reaction will be fast. When a reaction takes place by dissociative mechanism, when a ligand leaves, the metal becomes electron deficient. If there is a cis-ligand and if it is capable of donating electrons by forming  $\pi$ -bond with the electron deficient metal, then it stabilizes the transition state by lowering the energy and hence the reaction takes place faster.

### **Effect of charge**

The increase in positive charge decreases the rate of reaction following a dissociative mechanism because the breaking the metal-ligand bond becomes difficult.

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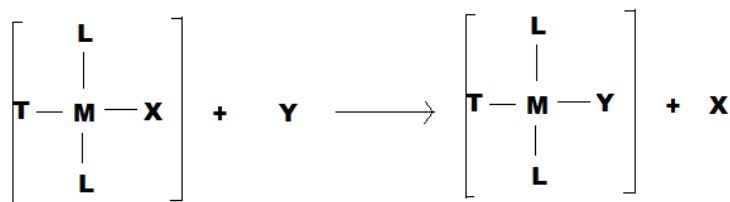
## **2.4 Substitution Reactions In Square Planar Complexes.**

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Square planar complexes with  $d^8$  configurations undergo substitution reactions of the type,

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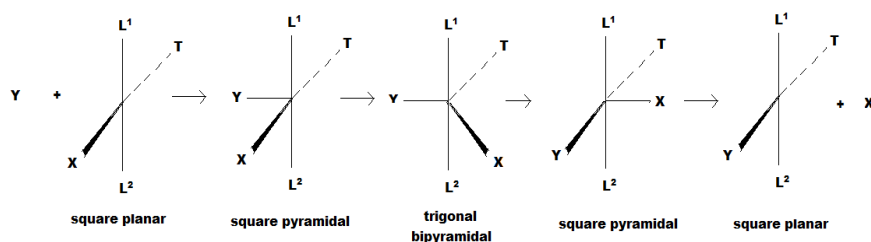
## NOTES



in which Y is the entering nucleophilic ligand, X is the leaving ligand and T is the ligand trans to X.

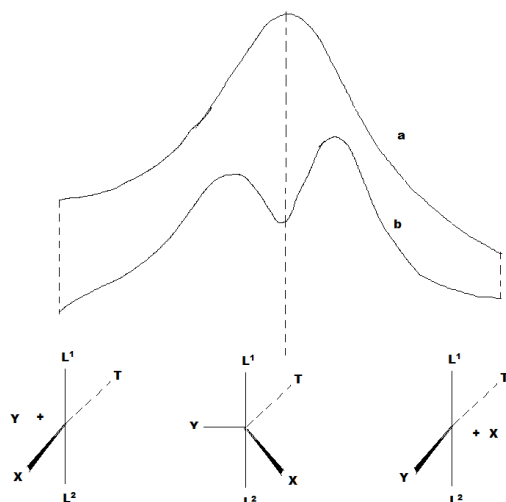
**Mechanism**

Pt(II) complexes are widely used for studying the mechanism and kinetics since the substitutions are comparatively slow and hence easier to study. From kinetic studies scientists have arrived at an associative  $S_N2$  mechanism for substitution reactions in square planar complexes. Consider a nucleophile Y attacking a  $d^8$  complex from either side of the plane. In addition to being attracted to the electron deficient metal centre, the ligand experiences repulsion from the filled metal d orbitals and from the bonding electrons. However, it coordinates to the metal through an empty  $p_z$  orbital to form a square pyramidal species, though electronic repulsions as well as steric factors slow the attack. Once formed, the square pyramidal species will undergo a transformation to a trigonal bipyramidal structure. It will have three ligands (Y, T and X) in its equatorial plane and two of the groups that were trans to each other in the original complex will occupy the axial positions. As X departs from the trigonal plane, the T-M-Y angle opens up and the geometry will pass through a square pyramid on its way to the square planar product.



The trigonal bipyramidal species that forms during the reaction may exist either as an activated complex or as a true intermediate. The distinction between the two depends on the lifetime of the species. The term activated complex refers to the configuration of the reactants and products at a peak in the reaction profile energy curve. i.e at the transition state. The term intermediate implies that a species has a detectable state.

lifetime (though short) and that it is at least somewhat more stable than any activated complexes.



Reaction coordinate/energy profile for a square planar substitution reaction having a) trigonal bipyramidal activated complex and b) a trigonal bipyramidal intermediate.

#### Evidences for the mechanism

The mechanism of substitution reactions of square planar complexes appears to be associative  $S_N2$  rather than dissociative  $S_N1$ . The evidences for this are,

1. In the case of square planar complexes of Ni(II), Pd(II) and Pt(II), five empty orbitals of comparable energy can be made available for bonding of which four are used up for bonding with ligands. The fifth orbital can easily accommodate electrons from the attacking ligand forming a five coordinate intermediate. i.e an associative  $S_N2$  mechanism.
2. There exists a parallelism between the reactivity of the square planar complexes of Ni(II), Pd(II) and Pt(II) complexes (Ni(II) > Pd(II) > Pt(II)) and their ease with which these expand their coordination no: which indicates the formation of an intermediate with a higher coordination no:.
3. The rates of aquation reactions of  $[\text{PtCl}_4]^{2-}$ ,  $[\text{PtCl}_3\text{NH}_3]^-$ , cis  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$  changes only by a factor of 2 whereas the charge of the complex changes from -2 to +1. This suggests that both bond breaking and bond making are important, which is characteristic of an associative  $S_N2$  mechanism.
4. Nature of the entering ligand greatly affects the rate of substitution in square planar complexes indicating that the entering ligand takes part in the rate determining step. This is another evidence for  $S_N2$  mechanism.

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5. The nature of the departing group, does not affect much the rate constants of these reactions indicating that the dissociative  $S_N1$  mechanism in which the departing ligand has a greater role is not operative.
6. It has been observed that substitution in Pt(II) square planar complexes occurs with retention of configuration. i.e  $cis \rightarrow cis$  and  $trans \rightarrow trans$ . This is in agreement with a trigonal bipyramidal intermediate. With a 3 coordinate intermediate (dissociative mechanism), the entering group can lead to both  $cis$  and  $trans$  isomers.
7. As the bulkiness of the ligands other than the entering and departing ligands increases, the reaction rate decreases, indicating an associative mechanism.

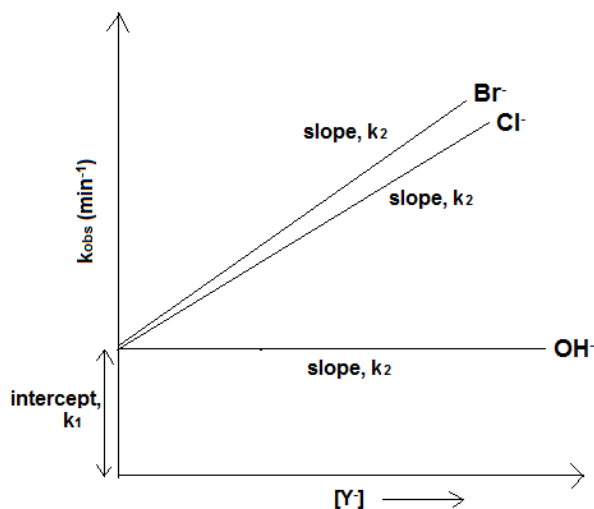
**Kinetics**

The kinetics of the reaction can be illustrated by the reaction,  $[PtA_3X]^{n+} + Y^- \rightarrow [PtA_3Y]^{n+} + X^-$  in the presence of water.

For this reaction, a two term rate law was found out.

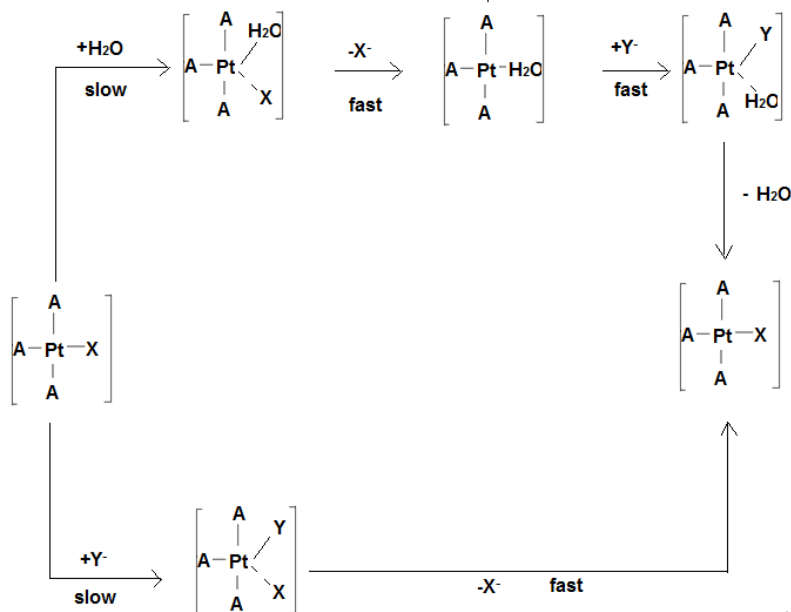
$$\text{Rate} = k_1[PtA_3X]^{n+} + k_2[PtA_3X]^{n+}[Y]$$

where  $k_1$ = first order rate constant for solvent controlled reaction and  $k_2$ = second order rate constant for reaction with  $Y^-$ . The analysis of the rate constants is made by conducting the reactions with a large excess of nucleophile,  $Y^-$ . Then the observed rate constant,  $k_{obs}$  is pseudo first order and is related to  $k_1$  and  $k_2$  as  $k_{obs} = k_1 + k_2[Y]$ . Thus for the same complex, linear plots of  $k_{obs}$  against different nucleophile concentration,  $[Y]$  should be obtained, having the same intercept  $k_1$  and different slopes,  $k_2$ .



Plots of  $k_{\text{obs}}$  for the reaction:  $[\text{Pt}(\text{dien})\text{Cl}]^+ + \text{Y}^- \rightarrow [\text{Pt}(\text{dien})\text{Y}]^+ + \text{Cl}^-$  against concentration of nucleophile,  $[\text{Y}^-]$

The obtained rate law indicates that the reaction of  $[\text{PtA}_3\text{X}]^{n+}$  with  $\text{Y}^-$  to yield  $[\text{PtA}_3\text{Y}]^{n+}$  is occurring by a two path mechanism, of which only one involves  $\text{Y}^-$  in the rate determining step.



The upper path is the solvent path (also called  $\text{Y}^-$ -independent path) and the lower path is the direct path (reagent path). In the solvent path, the solvent  $\text{H}_2\text{O}$  replaces  $\text{X}^-$  in a slow step. It is subsequently replaced by  $\text{Y}^-$  in a rapid step. Experiments show that  $\text{Y}^-$ -independent path is not an  $\text{S}_{\text{N}}1$  process, but is a direct  $\text{S}_{\text{N}}2$  displacement of leaving group by nucleophile in probably second order path while the solvent path gives pseudo first order kinetics.

The rate constant  $k_1$  is due to solvent path, while  $k_2$  is due to the direct displacement of the leaving group by nucleophile. Hence solvent path  $k_1$  can be designated as  $k_s$  and the direct displacement path  $k_2$  as  $k_Y$  so that

$$k_{\text{obs}} = k_s + k_Y[\text{Y}^-]$$

### Factors affecting the rates of substitution reactions in square planar complexes

1. Trans Effect (discussed later)
2. Effect of leaving group

For the reaction,  $[\text{Pt}(\text{dien})\text{X}]^+ + \text{py} \rightarrow [\text{Pt}(\text{dien})\text{py}]^{2+} + \text{X}^-$ , the rates of the reaction show that if the leaving group  $\text{X}^-$  is replaced by  $\text{NO}_3^-$ ,  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{N}_3^-$ ,  $\text{SCN}^-$ ,  $\text{NO}_2^-$  and  $\text{CN}^-$ , the rates decrease in the order,  $\text{NO}_3^- > \text{H}_2\text{O} > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{N}_3^- > \text{SCN}^- > \text{NO}_2^- > \text{CN}^-$

3. Solvent Effect

### NOTES

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Since in the solvent path, the solvent replaces directly, as the coordinating ability of the solvent increases, contribution made by this path to the overall rate of the reaction would also increase.

4. Effect of charge on the complex

The charge on the complex does not have appreciable effect on the rate of nucleophilic substitution of square planar complexes. For example, the rates of aquation reactions of  $[\text{PtCl}_4]^{2-}$ ,  $[\text{PtCl}_3\text{NH}_3]^-$ , cis  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$  changes only by a factor of 2 whereas the charge of the complex changes from -2 to +1.

In general there are two factors contributing to trans direction of substitution as described below:

**1) Trans influence:** This is a thermodynamic factor. Some ligands weaken the M-L bond trans to them in *the ground state* and thus by facilitating the substitution.

E.g. Strong  $\sigma$ - donors like  $\text{H}^-$ ,  $\text{I}^-$ ,  $\text{Me}^-$ ,  $\text{PR}_3$  etc., destabilize the M-L bond trans to themselves and thus by bringing the easy substitution of that ligand.

**2) Trans effect:** This is a kinetic factor and considered as true trans effect. It occurs by the stabilization of the transition state.

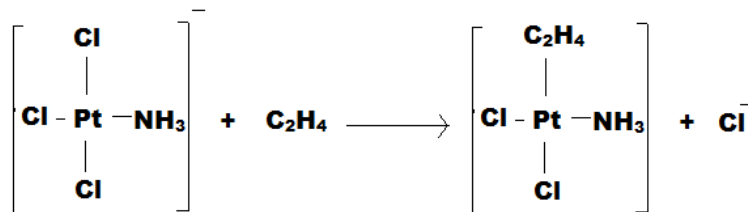
E.g. The strong  $\pi$ -acceptors like  $\text{NO}^+$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CO}$ ,  $\text{CN}^-$  etc., stabilize *the transition state* by accepting electron density that the incoming nucleophilic ligand donates to the metal through  $\pi$ -interaction.

Note: This is debatable since the  $\pi$ -interaction may increase the strength of M-L bond especially in the trans position.

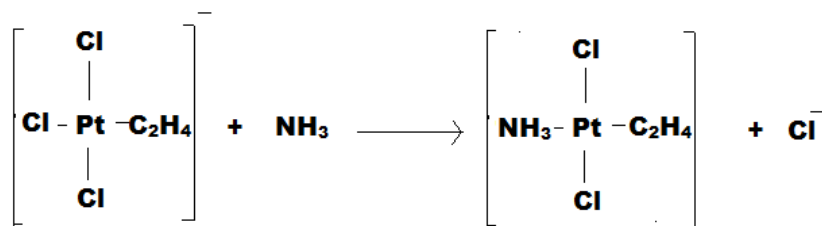
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### 2.4.1 Trans Effect

The ability of an attached group to direct substitution into a position trans to itself is called trans effect. Such a group has a marked influence (trans influence) on the rate of a reaction. For example, in the substitution reaction,



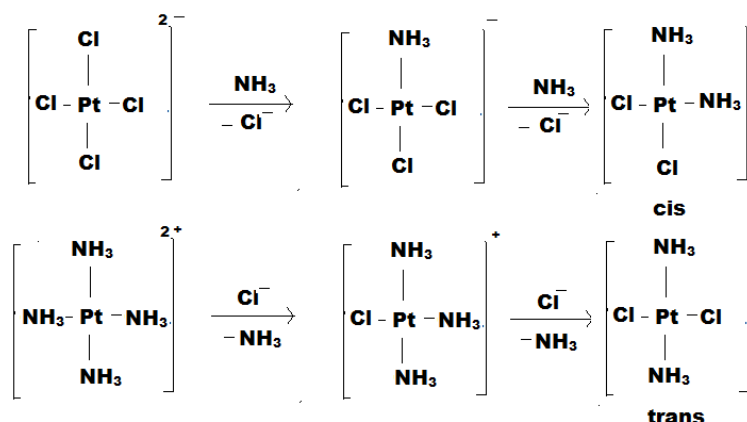
Since  $\text{Cl}^-$  has greater trans effect than  $\text{NH}_3$ , the  $\text{Cl}^-$  trans to  $\text{Cl}^-$  and not the one trans to  $\text{NH}_3$  is replaced by  $\text{C}_2\text{H}_4$ . Also,



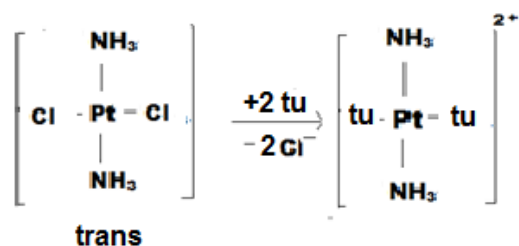
Since  $\text{C}_2\text{H}_4$  has greater trans effect than  $\text{Cl}^-$ , the  $\text{Cl}^-$  trans to  $\text{C}_2\text{H}_4$  and not the one which is trans to  $\text{Cl}^-$  is replaced by  $\text{NH}_3$ . The approximate ordering of ligands in a trans directing series is,

$\text{CN}^-$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{C}_2\text{H}_4$  >  $\text{PR}_3$ ,  $\text{H}^-$  >  $\text{CH}_3^-$ ,  $\text{C}_6\text{H}_5^-$ ,  $\text{SC}(\text{NH}_2)_2$ ,  $\text{SR}_2$  >  $\text{SO}_3\text{H}^-$  >  $\text{NO}_2^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$  >  $\text{Br}^-$  >  $\text{Cl}^-$  >  $\text{py}$  >  $\text{RNH}_2$ ,  $\text{NH}_3$  >  $\text{OH}^-$  >  $\text{H}_2\text{O}$

Trans effect is used in synthesizing certain specific complexes. For example cis and trans diamminedichloro Pt(II) complexes have been synthesized separately as,

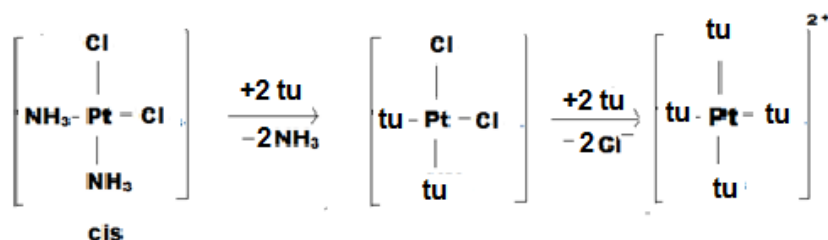


Another application of trans effect is in distinguishing cis and trans isomers of the formula  $[\text{PtCl}_2(\text{NH}_3)_2]$ . Addition of thiourea (tu) to the trans isomer results in the replacement of the two trans  $\text{Cl}^-$  ions. The reaction stops at this stage because the trans  $\text{NH}_3$  molecules do not labilise each other.



NOTES

But the addition of thiourea to the cis isomer results in the displacement of all the original ligands and gives  $[\text{Pt}(\text{tu})_4]^{2+}$  as the final product.



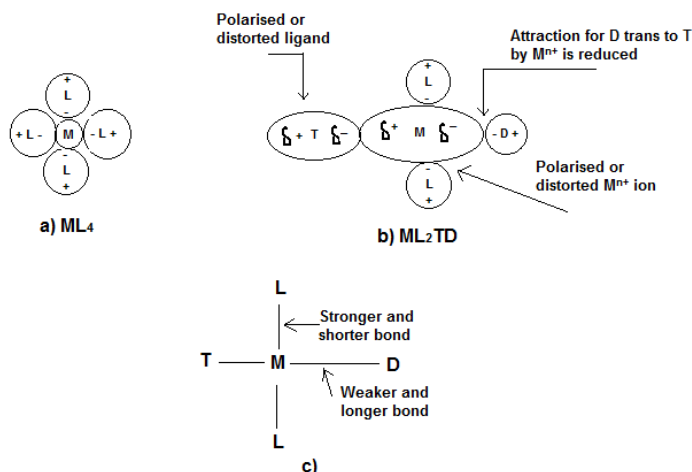
The trans effect of the ligands decreases in the order  $\text{tu} > \text{Cl}^- > \text{NH}_3$ . This method of differentiating the geometrical isomers is called the **Kurnakov effect**.

**Theories of trans effect**

Several theories have been proposed for the explanation of trans effect.

**1) Polarisation theory**

This is a thermodynamic approach. According to this theory, the primary positive charge of  $\text{M}^{n+}$  induces a dipole in all the four ligands. If all the four ligands are identical as in (a), then the dipoles induced by the metal ions cancel each other and the resultant dipole is zero. None of the four ligands show trans effect. But if the four ligands are not identical, then the induced dipoles do not cancel each other. The two L ligands which are similar and trans to each other balance each other. But the other two trans ligands T and D, which are not similar do not balance each other. T is large and has greater polarisability than D. Polarisation takes place in such a way that the positive charge of  $\text{M}^{n+}$  central ion at a point trans to T is reduced. Hence the attraction of D for  $\text{M}^{n+}$  is also reduced and the bond trans to T is weakened and hence lengthened. This facilitates the replacement of D by E (entering ligand) at a point trans to T.



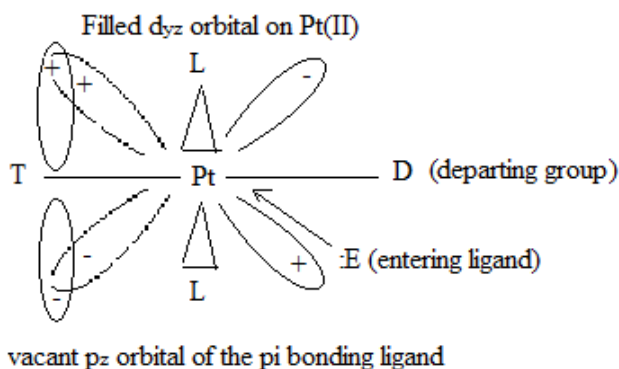


Evidences: 1) The theory predicts that trans effect is important only when the central metal ion itself is polarisable and large in size. Actually, trans effect is observed predominantly in Pt(II) complexes than in Pd(II) or Ni(II) complexes. 2) If the ligand T is highly polarisable in  $[\text{PtL}_2\text{TD}]$  complex, then Pt-D bond trans to T is longer than Pt-L bond cis to T. The complex  $[\text{Pt}(\text{C}_2\text{H}_4)\text{X}_3]$  type where  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{C}_2\text{H}_4$  has large trans effect. The Pt-Cl or Pt-Br bond trans to  $\text{C}_2\text{H}_4$  is longer than that cis to  $\text{C}_2\text{H}_4$ .

Limitations: The theory can well explain the ligands at the low end of the trans effect series like  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{NH}_3$  etc. However, this theory cannot explain the high trans effect of the  $\pi$  bonding ligands like  $\text{C}_2\text{H}_4$ ,  $\text{CN}^-$ ,  $\text{CO}$  etc which lie at the other end of trans effect series.

## 2) $\pi$ bonding theory

According to this theory, the vacant  $\pi$  or  $\pi^*$  orbitals of the  $\pi$  bonding ligands accept a pair of electrons from the filled d orbitals of the metal ( $d_{xz}$  or  $d_{yz}$ ) to form M-L  $\pi$  bond. In the case of Pt(II) square planar complex,  $[\text{PtL}_2\text{TD}]$  (T is the  $\pi$  bonding ligand, D is the departing ligand trans to T), the filled orbital of Pt(II) overlaps with the empty orbital of the ligand T to form M-T  $\pi$  bond. The formation of this  $\pi$  bond increases the electron density in the direction of T and diminishes it in the direction of the ligand trans to T. The electron shift towards T facilitates the approach of the entering ligand E with its lone pair in the direction of trans directors.



The formation of  $d_\pi - p_\pi$  bond between Pt(II) and the  $\pi$ -bonding ligand, T in the five coordinated transition complex.

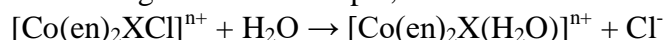
## 3) Molecular Orbital approach

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In this approach, there is the formation of a five coordinated intermediate with trigonal bipyramidal arrangement in which the more electronegative atoms occupy the axial positions. The loss of the ligand L from the triangular plane will take place from trans position to the least electronegative group T so that the entering group E is trans to T.

### Cis Effect

Certain ligands such as thiocyanate and hydroxide ions greatly accelerate the hydrolysis of a complex when they are cis to the leaving group as compared to the analogous reaction in which the leaving group is trans to these ligands. For example,



where X is a cis activating ligand like  $\text{OH}^-$ ,  $\text{SCN}^-$  etc. When  $\text{OH}^-$  is cis to the leaving  $\text{Cl}^-$ , the reaction rate is about ten times as great as that when it is in the trans position. The ligands that possess a strong cis effect are those that have unshared pairs of electrons in addition to the pair used in the sigma dative bond.

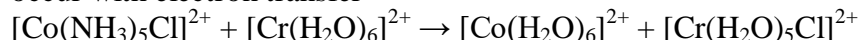
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## 2.5 Electron Transfer Reactions Or Redox Reactions

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Transition metals can undergo several oxidation- reduction reactions where in there is a change in oxidation state. There are formally two types of reactions of this type.

- Reactions involving simple electron transfer  
 $[\text{Fe}(\text{CN})_6]^{4-} + [\text{Ir}(\text{Cl})_6]^{2-} \rightarrow [\text{Fe}(\text{CN})_6]^{3-} + [\text{Ir}(\text{Cl})_6]^{3-}$
- Reactions that can be considered as atom transfer reactions that occur with electron transfer



Simple electron transfer reactions involving transition metal complexes in solutions are complicated by the fact that the oxidised and the reduced species are often metal ions surrounded by shields of ligands and solvating molecules. No heat change is associated with the reaction. The reactions can be between two metal ions or between single element in different oxidation states (self exchange reactions). The electron transfer can be broadly divided into two mechanistic classes called outer sphere mechanism and inner sphere mechanism.

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## 2.6 Check Your Progress

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1. What is meant by inert and labile complexes?
2. Give any two factors affecting inert and labile complexes?
3. Give some ligand displacement reactions in octahedral complexes.
4. Define the term Trans effect

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## 2.7 Answers to check your progress questions

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1. Transition metal complexes which undergo rapid substitution of one ligand for another are labile, whereas complexes in which substitution proceed slowly or not at all are inert. Labile means a relatively stable but reactive species whereas inert means unreactive. A compound in which metal-ligand bonds are easily broken is referred to as "labile." A labile complex has a very low activation energy for ligand substitution whereas an inert complex has a very high activation energy.

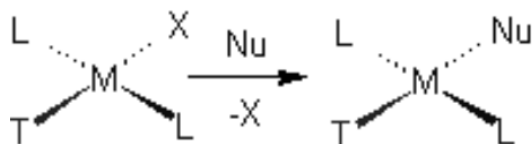
2. The factors affecting inert and labile complexes are

- Size of the central metal ion.
- Charge on the central metal ion.

3. The ligand displacement reactions in octahedral complexes are

- Aquation reaction (Acid hydrolysis)
- Anation reaction

4. The Trans effect can be defined as the effect of a ligand over rate of substitution of another ligand positioned Trans to it in the square planar complexes.




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## 2.8 Summary

- The rate at which one complex converts into another is governed by the height of the activation energy barrier that lies between them. Thermodynamically unstable complexes that survive for long periods (by convention, at least a minute) are commonly called 'inert' (non-labile) and the complexes that undergo more rapid equilibration (less than a minute) are called 'labile'.
- The reactions in which an aqua complex is formed by the replacement of a ligand by H<sub>2</sub>O molecule are called acid hydrolysis or aquation.
- The reactions in which a hydroxo complex is formed by the replacement of a ligand by OH<sup>-</sup> group are called base hydrolysis.
- An anation reaction is the reverse of acid hydrolysis reaction (aquation) in which the water molecule is replaced by any ligand.
- The spectator ligands T that are trans to the leaving group in square-planar complexes influence the rate of substitution. This phenomenon is called the trans effect. A strong  $\sigma$ -donor ligand or  $\pi$ -acceptor ligand greatly accelerates substitution of a ligand that lies in the trans position.

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## 2.9 Keywords

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Inert complex - Thermodynamically unstable complexes that survive for long periods

Labile complex - Thermodynamically stable complexes that survive for a very short period of time i.e., the half-life of the complex is less than a minute.

Trans effect - The Trans effect can be defined as the effect of a ligand over rate of substitution of another ligand positioned trans to it in the square planar complexes.

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### 2.10 Self-assessment questions and exercises

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1. Explain in detail about labile and inert complexes with example.
2. Give a brief review about ligand displacement reactions in octahedral complexes.
3. Give a brief overview about the ligand substitution reactions in square planar complexes.
4. Explain the trans effect.
5. What is meant by electron transfer reactions?

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### 2.11 Further readings

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1. Huheey, J.E., E.A. Keiter and R.L. Keiter. 2002. Inorganic Chemistry: Principles of Structure and Reactivity, 4th Edition. New York: HarperCollins Publishers.
2. Gary L. Miessler., Paul J. Fischer., Donald A. Tarr. Inorganic Chemistry, 5th ed : Pearson
3. Shriver and Atkins., Inorganic Chemistry, 5th ed : W. H. Freeman and Company New York.
4. Ajai Kumar., Coordination chemistry, 2<sup>nd</sup>ed :Aaryush educations.

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# UNIT- 3 COMPLEMENTARY AND NON-COMPLEMENTARY REACTIONS

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## Structure

- 3.0 Introduction
  - 3.1 Objectives
  - 3.2 Complementary and Non- Complementary reactions
  - 3.3 The classification of redox reactions
  - 3.4 Outer-sphere mechanism
  - 3.5 Inner-sphere mechanism
  - 3.6 Isomerization and racemization
  - 3.7 Template effect and synthesis of macrocyclic ligands
  - 3.8 Check Your Progress
  - 3.9 Answers to check your progress questions
  - 3.10 Summary
  - 3.11 Keywords
  - 3.12 Self-assessment questions and exercises
  - 3.13 Further readings
- 

## NOTES

### 3.0 Introduction

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Redox reactions in which the oxidant and reductant change their oxidation states by an equal number of units are called complementary reactions. Non- complementary reactions proceed through multistep, each step involving a single electron transfer in which the intermediates of unstable oxidation states are formed. Oxidation–reduction reactions of transition-metal complexes involve electron transfer from one complex to another. The two molecules may be connected by a common ligand through which the electron is transferred (inner-sphere reaction), or the exchange may occur between two separate coordination spheres (outer-sphere reaction). Electron transfer rates depend on the rate of ligand substitution within the reactants, the match of the reactant orbital energies, solvation of reactants, and the nature of the ligands.

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### 3.1 Objectives

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After going through this unit, you will be able to:

- Explain about the electron transfer mechanisms or classification of redox reactions.
- Understand about the inner sphere and outer sphere mechanisms.
- Understand the concept of racemization and isomerization in a precise manner.
- Explain about the template effect.
- Learn about the synthesis of macrocyclic ligands

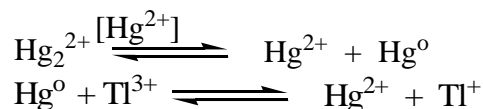
## NOTES

### 3.2 Complementary and Non-Complementary Reactions

Complementary reactions are reactions in which number of electrons gained by one species is equal to number of electrons lost by the other.

There are some elements that have stable oxidation states differing by two electrons, without a stable state in between. It has been shown that in the majority of these cases, if not in all, two – electron transfer occurs. Two electron transfers have been suggested for the oxidation of  $\text{Hg}_2^{2+}$  by  $\text{Tl}^{3+}$  and for the  $\text{Tl}^{3+} - \text{Tl}^+$  exchange reaction. In the latter case, the formation of  $\text{Tl}^{2+}$  is also possible, but the rate law for the former reaction.

$$K \frac{[\text{Hg}^{2+}]}{[\text{Tl}^{3+}]}$$

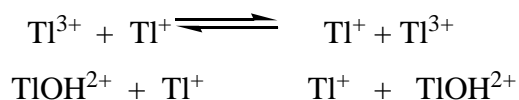


The exchange reaction of  $\text{Tl}^+ - \text{Tl}^{3+}$  which has been extensively studied is considered. Nevertheless, there is still not agreement as to whether the reaction occurs in a single two – electron transfer step or in a series of steps with unstable  $\text{Tl}^{2+}$  as an intermediate. The extreme sensitivity which  $\text{Tl}^{2+}$  shows that the exchange goes by this intermediate. The hydrolysis reaction,

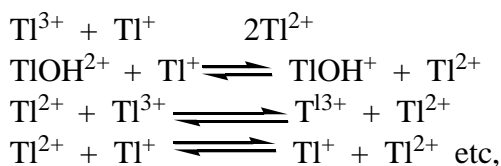


introduces a pH dependence for the rate.

The mechanism would be

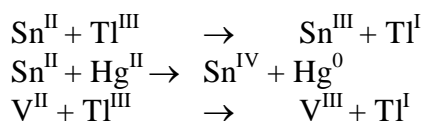


or



In the presence of other anions more complicated rate laws are found, indicating that two – electron transfers occurs through various  $\text{Tl}^{3+}$  complexes.

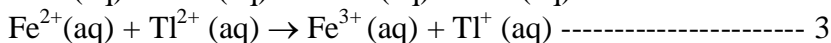
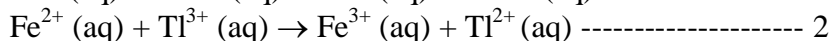
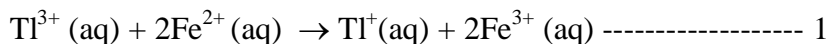
A number of other redox reactions also appear to proceed by two electron transfers, examples are,



All these reactions are complementary meaning that in the overall stoichiometry the oxidant gains and the reductant loses two electrons.

### **Non – Complementary Reactions**

Reactions of a non – complementary type, ie the number of electrons gained by one ion of one species is not equal to the number, lost by the other, must have multistep mechanisms, since ternary activated complexes are not likely and are not supported by an experimental evidence. This, in turn, means that some relatively unstable intermediate must be generated. For eg, the overall reaction of  $\text{Fe}^{2+}$  with  $\text{Tl}^{3+}$  (eqn1) might have as its initial step either a one – electron transfer to generate  $\text{Fe}^{3+}$  and the unstable  $\text{Tl}^{2+}$  or a two – electron transfer to generate  $\text{Tl}^+$  and the unstable  $\text{Fe}^{4+}$ . It has been reported that the addition of  $\text{Fe}^{3+}$  reduces the rate of reaction, but the addition of  $\text{Tl}^+$  is without effect. This indicates that the mechanism would be that of eqn2 and 3.



### **3.3 The Classification Of Redox Reactions**

In the 1950s, Henry Taube identified two mechanisms of redox reactions for metal complexes. One is the inner-sphere mechanism, which includes atom-transfer processes. In an inner-sphere mechanism, the coordination spheres of the reactants share a ligand temporarily and form a bridged transition state. The other is an outer-sphere mechanism, which includes many simple electron transfers. In an outer-sphere mechanism, the complexes come into contact without sharing a bridging ligand and the electron tunnels from one metal atom to the other.

### **3.4 Outer Sphere Electron-Transfer**

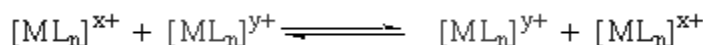
In principle outer sphere mechanism involves electron transfer from reductant to oxidant with the coordination shells or spheres of each staying intact. That is one reactant becomes involved in the outer or second coordination sphere of the other reactant and an electron flows from the reductant to oxidant. Such a mechanism is established when rapid electron transfer occurs between two substitution-inert complexes. No sharing of ligands and occurs when redox is faster than ligand substitution. The key to the mechanism is the matching of the energies of the reactants. i.e., the electron transfer should be between the same energies of reactants, so that electrons do not have to move (Frank-Condon Principle). In an outer-sphere mechanism, electron transfer occurs without a covalent linkage being formed between the reactants.

### **NOTES**

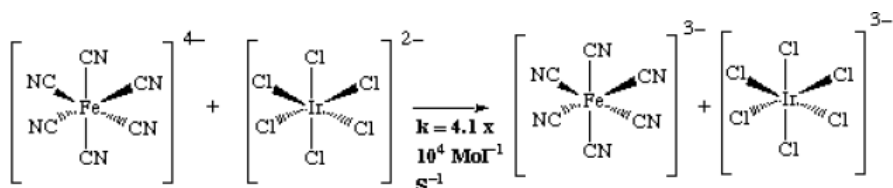
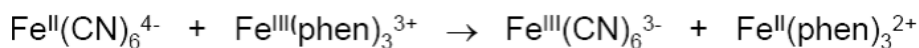
NOTES

To Enhance Outer-Sphere Electron Transfer Rates

1. Minimal solvent reorganisation (large ligands)
2. Small changes in M-L bond length
3. Good orbital overlap.



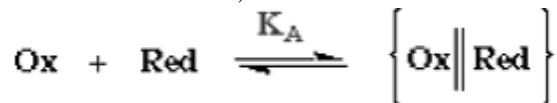
Two examples.



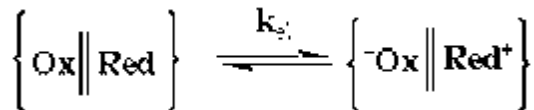
**Mechanism**

Electron transfer from the reductant to the oxidant, with the coordination shells or spheres of each staying intact. (One reactant becomes involved with outer sphere or second coordination sphere of the other reactant). Such reactions are observed in electron-transfer reactions of substitutionally inert complexes

**Step 1.** Formation of the Precursor Complex. This step is always considered to be fast,



**Step 2.** Chemical Activation and Electron Transfer. Chemical activation of the precursor and electron transfer and relaxation of the successor complex. Dissociation to the separated products.



Here  $k_{obs} = K_A k_{el}$ .

An outer sphere electron transfer rate of  $1.1 \text{ M}^{-1} \text{ sec}^{-1}$ , simply requires the transfer of electron from  $e_g$  orbital of one Co to the other.

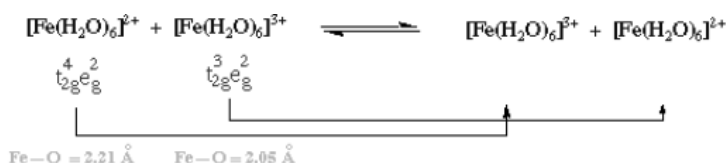




The reaction is very slow  $k = 10^{-9} \text{ M}^{-1} \text{ sec}^{-1}$  requires a change of spin multiplicity as well.



In addition the oxidant and reductant must structurally reorganise themselves before electrontransfer so that the energies of their transition states are equal.



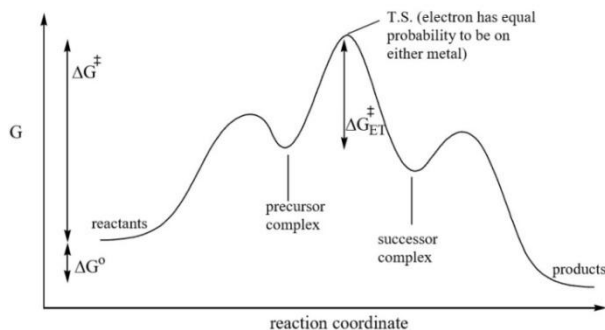
### Marcus-Hush equation $k_{12} = (k_{11} k_{22} K_{12} f_{12})$

Where  $k$  = rate constants,  $K_{12}$  = equilibrium constant for cross-reaction,

$$\log f = (\log K_{12})^2 / 4 \log k_{11} k_{22} / Z^2$$

$Z$  = effective collision frequency in solution

If the value of  $k_{12}$  calculated from the Marcus-Hush equation agrees with the experimental value, this provides strong evidence that the cross-reaction proceeds by an outer-sphere mechanism. If the Marcus-Hush equation is not fulfilled, this indicates that another mechanism (e.g. inner-sphere mechanism) is probably operative.

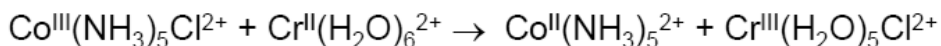


From thermodynamics, Driving force  $\Delta G^0 = -nF\Delta E^0$

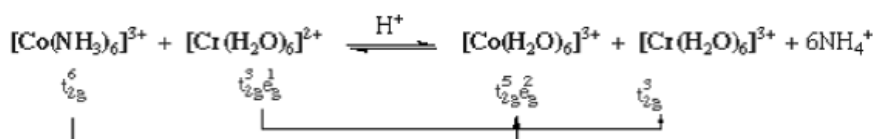
NOTES

### 3.5 Inner Sphere Electron Transfer

An inner sphere mechanism is one in which the reactant and oxidant share a ligand in their inner or primary coordination spheres the electron being transferred across a bridging group. In an inner-sphere mechanism, electron transfer occurs via a **covalently bound bridging ligand**.

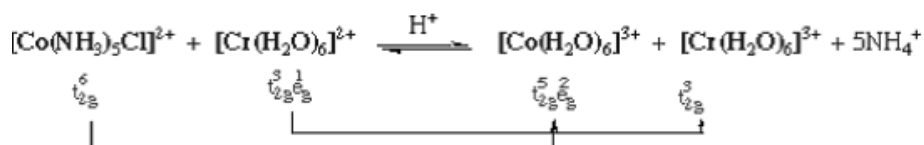


Reduction of hexaamminecobalt(<sup>3+</sup>) by hexaaquochromium(<sup>2+</sup>) occurs slowly ( $k = 10^{-3} \text{ M}^{-1}\text{sec}^{-1}$ ) by an outer sphere mechanism.



However, if one ammonia ligand on Co(III) is substituted by Cl<sup>-</sup>, reaction now occurs with a

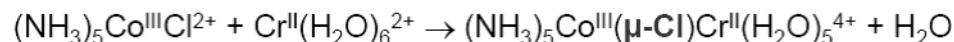
substantially greater rate ( $k = 6 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ )



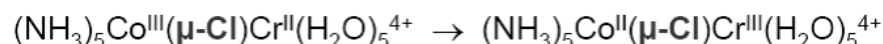
One reactant (usually the oxidant) possesses at least one ligand capable of binding simultaneously to two metal ions. The other reactant is substitutionally labile; i.e. one ligand must be replaced by the bridging ligand. Ligand transfer is not a requirement for inner sphere mechanism.

#### Steps and Rate Expression for the Inner Sphere Mechanism

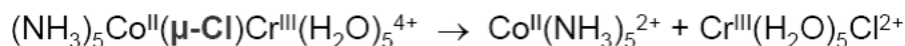
1. Formation of a precursor complex (bridge formation)



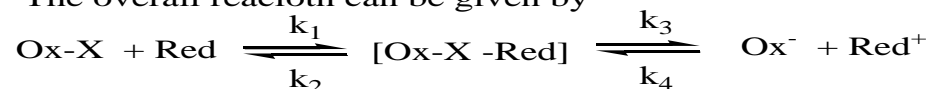
2. Activation of the precursor, and electron transfer via bridge



3. Dissociation to the separated products



The overall reaction can be given by



$$k_{\text{obs}} = \frac{k_1 k_3}{k_2 + k_3} [\text{Ox-X}][\text{Red}]$$

$k_1$  is rate limiting, formation of the precursor complex (usually substitution of the bridging ligand for  $H_2O$  on the Red complex).  $k_3$  is rate determining, electron transfer within the complex, or fission of the successor complex. Both extremes give 2 order kinetics. Most inner-sphere processes exhibit second order kinetics. Any of the three steps (bridge formation, electron transfer, bridge cleavage) can be rate-determining.

If the reaction is carried out in the presence of free  $^*Cl$ , labelled Cl is not incorporated into the product complex. The transferred Cl must have been bound to both metal centres during the reaction.

Common bridging ligands in inner-sphere mechanisms: halides,  $OH^-$ ,  $CN^-$ , NCS.

### 3.6 Isomerization And Racemization Of Octahedral Complexes

Tris-chelate complexes exist in enantiomeric configurations  $\Lambda$  and  $\Delta$  about the metal atom and when the chelating ligand is unsymmetrical, there are also geometrical isomers, cis and trans. Each geometrical isomer exists in enantiomeric forms; thus there are four different molecules.

In the case of tris complexes with symmetrical ligands, the process of inversion (interconversion of enantiomers) is of considerable interest. When the metal ions are of the inert type, it is possible to resolve the complex; then the process of racemization can be followed by measurement of optical rotation as a function of time. Possible paths of racemization fall into two broad classes, those without bond rupture and those with bond rupture.

There are two pathways without bond rupture that have been widely discussed. One is the trigonal, or Bailar twist and the other is rhombic, or Ray – Dutt Twist.

Twist processes are of course, not confined to chelate complexes. It has already been noted that some cis –  $M(CO)_4(PR_3)_2$  complexes are believed to isomerize in this way.

To illustrate the approach, let us consider some of the data and deductions for the system  $Co[CH_3COCHCOCH(CH_3)_2]_3$  measured in  $C_6H_5Cl$ . It was found that both the isomerization and the racemization are intramolecular processes, which occur at approximately the same rate and with activation energies that are identical within experimental errors. It thus appears likely that the two processes have the same transition state. This excludes the twist mechanism as the principal pathway for racemization.

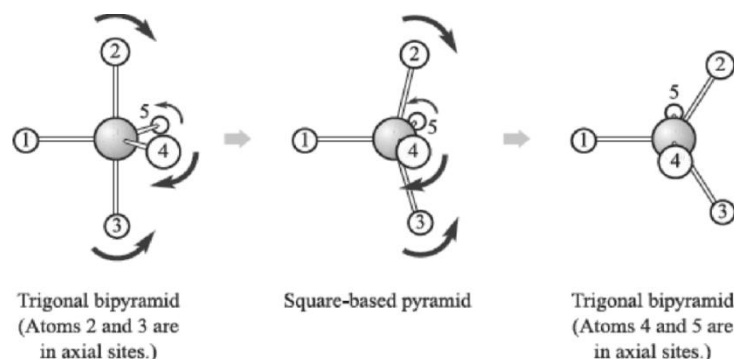
Moreover, it was found that isomerization occurs mainly with inversion of configuration. This imposes a considerable restriction on the acceptable pathways. Detailed consideration of the stereochemical consequences of the various dissociative pathways, and combinations thereof, leads to the conclusion that for this system the major pathway is through a *tdp* intermediate with the dangling ligand in an axial position.

### NOTES

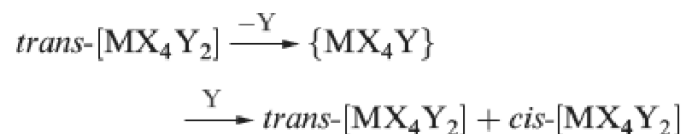
## NOTES

Evidence for the trigonal twist mechanism has been obtained in a few complexes in which the “bite” of the ligand is small, thus causing the ground state configuration to have a small twist angle  $\phi$ . A twist Mechanism is preferred in these cases because the structure is distorted away from an octahedral configuration of sulfur atoms towards a trigonal prismatic configuration. Thus the transition state, which is trigonal prismatic, is probably more energetically accessible than it would be if the complex had an essentially regular octahedral ground configuration. The three possible modes of intramolecular racemization of a trischelate complex.

**Example :** Octahedron is stereochemically rigid, loss of a ligand gives a 5-coordinate species which can undergo Berry pseudorotation.

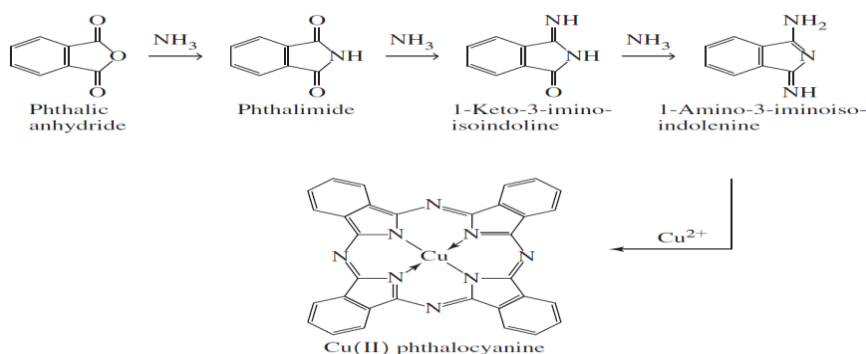


If the lifetime of the intermediate is long enough, it provides a mechanism for isomerization,



### 3.7 Template Effect and Synthesis of Macrocyclic Ligands

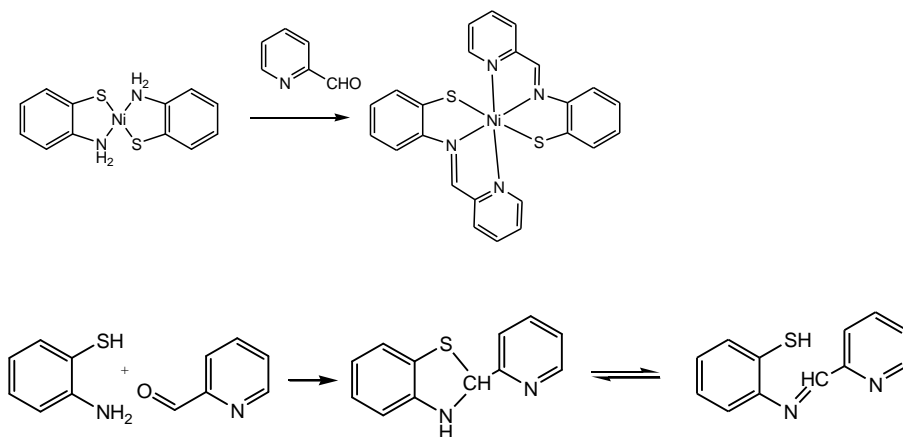
Template reactions are those in which formation of a complex places the ligands in the correct geometry for reaction. One of the earliest was for the formation of phthalocyanines..Phthalic acid and ammonia first form phthalimide, then 1-keto-3-iminoisoindoline, and then 1-amino-3-iminoisoindolenine. The cyclization reaction then occurs, probably with the assistance of the metal ion, which holds the chelated reactants in position. This is confirmed by the lack of cyclization in the absence of the metals. The essential feature of these reactions is the formation of the cyclic compound by coordination to a metal ion.



**NOTES**

**Phthalocyanine synthesis**

A major feature of template reactions is that formation of the complex brings the reactants into close proximity with the proper orientation for reaction. Complexation also changes the electronic structure to promote the reaction. Both features are important in all coordinated ligand reactions, but the orientation factor is more obvious because the final product has a structure determined by the coordination geometry.



Schiff Base Template Reaction.

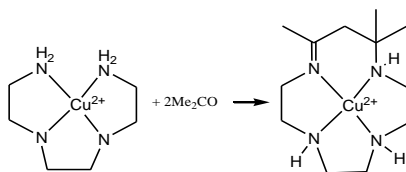
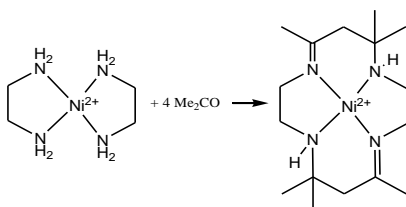
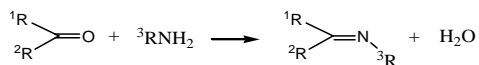
(a) The Ni(II)- *o*-aminothiophenol complex reacts with pyridine-1-carboxaldehyde to form the Schiff base complex.

(b) In the absence of the metal ion, the product is benzothiazoline; very little of the Schiff base is formed.

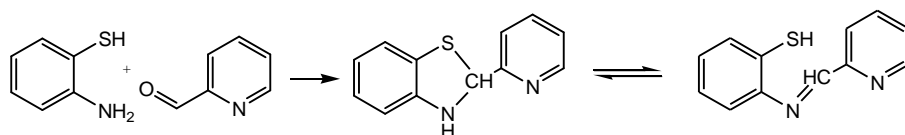
**Synthesis of Macrocyclic ligands**

Macrocycles that are saturated or have double bonds in only one part of the ring can be made independently or can be made by template synthesis where the presence of a metal ion controls the ligands synthesis. An important route is the Schiff base condensation reaction.

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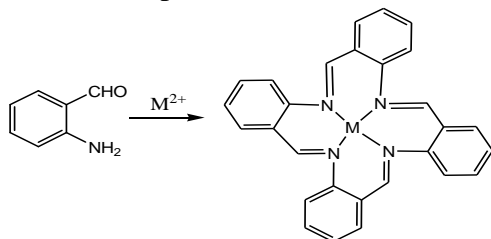


The condensation of O-aminothiophenol with pyridine – 1 – carboxaldehyde gives benzthiazoline in the absence of metal ions.

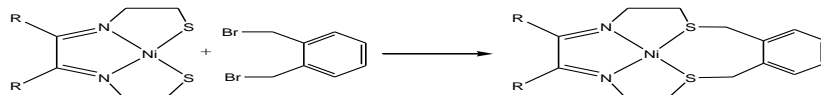
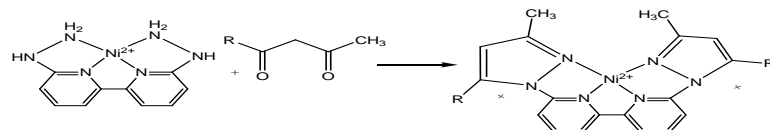


In the presence of metal ions, any small amount of the Schiff base that may be in equilibrium with benzthiazoline will be removed to give a metal complex

2. The self condensation of o-amino benzaldehyde in the presence of BF<sub>3</sub>.OEt<sub>2</sub> in acetic acid gives a macro cycle and when metal ion is also present, a complex is formed.



3. The reaction of chelate complexes as follows



### 3.8 Check Your Progress

1. What is meant by complementary reactions and non-complementary reactions?

2. Define Inner-sphere mechanism.
3. Define Outer-sphere mechanism.
4. What is meant by racemization and isomerization?
5. Define template effect.

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### 3.9 Answers To Check Your Progress Questions

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1. Redox reactions in which the oxidant and reductant change their oxidation states by an equal number of units are called complementary reactions. Non-complementary reactions proceed through multistep, each step involving a single electron transfer in which the intermediates of unstable oxidation states are formed.

2. In an inner-sphere redox reaction a ligand is shared to form a transition state; in an outer-sphere redox reaction there is no bridging ligand between the reacting species. The rate-determining step of an inner-sphere redox reaction may be any one of the component processes, but a common one is electron transfer.

3. An outer-sphere redox reaction involves electron tunnelling between two reactants without any major disturbance of their covalent bonding or inner coordination spheres; the rate constant depends on the electronic and geometrical structures of the reacting species and on the Gibbs energy of reaction.

4. Isomerization reactions are closely related to substitution reactions; indeed, a major pathway for isomerization is often via substitution. Isomerization of a complex can take place by mechanisms that involve substitution, bond cleavage, and reformation, or twisting.

5. Template reactions are those in which formation of a complex places the ligands in the correct geometry for reaction. A major feature of template reactions is that formation of the complex brings the reactants into close proximity with the proper orientation for reaction. Complexation also changes the electronic structure to promote the reaction. Both features are important in all coordinated ligand reactions, but the orientation factor is more obvious because the final product has a structure determined by the coordination geometry.

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### 3.9 Summary

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- Redox reactions in which the oxidant and reductant change their oxidation states by an equal number of units are called complementary reactions.
- Non-complementary reactions proceed through multistep, each step involving a single electron transfer in which the intermediates of unstable oxidation states are formed.
- In an inner-sphere redox reaction a ligand is shared to form a transition state; in an outer-sphere redox reaction there is no bridging ligand between the reacting species.
- An outer-sphere redox reaction involves electron tunnelling between two reactants without any major disturbance of their

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covalent bonding or inner coordination spheres; the rate constant depends on the electronic and geometrical structures of the reacting species and on the Gibbs energy of reaction.

- Isomerization reactions are closely related to substitution reactions; indeed, a major pathway for isomerization is often via substitution.
- Template reactions are those in which formation of a complex places the ligands in the correct geometry for reaction. A major feature of template reactions is that formation of the complex brings the reactants into close proximity with the proper orientation for reaction.

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### 3.10 Keywords

- Complementary reactions - Redox reactions in which the oxidant & reductant change their oxidation states by an equal number of units.
- Outer-sphere mechanism - Reaction involves electron tunnelling between two reactants without any major disturbance of their covalent bonding or inner coordination spheres.
- Template effect - A metal ion can be used to assemble a group of ligands which undergoes a reaction among themselves to form a *macrocyclic ligand*, acyclic molecule with several donor atoms. This phenomenon is known as template effect.

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### 3.11 Self-Assessment Questions and Exercises

1. Give the difference between complementary reactions and non-complementary reactions.
2. Give a brief review about inner-sphere mechanism.
3. Give a brief review about outer-sphere mechanism.
4. Explain about isomerization reactions.
5. What is template effect?
6. Give a detailed picture about the synthesis of macrocyclic ligands.

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### 3.12 Further Readings

1. Huheey, J.E., E.A. Keiter and R.L. Keiter. 2002. Inorganic Chemistry: Principles of Structure and Reactivity, 4th Edition. New York: HarperCollins Publishers.
2. Gary L. Miessler., Paul J. Fischer., Donald A. Tarr. Inorganic Chemistry, 5th edition : Pearson
3. Shriver and Atkins., Inorganic Chemistry, 5th ed : W. H. Freeman and Company New York.
4. Cotton, F.A. and G. Wilkinson. 1988. Advanced Inorganic Chemistry, 5th Edition. New Jersey: Wiley Eastern.
5. Ajai kumar.2014, Coordination chemistry, 2<sup>nd</sup> edition: Aaryush educations.



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# BLOCK 2 SPECTRAL PROPERTIES OF COMPLEXES, SPINELS, CAGES, CLUSTERS AND BORANES

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Spectral properties of complexes

## UNIT 4 SPECTRAL PROPERTIES OF COMPLEXES

### Structure

- 4.0 Introduction
- 4.1 Objectives
- 4.2 Types of spectra
  - 4.2.1 Electronic absorption spectroscopy principles
  - 4.2.2 Russel-Saunders or L-S coupling
  - 4.2.3 Term state for d ions in Octahedral complexes
  - 4.2.4 Number of microstates
  - 4.2.5 Selection rule
  - 4.2.6 Mechanism of breakdown of selection rules
- 4.3 Splitting of energy states
  - 4.3.1 Energy level diagram
  - 4.3.2 Orgeldiagrams
  - 4.3.3 Inter-electronic repulsion parameters
  - 4.3.4 Racah parameters
  - 4.3.5 Tanabe –Sugano diagrams
- 4.4 Check your progress questions
- 4.5 Answers to check your progress questions
- 4.6 Summary
- 4.7 Keywords
- 4.8 Self-assessment questions and exercises
- 4.9 Further readings

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### 4.0 Introduction

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#### Electronic spectra of coordination compounds

Explanation of electronic spectra of transition metal complexes, could become possible only after developments of CFT. Which considered splitting of a d-atomic orbitals of transition metal ions, after complex - formation. This splitting, and hence splitting energy was considered responsible for the visible and ultra-violet spectra of transition metal complexes. However, the detailed explanation of transition metal complex-spectra is obtained, with the knowledge of molecular orbitals of metal complexes. The bands obtained in the electronic spectra of transition metal complexes are considered to be due to transition of electrons from one d atomic orbital to the other d orbital (d – d transitions).

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Many transition metal complexes are colored. This is due to transitions of electrons between the molecular orbitals that are formed largely by the d orbitals on the metal. Many transitions are in the visible range, with the color of the complex taking on the complementary color of the frequency or frequencies absorbed.

Absorption of light occurs when electrons are promoted from lower to higher energy states. An interaction between electrons causes more than one peak in the UV/Vis spectra of these complexes. The electrons are not independent of each other, and the spin angular momenta and orbital angular momenta interact.

Absorption of radiation leading to electronic transitions within a molecule or complex. The UV/Vis spectra are used to determine the value of  $\Delta_o$  for the complex. The spectra arise from electronic transitions between the  $t_{2g}$  and  $e_g$  set of molecular orbitals. Electron-electron interactions can greatly complicate the spectra. The interaction of orbital angular momenta ( $m_l$  values) and spin angular momenta ( $m_s$  values) is called Russell-Saunders or LS coupling. The lower transition metals (4d and 5d) undergo further coupling (called j-j coupling or spin-orbit coupling).

Absorption bands in electronic spectra are usually broad, and occur much more rapidly than molecular vibrations. As a result, the spectra represent a “snapshot” of molecules in various vibrational and rotational states.

Extinction coefficients will range from  $<1$  up to  $50,000 \text{ M}^{-1}\text{cm}^{-1}$  depending upon the type of electronic transition and whether it is permitted based on selection rules.

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#### 4.1 Objectives

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The main aim of this unit is to see how to analyse the electronic spectra of transition metal complexes, and hence to enrich our understanding of their bonding. After going through this unit you should be able to :

- describe spectroscopic ground states and their correlation;
  - calculate values of  $dq$ ,  $B$  and  $B'$  parameter considering the bands obtained in the spectra of the complex;
  - explain charge transfer spectra (both the metal to ligand, and ligand to metal charge transfer); and
  - Explain the microstate and term symbol
  - Explain the selection rule for electronic spectrum
  - Draw the Orgel and Tanabe –Sugano diagrams
- 

#### 4.2 Types of spectra

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Spectra are broadly classified into two groups

(i) Emission spectra and (ii) Absorption spectra

**i. Emission spectra:** Emission spectra are of three kinds

- (a) continuous spectra,
- (b) bandspectra and
- (c) line spectra.

**Continuous spectra:** Solids like iron or carbon emit continuous spectra when they are heated until they glow. Continuous spectrum is due to the thermal excitation of the molecules of the substance.

**Band spectra:** The band spectrum consists of a number of bands of different colours separated by dark regions. The bands are sharply defined at one edge called the head of the band and shade off gradually at the other edge. Band spectrum is emitted by substances in the molecular state when the thermal excitement of the substance is not quite sufficient to break the molecules into continuous atoms.

**Line spectra:** A line spectrum consists of bright lines in different regions of the visible spectrum against a dark background. All the lines do not have the same intensity. The number of lines, their nature and arrangement depends on the nature of the substance excited.

Line spectra are emitted by vapours of elements. No two elements do ever produce similar line spectra.

**ii. Absorption spectra:** When a substance is placed between a light source and a spectrometer, the substance absorbs certain part of the spectrum. This spectrum is called the absorption spectrum of the substance.

#### **Beer-Lambert Law**

The absorption at any wavelength obeys the Beer-Lambert Law:

$A = \log(I_0/I) = \epsilon cb$ ; where  $A$  = absorbance,  $I_0$  = incident light intensity

$I$  = transmitted light intensity,  $\epsilon$  = molar absorptivity at a particular wavelength

$c$  = molar concentration,  $b$  = path length through the absorbing medium

It should be mentioned that not all bands in the visible and ultraviolet spectra of transition metal complexes are d – d spectra. Some arise from electron transfer (may be in either direction) between metal ion and ligand. Such charge transfer spectra are of high intensity and usually occur at somewhat higher frequency than d-d transition. Generally, electronic spectra are of four types :

#### **The d-d or Ligand Field Spectra**

This occurs in the near infrared, visible, and ultraviolet regions. Lower frequencies are not accessible experimentally; the higher frequencies though accessible, are overshadowed by the charge transfer and the interligand transitions. This limits the study of the d-d transitions to only the visible regions of spectrum. These transitions are considered to be totally within the metal ion in the CFT model, though some ligand contribution is included in LFT or ACFT models. MOT treats these transitions as arising due to the excitation of the electron from the  $t_{2g}$  level to  $e_g^*$  levels belonging largely to the metal itself.

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**Ligand-to-Metal Charge Transfer Bands**

When the electron transition takes place from a MO located primarily on the ligand (M – L bonding  $\sigma$  or  $\pi$  orbitals) to a nonbonding or antibonding MO located primarily on the metal atom, the ligand-to-metal charge transfer bands are observed. These cannot be explained by CFT and represent the tendency of ligands to reduce the metal ion. The semiempirical MOT is adequate for explaining it.

**Metal-to-Ligand Charge Transfer Bands**

These involve the transition of electron from an antibonding or nonbonding orbital, concentrated on the metal atom, to the antibonding orbital located primarily on the ligand, and measures the tendency of the metal ion to reduce the ligand. These bands are observed generally for the metal ions in low oxidation states in the ultraviolet region, but are seen many times to tail into the visible regions, e.g.  $[\text{Fe}(\text{dipy})_3]^{2+}$ .

**The Intraligand Transitions**

When an electron transition takes place from one ligand orbital to another ligand orbital, the intraligand transitions are observed. They are found in the ultraviolet regions and can be readily separated from the equally intense M – L charge transfer bands as they are not affected much by the other ligands. They, however, depend on the M – L bond strength.

**4.2.1 Electronic absorption spectroscopy principles**

***Franck-Condon Principle:*** Electronic transitions occur in a very short time (about 10-15sec.) and hence the atoms in a molecule do not have time to change position appreciably during electronic transition. So the molecule will find itself with the same molecular configuration and hence the vibrational kinetic energy in the excited state remains the same as it had in the ground state at the moment of absorption.

***Electronic transitions between vibrational states:*** Frequently, transitions occur from the ground vibrational level of the ground electronic state to many different vibrational levels of particular excited electronic states. Such transitions may give rise to vibrational fine structure in the main peak of the electronic transition. Since all the molecules are present in the ground vibrational level, nearly all transitions that give rise to a peak in the absorption spectrum will arise from the ground electronic state. If the different excited vibrational levels are represented as  $\nu_1$ ,  $\nu_2$ , etc., and the ground state as  $\nu_0$ , the fine structure in the main peak of the spectrum is assigned to  $\nu_0 \rightarrow \nu_0$ ,  $\nu_0 \rightarrow \nu_1$ ,  $\nu_0 \rightarrow \nu_2$  etc., vibrational states. The  $\nu_0 \rightarrow \nu_0$  transition is the lowest energy (longest wave length) transition.

Electronic transitions occur between split 'd' levels of the central atom giving rise to so called d-d or ligand field spectra.

The spectral region where these occur spans the near

Ultraviolet (UV)	Visible (Vis)	Near infrared (NIR)
50,000 - 26300	26300 - 12800	12800 - 5000 $\text{cm}^{-1}$
200 - 380	380 - 780	780 - 2000 nm

### 4.2.2 Russel-Saunders or L-S coupling

An orbiting electronic charge produces magnetic field perpendicular to the plane of the orbit. Hence the orbital angular momentum and spin angular momentum have corresponding magnetic vectors. As a result, both of these momenta couple magnetically to give rise to total orbital angular momentum. There are two schemes of coupling: Russel-Saunders or L-S coupling and j-j coupling.

### 4.2.3 Term state for d ions in octahedral complexes

In quantum mechanics, the **term symbol** is an abbreviated description of the (total) angular momentum quantum numbers in a multi-electron atom. Each energy level of an atom with a given electron configuration is described by not only the electron configuration but also its own term symbol, as the energy level also depends on the total angular momentum including spin. The usual atomic term symbols assume LS coupling (also known as Russell–Saunders coupling or spin–orbit coupling). The ground state term symbol is predicted by Hund's rules.

Atomic states are then well described by term symbols of the

$$\text{form } {}^{2S+1}L_J$$

$S$  is the total spin quantum number.  $J$  is the total angular momentum quantum number.  $2S + 1$  is the spin multiplicity, which represents the number of possible states of  $J$  for a given  $L$  and  $S$ , provided that  $L \geq S$ . (If  $L < S$ , the maximum number of possible  $J$  is  $2L + 1$ ).

This is easily proven by using  $J_{\max} = L + S$  and  $J_{\min} = |L - S|$ , so that the number of possible  $J$  with given  $L$  and  $S$  is simply  $J_{\max} - J_{\min} + 1$  as  $J$  varies in unit steps.  $L$  is the total orbital quantum number in spectroscopic notation. The first 17 symbols of  $L$  are:

$$L = 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ 8 \ 9 \ 10 \ 11 \ 12 \ 13 \ 14 \ 15 \ 16 \ \dots$$

S P D F G H I K L M N O Q R T U V (continued  
alphabetically)

The nomenclature (S, P, D, F) is derived from the characteristics of the spectroscopic lines corresponding to (s, p, d, f) orbitals: sharp, principal, diffuse, and fundamental.

The rules governing the term symbol for the ground state according to L-S coupling scheme are given below:

1. The spin multiplicity is maximized i.e., the electrons occupy degenerate orbitals so as to retain parallel spins as long as possible (Hund's rule).

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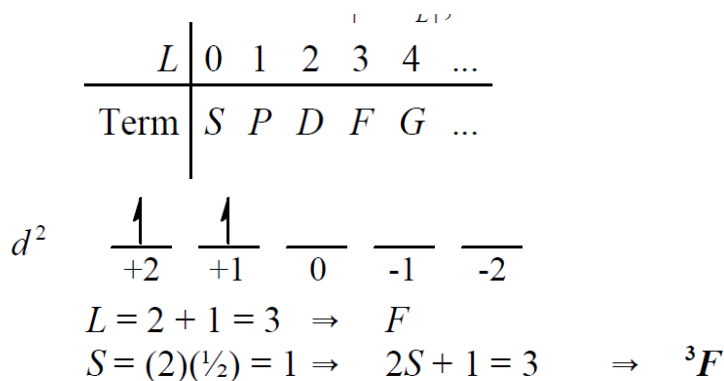
2. The orbital angular momentum is also maximized i.e., the orbitals are filled with highest positive  $m$  values first.

3. If the sub-shell is less than half-filled,  $J = L - S$  and if the sub-shell is more than half-filled,  $J = L + S$ .

It should be noted that  $S$  is used to represent two things-

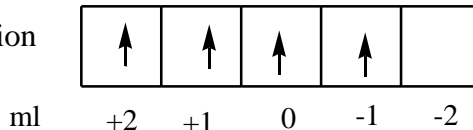
(a) total spin angular momentum and (b) total angular momentum when  $L = 0$ .

The above rules are illustrated with examples.



$$J = 3 - 1 = 2; {}^3F_2$$

For  $d^4$  configuration

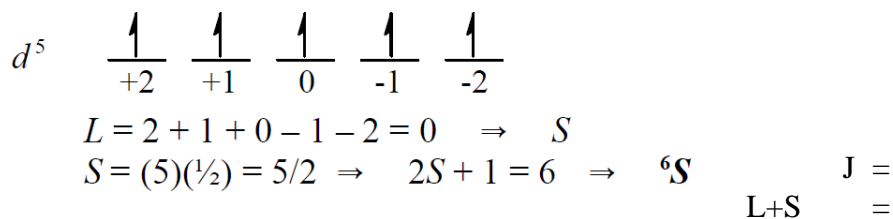


Hence,  $L = 3 - 1 = 2$  i.e.,  $D$ ;

$$S = 2; 2S + 1 = 5;$$

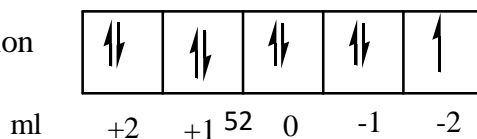
$$\text{and } J = L - S = 2 - 2 = 0;$$

**Term symbol =  ${}^5D_0$**



$$0 + 5/2; {}^6S_{5/2}$$

For  $d^9$  configuration



Hence,  $L = +2+2+1+1+0+0-1-1-2 = 2$  i.e., D ;

$S = 1/2$  ;  $2S+1 = 2$  ;

and  $J = L + S = 3/2$  ; Term symbol =  ${}^2D_{5/2}$

$d^n$	Term	$d^n$	Term
$d^0$	${}^1S_0$	$d^{10}$	${}^1S_0$
$d^1$	${}^2D_{3/2}$	$d^9$	${}^2D_{5/2}$
$d^2$	${}^3F_2$	$d^8$	${}^3F_4$
$d^4$	${}^5D_0$	$d^6$	${}^5D_4$
$d^5$	${}^6S_{5/2}$		

${}^1S_0$  (singlet S nought);  ${}^2S_{1/2}$  (doublet S one-half);  ${}^3P_2$  (triplet P two );  
 ${}^5I_8$ (quintet I eight).

d electrons are only of importance in deciding term symbols of transitionmetals.

#### 4.2.4 Number of microstates

The electrons may be filled in orbitals by different arrangements since the orbitals havedifferent  $m_l$  values and electrons may also occupy singly or get paired. Each different typeof electronic arrangement gives rise to a microstate. Thus each electronic configuration willhave a fixed number of microstates. The numbers of microstates for  $p^2$  configuration aregiven in Table (for both excited and ground states).

The number of microstates possible for any electronic configuration may be calculated from

the formula, Number of microstates =  $n! / r! (n - r)!$

Where n is the twice the number of orbitals, r is the number of electrons and !is the factorial.

For  $p^2$  configuration,  $n = 3 \times 2 = 6$ ;  $r = 2$ ;  $n - r = 4$

$6! = 6 \times 5 \times 4 \times 3 \times 2 \times 1 = 720$ ;  $2! = 2 \times 1 = 2$ ;  $4! = 4 \times 3 \times 2 \times 1 = 24$

Substituting in the formula, the number of microstates is 15.

$m_l$		↑	↑		↓	↓		↓	↓		↑		↑↓	
0	↑		↑	↓		↓	↓		↑	↑	↑	↓	↑↓	
+1	↑	↑		↓	↓		↑	↑		↓	↓		↑↓	
ML	+1	0	-1	+1	0	-1	+1	0	-1	+1	+1	-1	+2	0

Number of microstates for  $p^2$  configuraion

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Similarly for a  $d^2$  configuration, the number of microstates is given by  $10! / 2! (10 - 2)!$

$$\frac{10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{2 \times 1 (8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1)} = 45$$

Thus a  $d^2$  configuration will have 45 microstates. Microstates of different  $d^n$  configuration are given in Table.

Microstates of different  $dn$  configuration

$d^n$ configuration	$d^1$	$d^2, d^8$	$d^3, d^7$	$d^4, d^6$	$d^5$	$d^{10}$
No. of microstates	10	45	120	210	252	1

#### 4.2.5 Selection rule

The magnitude of the extinction coefficient (intensity of the colour) is affected by two quantum mechanical *selection rules* that state whether transitions are *allowed* (intense colour) or *forbidden* (pale colour).

- ❖ **Spin selection rule**—the number of unpaired electrons in a molecule cannot change upon excitation (*i.e.*, an electron “spin-flip” is forbidden).

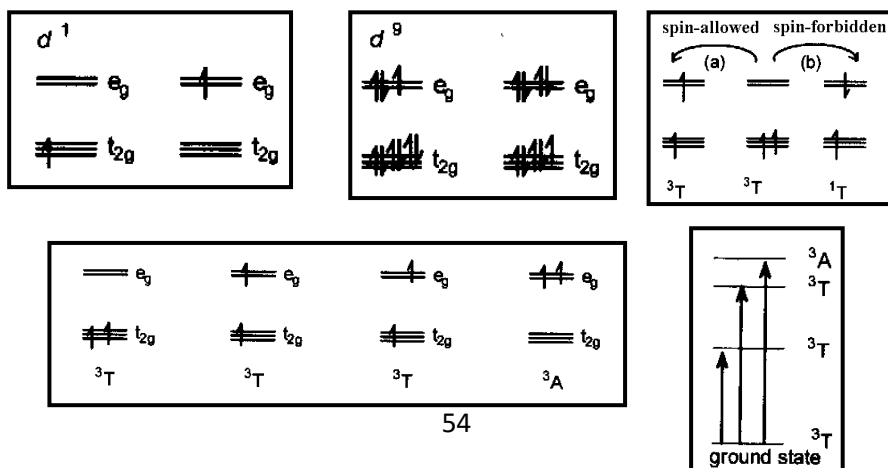
$$\Delta S = 0$$

$2S \rightarrow 2P$  and  $3D \rightarrow 3P$  are allowed, but transition such as  $1S \rightarrow 3P$  is forbidden.

-Transitions may occur from singlet to singlet, or from triplet to triplet states etc., but a change in spin multiplicity is *forbidden*.

$S = 0$ , spin-allowed transition transition between states of same spin multiplicity

$S \neq 0$ , spin-forbidden transition transition between states of different spin multiplicity





- ❖ *Symmetry selection rule -Laporte selection rule*; if the molecule has a center of symmetry (inversion center), transitions from one centrosymmetric orbital to another are forbidden (*i.e.*, all d orbitals are centrosymmetric, so d-d transitions are forbidden in a complex that has an inversion center. If the molecule does not have an inversion center, d-d transitions are symmetry allowed).

This means that all d-d transitions in octahedral complexes are formally forbidden as there is center of symmetry

Hence all d-d transitions in octahedral complexes are weak

– For tetrahedral complexes there is no center of symmetry are typically stronger than those in octahedral complexes

**Laporte selection rule:** There must be a change in parity:

$1S \rightarrow 1P$  and  $2D \rightarrow 2P$  are allowed but transition such as  $3D \rightarrow 3S$  is forbidden since  $\Delta L = -2$

allowed transitions:  $g \leftrightarrow u$

forbidden transitions:  $g \leftrightarrow g$ ,  $u \leftrightarrow u$

This leads to the selection rule:  $\Delta L = \pm 1$

allowed transitions are:  $s \rightarrow p$ ,  $p \rightarrow d$ ,  $d \rightarrow f$ ,

forbidden transitions are:  $s \rightarrow s$ ,  $p \rightarrow p$ ,  $d \rightarrow d$ ,  $f \rightarrow f$ ,  $s \rightarrow d$ ,  $p \rightarrow f$ ,

#### 4.2.6 Mechanism of breakdown of selection rules

##### Spin-orbit coupling

For electronic transition to take place,  $\Delta S = 0$  and  $\Delta L = \pm 1$  in the absence of spin-orbit coupling. However, spin and orbital motions are coupled. Even, if they are coupled very weakly, a little of each spin state mixes with the other in the ground and excited states by an amount dependent upon the energy difference in the orbital states and magnitude of spin-orbit coupling constant. Therefore electronic transitions occur between different states of spin multiplicity and also between states in which  $\Delta L$  is not equal to  $\pm 1$ . For example, if the ground state were 99% singlet and 1% triplet (due to spin-orbit coupling) and the excited state were 1% singlet and 99% triplet, then the intensity would derive from the triplet-triplet and singlet-singlet interactions. Spin-orbit coupling provides small energy differences between degenerate state.

## NOTES

**La Porte selection rule**

Physically 3d (even) and 4p (odd) wave functions may be mixed, if centre of inversion (i) is removed.

The central metal ion is placed in a distorted field (tetrahedral field, Tetragonal distortions, etc.,) The most important case of distorted or asymmetric field is the case of a tetrahedral complex. Tetrahedron has no inversion centre and so d-p mixing takes place. So electronic transitions in tetrahedral complexes are much more intense, often by a factor 100, than in analogous octahedral complexes. Trans isomer of  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  in aqueous solution is three to four times less intense than the cis isomer because the former is centro-symmetric. Other types of distortion include Jahn – Teller distortions.

Odd vibrations of the surrounding ligands create the distorted field for a time that is long enough compared to the time necessary for the electronic transition to occur (Franck-Condon Principle). Certain vibrations will remove the centre of symmetry. Mathematically this implies coupling of vibrational and electronic wave functions. Breaking down of LaPorte rule by vibronic coupling has been termed as “Intensity Stealing”. If the forbidden excited term lies energetically nearby a fully allowed transition, it would produce a very intense band. Intensity Stealing by this mechanism decreases in magnitude with increasing energy separation between the excited term and the allowed level.

The molar absorptivity ( $\epsilon_{\text{max}}$ , extinction coefficient) is a good indicator of the type of electronic transition

Electronic transition	$\epsilon_{\text{max}}$	Example
Laporte allowed (charge transfer)	1000—50000	Organic chromophores, $\text{MnO}_4^-$
Laporte forbidden (d-d transition) spin allowed; noncentrosymmetric	100 - 500	Most 3d Oh complexes Td complexes, $\text{CoCl}_4$
spin allowed; centrosymmetric	5—100	$[\text{Co}(\text{OH}_2)_6]^{2+}$ complexes
spin forbidden	0.01—1	$[\text{Mn}(\text{OH}_2)_6]^{2+}$ complexes

**4.3 Splitting of energy states**

The symbols A (or a) and B (or b) with any suffixes indicate wave functions which are singly degenerate. Similarly E (or e) indicates double

degeneracy and T (or t) indicates triple degeneracy. Lower case symbols,  $a_{1g}$ ,  $a_{2g}$ ,  $e_g$ , etc., are used to indicate electron wavefunctions (orbitals) and upper case symbols are used to describe electronic energy levels. Thus  ${}^2T_{2g}$  means an energy level which is triply degenerate with respect to orbital state and also doubly degenerate with respect to its spin state. Upper case symbols are also used without any spin multiplicity term and they then refer to symmetry (ex.,  $A_{1g}$  symmetry). The subscripts g and u indicate *gerade* (even) and *ungerade* (odd). d orbitals split into two sets -  $t_{2g}$  orbitals and  $e_g$  orbitals under the influence of crystal field. These have  $T_{2g}$  and  $E_g$  symmetry respectively.

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#### 4.3.1 Energy level diagram

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Energy Level Diagrams are described by two independent schemes - Orgel Diagrams which are applicable to weak field complexes and Tanabe-Sugano (or simply T-S) Diagrams which are applicable to both weak field and strong field complexes.

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#### 4.3.2 Orgel Diagrams

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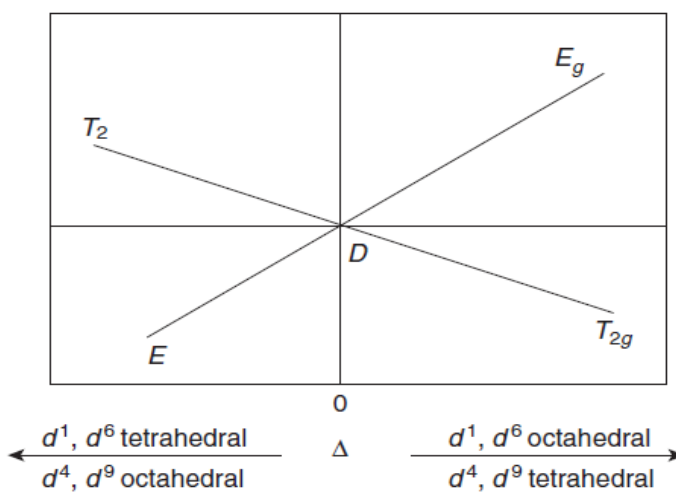
Orgel Diagrams are correlation diagrams which show the relative energies of electronic terms in transition metal complexes that shows how ligand field strength affects the energy of the crystal field terms. They are named after their creator, Leslie Orgel. Orgel diagrams are restricted to weak ligand fields of both octahedral ( $Oh$ ) and tetrahedral ( $Td$ ) complexes (i.e. high-spin complexes). Because Orgel diagrams are qualitative, no energy calculations can be performed from these diagrams. Orgel diagrams only show the symmetry states of the highest spin multiplicity instead of all possible terms, unlike a Tanabe-Sugano diagram. Orgel diagrams will, however, show the number of spin allowed transitions, along with their respective symmetry designations. Orgel diagrams are for qualitative purposes only. Tanabe-Sugano diagrams must be used for low-spin cases and any spin-forbidden transitions (high-spin or low-spin).

In an Orgel diagram, the parent term (P, D, or F) in the presence of no ligand field is located in the center of the diagram, with the terms due to that electronic configuration in a ligand field at each side. There are only two Orgel diagrams, one for  $d^1$ ,  $d^4$ ,  $d^6$ , and  $d^9$  configurations and the other with  $d^2$ ,  $d^3$ ,  $d^7$ , and  $d^8$  configurations. Only terms with same multiplicity as the ground state are shown because only these can be involved in transition from the ground state (spin selection rule). Remember that  $d^1 Td$  splitting is just the opposite of  $d^1 Oh$ , so  $d^1 Td$  and  $d^9 Oh$  have similar Orgel Diagrams; same with  $d^9 Td$  and  $d^1 Oh$ . In an Orgel diagram, energy is represented as the vertical dimension, and the vertical line in the center of the diagram represents the gaseous ion where there is no ligand field ( $\Delta_0$ ). Note that the right-hand side of the diagram applies to  $d^1$  and  $d^6$  ions in octahedral fields or  $d^4$  and  $d^9$  ions in tetrahedral fields. This situation arises because the ligand field states are inverted for the two cases, and the electron-hole formalism also causes the

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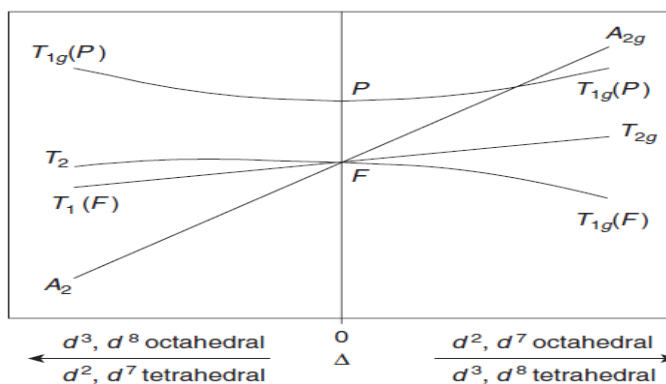
## NOTES

orbitals to be inverted. As a result, the ligand field states are the same for a  $d^1$  ion in an octahedral field as they are for a  $d^4$  ion in a tetrahedral field.



An Orgel diagram for metal ions having D spectroscopic ground states. The multiplicity of the D state is not specified because it is determined by the number of electrons in the d orbitals of the metal ion.

- First look at splitting of the ground state,  $^3F$  term as we move from a spherically symmetric to octahedral (or tetrahedral) field.
- Next, add  $^3P$  component in octahedral field,  $^3T_{1g}$ .
- Note that there is a problem on the left hand side of the diagram as two  $^3T_{1g}$  components are crossing. As we saw with MO diagrams, two energy components with identical symmetry will mix rather than cross.
- So, the *predicted* transitions would be:  $T_{1g} \rightarrow T_{2g}$ ,  $T_{1g} \rightarrow T_{1g}(P)$  and  $T_{1g} \rightarrow A_{2g}$ . However, this last transition would involve the simultaneous excitation of two electrons and so is relatively impossible; for  $d^8$  Oh all 3 transitions are possible.
- Although Orgel Diagrams are good for qualitatively predicting transitions, they are not good for predicting  $10Dq$  value, nor do they account for high spin /low spin.



An Orgel diagram for metal ions having F spectroscopic ground states. The multiplicity of the F state is not specified. The P state having the same multiplicity as the ground state is also shown.

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### 4.3.3 Inter-electronic repulsion parameters

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The inter-electronic repulsions within a configuration are linear combinations of Coulombic and exchange integrals above the ground term. They are expressed by either of the two ways: Condon - Shortley parameters,  $F_0$ ,  $F_2$  and  $F_4$  and Racah parameters, A, B and C. The magnitude of these parameters varies with the nature of metal ion.

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### 4.3.4 Racah parameters

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The Racah parameters are A, B and C. The Racah parameter A corresponds to the partial shift of all terms of a given electronic configuration. Hence in the optical transition considerations, it is not taken into account. The parameter, B measures the inter-electronic repulsion among the electrons in the d-orbitals. The decrease in the value of the interelectronic repulsion parameter, B leads to formation of partially covalent bonding. The ratio between the crystal B<sup>1</sup> parameter and the free ion B parameter is known as nephelauxetic ratio and it is denoted by  $\beta$ . The value of  $\beta$  is a measure of covalency. The smaller the value, the greater is the covalency between the metal ion and the ligands. The B and C values are a measure of spatial arrangement of the orbitals of the ligand and the metal ion.

Racah redefined the empirical Condon - Shortley parameters so that the separation between states having the maximum multiplicity (for example, difference between  $^3F$  and  $^3P$  or  $^4F$  and  $^4P$  is a function of a single parameter, B. However, separations between terms of different multiplicity involve both B and C.

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### 4.3.5 Tanabe - Sugano diagrams

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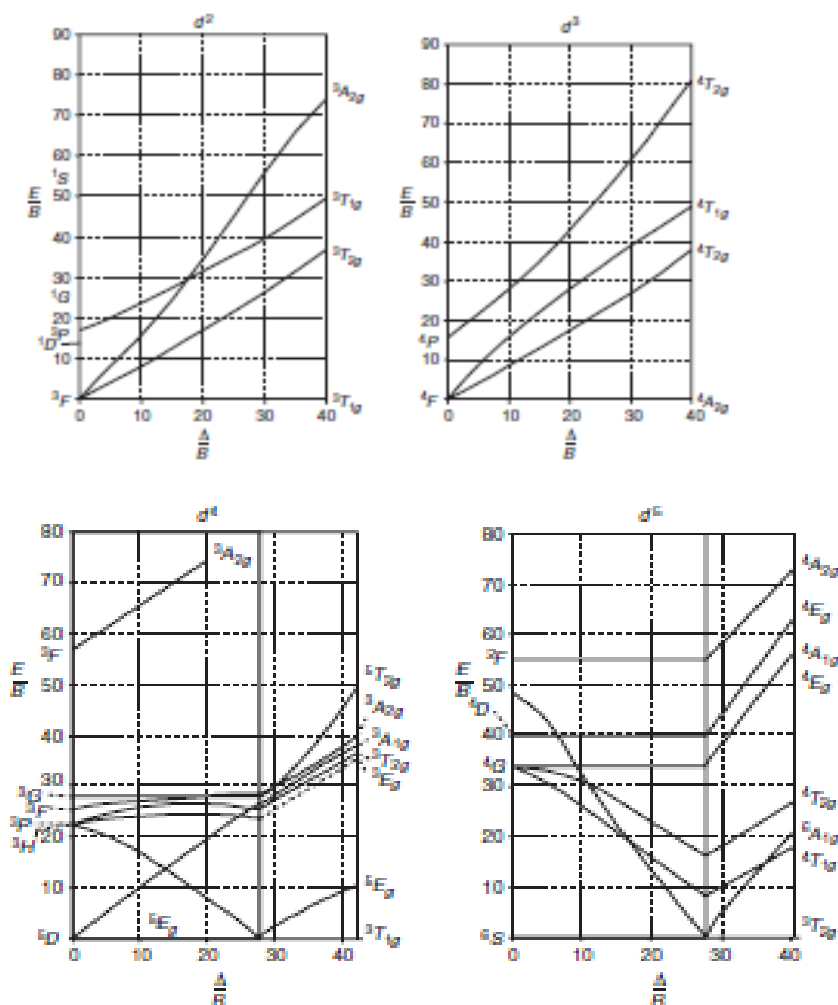
Exact solutions for the excited state energy levels in terms of Dq, B and C are obtained from Tanabe-Sugano matrices. The T-S diagrams are valid only if the value of B, C and Dq are lower for a complex than for the free ion value. Quantitative interpretation of electronic absorption spectra is possible by using Tanabe - Sugano diagrams or simply T-S diagrams. These diagrams are widely employed to correlate and interpret spectra for ions of all types, from  $d^2$  to  $d^8$ . Orgel diagrams are useful only qualitatively for high spin complexes whereas T-S diagrams are useful both for high spin and low spin complexes. The x-axis in T-S diagrams represent the ground state term. Further, in T-S diagrams, the axes are divided by B, the interelectronic repulsion parameter or Racah Parameter. The x-axis represents the crystal field strength in terms of Dq/

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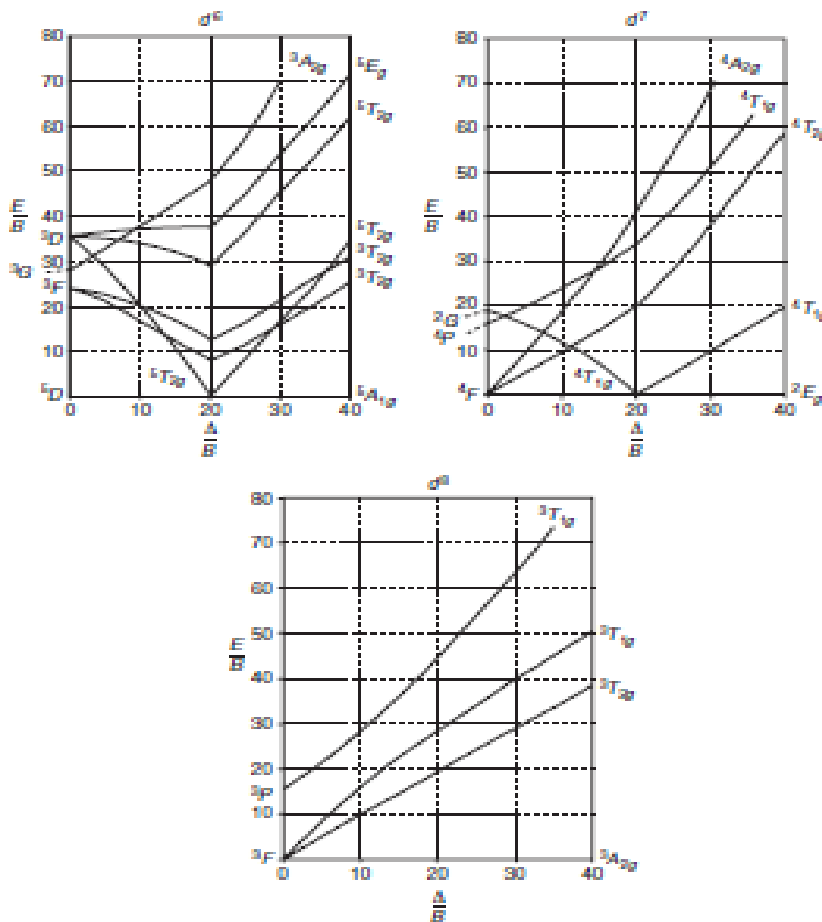
## NOTES

B or  $\Delta$  / B and the Y-axis represents the energy in terms of E/B. The energies of the various electronic states are given in the T-S diagrams on the vertical axis and the ligand field strength increases from left to right on the horizontal axis. The symbols in the diagram omit the subscript, g, with the understanding that all states are gerade states. Also, in T.S. diagrams, the zero of energy for any particular  $d^n$  ion is taken to be the energy of the ground state. Regardless of the ligand field strength, then, the horizontal axis represents the energy of the ground state because the vertical axis is in units of E/B and x-axis is also in units of  $\Delta/B$ . Thus, the unit of energy in T-S diagram is B, Racah Parameter. The values of B are different for different ions of the same  $d^n$  Configuration which is shown on the top of each diagram. One T-S diagram is used for all members of an isoelectronic group. Also some assumption is made about the relative value of C/B.

It is used for the interpretation of the spectra. Tanabe-Sugano diagrams are similar to Orgel diagrams that they depict variation of the term energies with field strength, but they differ in following aspects, .



## NOTES



Simplified Tanabe-Sugano diagrams for  $d^n$  metal ions in octahedral fields. The drawings have been simplified by omitting several states that have multiplicities that do not permit spin allowed transitions.

### f-f Transitions

f-f transitions in lanthanide complexes are weak and sharp and have energies close to those expected for free lanthanide ions. Together with the magnetic properties, this confirms that 4f orbitals have very little overlap with surrounding atoms. High-resolution spectra measured in crystals at low temperatures do show small ligand field splittings but they are small (of the order of  $10\text{ cm}^{-1}$ ) compared with splittings in transition metal complexes. Actinides show larger ligand field effects than lanthanides, especially ions early in the series (e.g.  $\text{U}^{4+}$ ). The interpretation of spectra is complicated by strong spin-orbit splitting. f-f transitions in centrosymmetric complexes are Laporte forbidden as with d-d spectra. Intensities are in the order  $4f < 5f < d$  reflecting the order of strength of metal-ligand interactions.

### Charge Transfer Spectra

All electronic transition between orbitals that are centered on different atoms is called a charge-transfer transition and the absorption band is usually very strong.

## NOTES

Two types of the charge transfer (CT) bands appear in the metal complexes:

(1) The L→M CT bands as shown by oxide, chloride bromide and iodide complexes. For  $d^0$  ions, where the d-d transitions are not possible, the CT bands are used for the determination of the  $10Dq$  values.

(2) The M→L CT bands that occur in the  $\pi$  acceptor ligands (CO, NO, CN-) containing empty low energy orbitals. As the CT bands are neither multiplicity forbidden, nor Laporte forbidden, they have high absorption intensities ( $50-2001 \text{ mm}^{-1} \text{ mol}^{-1}$ ).

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#### 4.4 Check Your Progress

1. Explain term symbol
2. Define Franck-Condon Principle
3. Why tetrahedral complexes are normally bright in colour?
4. Why Au(II) is unstable?
5. Define Microstates?
6. Give formula for Spin selection rule in the electronic spectra?

---

#### 4.5 Answers to check your progress questions

- Atomic states are then well described by term symbols of the form  $^{2S+1}L_J$
- Electronic transitions occur in a very short time (about 10-15sec.) and hence the atoms in a molecule do not have time to change position appreciably during electronic transition. So the molecule will find itself with the same molecular configuration and hence the vibrational kinetic energy in the excited state remains the same as it had in the ground state at the moment of absorption.
- There is no center of symmetry and Laporte rule does not hold good for d-d transition.
- $\Delta_0$  value is very high and increases from Cu(II) to Au(II). Further the  $2Au^{2+}$  convert like  $Au^{3+} + Au^+$
- The different ways in which electrons can occupy certain orbitals.
- $\Delta S = 0$

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#### 4.6 Summary

The Selection Rules governing transitions between electronic energy levels of transition metal complexes are:

(i)  $\Delta S = 0$  The Spin Rule The first rule says that allowed transitions must involve the promotion of electrons without a change in their spin.

(ii)  $\Delta L = \pm 1$  The Orbital Rule (Laporte) The second rule says that if the molecule has a centre of symmetry, transitions within a given set of p or d orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are forbidden.



d-d, these can occur in both the UV and visible region but since they are forbidden transitions have small intensities.

Relaxation of the Rules can occur through a) Spin-Orbit coupling - this gives rise to weak spin forbidden bands. b) Vibronic coupling - an octahedral complex may have allowed vibrations where the molecule is asymmetric. Absorption of light at that moment is then possible.

1.  $d^1$ ,  $d^4$ ,  $d^6$  and  $d^9$  complexes show one absorption.
2.  $d^2$ ,  $d^3$ ,  $d^7$  and  $d^8$  complexes show three absorptions, with the 3<sup>rd</sup> peak often obscured.
3.  $d^5$  complexes show very weak, sharp absorptions.

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#### 4.7 Keywords

**UV/Vis spectra:** UV/Vis spectra are used to determine the value of  $\Delta_o$  for the complex.

**Charge-transfer transition:** All electronic transition between orbitals that are centered on different atoms is called a charge-transfer transition and the absorption band is usually very strong.

**Term symbols:** Atomic states are then well described by term symbols of the form  $^{2S+1}L_J$

**Selection rule:** The magnitude of the extinction coefficient (intensity of the colour) is affected by two quantum mechanical *selection rules* that state whether transitions are *allowed* (intense colour) or *forbidden* (pale colour).

**Orgel Diagrams** are correlation diagrams which show the relative energies of electronic terms in transition metal complexes that shows how ligand field strength affects the energy of the crystal field terms.

**The inter-electronic repulsions** within a configuration are linear combinations of Coulombic and exchange integrals above the ground term.

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#### 4.8 Self-assessment questions and exercises

1. Define Racah parameters
2. Draw Orgel and TS diagram for  $d^2$  configuration
3. Give selection rule of Electronic spectra
4. Explain Charge-transfer transition

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#### 4.9 Further Readings

1. Huheey, J.E.; Keiter, E.A.; Keiter, R.L. *Inorganic Chemistry: Principles of Structure and Reactivity*; 4th ed.; HarperCollins: New York, 1993, pp. 394-408, 433-459.
2. Brisdon, A.K. *Inorganic Spectroscopic Methods*, Oxford University Press: Oxford, 1998, pp. 57-73.
3. Shriver and Atkins, "Inorganic Chemistry", 3/e, Oxford University Press, 2002,

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# UNIT -5 SPINELS

## Structure

- 5.0 Introduction
- 5.1 Objective
- 5.2 Classification of spinels
- 5.3 Normal Spinel
- 5.4 Inverse Spinel
- 5.5 Perovskite Structure
- 5.6 Answer to check your progress
- 5.7 Summary
- 5.8 Keywords
- 5.9 Self Assessment and exercise
- 5.10 Further Reading

## 5.0 Introduction

Spinel is a name of mixed ore of magnesium(Mg) and aluminium(Al), its molecular formula is  $MgAlO_4$  ( $MgO \cdot Al_2O_3$ ). Here Mg is in +2 oxidation state and Al is in +3 oxidation state. The spinels are any class of minerals are general formation  $AB_2X_4$  which crystallise in the cubic crystal system, with the X anion arranged in a cubic close-packed and the cations. A and B occupying some or all of the octahedral and tetrahedral sites in the lattice. A and B can be same metal with different valencies, as is with magnetite which is the most abundant member of the spinel group. Spinel are grouped in series by the B cation. Spinel are often referred to as rubies, but the ruby is not a spinel. A = any divalent metal (eg.  $Mg^{+2}$ ,  $Ni^{+2}$ )

B = any trivalent metal (eg.  $Fe^{+3}$ ,  $Al^{+3}$ ,  $La^{+3}$ ). X = O, S, Se etc. ,

## 5.1 Objective

After going through this unit, you will be able to;

- ✓ To know the meaning of the spinels
- ✓ Understand the classification of spinels
- ✓ Discuss about the perovskite structure

## 5.2 Classification of Spinel

- 1 Spinel are mixed oxides having formula  $AO \cdot B_2O_3$
- 2 They have Face Centred Cubic (CCP) structures.
- 3 Total No. of Atoms per unit cell = 4
- 4 No. of Tetrahedral (Td) voids per unit cell = 8
- 5 No. of Octahedral (Oh) voids per unit cell = 4

On the basis of position occupied by  $A^{+2}$  ions and  $B^{+3}$  ions,

Spinel are of two types

1. Normal Spinel
2. Inverse Spinel

## 5.3 Normal Spinel

The divalent  $A^{+2}$  ions occupy the tetrahedral voids, whereas the trivalent  $B^{+3}$  ions occupy the octahedral voids in the close packed

arrangement of oxide ions. A normal spinel can be represented as:  $(A^{+2})^{tet}(B^{+3})_2^{oct}O_4$  e.g.  $Mn_3O_4$ ,  $ZnFe_2O_4$ ,  $FeCr_2O_4$

In the **normal spinel** structure, there is a close-packed array of anions. The A-site cations fill 1/8 of the tetrahedral holes and the B-site cations fill 1/2 of the octahedral holes.

#### **Prediction Of Structure Of Spinel:**

Basic rule for determining whether a complex is Normal or Inverse Spinel,  
CFSE of  $B^{+3}$  ions in Octahedral Field > CFSE of  $B^{+3}$  ions in Tetrahedral Field  
> CFSE of  $A^{+2}$  ions in Octahedral Field  
> CFSE of  $A^{+2}$  ions in Tetrahedral Field

*i.e. if CFSE of  $B^{+3}$  ions in Octahedral Field is largest of all CFSE*

#### **For Inverse Spinel:**

CFSE of  $A^{+2}$  ions in Octahedral Field > CFSE of  $A^{+2}$  ions in Tetrahedral Field  
> CFSE of  $B^{+3}$  ions in Octahedral Field  
> CFSE of  $B^{+3}$  ions in Tetrahedral Field

*i.e. if CFSE of  $A^{+2}$  ions in Octahedral Field is largest of all CFSE*

A spinel unit cell is made up of 8 FCC cells. The anions (usually oxide ions:  $O^{2-}$ ) occupy the FCC lattice points. The divalent  $A^{II}$  cations occupy 1/8<sup>th</sup> of the tetrahedral voids, whereas the trivalent  $B^{III}$  cations occupy one half (1/2) of octahedral voids. Thus a normal spinel can be represented as:  $(A^{II})^{tet}(B^{III})_2^{oct}O_4$

Note: We know that in one FCC lattice unit cell, the effective numbers of atoms (or ions) occupying the lattice points is 4. At the same time, the effective number of tetrahedral voids (holes) = 8 and that of octahedral voids = 4. That means, in a normal spinel, there are  $8 \times 4 = 32$  anions occupying the lattice points of 8 FCC unit cells. Whereas, the number of divalent  $A^{II}$  cations occupying tetrahedral voids is  $8 \times 1/8 \times 8 = 8$  and the number of trivalent  $B^{III}$  ions occupying the octahedral voids =  $8 \times 1/2 \times 4 = 16$ . i.e. The ratio of  $A^{II} : B^{III} : O^{2-} = 8 : 16 : 32 = 1:2:4$  which confirms with the formula of normal spinels.

### **5.4 Inverse Spinel**

The  $A^{+2}$  ions occupy the octahedral voids, whereas half of  $B^{+3}$  ions occupy the tetrahedral voids. It can be represented as:  $(B^{+3})^{tet}(A^{+2}B^{+3})^{oct}O_4$  E.g.  $Fe_3O_4$  (ferrite),  $CoFe_2O_4$ ,  $NiFe_2O_4$  etc., **Inverse spinels** have a closely related structure (with the same large unit cell) in which the A-site ions and half of the B-site ions switch places. Inverse spinels are thus formulated  $B(AB)O_4$ , where the AB ions in parentheses occupy octahedral sites, and the other B ions are on tetrahedral sites. Many magnetic oxides, such as  $Fe_3O_4$  and  $CoFe_2O_4$ , are spinels.

**Structures of Inverse spinels ( $B(AB)O_4$ ):** The  $A^{II}$  ions occupy the octahedral voids, whereas one half of  $B^{III}$  ions occupy the tetrahedral

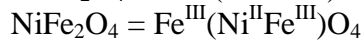
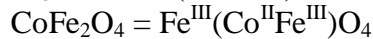
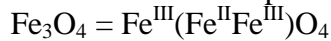
Spinel

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voids and the other half occupy octahedral sites. It can be represented as:  $(B^{III})^{tet}(A^{II}B^{III})^{oct}O_4$ .

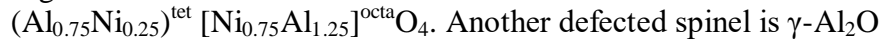
E.g.  $Fe_3O_4$  (ferrite),  $CoFe_2O_4$ ,  $NiFe_2O_4$  etc.

The above inverse spinels can also be written as:



The number of octahedral sites occupied may be ordered or random. The random occupation leads to defected spinels.

E.g.  $NiAl_2O_4$  for which the formula can be written as



#### Rules:

1. If both  $A^{+2}$  and  $B^{+3}$  are non transition metals then spinel will be NORMAL.
2. If  $A^{+2}$  is Non transition metal and  $B^{+3}$  is transition metal (having  $d^1 d^2 d^3 d^4 d^6 d^7 d^8 d^9$ ) then spinel will be NORMAL.
3. If is transition metal with ( $d^1 d^2 d^3 d^4 d^6 d^7 d^8 d^9$ ) and B is also transition metal with ( $d^0 d^5$  and  $d^{10}$ ) system then spinel will be INVERSE

#### EXAMPLES FOR SPINEL AND INVERSE SPINEL STRUCTURES

1)  $MgAl_2O_4$  is a normal spinel since both the divalent and trivalent ions are non transition metal ions. There is no question of CFSE.

2)  $Mn_3O_4$  is a normal spinel since the  $Mn^{2+}$  ion is a high spin  $d^5$  system with zero LFSE. Whereas,  $Mn^{3+}$  ion is a high spin  $d^4$  system with considerable LFSE.

3)  $Fe_3O_4$  is an inverse spinel since the  $Fe(III)$  ion is a high spin  $d^5$  system with zero CFSE. Whereas the divalent  $Fe(II)$  is a high spin  $d^6$  system with more CFSE.

4)  $NiFe_2O_4$  is again an inverse spinel since the divalent  $Ni^{2+}$  (a  $d^8$  ion) has more CFSE than the trivalent  $Fe^{3+}$  (a  $d^5$  ion).

5)  $FeCr_2O_4$  is a normal spinel since the divalent  $Fe^{2+}$  is a high spin  $d^6$  ion with  $CFSE = 4 Dq$  and the trivalent  $Cr^{3+}$  is a high spin  $d^3$  ion with  $CFSE = 12 Dq$ . Hence  $Cr^{3+}$  gets more OSSE while occupying octahedral sites.

6)  $Co_3O_4$  is a normal spinel. Even in the presence of weak field oxo ligands, the  $Co^{3+}$  is a low spin  $d^6$  ion with very high CFSE. It is due to high charge on  $Co^{3+}$ . Hence all the  $Co^{3+}$  ions occupy the octahedral sites.

## NORMAL VS. INVERSE SPINEL STRUCTURE

For transition metal oxide spinels, the choice of the normal vs. inverse spinel structure is driven primarily by the **crystal field stabilization energy (CFSE)** of ions in the tetrahedral and octahedral sites. For spinels that contain 3d elements such as Cr, Mn, Fe, Co, and Ni, the electron configuration is typically **high spin** because  $O^{2-}$  is a **weak field ligand**. As an example, we can consider magnetite,  $Fe_3O_4$ . This compound contains one  $Fe^{2+}$  and two  $Fe^{3+}$  ions per formula unit, so we could formulate it as a normal spinel,  $Fe^{2+}(Fe^{3+})_2O_4$ , or as an inverse spinel,  $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$ . Which one would have the lowest energy?

Spinel

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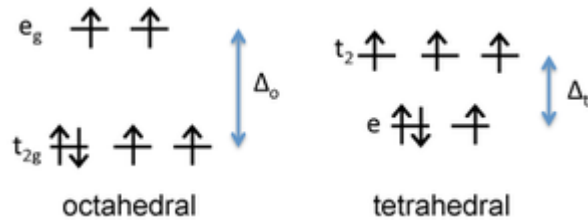


Figure: d-orbital energy diagram for  $Fe^{2+}$

First we consider the crystal field energy of the  $Fe^{2+}$  ion, which is  $d^6$ . Comparing the tetrahedral and high spin octahedral diagrams, we find that the CFSE in an **octahedral** field of  $O^{2-}$  ions is  $[(4)(2/5) - (2)(3/5)]\Delta_o - P = 0.4 \Delta_o - P$ . In the **tetrahedral** field, the CFSE is  $[(3)(3/5) - (3)(2/5)]\Delta_t - P = 0.6 \Delta_t - P$ . Since  $\Delta_o$  is about 2.25 times larger than  $\Delta_t$ , the octahedral arrangement has a larger CFSE and is preferred for  $Fe^{2+}$ .

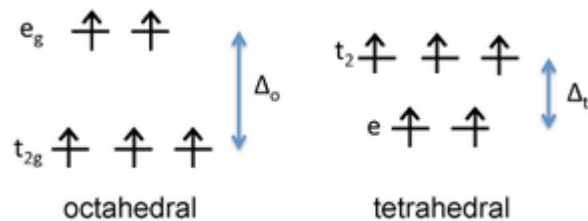


Figure : d-orbital energy diagram for  $Fe^{3+}Fe^{3+}$

In contrast, it is easy to show that  $Fe^{3+}$ , which is  $d^5$ , would have a CFSE of zero in either the octahedral or tetrahedral geometry. This means that  $Fe^{2+}$  has a preference for the octahedral site, but  $Fe^{3+}$  has no preference. Consequently, we place  $Fe^{2+}$  on octahedral sites and  **$Fe_3O_4$  is an inverse spinel**,  $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$ . **Ferrites** are compounds of general formula.

**$M^{II}Fe_2O_4$** . We can see that magnetite is one example of a ferrite (with  $M = Fe$ ). Other divalent metals ( $M = Mg, Mn, Co, Ni, Zn$ ) also form ferrites. Ferrites can be normal or inverse spinels, or mixed spinels, depending on the CFSE of the  $M^{II}$  ion. Based on their CFSE,  $Fe^{2+}$ ,  $Co^{2+}$ , and  $Ni^{2+}$  all have a strong preference for the octahedral site, so those

compounds are all inverse spinels.  $\text{ZnFe}_2\text{O}_4$  is a normal spinel because the small  $\text{Zn}^{2+}$  ion ( $d^{10}$ ) fits more easily into the tetrahedral site than  $\text{Fe}^{3+}$  ( $d^5$ ), and both ions have zero CFSE.  $\text{MgFe}_2\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$ , in which all ions have zero CFSE and no site preference, are mixed spinels. **Chromite spinels,  $\text{M}^{\text{II}}\text{Cr}_2\text{O}_4$** , are always **normal spinels** because the  $d^3$   $\text{Cr}^{3+}$  ion has a strong preference for the octahedral site.

## NOTES

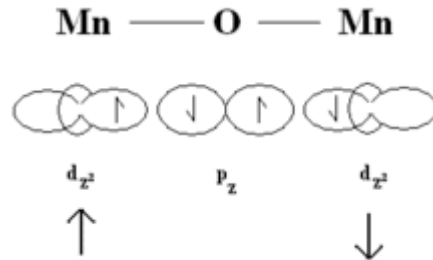


Figure: Illustration of antiferromagnetic superexchange between two transition metal cations through a shared oxygen atom.

### Factors Of Affecting Of The Structure Of Spinel

- **The relative sizes of A and B:** In general, the smaller cation prefers to occupy the site of lower coordination i.e., tetrahedral site. However, in the spinel,  $\text{MgAl}_2\text{O}_4$  itself this factor is outweighed by greater lattice energy of smaller cation,  $\text{Al}^{3+}$ , which occupies the octahedral site and thus by giving normal spinel structure. Otherwise the "spinel" will have the inverse spinel structure!
- **The Madelung constants for the normal and inverse structures:** It is observed that the Madelung constants are same for both normal and inverse spinels and hence are not that much important in arriving at the structure.
- **Ligand-Field Stabilization Energies:** Applicable whenever there are transition metal ions and is discussed below.
- The structures of spinels are affected by the relative LFSE values of metal ions. The ion with more LFSE value in octahedral geometry when compared to the LFSE in tetrahedral geometry tends to occupy octahedral sites.
- The difference between the LFSE values in octahedral and tetrahedral geometries is referred to as Octahedral Site Stabilization Energy (OSSE).
- "If the  $\text{B}^{\text{III}}$  ion has more CFSE gain in octahedral site than that of  $\text{A}^{\text{II}}$  ion, a normal spinel is expected."
- "Whereas an inverse spinel is formed whenever the divalent  $\text{A}^{\text{II}}$  ion has comparatively more CFSE gain in octahedral geometry than the trivalent  $\text{B}^{\text{III}}$  ion."

## Some Generalizations Regarding The Structure Of Spinel

- 1 A normal spinel structure is assumed if both the divalent and the trivalent metals are non transition metals since no CFSE is involved.
- 2 There is a tendency of formation of inverse spinel structure in some cases (not all the cases) which contain transition metal ions. This is because, the transition metal ion may get extra stability (LFSE) in octahedral geometry, prefers octahedral voids over tetrahedral ones.
- 3 The  $d^0$ ; high spin  $d^5$ ,  $d^{10}$  ions have no preference between tetrahedral and octahedral coordination since the LFSE is zero.
- 4 Usually  $d^3$  &  $d^8$  ions have strongest preference for octahedral geometry.
- 5 Other ions with  $d^1$ ,  $d^2$ ,  $d^4$ ,  $d^6$ ,  $d^7$ ,  $d^9$  too have slightly more preference for octahedral symmetry.
- 6 That means, if **A<sup>II</sup> has  $d^3$  or  $d^8$  configuration** and the **B<sup>III</sup> ion** has configuration other than these, then the **spinel is inverted**.
- 7 If the divalent **A<sup>II</sup>** is a transition metal (with configurations other than  $d^0$ ; highspin  $d^5$  &  $d^{10}$ ) and the **B<sup>III</sup> ion** is a non transition metal, there is a tendency to form inverse spinel.
- 8 But there are exceptions like  $\text{FeAl}_2\text{O}_4$  which has normal spinel structure.
- 9 Above generalizations are valid for high spin systems as the oxide ion is expected to be a weak field ligand.
- 10 For example,  $\text{Co}^{3+}$  is a low spin system even in presence of oxo ligands due to high charge on the ion.

A <sup>II</sup>	B <sup>III</sup>	Structure
Non transition metal $d^0$ or $d^5$ or $d^{10}$ transition metal	Non transition metal	Spinel structure
Non transition metal or $d^0$ or $d^5$ or $d^{10}$ transition metal	A transition metal with $d^1$ or $d^2$ or $d^3$ or $d^4$ or $d^6$ or $d^7$ or $d^8$ or $d^9$ configurations	Spinel structure
A transition metal with $d^1$ or $d^2$ or $d^3$ or $d^4$ or $d^6$ or $d^7$ or $d^8$ or $d^9$ configurations	Non transition metal or transition metal with $d^0$ or $d^5$ or $d^{10}$ configurations	Inverse spinel
Transition metal with higher CFSE value	Transition metal with lower CFSE value	Inverse spinel

### Magnetism In Spinel

The spinels can be ferromagnetic or anti ferrimagnetic depending on the structure and nature of metal ions. The unpaired spins of metal ions

Spinel

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are coupled through shared oxide ions by super exchange process. In ferrite spinels, the spins of electrons at tetrahedral sites have one orientation, whereas the spins of electrons at octahedral sites have opposite orientation. If the number of spins in these two types of sites is equal, then that spinel will be antiferromagnetic. Otherwise, it will be ferromagnetic.

E.g. The inverse spinels -  $\text{Fe}_3\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  are ferrimagnetic. In these cases, the spins of trivalent ions are cancelled out since half of them belong to tetrahedral sites and the other half belong to octahedral sites. However, the spins of divalent ions are not cancelled. Hence they show ferrimagnetism.

In case of  $\text{FeCr}_2\text{O}_4$  - a normal spinel, the number of spins of high spin  $\text{Cr}^{3+}$  ( $d^3$ ) ions is equal to the number of spins of high spin  $\text{Fe}^{2+}$  ( $d^6$ ) ions. Hence it is antiferromagnetic.

$\text{MgAl}_2\text{O}_4$  is diamagnetic since all the electrons in the metal ions are paired up.

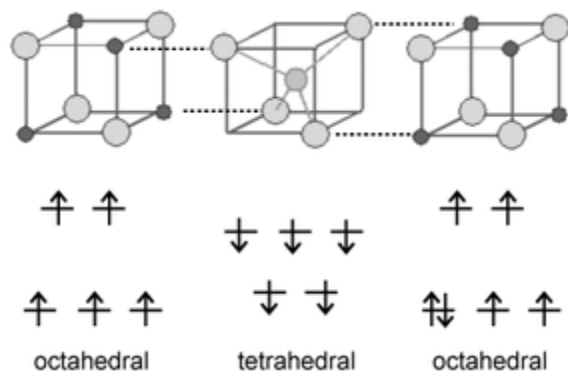
Note: Antiferro magnetic substances show weak magnetism, whereas diamagnetic substances show no magnetism at all.

### Magnetism Of Ferrite Spinel

Ferrite spinels are of technological interest because of their magnetic ordering, which can be ferrimagnetic or antiferromagnetic depending on the structure (normal or inverse) and the nature of the metal ions.  $\text{Fe}_3\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ , and  $\text{NiFe}_2\text{O}_4$  are all inverse spinels and are ferrimagnets. The latter two compounds are used in magnetic recording media and as deflection magnets, respectively.

In order to understand the magnetism of ferrites, we need to think about how the unpaired spins of metal ions are coupled in oxides. If an oxide ion is shared by two metal ions, it can mediate the coupling of spins by superexchange as shown at the right. The coupling can be antiferromagnetic, as shown, or ferromagnetic, depending on the orbital filling and the symmetry of the orbitals involved. The **Goodenough-Kanamori rules** predict the local magnetic ordering (ferromagnetic vs. antiferromagnetic) that results from superexchange coupling of the electron spins of transition metal ions. For ferrites, the strongest coupling is between ions on neighboring **tetrahedral and octahedral sites**, and the ordering of spins between these two sites is reliably **antiferromagnetic**.





Because all the tetrahedral and octahedral sites in a spinel or inverse spinel crystal are coupled together identically, it works out that ions on the tetrahedral sites will all have one orientation (e.g., spin down) and ions on all the octahedral sites will have the opposite orientation (e.g., spin up). If the number of spins on the two sites is the same, then the solid will be antiferromagnetic. However, if the **number of spins is unequal** (as in the case of  $\text{Fe}_3\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ , and  $\text{NiFe}_2\text{O}_4$ ) then the solid will be **ferrimagnetic**. This is illustrated above for  $\text{Fe}_3\text{O}_4$ . The spins on the  $\text{Fe}^{3+}$  sites cancel, because half of them are up and half are down. However, the four unpaired electrons on the  $\text{Fe}^{2+}$  ions are all aligned the same way in the crystal, so the compound is ferrimagnetic.

### 5.5 Perovskite Structure

**Perovskites** are **ternary oxides** of general formula  $\text{ABO}_3$ . More generally, the perovskite formula is  $\text{ABX}_3$ , where the anion X can be **O**, **N**, or **halogen**. The A ions are typically large ions such as  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Rb}^+$ , or a lanthanide 3+ ion, and the B ions are smaller transition metal ions such as  $\text{Ti}^{4+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ru}^{4+}$ , etc. The mineral after which the structure is named has the formula  $\text{CaTiO}_3$ .

The perovskite structure has simple cubic symmetry, but is related to the fcc lattice in the sense that the A site cations and the three O atoms comprise a fcc lattice. The B-site cations fill 1/4 of the octahedral holes and are surrounded by six oxide anions.

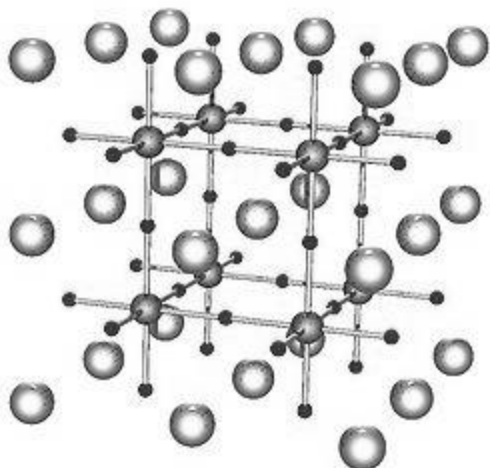


Figure:  $ABX_3$  perovskite structure. A, B, and X are white, blue, and red, respectively.

The coordination of the A ions in perovskite and the arrangement of  $BO_6$  octahedra is best understood by looking at the  $ReO_3$  structure, which is the same structure but with the A-site cations removed. In the polyhedral representation of the structure shown below, it can be seen that the octahedra share all their vertices but do not share any octahedral edges. This makes the  $ReO_3$  and perovskite structures flexible, like three-dimensional wine racks, in that the octahedra can **rotate and tilt cooperatively**. Eight such octahedra surround a large **cuboctahedral cavity**, which is the site of the A ions in the perovskite structure. Cations in these sites are coordinated by 12 oxide ions, as expected from the relationship between the perovskite and fcc lattices.

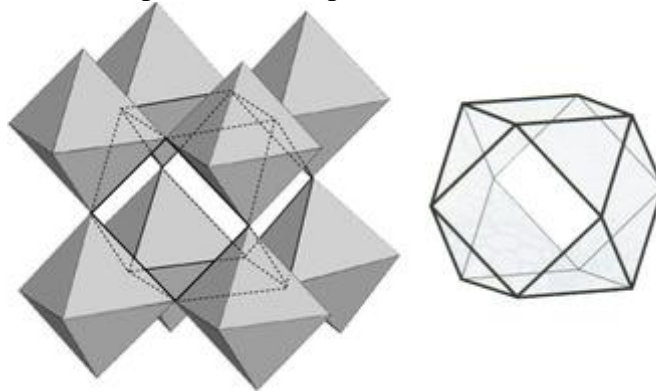


Figure: Polyhedral representation of the  $ReO_3$  structure showing the large cuboctahedral cavity that is surrounded by 12 oxygen atoms.

Because the A-site is empty in the  $ReO_3$  structure, compounds with that structure can be reversibly **intercalated** by small ions such as  $Li^+$  or  $H^+$ , which then occupy sites in the cuboctahedral cavity. For example, smart windows that darken in bright sunlight contain the **electrochromic** material  $WO_3$ , which has the  $ReO_3$  structure.  $WO_3$  is a light yellow compound containing  $d^0$  W(VI). In contrast,  $H_xWO_3$ , which is mixed-valent W(V)-W(VI) =  $d^1-d^0$ , has a deep blue color. Such coloration is typical of mixed-valence transition metal complexes because their d-electrons can be excited to delocalized conduction band levels by red light. Because the electrochemical intercalation-deintercalation process is powered by a solar cell, the tint of the windows can adjust automatically to the level of sunlight.

### **FERROELECTRIC PEROVSKITES:**

The flexibility of the network of corner-sharing  $BO_6$  octahedra is also very important in ferroelectric oxides that have the perovskite structure. In some perovskites with small B-site cations, such as  $Ti^{4+}$  and  $Nb^{5+}$ , the cation is too small to fit symmetrically in the  $BO_6$  octahedron. The octahedron distorts, allowing the cation to move off-center. These

distortions can be **tetragonal** (as in the figure shown below), **rhombohedral**, or **orthorhombic**, depending on whether the cation moves towards a vertex, face, or edge of the  $\text{BO}_6$  octahedron. Moving the cation off-center in the octahedron creates an **electric dipole**. In ferroelectrics, these dipoles align in neighboring unit cells through cooperative rotation and tilting of octahedra. The crystal thus acquires a net electrical polarization.

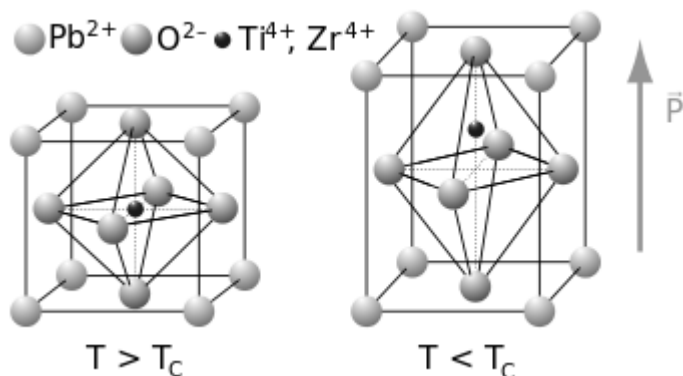


Figure: Tetragonal distortion of the perovskite unit cell in the ferroelectric oxide PZT,  $\text{PbTi}_x\text{Zr}_{1-x}\text{O}_3$

**Ferroelectricity** behaves analogously to **ferromagnetism**, except that the polarization is electrical rather than magnetic. In both cases, there is a **critical temperature** ( $T_c$ ) above which the **spontaneous polarization** of the crystal disappears. Below  $T_c$ , the electric polarization of a ferroelectric can be switched with a coercive field, and hysteresis loop of polarization vs. field resembles that of a ferromagnet. Above  $T_c$ , the crystal is **paraelectric** and has a high dielectric permittivity.

Ferroelectric and paraelectric oxides (along with piezoelectrics and pyroelectrics) have a wide variety of applications as switches, actuators, transducers, and dielectrics for capacitors. **Ferroelectric capacitors** are important in memory devices (FRAM) and in the tuning circuits of cellular telephones. **Multiferroics**, which are materials that are simultaneously ferroelectric and ferromagnetic, are rare and are being now intensively researched because of their potential applications in electrically addressable magnetic memory.

**Halide perovskites** ( $\text{ABX}_3$ ,  $X = \text{Cl}, \text{Br}, \text{I}$ ) can be made by combining salts of monovalent A ions ( $A^+ = \text{Cs}^+, \text{NH}_4^+, \text{RNH}_3^+$ ) and divalent metal salts such as  $\text{PbCl}_2$  or  $\text{PbI}_2$ . These compounds have sparked recent interest as light absorbers for **thin film solar cells** that produce electricity from sunlight. Lead and tin halide perovskites can be grown as thin films from solution precursors or by thermal evaporation at relatively low temperatures. In some lead halide perovskites, the mobility of electrons and holes is very high, comparable to that of more expensive III-V semiconductors such as GaAs, which must be grown as very pure single

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crystals at high temperatures for use in solar cells. Because of their high carrier mobility, some lead halide perovskites are also electroluminescent and are of interest as inexpensive materials for light-emitting diodes (LEDs).

Despite their very impressive efficiency, perovskite solar cells are stable for relatively short periods of time and are sensitive to air and moisture. Current research is focused on understanding the degradation mechanisms of these solar cells and improving their stability under operating conditions.

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### 5.6 Answer To Check Your Progress

- 1 The spinels are any class of minerals are general formation  $AB_2X_4$  which crystallise in the cubic crystal system, with the X anion arranged in a cubic close-packed and the cations A and B occupying some or all of the octahedral and tetrahedral sites in the lattice.
- 2 In the **normal spinel** structure, there is a close-packed array of anions.
- 3 **Inverse spinels** have a closely related structure (with the same large unit cell) in which the A-site ions and half of the B-site ions switch places.
- 4 The flexibility of the network of corner-sharing  $BO_6$  octahedra is also very important in ferroelectric oxides that have the perovskite structure.

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### 5.7 Summary

- The spinels are any class of minerals are general formation  $AB_2X_4$  which crystallise in the cubic crystal system, with the X anion arranged in a cubic close-packed and the cations A and B occupying some or all of the octahedral and tetrahedral sites in the lattice.
- Spinel classified can into two types. They are normal and Inverse spinels.
- $MgAl_2O_4$  is a normal spinel since both the divalent and trivalent ions are non transition metal ions. There is no question of CFSE.
- $Fe_3O_4$  is an inverse spinel since the Fe(III) ion is a high spin  $d^5$  system with zero CFSE. Whereas the divalent Fe(II) is a high spin  $d^6$  system with more CFSE.
- The flexibility of the network of corner-sharing  $BO_6$  octahedra is also very important in ferroelectric oxides that have the perovskite structure.

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## 5.8 Keywords

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Spinel: The **spinel** has the general formula  $AB_2X_4$ .

Where:  $A^{II}$  = a divalent cation like Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn

$B^{III}$  = a trivalent cation like Al, Ga, In, Ti, V, Cr, Mn, Fe, Fe, Co, Ni

X = O, S, Se etc.

Normal And Inverse Spinel:

In the **normal spinel** structure, there is a close-packed array of anions.

**Inverse spinels** have a closely related structure (with the same large unit cell) in which the A-site ions and half of the B-site ions switch places.

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## 5.9 Self Assessment And Exercise

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### Short Answer Questions

- 1 Define Spinel
- 2 Write the classification of the spinels
- 3 Give examples for Spinel
- 4 What are the factors affecting the structure of the spinels?

### Long Answer Questions

- 1 Define Spinel and write the classification of the spinels?
  - 2 What is meant by perovskite Structure?
- 

## 5.10 FURTHER READING

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- 1 Puri, Sharma and Kalia Principles Of Inorganic Chemistry. Mulesons Publishers and Distributors
- 2 Huheey, J.E., E.A. Keiter and R.L. Keiter. 2002. Inorganic Chemistry: Principles of Structure and Reactivity, 4th Edition. New York: HarperCollins Publishers.

Spinel

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# UNIT -6 CAGES AND CLUSTERS

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## Structure

### 6.0 Introduction

#### 6.1 Objectives

#### 6.2 Classification of metal clusters

#### 6.3 Criteria for metal Clusters

#### 6.4 Types of metal clusters

##### 6.4.1 Dinuclear Clusters

##### 6.4.2 Trinuclear Clusters

##### 6.4.3 Tetranuclear Clusters

##### 6.4.4 Hexanuclear Clusters

#### 6.5 Answers to check your progress

#### 6.6 Summary

#### 6.7 Key words

#### 6.8 Self Assessment and exercise

#### 6.9 Further Reading

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### 6.0 Introduction

Metal-metal bond is a bond between two metal centers, particularly between two transition metal atoms, which ranges from a single to a quadruple bond. The existence of metal-metal bond is mainly because of the presence of  $(n+1)s$ ,  $(n+1)p$  and  $nd$  orbitals as valence shell electronic configuration. The transition metals can form three general types of bonds such as covalent bonds, dative bonds and weak metal-metal symmetry interactions where covalent bonds being the strongest and symmetry interactions are the weakest. The compounds containing a large number of metal-metal bonds forming triangular and larger structures are called cluster compounds, however these also include linear M-M bonds. The metal clusters can also be defined as any entity that contains a metal-metal bond. The journey started with the identification of the Hg-Hg in the  $\text{Hg}^{2+}$  ion ( $\text{Hg}_2\text{Cl}_2$ ) which was the first d-block metal-metal bonded species. Most of these cluster compounds are homo-metallic, however there are few exceptions with heterometallic cluster compounds.

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### 6.1 Objectives

After going through this unit, you will be able to;

- ✓ To know the meaning of Cages and Clusters
- ✓ Discuss about the classification of metal Clusters
- ✓ Understand the types of metal Clusters

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## Definition of Clusters And Metal Clusters

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Clusters are aggregates of  $2-10^n$  ( $n \rightarrow 6$  or  $7$ ) particles (atoms or molecules). Constituent particles may be identical or they can be two or more different species. Clusters may be studied in the gas phase, in a cluster “molecular” beam, adsorbed onto a surface or trapped in an inert matrix. Clusters are formed by most of the elements in the periodic table – even the noble gases. Clusters of the coinage metals (copper, silver and gold) are found in stained glass windows. Silver clusters are important in photography. Molecular clusters are present in the atmosphere. Carbon nanoclusters (*e.g.*  $C_{60}$  and related fullerenes) may be present in soot and even in space.

Clusters are of fundamental interest, because

due to their intrinsic properties

because of their central position between molecular and condensed matter science.

Clusters span a wide range of particle size – from molecular to micro-crystalline.

Clusters constitute new materials (nano-particles) which may have properties that are distinct from those of discrete molecules or bulk matter.

### Cluster

It is defined as ensemble of atoms or molecules intermediate in size between a molecule and a bulk solid. They can be made up of diverse nuclearities and stoichiometry. Examples: Fullerene, Diborane, Water

**Metal Cluster:** (1) Compounds that contain metal-metal bonds. (2) A compound that contains a group of two or more atoms where direct and substantial metal bonding is present.

Examples:  $Co_2(CO)_8$ ,  $Rh_2(OAc)_4$ , Stryker’s reagent.

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## 6.2 Classification of Metal Clusters

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Metal clusters have been classified into two major categories:

- ✓ The polynuclear carbonyl, nitrosyl and related clusters can be categorized as Class I. These clusters are mainly formed by metals in lower oxidation states ( $-1$ ,  $+1$ ) which include the metal ions residing on the right hand side of the periodic table.
  - ✓ The other category (Class II) includes clusters formed as halides and oxides of transition metal complexes in their higher oxidation states. The transition metals lying on the left hand side of the periodic table (second or third row transition metals) form such type of cluster compounds. For example, the  $[Re_2Cl_8]^{2-}$  cluster contains a Re-Re single bond with  $+3$  oxidation state on each rhenium center in the cluster.
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## 6.3 Criteria For Metal Cluster Formation

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There is a general trend that transition metals having large energies of atomization (Zr, Nb, Mo, Tc, Ru, Rh, Hf, Ta, W, Re, Os, Ir and Pt) display a higher tendency to form metal clusters.

Model Question  
paper

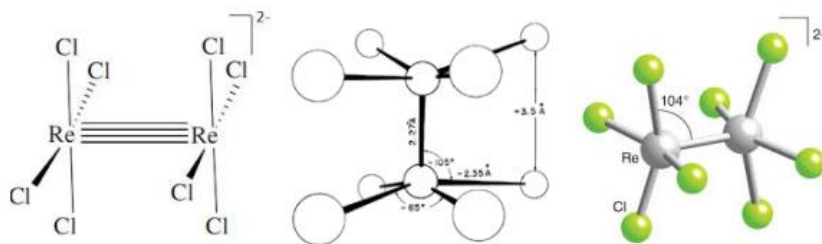
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Nature of the d-orbital: The effective nuclear charge is inversely related to the size of the d-orbital. Higher nuclear charge tends to reduce the effective overlap of the d-orbitals which is unfavourable for cluster formation. For example, the first row transition metals with higher oxidation states (+2, +3) do not offer sufficient orbital overlap and therefore poses an unfavourable situation towards cluster formation.

## 6.4 Types of Metal Clusters

### 6.4.1 Dinuclear clusters

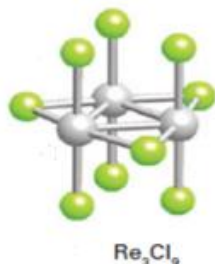
The first dinuclear cluster studied in detail was the species  $[\text{Re}_2\text{X}_8]^{2-}$ . The structural features were studied by Prof. F. A. Cotton. Surprisingly, the Re-Re bond distance was found to be 224 pm which is very less than the average Re-Re distance 275 pm in Re metal. Secondly, the distance between the chlorine atoms is nearly 330 pm which is less than the sum of their Van der Waals radii (340-360 pm)



Cotton introduced the concept of a quadruple bond between the two rhenium centers. The chlorine atoms are connected to the rhenium ion in a square planar array. These are arranged in a staggered configuration forming a square anti-prism rather than a cube. Few other examples which involves metal-metal multiple bonded cluster are the hexa-alkoxo dinuclear tungsten and molybdenum complexes of the formula  $[\text{M}_2(\text{OR})_6]$  where  $\text{M} = \text{Mo}, \text{W}$ .

### 6.4.2 Trinuclear cluster

Among all, the best studied examples of trinuclear clusters are those of Re such as rhenium trihalides  $[(\text{ReCl}_3)_3]$  and their derivatives.



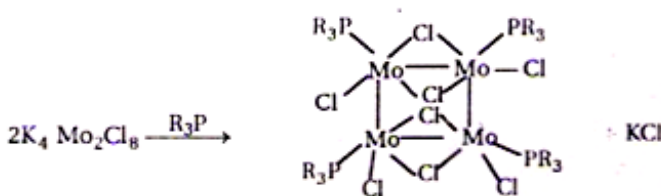
Each rhenium atom is bonded with the other two rhenium atoms by a metal-metal single bond. They are also bonded indirectly to three



bridging chloride atom whereas each rhenium ion is also bonded with two chloride ions above and below Re triangular planes. The rhenium atoms form a triangle. The Re(III) ions have a  $d^4$  configuration. If Re ions are bonded with Re-Re single bonds only, the complex would have been a paramagnetic complex. However, the complex is diamagnetic which implies that the Re ions are doubly bonded.

### 6.4.3 Tetranuclear cluster

A number of tetranuclear cluster are known in which most of them exist as halides and oxides of tungsten and molybdenum, metals. Only a few examples of tetranuclear clusters of halides and oxides are known. Most important example is the dimeric  $[\text{Mo}_2\text{Cl}_8]^{4-}$  cluster giving a tetra nuclear molecule :



### 6.4.4 Hexanuclear Cluster

Metal clusters containing six metal atoms have been known for many years; mostly consist of molybdenum, niobium and tantalum atoms. Considering the case of metal chlorides, the first type of hexanuclear cluster consist of an octahedron of six metal atoms surrounded by eight chloride ions one on each face of the octahedron. In this way, the chloride ions are forming a cube around the metal octahedron. For example, such kind of arrangement can be seen in 'molybdenum dichloride'  $\text{Mo}_6\text{Cl}_{12}$  which can also be formulated as  $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$ . In this case, each Mo(II) ion is sharing four single bonds with four other Mo(II) ions and also receive four dative bonds from four chloride ions. In the second type, twelve halide ions are surrounding the Mo octahedron and placed along the edges. Such types of clusters are formed by niobium and tantalum. Unlike the bonding situation in hexanuclear metal clusters discussed above, each metal ion is surrounded by a distorted square prism of four metals and four chloride ions. These compounds are electron deficient.



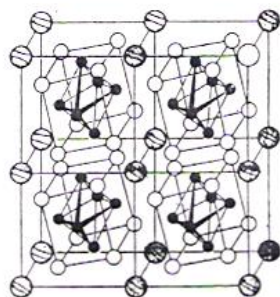
## COMPOUNDS WITH METAL-METAL MULTIPLE BONDS

As has been shown earlier, the earlier metals in d-block series in their lower oxidation states have tendency to form metal-metal multiple

bonds. These metal-metal bonds may be present in smaller molecules and also in macro-chain solids.

### CHEVREL-PHASES

Chevrel phases generally involve tertiary molybdenum chalcogenides,  $M_xMoX_6$ , polynuclear clusters, which have characteristic properties (specially electrical and magnetic). Their structures are also abnormal. An important example of these phases is a super-conductor substance,  $PbMo_6S_8$ . Its structure consists of an octahedral cluster of molybdenum atoms, which is surrounded by cubic cluster of sulphur atoms. Then this whole structure is enclosed in to a cubic structure of lead atoms. The internal  $Mo_6S_8$  cubic structure rotates with respect to lead lattice. This rotation is due to strong repulsion between sulphur atoms. Similarly, the superconductivity originates due to overlapping of d-orbital of molybdenum.



● = Mo, ○ = S, ◐ = Pb

### Metal Carbonyl And Halide Clusters

As has been described earlier, metal carbonyl clusters are rarely formed by earlier d-block metals; while that of f-metals are unknown, i.e. these clusters are formed by group 6 to 10 elements.







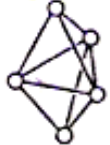

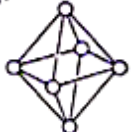
An alternative method for counting skeletal electrons in these compounds is due to D.M.P. Mingos and J. Lauher. This method is also based on Wade's rule and is known as Wade-Mingos-Lauher rule. In this method the total number of valence electrons in all the metal atoms present in the complex are counted and then electrons donated by ligands are added. Thus in  $Rh_6(CO)_{16}^-$

$$\begin{array}{rclcl}
 6Rh & = & 6 \times 9 & = & 54 e^- \\
 16CO & = & 16 \times 2 & = & 32 e^- \\
 & & & & \hline
 \text{Total} & = & & = & 86 e^-
 \end{array}$$

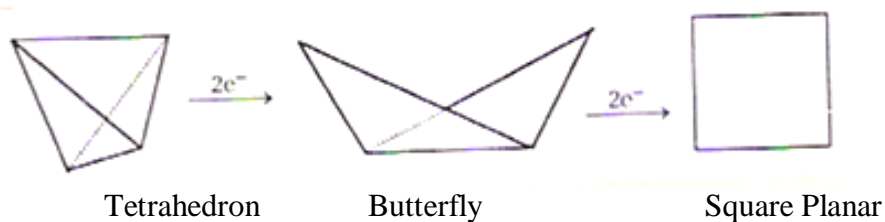
Out of the total  $86e^-$ , twelve electrons per rhodium atom are used for non framework bonding, and remaining  $14e^-$  are obtained for skeletal bonding. These include seven bonding pairs, equal to  $2n+2$  electron. Hence,  $Rh_6(CO)_{16}$  should have closo- structure

Some examples showing inter-relation between cluster-valency electrons and structures are given in Table

**NOTES**

No. of Metal Atoms	Geometry	Metal Skeleton Structure	Bonding Molecular Orbital	No. of Cluster electrons	Examples
1.	Monomer		9	18	Ni(CO) <sub>4</sub>
2.	Dimer		17	34	Fe(CO) <sub>9</sub> , Mn <sub>2</sub> (CO) <sub>10</sub>
3.	Triangle		24	48	Os <sub>3</sub> (CO) <sub>12</sub> , Co <sub>3</sub> (CO) <sub>9</sub> CH
4.	Tetrahedron		30	60	Co <sub>4</sub> (CO) <sub>12</sub> , Rh <sub>4</sub> (CO) <sub>12</sub>
	Butterfly		31	62	Re <sub>4</sub> (CO) <sub>16</sub> <sup>2-</sup> , [Fe <sub>4</sub> (CO) <sub>12</sub> C] <sub>2-</sub>
	Square		32	64	Os <sub>4</sub> (CO) <sub>16</sub> , Pt <sub>4</sub> (O <sub>2</sub> CMe) <sub>8</sub>
5.	TBP		36	72	Os <sub>5</sub> (CO) <sub>16</sub>
	Octahedral		37	74	Fe <sub>5</sub> (CO) <sub>15</sub> C
6.	Trigonal prism		43	86	Ru <sub>6</sub> (CO) <sub>17</sub> C

It is quite clear from table in tetranuclear metal cluster three structures, tetrahedral, butterfly and square planar, are seen, with 60, 62 and 64 cluster electrons respectively.



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### 6.5 Answer To Check Your Progress

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- Metal-metal bond is a bond between two metal centers, particularly between two transition metal atoms, which ranges from a single to a quadruple bond.
  - Metal classified into two types based on their Oxidation states.
  - It is important to understand the criteria for the metal clusters.
  - First Dinuclear compound found by Prof. F. A. Cotton
- 

### 6.6 SUMMARY

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- The transition metals can form three general types of bonds such as covalent bonds, dative bonds and weak metal-metal symmetry interactions where covalent bonds being the strongest and symmetry interactions are the weakest
  - The important criteria for the formation of metal clusters the large energy of atomization of transition metal and nature of the d-orbital.
  - Metal clusters can be classified into four types. They are Dinuclear metal clusters, Trinuclear metal clusters, Tetranuclear clusters and Hexanuclear clusters.
- 

### 6.7 Keywords

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**CAGES:** It is defined as three dimensional ordered structure in solution.

**CLUSTERS:** A metal clusters may be defined as a group of two or more metal atoms that are directly linked to one another through metal-metal bonds.

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### 6.8 Self Assessment Questions And Exercises

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#### Short Answer Questions

1. Define Cages and Clusters
2. What is the criteria for the formation of the metal clusters?
3. What is the classification of metal clusters based on oxidation state?

#### Long Answer Questions

Define Cages and classify the types of metal clusters?

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### 6.9 Further Reading

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1. Puri, Sharma And Kalia Principles Of Inorganic Chemistry. Milesone Publishers And Distributors
2. Huheey, J.E., E.A. Keiter and R.L. Keiter. 2002. Inorganic Chemistry: Principles of Structure and Reactivity, 4th Edition. New York: Harpercollins Publishers.

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# UNIT 7 BORANES

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## Structure

### 7.0 Introduction

### 7.1 Objectives

### 7.2 Boranes & Higher Boranes

#### 7.2.1 Nomenclature of boranes

#### 7.2.2 Classification

#### 7.3.3 Synthesis

### 7.3 Carboranes

#### 7.3.1 Nomenclature

#### 7.3.2 Preparation

### 7.4 Wade's rules

### 7.5 STYX notation

#### 7.5.1 Predicting structures of cluster compounds

#### 7.5.2 $4n$ rules

#### 7.5.3 $5n$ rules

#### 7.5.4 $6n$ rules

#### 7.5.5 Isolobal vertex units

#### 7.5.6 Isolobal Analogy

### 7.6 Check your progress question

### 7.7 Answers to Check Your Progress Questions

### 7.8 Summary

### 7.9 Keywords

### 7.10 Self-Assessment Questions and Exercises

### 7.11 Further Readings

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## 7.0 Introduction

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Boranes is the name given to the class of synthetic hydrides of boron with a general formula of  $B_xH_y$ . Lipscomb was awarded the Nobel prize in Chemistry in 1976 for his achievements in this field. Polyhedral skeletal electron pair theory (Wade's rules) can be used to predict the structures of boranes. In this unit, we are going in detail about the structural classification of boranes, bonding in polyhedral boranes, LIPCOMB's styx rule and Wades rule. Further, we are also going to discuss carboranes, borazines and isolable analogy with suitable examples.

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## 7.1 Objectives

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The main aim of this unit is to study the nature, methods of preparation and structures of metal-clusters. After going through this unit you should be able to:

- describe boranes and higher boranes with reference to their classification, synthesis reactions and structures;
- discuss carboranes and explain their synthesis and properties in the light of their structures;
- identify compounds with metal-metal multiple bonds and their structures.

Boranes

NOTES

- Learn about the Lipcomb's STYX codes.
- Understand the concepts behind bonding in polyhedral boranes.
- Explain about Wade's rule.
- Explain about carboranes
- Learn about the Isolobal Analogy.

## 7.2 Boranes & Higher Boranes

### NOTES

Boron hydrides are known as Boranes. These are named boranes in analogy with alkanes. These are gaseous substance at ordinary temperatures. **Boranes** is the name given to the class of synthetic hydrides of boron with generic formula  $B_xH_y$ . In the past, borane molecules were often labeled "electron-deficient" because of their multicenter bonding (in which a pair of bonding electrons links more than two atoms, as in 3-center-2-electron bonds); this was done in order to distinguish such molecules from hydrocarbons and other classically bonded compounds.

### 7.2.1 Nomenclature of boranes

A) The latin prefixes mono, di, tri, etc are used before "BORANCES" to indicate the number of boron atoms in the compound.

B) Immediately following the 'e' in 'borane' the number of hydrogen atoms is placed in parentheses using Arabic numerals.

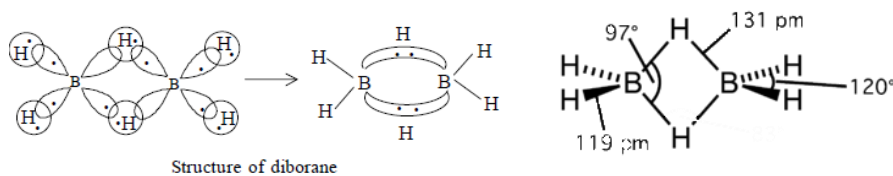
Examples;  $B_5H_{11}$  is pentaborane (11)

C) Whereas the names of anions end in "ate" rather "ane". The numbers of both borane and hydrogens are indicated by latin prefixes.

Examples:  $B_{10}H_{10}^{2-}$  is decahydrodecaborate (2- )

It is expected that boron would form the hydride  $BH_3$ , but this compound is unstable at the room temperature. However, higher hydrides like  $B_2H_6$ (diborane).  $B_4H_{12}$  (tetraborane),  $B_6H_{10}$ (hexaborane),  $B_{10}H_{14}$ (decaborane) etc. are known. The general formula of boranes are  $B_nH_{n+4}$  and  $B_nH_{n+6}$ . In addition to these is one, recently discovered series of closed polyhedral structures with the formula  $[B_nH_n]^{2-}$ . Higher boranes have different shapes, some resemble with nests, some with butterfly and some with spider's web.

The modern explanation of the structure of boranes is due to C.L.Higgins, who proposed the concept of three centred two electron bond ( $\delta$ -bond). He also proposed the concept of completely delocalised molecular orbitals to explain structures of boron polyhedrons.



In higher boranes, in addition to two centred two electron (2c, 2e) and the three centred two electron bond (3c, 2e bond) present in diborane, B-B 2C, 2e and B-B-B (3c, 2e) bonds are also important. In B-B-B bonds, three atoms of boron with their sp<sup>3</sup> hybridisation are placed at the corners of an equilateral triangle.

### 7.2.2 Classification

The structures of boranes can be classified according to the following scheme:

- **closo boranes** have the formula  $B_nH_n^{2-}$  (n vertices of cornered polyhedron are occupied by boron atoms)
- **nido boranes** are formally derived from  $B_nH_n^{4-}$  ions (1 vertex is missing from parent closo borane)
- **arachno boranes** are formally derived from  $B_nH_n^{6-}$  ions (2 vertex is missing from parent closo borane)
- **hypoh boranes** are formally derived from  $B_nH_n^{8-}$  ions (3 vertex is missing from parent closo borane)
- **klado boranes** are formally derived from  $B_nH_n^{10-}$  ions (4 vertex is missing from parent closo borane)

Name	Formula	Skeletal Electron Pair	Examples
Closo	$[B_nH_n]^{2-}$	n+1	$[B_5H_5]^{2-}$ to $[B_{12}H_{12}]^{2-}$
Nido	$[B_nH_{n+4}]$	n+2	$B_2H_6$ , $B_5H_9$ , $B_6H_{10}$
Arachno	$[B_nH_{n+6}]$	n+3	$B_4H_{10}$ , $B_5H_{11}$
Hypo	$[B_nH_{n+8}]$	n+4	Only derivatives are known.

#### Closo Boranes

These are closed structured (Closo, Greek, meaning cage) boranes with the molecular formula  $[B_nH_n]^{2-}$  and skeletal electrons = n+1 pairs (= 2n+2 electrons). In this structure, there is one boron atom placed at each apex and there are no B-H-B bonds present in the molecule. All the members of the series from n=5 to 12 are known.  $[B_5H_5]^{2-}$  is trigonal bipyramidal,  $[B_6H_6]^{2-}$  is octahedral and  $[B_{12}H_{12}]^{2-}$  is icosahedral. All are stable on heating and are quite inert.

#### Nido-Boranes

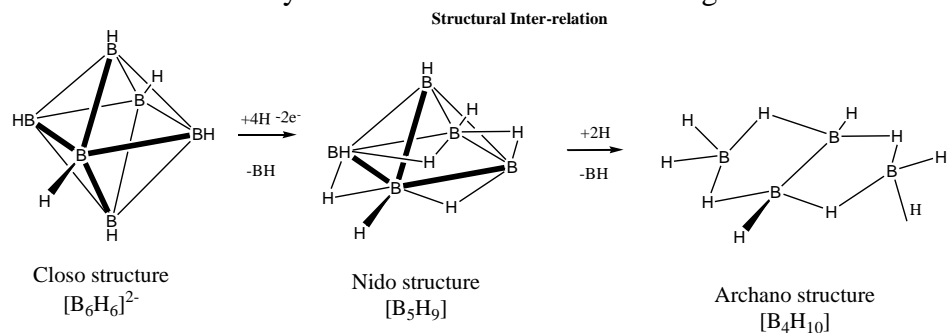
These boranes have nest (Nido, Latin, meaning Nest) like structure. Their general formula is  $B_nH_{n+4}$  and have (n+2) pairs = 2n+4 skeletal electrons on removing one boron atom from an apex of closo structure, nido structure is obtained. Because, of the lost boron atom, these boranes have extra hydrogens for completing the valency. The polyhedra in this series have B-H-B bridge bonds in addition to B-B bonds. They are comparatively less stable than 'Closo', but more than 'Arachno' on heating.

#### Arachno-Boranes

NOTES

These boranes have the general formula ( $B_nH_{n+6}$ ) and skeletal electrons of  $(n+3)$  pairs =  $2n+6$  = electrons. These molecules are obtained by removing two boron atoms from two apexes of the closo structure and have spider-web like structure. They have B-H-B bridge-bonds in their structures and are very reactive and unstable on heating.

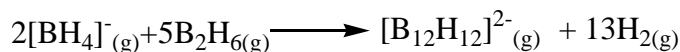
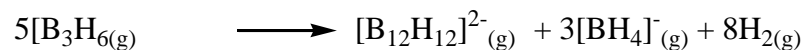
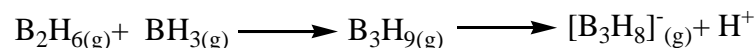
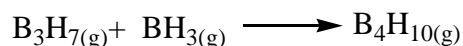
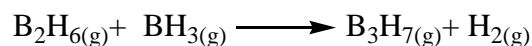
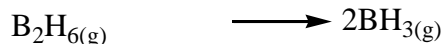
## NOTES



This is based on the observation that the structures having same number of skeletal electrons are related with one another by the removal of BH unit one by one and the addition of suitable number of electrons and hydrogen atoms.

### 7.2.3 Synthesis

The simplest method for synthesis of higher boranes is the controlled pyrolysis of diborane,  $B_2H_6$  it is a gas phase reaction,  $BH_3$  formed in the first step reacts with borane to give higher boranes



### Reactions

The important reactions of higher boranes are with Lewis bases, which involve removal of  $BH_2$  or  $BH_n$  from the cluster, growth of the cluster or removal of one or more number of protons:

#### 1. Decomposition by Lewis-bases:





The reaction is analogous to the reaction of diborane with ammonia.

## 2. Deprotonation :

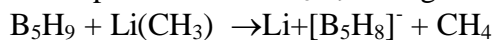
Higher boranes give deprotonation reaction easily rather than decomposition:



This deprotonation takes place from 3c, 2e BHB-bond. The bronsted acidity of boranes increases with their size:

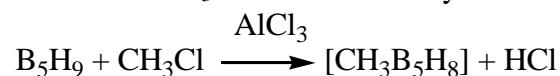


For deprotonation of  $\text{B}_5\text{H}_9$  strong-base like  $\text{Li}_4(\text{CH}_3)_4$  is required:



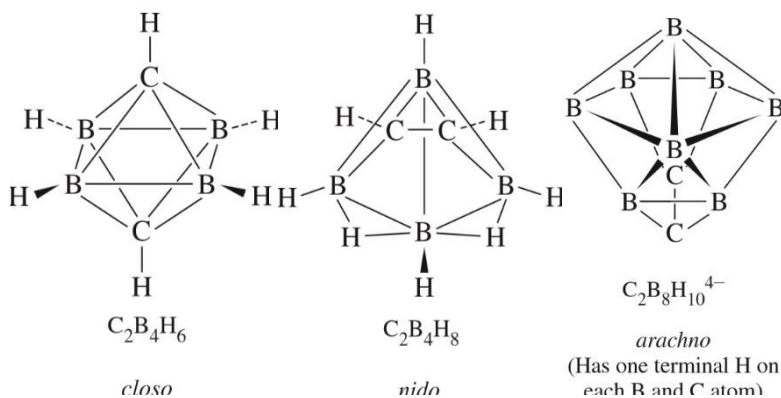
## 4. Electrophilic displacement of proton:

Electrophilic displacement of proton by the catalytic activity of Lewis acids like  $\text{AlCl}_3$  is the basis of alkylation and halogenation of boranes:



## 7.3 Carboranes

Carborane, any member of a class of organometallic compounds containing carbon (C), boron (B), and hydrogen(H). The general formula of carboranes is represented by  $\text{C}_2\text{B}_n\text{H}_{n+2}$ , in which  $n$  is an integer; carboranes with  $n$  ranging from 3 to 10 have been characterized. The first carboranes were produced in the 1950s, but the results were not declassified and published until 1962–63. Since then, many thousands of carboranes have been prepared, and they have been combined with transition metals to yield derivatives called metallocarboranes, some of which show catalytic activity. Carboranes are electron-delocalized (non-classically bonded) clusters composed of boron, carbon and hydrogen atoms that may also contain other metallic and nonmetallic elements in the cluster framework. Like many of the related boron hydrides, these clusters are polyhedra or fragments of polyhedra, and are similarly classified as *closo*-, *nido*-, *arachno*-, *hypho*-, etc. based on whether they represent a complete (*closo*-) polyhedron, or a polyhedron that is missing one (*nido*-), two (*arachno*-)three (*hypho*-), or more vertices. Carboranes are a notable example of heteroboranes.

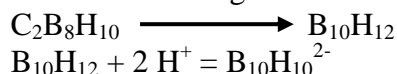


The utility of carboranes as pharmacophores in drug design (molecules that facilitate recognition and binding by biological macromolecules) motivates medicinal applications. Unlike boranes, which are generally quite moisture sensitive, some carboranes are kinetically stable to hydrolysis, permitting their use *in vivo*. Carboranes may be classified by structural type using the same method described previously for boranes. Because a carbon atom has the same number of valence electrons

Type	Borane	Example	Carborane	Example
<i>closo</i>	$B_nH_n^{2-}$	$B_{12}H_{12}^{2-}$	$C_2B_{n-2}H_n$	$C_2B_{10}H_{12}$
<i>nido</i>	$B_nH_{n+4}$	$B_{10}H_{14}$	$C_2B_{n-2}H_{n+2}$	$C_2B_8H_{12}$
<i>arachno</i>	$B_nH_{n+6}$	$B_9H_{15}$	$C_2B_{n-2}H_{n+4}$	$C_2B_7H_{13}$

*Examples of Formulas of Boranes and Carboranes*

as a boron atom plus a hydrogen atom, formally each C should be converted to BH in the classification scheme. For example, for a carborane having the formula  $C_2B_8H_{10}$ ,



the classification of the carboranes  $C_2B_8H_{10}$  is therefore *closo*.

**Closo-Carboranes:** These have closed cage structures in which hydrogen bridges are structurally analogous to the  $B_nH_{n-2}$  anions with B-replaced by isoelectronic carbon. These carboranes have the general formula.  $C_2B_{n+2}$  ( $n=3$ ) to 12. The important member is  $C_2B_{10}H_{12}$  which is isoelectronic with  $[B_{12}H_{12}]^{2-}$  similarly  $B_4C_2H_6$  is isoelectronic with  $[B_6H_6]^{2-}$ .

**Nido Carboranes:** They are having an open case structure in which some framework members are attached likely by hydrogen bridges. These are derived formally from one or other of several boranes.

These contain one to four carbon atoms in the skeleton.

In addition to the above types of carboranes, there are a number of carboranes with an additional heteroatom such as phosphorus built into the basic structure and a family of metallo carboranes, some of which are similar to ferrocene. One peculiar feature common to all carboranes is that to date no compound has been synthesized with either carbon bridging two boron atoms in a three centre two electron bond or acting as one end off a hydride bridge.

First carborane was obtained in 1953 when mixtures of diborane and acetylene were ignited with a hot wire. Since that time, many new carboranes have been isolated.

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### 7.3.1 Nomenclature

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Rules for naming carboranes are as follows:

i. First of all, give the positions and number of carbon atoms, then the type of carborane (either closo or nido) and finally the name of the borane from which the carborane is formally derived and the number of hydrogen atoms shown in bracket. For example  $\text{CB}_5\text{H}_9$  is name as monocarbonido hexaborane (9). Similarly, the three isomers of  $\text{C}_2\text{B}_{10}\text{H}_{12}$  are named as 1, 2; 1, 7 and 1, 12 dicarbo-closo-dodecaborane (12).

ii. Number of atoms in these structure are counted by starting the numbering from that in the apical position and proceeding through successive rings in a clockwise direction.

This rule is important in naming the isomers.

#### Closo-Carboranes or Closed Cage Carboranes

These carboranes are having general formula  $\text{C}_2\text{B}_n\text{H}_{n+2}$  ( $n=3$  to 10) in which the constituents are only terminal. These are isoelectronic with the corresponding  $[\text{B}_n\text{H}_n]^{2-}$  ions and have the same closed polyhedral structures, with one hydrogen atom bonded to each carbon and boron. No bridging hydrogen atoms are present in the  $\text{C}_2\text{B}_n$  skeleton. They are considered in three groups.

a. small,  $n = 3 - 5$

b. large,  $n = 6-10$  and

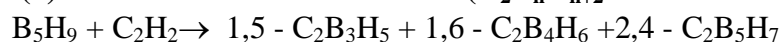
c. dicarbo-closo-dodecaborane

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### 7.3.2 Preparation

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(a) **The Small Closo Carboranes ( $\text{C}_2\text{B}_n\text{H}_{n+2}$  where  $n = 3$  to 5)**



Example - The closo hexaborane isomers,  $\text{C}_2\text{B}_n\text{H}_6$ ,

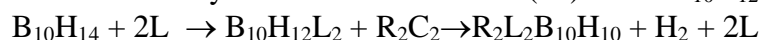
(b) **The Large Closo Carboranes ( $\text{C}_2\text{B}_n\text{H}_{n+2}$  where  $n = 6$  to 9)**

The first three members of this group of carboranes are obtained by the thermolysis of 1,3 -  $\text{C}_2\text{B}_7\text{H}_{13}$  and 1,3 -  $\text{C}_2\text{B}_8\text{H}_{14}$ .

**Example :**  $\text{C}_2\text{B}_6\text{H}_8$  is made from hexaborane (10) and dimethylacetylene. The structure of 1,7 -  $\text{Me}_2\text{C}_2\text{B}_6\text{H}_6$  is based on the bicapped triangular prism. The carbon atoms are present one on the prism and the other above the face opposite.

(c) **Dicarbo-closo-dodecaborane:**

**Preparation:** The orthocarborane is the only isomer which can be synthesized directly. However, it is synthesized by the base catalysed reaction of acetylenes with decaborane (14) or via  $\text{B}_{10}\text{H}_{12}\text{L}_2$ .



**Example:**  $\text{C}_2\text{B}_{10}\text{H}_{12}$  gives three isomeric structure - 1,2 (ortho), 1-7 (meta) and 1, 12 (para)

#### Nido-Carboranes or Open Cage Carboranes

These structures are derived formally from one or other of several boranes and contain from one to four carbon atoms in the skeleton.

Boranes

NOTES

Boranes

**Examples:**  $\text{CB}_5\text{H}_9$ ,  $\text{C}_2\text{B}_4\text{H}_8$ ,  $\text{C}_3\text{B}_3\text{H}_7$ ,  $\text{C}_4\text{B}_2\text{H}_6$  etc.

**Preparation:** The smaller nido-carboranes are generally prepared by reacting a borane with acetylene under mild conditions.

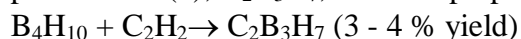
**Example:**  $\text{B}_5\text{H}_9$  and  $\text{C}_2\text{H}_2$  undergo reaction in the gas phase at  $215^\circ\text{C}$  to give mainly the nidocarborane 2,3 -  $\text{C}_2\text{B}_4\text{H}_8$  together with methyl derivatives of  $\text{CB}_5\text{H}_9$ .

NOTES

The preparation method described above does not yield a single product but a mixture of several products whose separation is not an easy task. However some smaller nidocarboranes are prepared by the following specific methods:

i. Mono carbo-nido-hexaborane (7)  $\text{CB}_5\text{H}_7$  is formed by passing silent electric discharge through 1-methyl pentaborane (9).

ii. The only example isoelectronic with  $\text{B}_5\text{H}_9$  is 1,2- dicarbonido - pentaborane(7),  $\text{C}_2\text{B}_3\text{H}_7$ , which is prepared as follows:

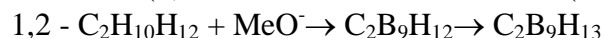


iii. Monocarbonidohexaborane (9),  $\text{CB}_5\text{H}_9$  is formed from ethyldifluoroborane and lithium.

The nido-carboranes are formally related to  $\text{B}_6\text{H}_{10}$ . All are having eight pairs of electrons which are bonding the six cage atoms together.

### Large Nido-Carborane:

Dicarbo-nido-undecaborane,  $\text{C}_2\text{B}_9\text{H}_{13}$ , is the second member of the class of nido-carboranes  $\text{C}_2\text{B}_n\text{H}_{n+4}$  ( $n = 4$  or  $9$ ), The parent carborane and its substituted derivatives can be prepared by the base degradation of ortho-carborane (1,2-dicarbocloso-dodecaborane ( $\text{C}_2\text{B}_{10}\text{H}_{12}$ )).



When  $\text{C}_2\text{B}_9\text{H}_{13}$  is heated, the closo-undeca-Borone (11) cage is formed.

### 7.3.3 Properties

Properties of carboranes resemble with that of the corresponding boranes closely. Thus, 1.2 dicarbo closo-dodecaborane-12 is stable in both air and heat. On heating in inert atmosphere at  $500^\circ\text{C}$ , it is converted into 1, 7 isomer i.e. meta or neo isomer; while at  $700^\circ\text{C}$  it is converted to 1, 12 isomer i.e. para-isomer.

### 7.4 Wade's rules

Ken Wade developed a method for the prediction of shapes of borane clusters; however, it may be used for a wide range of substituted boranes (such as carboranes) as well as other classes of cluster compounds. Wade's rules are used to rationalize the shape of borane clusters by calculating the total number of skeletal electron pairs (SEP) available for cluster bonding. In using Wade's rules it is key to understand structural relationship of various boranes.

The general methodology to be followed when applying Wade's rules is as follows:

1. Determine the total number of valence electrons from the chemical formula, i.e., 3 electrons per B, and 1 electron per H.
2. Subtract 2 electrons for each B-H unit (or C-H in a carborane).
3. Divide the number of remaining electrons by 2 to get the number of skeletal electron pairs (SEP).
4. A cluster with  $n$  vertices (i.e.,  $n$  boron atoms) and  $n+1$  SEP for bonding has a *closo* structure.
5. A cluster with  $n-1$  vertices (i.e.,  $n-1$  boron atoms) and  $n+1$  SEP for bonding has a *nido* structure.
6. A cluster with  $n-2$  vertices (i.e.,  $n-2$  boron atoms) and  $n+1$  SEP for bonding has an *arachno* structure.
7. A cluster with  $n-3$  vertices (i.e.,  $n-3$  boron atoms) and  $n+1$  SEP for bonding has an *hypho* structure.
8. If the number of boron atoms (i.e.,  $n$ ) is larger than  $n+1$  SEP then the extra boron occupies a capping position on a triangular phase.

What is the structure of  $B_5H_{11}$ ?

1. Total number of valence electrons =  $(5 \times B) + (11 \times H) = (5 \times 3) + (11 \times 1) = 26$
2. Number of electrons for each B-H unit =  $(5 \times 2) = 10$
3. Number of skeletal electrons =  $26 - 10 = 16$
4. Number SEP =  $16/2 = 8$
5. If  $n+1 = 8$  then  $n = 7$  and  $n-2 = 5$  boron atoms,
6. Structure of  $n = 7$  is pentagonal bipyramid, therefore  $B_5H_{11}$  is an *arachno* based upon a pentagonal bipyramid with two apexes missing.

What is the structure of  $B_6H_6^{2-}$ ?

1. Total number of valence electrons =  $(6 \times B) + (3 \times H) = (6 \times 3) + (6 \times 1) + 2 = 26$
2. Number of electrons for each B-H unit =  $(6 \times 2) = 12$
3. Number of skeletal electrons =  $26 - 12 = 14$
4. Number SEP =  $14/2 = 7$
5. If  $n+1 = 7$  and  $n$  boron atoms, then  $n = 6$
6. Structure of  $n = 6$  is octahedral, therefore  $B_6H_6^{2-}$  is a *closo* structure based upon an octahedral structure.

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## 7.5 STYX notation

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The description of the bonding in the larger boranes formulated by William Lipscomb which accounts for

- 3-center 2-electron B-H-B hydrogen bridges
- 3-center 2-electron B-B-B bonds
- 2-center 2-electron bonds (in B-B, B-H and BH<sub>2</sub>)

The *styx number* was introduced to aid in electron counting. Lipscomb's methodology has largely been superseded by a molecular orbital approach, although it still affords insights. The results of this have been summarized in a simple but powerful rule, PSEPT (Polyhedral Skeletal Electron Pair Theory), often known as Wade's rules, that can be used to predict the cluster type, *closo*-, *nido*-, etc. The power of this rule is its ease of use and general applicability to many different cluster types other than boranes.

where

s = count of 3-center B-H-B bonds;

t = count of 3-center B-B-B bonds;

y = count of 2-center B-B bonds and

x = count of BH<sub>2</sub> groups.

The polyhedral skeletal electron pair theory (PSEPT) provides electron counting rules useful for predicting the structures of clusters such as borane and carborane clusters. The electron counting rules were originally formulated by Kenneth Wade and were further developed by Michael Mingos and others; they are sometimes known as Wade's rules or the Wade-Mingos rules. The rules are based on a molecular orbital treatment of the bonding. These rules have been extended and unified in the form of the Jemmis *mno* rules.

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### 7.5.1 Predicting structures of cluster compounds

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Different rules ( $4n$ ,  $5n$ , or  $6n$ ) are invoked depending on the number of electrons per vertex.

The  $4n$  rules are reasonably accurate in predicting the structures of clusters having about 4 electrons per vertex, as is the case for many boranes and carboranes. For such clusters, the structures are based on deltahedra, which are polyhedra in which every face is triangular. The  $4n$  clusters are classified as *closo*-, *nido*-, *arachno*- or *hypho*-, based on whether they represent a complete (*closo*-) deltahedron, or a deltahedron that is missing one (*nido*-), two (*arachno*-) or three (*hypho*-) vertices.

However, *hypho* clusters are relatively uncommon due to the fact that the electron count is high enough to start to fill antibonding orbitals and destabilize the  $4n$  structure. If the electron count is close to 5 electrons per vertex, the structure often changes to one governed by the  $5n$  rules, which are based on 3-connected polyhedra.

As the electron count increases further, the structures of clusters with  $5n$  electron counts become unstable, so the  $6n$  rules can be implemented. The  $6n$  clusters have structures that are based on rings.

A molecular orbital treatment can be used to rationalize the bonding of cluster compounds of the  $4n$ ,  $5n$ , and  $6n$  types.

### 7.5.2 $4n$ rules

The following polyhedra are *closo* polyhedra, and are the basis for the  $4n$  rules; each of these have triangular faces. The number of vertices in the cluster determines what polyhedron the structure is based on.

Number of vertices	Polyhedron
4	Tetrahedron
5	Trigonal bipyramid
6	Octahedron
7	Pentagonal bipyramid
8	$D_{2d}$ (trigonal) dodecahedron (snub disphenoid)
9	Tricapped trigonal prism
10	Bicapped square antiprism
11	Edge-contracted icosahedron (octadecahedron)
12	Icosahedron (bicapped pentagonal antiprism)

using the electron count, the predicted structure can be found.  $n$  is the number of vertices in the cluster. The  $4n$  rules are enumerated in the following table.

Electron count	Name	Predicted structure
$4n - 2$	Bicapped <i>closo</i>	$n - 2$ vertex <i>closo</i> polyhedron with 2 capped (augmented) faces
$4n$	Capped <i>closo</i>	$n - 1$ vertex <i>closo</i> polyhedron with 1 face capped
$4n + 2$	<i>closo</i>	<i>closo</i> polyhedron with $n$ vertices
$4n + 4$	<i>nido</i>	$n + 1$ vertex <i>closo</i> polyhedron with 1 missing vertex
$4n + 6$	<i>arachno</i>	$n + 2$ vertex <i>closo</i> polyhedron with 2 missing vertices
$4n + 8$	<i>hypho</i>	$n + 3$ vertex <i>closo</i> polyhedron with 3 missing vertices
$4n + 10$	<i>klado</i>	$n + 4$ vertex <i>closo</i> polyhedron with 4 missing vertices

When counting electrons for each cluster, the number of valence electrons is enumerated. For each transition metal present, 10 electrons are subtracted from the total electron count

Example:



Boranes

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Electron count:  $5 \times B + 5 \times H + 4$  (for the negative charge) =  $5 \times 3 + 5 \times 1 + 4 = 24$

Since  $n = 5$ ,  $4n + 4 = 24$ , so the cluster is nido.

Starting from an octahedron, one of the vertices is removed.

## NOTES

The rules are useful in also predicting the structure of carboranes.  
Example:  $C_2B_7H_{13}$

Electron count =  $2 \times C + 7 \times B + 13 \times H = 2 \times 4 + 7 \times 3 + 13 \times 1 = 42$

Since  $n$  in this case is 9,  $4n + 6 = 42$ , the cluster is *arachno*.

### 7.5.3 $5n$ rules

As more electrons are added per vertex, the number of the electrons per vertex approaches 5. Rather than adopting structures based on deltahedra, the  $5n$ -type clusters have structures based on a different series of polyhedra known as the 3-connected polyhedra, in which each vertex is connected to 3 other vertices. The 3-connected polyhedra are the duals of the deltahedra.

Number of vertices	Type of 3-connected polyhedron
4	Tetrahedron
6	Trigonal prism
8	Cube
10	Pentagonal prism
12	$D_{2d}$ pseudo-octahedron (dual of snub disphenoid)
14	Dual of triaugmented triangular prism ( $K_5$ associahedron)
16	Square truncated trapezohedron
18	Dual of edge-contracted icosahedron
20	Dodecahedron

The  $5n$  rules are as follows.

Total electron count	Predicted structure
$5n$	$n$ -vertex 3-connected polyhedron
$5n + 1$	$n - 1$ vertex 3-connected polyhedron with one vertex inserted into an edge
$5n + 2$	$n - 2$ vertex 3-connected polyhedron with two vertices inserted into edges
$5n + k$	$n - k$ vertex 3-connected polyhedron with $k$ vertices inserted into edges



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### 7.5.4 6n rules

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As more electrons are added to a  $5n$  cluster, the number of electrons per vertex approaches 6. Instead of adopting structures based on  $4n$  or  $5n$  rules, the clusters tend to have structures governed by the  $6n$  rules, which are based on rings. The rules for the  $6n$  structures are as follows.

Total electron count	Predicted structure
$6n - k$	$n$ -membered ring with $k/2$ transannular bonds
$6n - 4$	$n$ -membered ring with 2 transannular bonds
$6n - 2$	$n$ -membered ring with 1 transannular bond
$6n$	$n$ -membered ring
$6n + 2$	$n$ -membered chain ( $n$ -membered ring with 1 broken bond)

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### 7.5.5 Isolobal vertex units

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Provided a vertex unit is isolobal with BH then it can, in principle at least, be substituted for a BH unit, even though BH and CH are not isoelectronic. The  $\text{CH}^+$  unit is isolobal, hence the rules are applicable to carboranes. This can be explained due to a frontier orbital treatment. Additionally there are isolobal transition-metal units.

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### 7.5.6 Isolobal Analogy

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An important contribution to the understanding of parallels between organic and inorganic chemistry has been the concept of isolobal molecular fragments, described elaborately by Roald Hoffmann in his 1981 Nobel lecture. Hoffmann defined molecular fragments to be isolobal if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar not identical, but similar.

The fragments can be combined into molecules; two  $\text{CH}_3$  fragments form ethane, and two  $\text{Mn}(\text{CO})_5$  fragments form  $(\text{OC})_5\text{Mn}-\text{Mn}(\text{CO})_5$ . Furthermore, these organic and organometallic fragments can be combined to afford  $\text{H}_3\text{C}-\text{Mn}(\text{CO})_5$ .

The organic and organometallic parallels are not always this complete. For example, although two 6-electron  $\text{CH}_2$  fragments form ethylene,  $\text{H}_2\text{C}=\text{CH}_2$ , the neutral dimer of the isolobal  $\text{Fe}(\text{CO})_4$  is known only as a transient species, obtained photochemically from  $\text{Fe}_2(\text{CO})_9$ . However, both  $\text{CH}_2$  and  $\text{Fe}(\text{CO})_4$  form three-membered rings, cyclopropane and  $\text{Fe}_3(\text{CO})_{12}$ . Although cyclopropane is a trimer of three  $\text{CH}_2$  fragments,  $\text{Fe}_3(\text{CO})_{12}$  has two bridging carbonyls and is therefore not a perfect trimer of  $\text{Fe}(\text{CO})_4$ . The isoelectronic  $\text{Os}_3(\text{CO})_{12}$ , on the other hand, is a trimeric combination of three  $\text{Os}(\text{CO})_4$  fragments, which are isolobal with both  $\text{Fe}(\text{CO})_4$  and  $\text{CH}_2$ , and can correctly be described as  $[\text{Os}(\text{CO})_4]_3$ .

Boranes

NOTES

The isolobal species  $\text{Ir}(\text{CO})_3$ ,  $\text{Co}(\text{CO})_3$ , CR (R = H, alkyl, aryl), and P may also be combined in several different ways. The  $\text{Ir}(\text{CO})_3$ , a 15-electron fragment, forms  $[\text{Ir}(\text{CO})_3]_4$ , which has  $T_d$  symmetry. The isoelectronic complex  $\text{Co}_4(\text{CO})_{12}$  has a nearly tetrahedral array of cobalt atoms but has three bridging carbonyls and hence  $C_{3v}$  symmetry. Compounds are also known that have a central tetrahedral structure, with one or more  $\text{Co}(\text{CO})_3$  fragments replaced by the isolobal CR fragment. This is similar to the replacement of phosphorus atoms in the  $\text{P}_4$  tetrahedron by  $\text{Co}(\text{CO})_3$  fragments; P is isolobal with CR.

### Bonding in cluster compounds

#### $\text{B}_2\text{H}_6$ :

The bonding in diborane is best described by treating each B as  $\text{sp}^3$ -hybridized. Two  $\text{sp}^3$ -hybrid orbitals on each boron form the bonds to the terminal hydrogens. The remaining  $\text{sp}^3$ -orbitals create the bonds with the bridging hydrogens. Because the angles in the diborane structure are not tetrahedral the orbitals also likely contain some  $\text{sp}^2$  character.

#### *closo*- $\text{B}_6\text{H}_6^{2-}$

MO diagram of  $\text{B}_6\text{H}_6^{2-}$  showing the orbitals responsible for forming the cluster. The boron atoms lie on each vertex of the octahedron and are sp hybridized. One sp-hybrid radiates away from the structure forming the bond with the hydrogen atom. The other sp-hybrid radiates into the center of the structure forming a large bonding molecular orbital at the center of the cluster. The remaining two unhybridized orbitals lie along the tangent of the sphere like structure creating more bonding and antibonding orbitals between the boron vertices. The orbital diagram breaks down as follows: The 18 framework molecular orbitals, (MOs), derived from the 18 boron atomic orbitals are:

- One bonding MO at the center of the cluster and 5 antibonding MOs from the 6 sp-radial hybrid orbitals
- 6 bonding MOs and 6 antibonding MOs from the 12 tangential p-orbitals.

The total skeletal bonding orbitals is therefore 7, i.e.  $n + 1$ .

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### 7.6 Check your progress

1. Give the classification of boranes.
2. Classify the following boranes by structural type: a.  $\text{B}_{11}\text{H}_{13}^{2-}$  b.  $\text{B}_5\text{H}_8^-$  c.  $\text{B}_7\text{H}_7^{2-}$
3. What are the STYX number?

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### 7.7 Answers to Check Your Progress Questions

1. Boranes fall into five structure categories:
  - closo* ( $\text{B}_n\text{H}_n^{2-}$ ), *nido* ( $\text{B}_n\text{H}_n^{+4}$ ), *arachno* ( $\text{B}_n\text{H}_n^{+6}$ ), *hypho* ( $\text{B}_n\text{H}_n^{+8}$ ), *klado* ( $\text{B}_n\text{H}_n^{10-}$ ).
2. a.  $\text{B}_{11}\text{H}_{13}^{2-}$  is derived from  $\text{B}_{11}\text{H}_{11}^{4-}$ , a nido species.  
 b.  $\text{B}_5\text{H}_8^-$  is derived from  $\text{B}_5\text{H}_5^{4-}$ , a nido species.  
 c.  $\text{B}_7\text{H}_7^{2-}$  is a closo species.

3. The *styx number* was introduced to aid in electron counting where

**s** = count of 3-center B-H-B bonds;

**t** = count of 3-center B-B-B bonds;

**y** = count of 2-center B-B bonds and

**x** = count of BH<sub>2</sub> groups.

Boranes

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## 7.8 Summary

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- **Boranes** is the name given to the class of synthetic hydrides of boron with generic formula B<sub>x</sub>H<sub>y</sub>. In the past, borane molecules were often labeled "electron-deficient" because of their multicenter bonding (in which a pair of bonding electrons links more than two atoms, as in 3-center-2-electron bonds); this was done in order to distinguish such molecules from hydrocarbons and other classically bonded compounds.
- Boranes fall into five structure categories: closo (B<sub>n</sub>H<sub>n</sub><sup>2-</sup>), nido (B<sub>n</sub>H<sub>n</sub><sup>+4</sup>), arachno (B<sub>n</sub>H<sub>n</sub><sup>+6</sup>), hypho (B<sub>n</sub>H<sub>n</sub><sup>+8</sup>), klado (B<sub>n</sub>H<sub>n</sub><sup>10-</sup>).
- The *styx number* was introduced to aid in electron counting where s = count of 3-center B-H-B bonds; t = count of 3-center B-B-B bonds; y = count of 2-center B-B bonds and x = count of BH<sub>2</sub> groups.
- Wade's rule states that clusters having n skeletal atoms (vertices) will adopt closo structures if it is held together by (n+1) skeletal bonding electron pairs; nido if held together by (n+2) skeletal electron pairs, arachno if held together by (n+3) skeletal electron pairs, hypho if held together by (n+4) skeletal electron pairs and klado if held together by (n+5) skeletal electron pairs.
- Two molecular fragments are isolable if the number, symmetry properties and shapes and approximate energies of their frontier orbitals are the same. They may or may not be isoelectronic.

NOTES

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## 7.9 Keywords

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**Boranes** - The name given to the class of synthetic hydrides of boron with generic formula B<sub>x</sub>H<sub>y</sub>.

**Carboranes**- Any member of a class of organometallic compounds containing carbon(C), boron (B), and hydrogen (H). The general formula of carboranes is represented by C<sub>2</sub>B<sub>n</sub>H<sub>n+2</sub>, in which n is an integer.

**Wade's rule** - used to rationalize the shape of borane clusters by calculating the total number of skeletal electron pairs (SEP) available for cluster bonding. In using Wade's rules it is key to understand structural relationship of various boranes.

**Borazine**- A non-polar inorganic compound with the chemical formula B<sub>3</sub>H<sub>6</sub>N<sub>3</sub>. It is isostructural and isoelectronic with benzene, and hence it is referred as inorganic benzene.

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## 7.10 Self-Assessment Questions and Exercises

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1. Explain Lipcomb's Styx rule with example.
2. Give the detailed picture of the classification of boranes with examples.
3. Give a detailed picture of carboranes.

Boranes

4. Classify the following carboranes by structural type:
  - a.  $C_3B_3H_7$
  - b.  $C_2B_5H_7$
  - c.  $C_2B_7H_{12}^-$
5. Explain Wade's rule with a suitable example.
6. Explain the preparation and properties of borazine.
7. Explain in detail about Isolable analogy suitable examples.

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#### 7.11 Further Readings

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NOTES

- 1 Cotton, F.A. and G. Wilkinson. 1988. Advanced Inorganic Chemistry, 5th Edition. New Jersey: Wiley Eastern.
- 2 Huheey, J.E., E.A. Keiter and R.L. Keiter. 2002. Inorganic Chemistry: Principles of Structure and Reactivity, 4th Edition. New York: HarperCollins Publishers.
- 3 Gary L. Miessler., Paul J. Fischer., Donald A. Tarr. Inorganic Chemistry, 5th edition : Pearson
- 4 Shriver and Atkins., Inorganic Chemistry, 5th ed : W. H. Freeman and Company New York.

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## BLOCK-3 ORGANOMETALLIC CHEMISTRY

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### UNIT-8 DEFINITION OF ORGANOMETALLICS

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Structure

8.0 Introduction

8.1 Objectives

8.2 Synthesis of Metal Alkyl Complexes

8.2.1 Reactions of Metal alkyls

8.3 Metal alkene complexes

8.4 Dewar-Chatt approach to bonding in olefins

8.5 Metal – alkyne complexes

8.5.1 Reactivity of Alkyne Complexes

8.6 Metal – Arene Complexs

8.7 Check your progress questions

8.8 Answers to check your progress questions

8.9 Summary

8.10 Keywords

8.11 Self-assessment questions and exercises

8.12 Further readings

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#### 8.0 Introduction

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Organometallic chemistry is the study of chemical compounds containing at least one chemical bond between a carbon atom of an organic molecule and a metal, including alkaline, alkaline earth, and transition metals, and sometimes broadened to include metalloids like boron, silicon, and tin, as well. Aside from bonds to organyl fragments or molecules, bonds to 'inorganic' carbon, like carbon monoxide (metal carbonyls), cyanide, or carbide, are generally considered to be organometallic as well. Some related compounds such as transition metal hydrides and metal phosphine complexes are often included in discussions of organometallic compounds, though strictly speaking, they are not necessarily organometallic. The related but distinct term "metalorganic compound" refers to metal-containing compounds lacking direct metal-carbon bonds but which contain organic ligands. Metal  $\beta$ -diketonates, alkoxides, dialkylamides, and metal phosphine complexes are representative members of this class. The field of organometallic chemistry combines aspects of traditional inorganic and organic chemistry.

Organometallic compounds are widely used both stoichiometrically in research and industrial chemical reactions, as well as in the role of catalysts to increase the rates of such reactions (e.g., as in uses of homogeneous catalysis), where target molecules include polymers, pharmaceuticals, and many other types of practical products.

Compounds that contain a metal-carbon bond, **R-M**, are known as "*organometallic*" compounds. Organometallic compounds of Li, Mg (Grignard reagents) are amongst some of the most important organic reagents. Many other metals have been utilised, for example Na, Cu and

## NOTES

Zn. Organometallic compounds provide a source of **nucleophilic carbon** atoms which can react with electrophilic carbon to form a new carbon-carbon bond. This is very important for the synthesis of complex molecules from simple starting materials. To rationalise the general reactivity of organometallics it is **convenient** to view them as ionic, so  **$R-M = R^{\ominus}M^{\oplus}$**

The most important reactions in this chapter are the reactions of organolithiums,  **$RLi$** , and Grignard reagents,  **$RMgX$** , with the carbonyl groups in aldehydes, ketones and esters to give alcohols. However, we will also look at some useful reactions involving Cu, Zn and Hg (mercury). Transition metal alkyl complexes play a critical role in a variety of important organometallic reactions such as olefin polymerization and hydroformylation. Early attempts to synthesize these complexes were unsuccessful, so it was originally thought that such species were inherently unstable due to weak metal-carbon bonds. In fact, the issue is not their thermodynamic stability (M-C bond dissociation energies are typically 40-60 kcal/mol with 20-70 kcal/mol being a practical range), but their kinetic stability.

### Hapticity

The term hapticity is used to describe how a group of *contiguous* atoms of a ligand are coordinated to a central atom. Hapticity of a ligand is indicated by the Greek character 'eta',  $\eta$ .

$\eta^n$ : n = the number of contiguous atoms of the ligand that are bound to the metal. The term is usually employed to describe ligands containing extended  $\pi$ -systems or where agostic bonding is not obvious from the formula.

Example

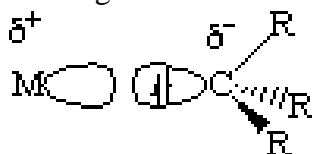
1. Ferrocene: bis( $\eta^5$ -cyclopentadienyl)iron

2. Zeise's salt:  $K[PtCl_3(\eta^2-C_2H_4)] \cdot H_2O$

Uranocene: bis( $\eta^8$ -1,3,5,7-cyclooctatetraene)uranium

### Structure and Bonding

Simple alkyls are simple sigma donors, that can be considered to donate one or two electrons to the metal center depending on which electron counting formalism.



For simple metal alkyls, the M-R bond distance is typically 190 to 220 pm. This is approximately the sum of the covalent radii of carbon and metal,  $r_C = 77$  pm and  $r_M \sim 120$  pm. Realize that the first row transition metals are smaller, so any M-X bond distance will usually be smaller by 10-20 pm or so.

Alkyls can bridge two metal centers, something that is well known from aluminum-alkyl chemistry. For  $Al_2Me_6$ , Bridging alkyls are also known

for other metals such as lanthanum and zirconium. Another type of unusual alkyl group involves agostic interactions in which part of the alkyl substituent coordinates to the metal in addition to the M-C bond.

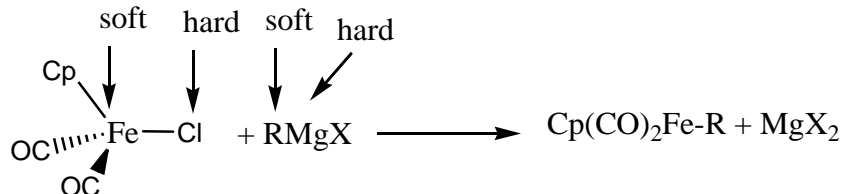
## 8.1 Objectives

After going through this unit, you will be able to:

- Understand about the stability of Metal carbon bond
- Understand the methods of synthesis of metal alkyl, alkene, arene complexes
- Explain the concept and structure of metal alkene complexes

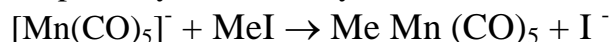
## 8.2 Synthesis of Metal Alkyl Complexes

**1. Metathetical exchange using a carbon nucleophile (R<sup>-</sup>).** Much of this alkylation chemistry can be understood with Pearson's "hard-soft" principles. Here are just a few examples of nucleophilic routes; notice that some of the homoleptic alkyls are rather unstable. This is because they have low d-counts, are susceptible to alpha- and/or beta-hydride elimination, and lack good pi-donating ligands to stabilize their high oxidation states:

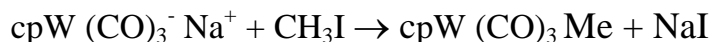


Beware of reactions where the hard-soft interactions are not so clear as these can represent equilibria instead of complete reactions

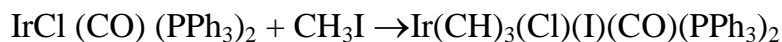
2) Metal alkyl complexes are prepared by taking advantage of the nucleophilicity of a carbonylate ion.



3) Interaction of sodium salts of anions with alkyl or aryl halides.



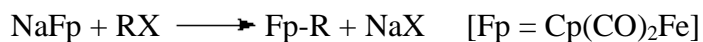
4) Oxidative – Addition reactions: This requires a covalently unsaturated, low-valent complex (16 e<sup>-</sup> or less). A classic example:



5) Metal atom reactions



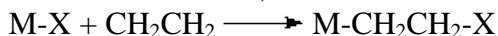
6) **Metal-centered nucleophiles** (i.e. using R<sup>+</sup> as a reagent): Typical examples are a metal anion and alkyl halide (or pseudohalogen). for example:



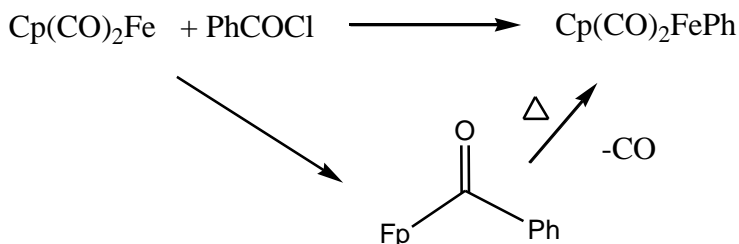
S<sub>N</sub><sup>2</sup> (associative mechanism) for this reaction, but a single electron transfer mechanism (SET) could also be postulated.

NOTES

7) **Insertion reactions:** To form an alkyl, this usually involves an olefin insertion. The simplest generic example is the insertion of ethylene into an M-X bond, i.e.



8) **Deinsertion.** This is not a highly common method. The reaction usually involves desinsertion of carbon monoxide from an intermediate acyl complex



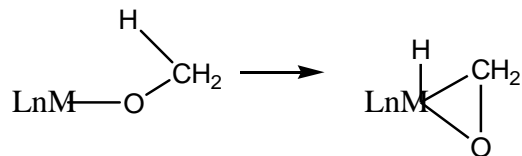
### 8.2.1 Reactions of Metal alkyls

(i)  $\alpha$  - hydride transfer

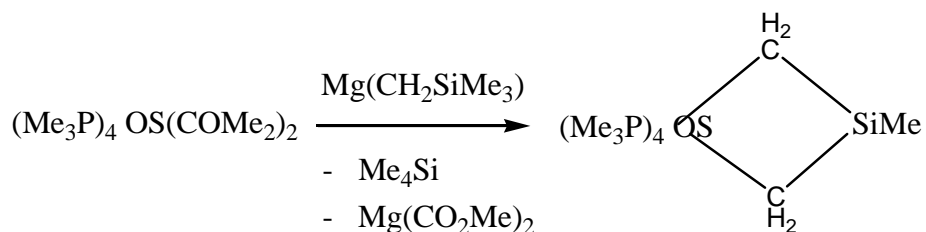
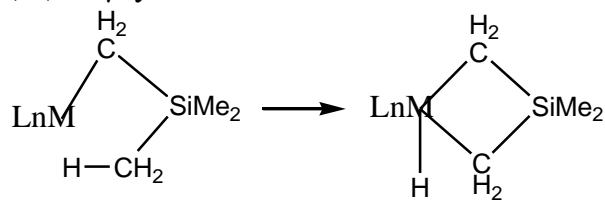
Methyl compounds like  $WMe_6$  decompose thermally to give  $CH_4$  and polymeric material.



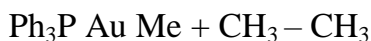
(ii)  $\beta$  - hydride transfer



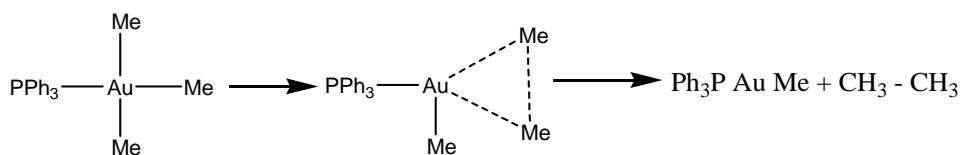
(iii)  $\gamma$  hydride transfer



(iv) Intermolecular reductive eliminations







## (v) Alkyl exchange reactions

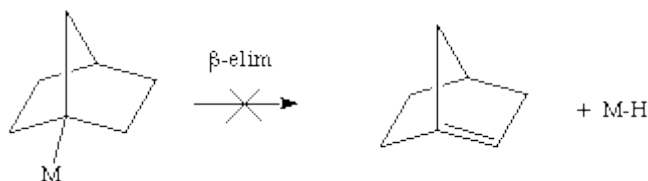


## NOTES

**Empirical order of stabilities**

The factors discussed above all influence the stability of metal alkyl complexes. We can come up with some experimental observations about the relative stabilities of different alkyl ligands:

- a. 1-norbornyl > benzyl > trimethylsilyl > neopentyl > Ph ~ Me >> Et (1° R) > 2, 3° R

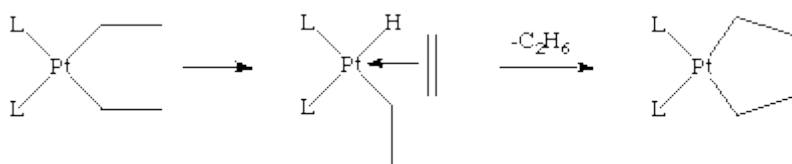


Notice that norbornyl not only has a difficult time approaching the metal center, but that the olefin that would be generated would be highly strained (and violate Bent's rule).

- b. Fluoroalkyl > alkyl (i.e.  $-\text{C}_n\text{F}_{2n+1} > -\text{C}_n\text{H}_{2n+1}$ )

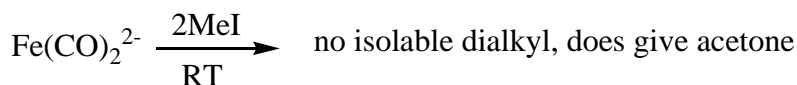
CF bonds are very strong (120-130 kcal/mol vs. 98-104 kcal/mol for alkyl C-H).

- c. Chelating (metallacycles) > nonchelating (acyclic)

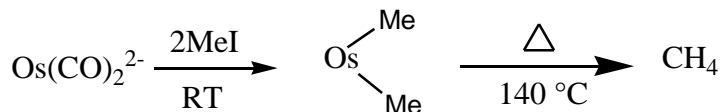


The dialkyl shown on the left decomposes at 110 °C with  $k_{\text{dec}} = 1.0 \text{ s}^{-1}$ . In contrast, the metallacycle has  $k = 5.3 \times 10^{-3} \text{ s}^{-1}$ . The beta-hydrogen has a close approach to the metal in the dialkyl case, but not the metallacycle.

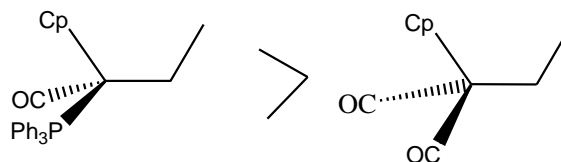
- d. 3rd row > 2nd row > 1st row transition metals.



but



e. Strong electron-donating ligands increase stability.

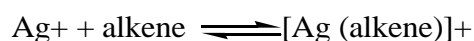
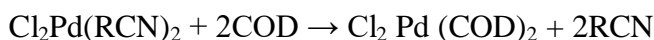


The carbonyl ligand reduces electron density on the metal through pi-backbonding, in contrast to the phosphine ligand, which is a good sigma donor.

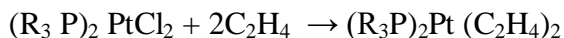
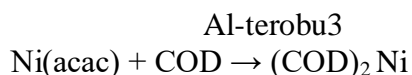
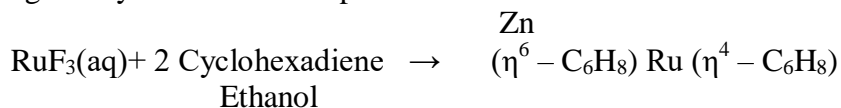
### 8.3 Metal alkene complexes

#### General Methods of Synthesis of Metal Alkene Complexes

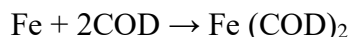
1) Substitution of CO in metal carbonyls or of weakly held ligands by alkene.  $\text{Cr}(\text{CO})_6 + \text{C}_7\text{H}_8 \rightarrow (\eta^6\text{-C}_7\text{H}_8)\text{Cr}(\text{CO})_3 + \text{CO}$



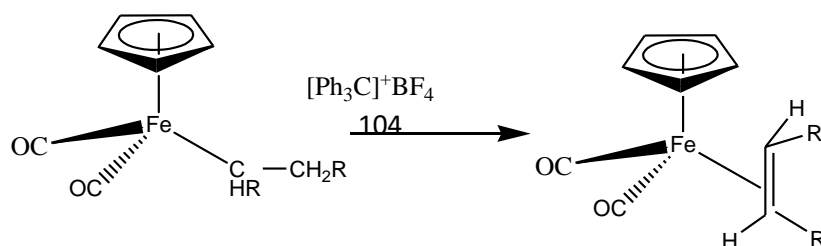
2) From halides and other compounds in the presence of reducing agents by use of anionic species.



3) CO – Condensation of metal vapours with alkene



4) Removal of a  $\beta$  – hydrogen from a coordinated alkyl ligand by triphenyl carbonium ion



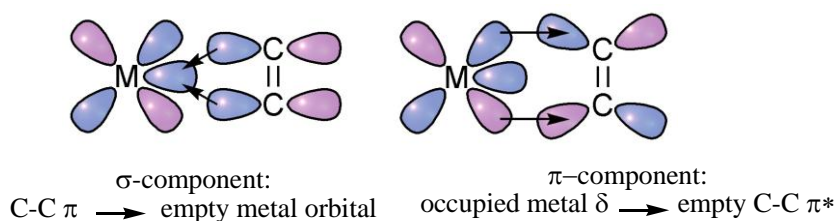
## 8.4 Dewar-Chatt approach to bonding in olefins

Simple alkyl ligands are dihapto two electron donors. The bond between the ethylene molecule and metal ion is a dative  $\sigma$  – bond from the filled  $\pi$  – orbital of the alkene to the suitably oriented metal orbital. The bonding scheme is analogous to that in CO complexes. There is a  $L \rightarrow M$   $\sigma$  donation and  $M \rightarrow L$   $\pi^*$  donation. i.e.,

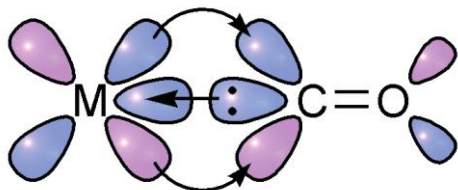
Two components

- $\sigma$ -donation from alkene  $\pi$ -orbital to metal  $\sigma$ -orbital ( $s, p_z$  or  $d_{z^2}$ )
- $\pi$ -donation from metal  $d$ -orbital to alkene  $\pi^*$  orbital

Evidence for this model?



Note the similarity to CO ligands

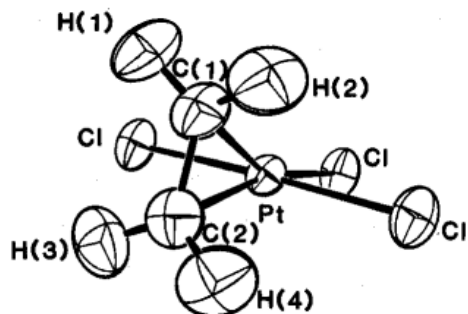


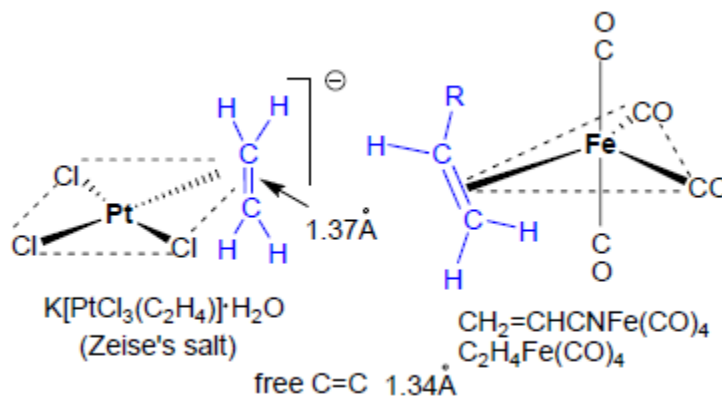
$\sigma$ -component: donation of C lone pair

$\pi$ -component: backbonding into CO  $\pi^*$

### Structural data

#### (a) bond distances





Zeise's salt

$[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$

C-C distance = 1.37 Å

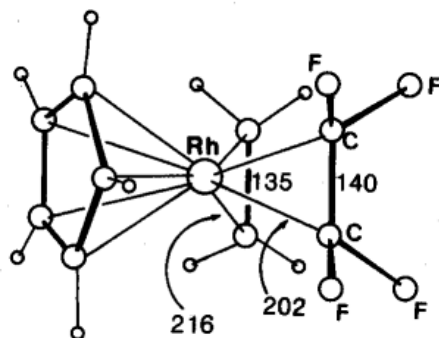
C-C distance in free ligand = 1.35 Å

**Conclusion** : in this complex most of bonding is ligand  $\rightarrow$  M  $\sigma$ -donation. Both components *strengthen* M-C bonds and *weaken* C-C bonds, but  $\pi$ -donation has greatest effect in weakening C-C bond.

### (b) bond angles

When backbonding occurs, hybridisation of alkene C- atoms changes from  $sp^2$  to approaching  $sp^3$ . This has an implication for the bond angles ( $sp^2$  C-atom is planar  $sp^3$  C-atom is pyramidal)

So - substituents "bend-back" from the metal - the greater the  $\pi$ -donation the greater the bend-back.



C-C distances  $\text{C}_2\text{H}_4 = 1.35 \text{ \AA}$

$\text{C}_2\text{F}_4 = 1.40 \text{ \AA}$

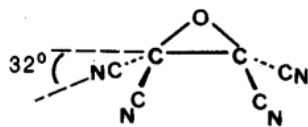
Rh-C distances  $\text{C}_2\text{H}_4 = 2.16 \text{ \AA}$

$\text{C}_2\text{F}_4 = 2.02 \text{ \AA}$

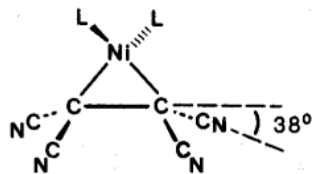
More  $\pi$ -donation in  $\text{C}_2\text{F}_4$  ligand because F atoms are electron withdrawing.

$\text{CpRh}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)$

"Bend-back" angle  $\text{C}_2\text{H}_4 = 17^\circ$   $\text{C}_2\text{F}_4 = 37^\circ$



Epoxide

 $(\eta^2\text{-Tetracyanoethylene})\text{Ni}$  complex  
(nickelacyclopropane)

NOTES

Alkene complexes can also be thought of as *metallacyclopropanes*. Two approaches are complementary.

### Hindered rotation of coordinated alkenes

Alkenes can rotate about M-C=C axis

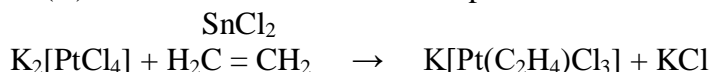
- M - alkene  $\sigma$ -bond is *invariant* to rotation (does not affect overlap)
- M - alkene  $\pi$ -bond is *strongly* dependent on rotation angle

Thus there is a energy cost (and hence a *energy barrier*) to this rotation. Barrier is of the size which can be detected by variable temperature NMR spectroscopy

### Preparation of Zeises salt

W.C. Zeises isolated stable yellow crystals after refluxing an alcoholic solution of  $\text{K}_2[\text{PtCl}_4]$  in 1827 which is known as Zeises salt  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$

Zeises salt is now prepared by bubbling ethene through an aqueous solution of potassiumtetrachloroplatinate(II) in the presence of Sn(II) which aids the coordination sphere.



### Structure of Zeises salt

A structural investigation of the anion in Zeises salt has shown that the ethylene occupies the four coordination sites of the square planar complex with the C - C axis perpendicular to the platinum ligand plane (Cl-Pt-Cl plane) i.e., xy plane. Relative to free ethylene the C - C bond is lengthened slightly from 1.35 Å to 137.5 Å and the hydrogens are slightly tilted back from the planar arrangement.

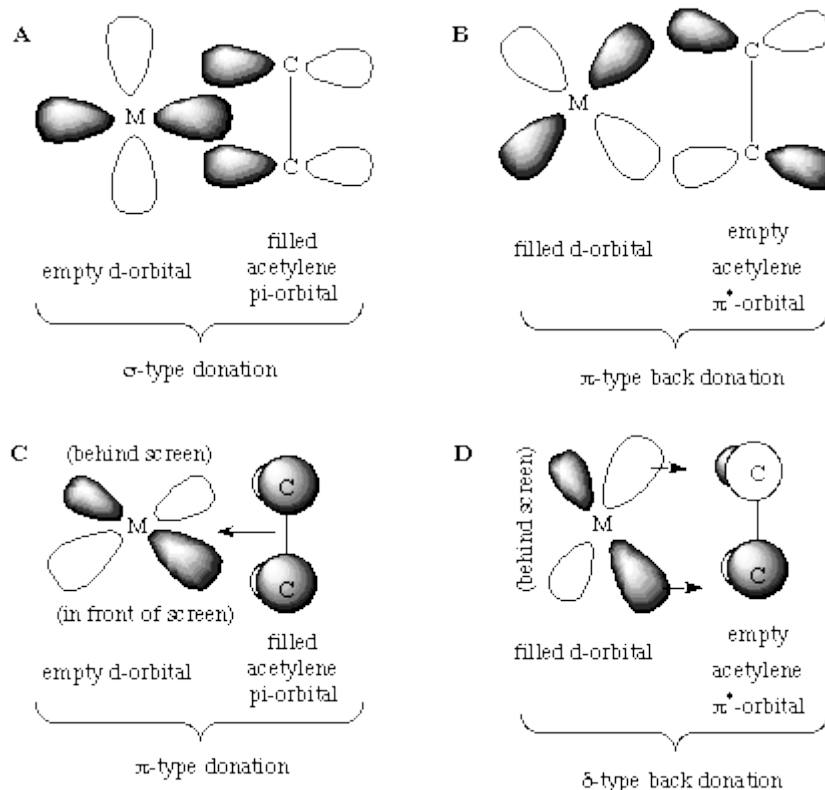
The extent of back bonding depends on the metal substituents on ethylene and the other ligands on the metal. For example in the complexes of the type  $\text{LRh}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)$  where (L - acacorcp), the tetrafluoroethylene molecule bonds more strongly and at a shorter distance. Rh - C = 201 - 202 pm than the unsubstituted ethylene Rh - C = 217 - 219 pm. This indicates that the  $\pi$  accepting ability of  $(\text{C}_2\text{F}_4 > \text{C}_2\text{H}_4)$  significantly influences the M - C bond in this compounds. Only metal atoms in low oxidation states are sufficiently good  $\pi$  - donors to stabilise alkene complexes.

## 8.5 Metal – alkyne complexes

### Structure and Bonding

The bonding of an alkyne (acetylene) to a transition metal complex is similar to that of an alkene complex. Alkynes tend to be more electropositive and therefore tend to bind more tightly to a transition metal than alkenes. In fact, alkynes will often displace alkenes.

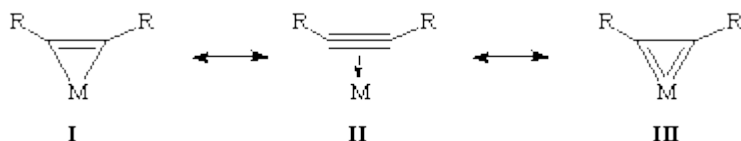
The primary difference in bonding between alkenes and alkynes is that an alkyne can act as either a 2 or 4 electron donor. Recall that alkynes have **two** sets of mutually orthogonal pi bonds. We can bind one of these to the transition metal in a sigma-type fashion (**A**) as we did for alkenes, including a pi-backbond (**B**). The orthogonal set can also bind in a pi-type fashion using an orthogonal metal d-orbital (**C**):



The back-donation to the antibonding orbital (**D**) is a delta-bond (there are two nodes in it), and the degree of overlap is quite small as the two orbitals meet side-to-side rather than engaging in direct overlap. Therefore, the contribution of **D** to the bonding of alkynes is minimal at best.

The net effect of this additional pi-donation is that alkynes are usually non-linear when coordinated to a transition metal complex. We can draw several resonance structures that depict the bonding of an alkyne. **I** is the **metallacyclopropene** resonance form. Support for this versus a simple two electron donor, **II**, can be inferred from the C-C bond distance as

well the R-C-C-R angles (see below). **III** generally does not contribute to the bonding of alkyne complexes.



Other than geometry, the other major difference between **I** and **II** is that **I** implies the metal oxidation state is greater by two. In other words, one can sometimes think of alkynes as dianionic ligands instead of as neutral ligands! Remember that electron counting is strictly a formalism.

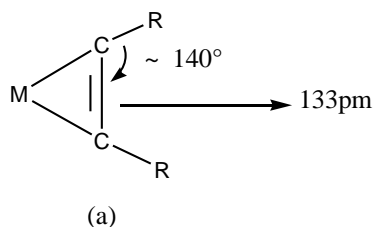
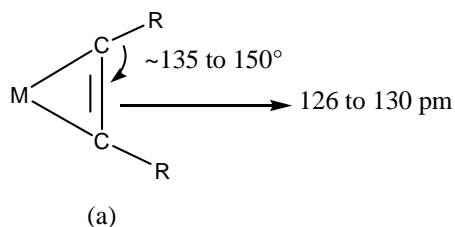
As expected from the reduced C-C bond order, the C-C bond distances for coordinated alkynes are typically larger (125 to 135 pm) than in the uncoordinated ligand (110 to 115 pm).

For 4-electron donors, the R-C-C bond angles are usually in the range of 130 to 146 degrees, with M-C bond distances of 199 to 209 pm. The C-C triple bond of free alkynes are normally observed around  $2200\text{ cm}^{-1}$  in the infrared or Raman spectrum.

Coordination to a transition metal reduces the C-C bond order, leading to a lower stretching frequency in the range of  $1700\text{ to }2000\text{ cm}^{-1}$ . 4-electron donors reflect their reduced nature in the IR: coordinated internal alkynes are typically  $1730 - 1820\text{ cm}^{-1}$  and coordinated terminal alkynes are typically  $1675 - 1715\text{ cm}^{-1}$ .

Remember that symmetric C-C stretches are not IR active, so that an asymmetric alkyne or the use of Raman spectroscopy may be required to observe this spectroscopic feature. In an alkyne molecule such as acetylene there are two mutually perpendicular  $\pi$  bonds. Acetylene can use one  $\pi$  bond and the associated  $\pi^*$  orbital in exactly the same way as found in olefin complexes.

This results in the lengthening of C - C bond distance and marked deviation from linearity.

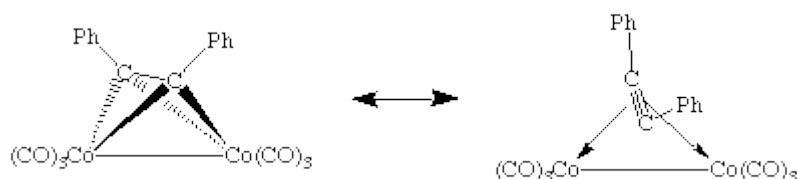


NOTES

## NOTES

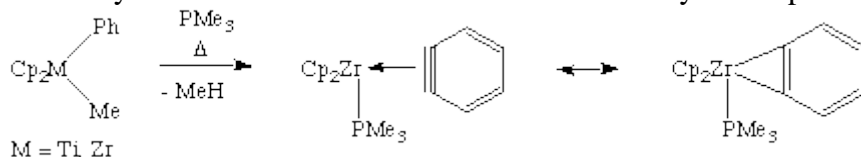
An alkyne can also behave as formal four electron donor to one metal atom. In addition to the above discussed interaction, the other pair of  $\pi$  electrons may be partially donated to a metal  $d \pi$  orbital lying perpendicular to the plane of three membered ring. Again a synergistic back donation may also occur if there is filled  $d$  – orbital perpendicular to both of the already used (fig b). This leads to even greater lengthening of C – C distance. Additional arrow is used to to represent this four electron bonding.

Finally, it is worth noting that alkynes can also bridge two metal centers. In these cases it is sometimes appropriate to describe the complex as a 1,2-dimetallatetrahedrane. In this case, the alkyne is a 2-electron donor to each metal center:

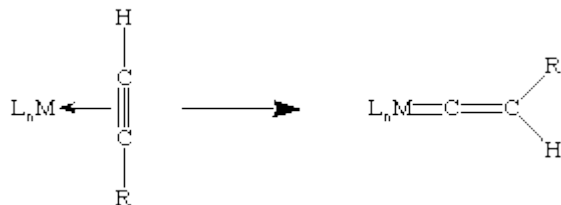


### 8.5.1 Reactivity of Alkyne Complexes

Coordination of alkynes permits the trapping of alkynes that would not ordinarily be stable. Consider this isolation of a benzyne complex

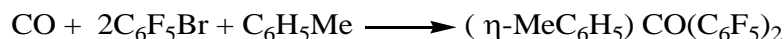
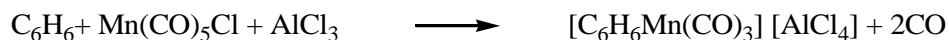


As one might expect, such species can act as a stoichiometric source of benzyne and display a correspondingly rich reaction chemistry and rearrangement of terminal acetylene complexes to the vinylidene tautomer is common noticed reaction.



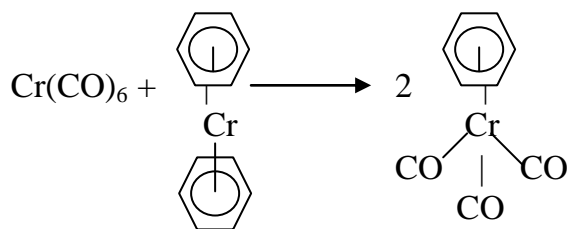
## 8.6 Metal – Arene Complexes

Arenes also form a variety of mono complexes that can be made by reactions such as.





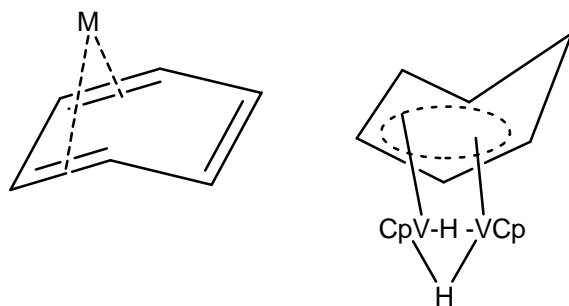
The rings of the dibenzene chromium, molybdenum and tungsten complexes are eclipsed and have a small rotational barrier. Unlike ferrocene, these complexes have labile rings which can be displaced.



The benzene rings can be removed completely by reaction with a more active ligand.



Other arene bonding modes.



### 8.7 Check your progress questions

1. What is meant by Hapticity?
2. How will you synthesis metal alkyl complexes
3. Give example for  $\alpha$  - hydride transfer of metal alkyl complexes
4. Dewar-Chatt approach to bonding in olefins

### 8.8 Answers to check your progress questions

- The term hapticity is used to describe how a group of *contiguous* atoms of a ligand are coordinated to a central atom.  $\eta^n$ : n = the number of contiguous atoms of the ligand that are bound to the metal
- Metal alkyl complexes are prepared by taking advantage of the nucleophilicity of a carbonylate ion.
 
$$[\text{Mn(CO)}_5]^- + \text{MeI} \rightarrow \text{Me Mn(CO)}_5 + \text{I}^-$$
  - Methyl compounds like  $\text{WMe}_6$  decompose thermally to give  $\text{CH}_4$  and polymeric material.  $\text{WMe}_6 \rightarrow 3\text{CH}_4 + \text{W}(\text{CH}_2)_3$
- Two components

$\sigma$ -donation from alkene  $\pi$ -orbital to metal  $\sigma$ -orbital ( $s$ ,  $p_z$  or  $d_{z^2}$ )

$\pi$ -donation from metal  $d$ -orbital to alkene  $\pi^*$  orbital.

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## 8.9 Summary

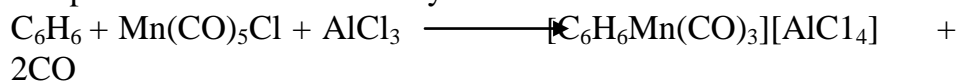
**Organometallic compounds:** Compounds that contain a metal-carbon bond, **R-M**, are known as "*organometallic*" compounds.

**Zeise's salt:**  $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$

**Dewar-Chat approach to bonding in olefins:** In this complex most of bonding is ligand  $\rightarrow$  M  $\sigma$ -donation. Both components *strengthen* M-C bonds and *weaken* C-C bonds, but  $\pi$ -donation has greatest effect in weakening C-C bond.

**Metal – alkyne complexes:** The primary difference in bonding between alkenes and alkynes is that an alkyne can act as either a 2 or 4 electron donor.

**Metal arene complexes:** Arenes also form a variety of mono complexes that can be made by reactions such as.




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## 8.10 Keywords

**Organometallic compounds:** Compounds that contain a metal-carbon bond, **R-M**, are known as "*organometallic*" compounds.

**Hapticity:** The term hapticity is used to describe how a group of *contiguous* atoms of a ligand are coordinated to a central atom.

**Metal – Arene Complexes:** Ferrocene is the best known Metal – Arene Complexes.

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## 8.11 Self-assessment questions and exercises

1. Define Organometallic compounds
2. Explain Hapticity
3. How will you synthesis metal alkyl complexes
4. How will you synthesis metal alkene complexes
5. How will you synthesis metal alkyene complexes
6. Explain Dewar-Chat approach to bonding in olefins

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## 8.12 Further readings

1. Dewar, M. Bull. Soc. Chim. Fr. **1951**, 1 8 , C79
2. J. Chatt and L. A. Duncanson, *Olefin co-ordination compounds. Part III. Infra-red spectra and structure: attempted preparation of acetylene complexes* J. Chem. Soc., **1953**, 2939.
3. Buchwald and coworkers (*Organometallics***1993**, 12 4182):
4. Jones, W. M.; Klosin, J. *Adv. Organomet. Chem.***1998**, 42, 147.

# UNIT-9 METALLOCENES

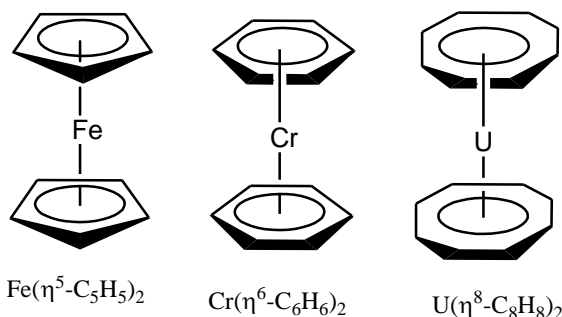
## Structure

- 9.0 Introduction
- 9.1 Objective
- 9.2 Comparison of ferrocene with other metallocenes with respect to their reactivity
- 9.3 Molecular orbital diagram of Ferrocene
- 9.4 preparation of Ferrocene ( $\eta^5\text{-C}_5\text{H}_5$ )<sub>2</sub>Fe
- 9.5 Properties of Ferrocene
- 9.6 Fluxional Molecules
- 9.7 Check your progress question
- 9.8 Answers to check your progress questions
- 9.9 Summary
- 9.10 Keywords
- 9.11 Self assessment question and exercise
- 9.12 Further Reading

## 9.0 Introduction

### Metallocenes

A metallocene consists of a metal atom between two planar polyhapto rings and they are called sandwich compounds. Example ferrocene  $\text{Fe}((\eta^5\text{-C}_5\text{H}_5)_2$ , bis(benzene) Chromium(0)  $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$  and uranocene  $\text{U}(\eta^8\text{-C}_8\text{H}_8)_2$ . The name metallocenes arose because they participated in reactions similar to those of aromatic molecules.



Some cyclic polyenes are known to form complexes in which they are bound to a metal atom through some but not all of their carbon atoms. In these cases the ring is non-planar. Besides these homoleptic cyclopolyene complexes in which organometallic such as halogens, CO, RNC and R<sub>3</sub>P share the coordination sphere of the metal with a cyclic polyene.

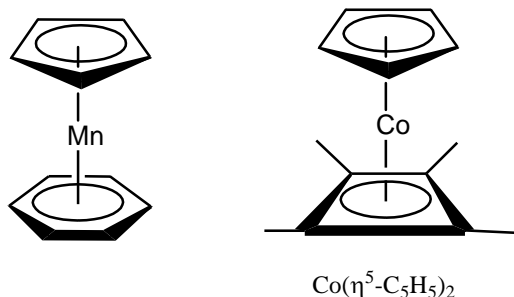
eg.  $(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ ,  $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$

There are also molecules in which two different types of arene rings are present, such that the total number of  $\pi$  electrons

Metallocenes

NOTES

they provide plus those possessed by the metal atom itself add to 18 for eg.



### 9.1 Objective

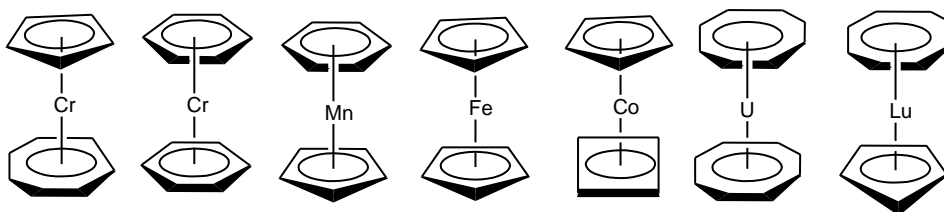
The main objective of this unit is to discuss the importance of metallocene. After going through this unit you will be able to:

- Discuss the ferrocene with other metallocenes
- Describing Molecular orbital diagram of Ferrocene
- Discuss behavior of Fluxional Molecules

### 9.2 Comparison of ferrocene with other metallocenes with respect to their reactivity

Ferrocene was the first of many complexes which came to be known as metallocenes. The name arises because they participated in reactions similar to those of aromatic molecules.

eg.

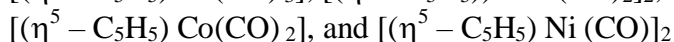
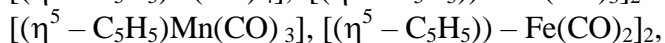
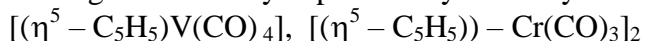


All of the complexes except the last two obey the 18 – electron rule.

In addition to ferrocene,  $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2$  compounds are known for most of the other elements of the first transition series. ( $\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Co}, \text{Ni}$ ) and these cannot obey the 18 – electron rule.

Ferrocene shows exceptional thermal stability (Stable to  $500^\circ\text{C}$ ) and is not oxidized by air. Furthermore cobaltocene, a 19 electron species, is readily oxidized to the 18 – electron cobaltocenium ion  $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$  which reflects much of the thermal stability of ferrocene.

Among the mixed cyclopentadienyl carbonyl complexes



The odd atomic number elements (V, Mn and Co) form monomers and the even atomic number elements (Cr, Fe and Ni) form dimers, which is in direct contrast to the behaviour shown by the simple carbonyl complexes.

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### 9.3 Molecular orbital diagram of Ferrocene

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The semiquantitative energy level diagram for ferrocene is shown. The set of ligand group orbitals (LGOS) in cyclopentadienyl in the left hand side of the diagram rings are also shown.

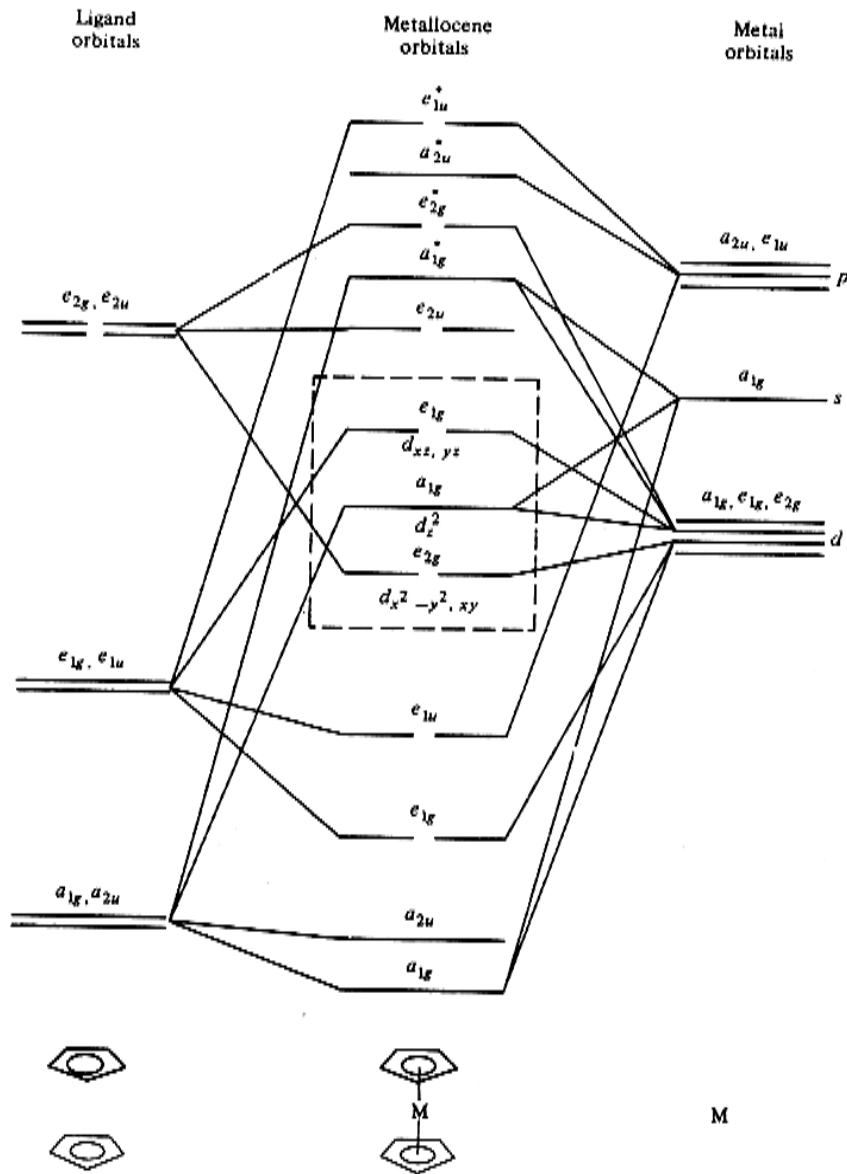
The  $a_{1g}$  ( $\sigma$ ) orbitals of cyclopentadiene are so stable relative to the metal orbitals that they interact but little (ie., the ligand is a poor  $\sigma$  donar). The  $e_{2g}$  ( $\Pi$ ) orbitals are so high in energy compared to the metal orbitals of the same symmetry, that they interact very little (ie., these empty orbitals are not good  $\Pi$  acceptors). The  $e_{1u}$  and  $a_{2u}$  (4p) orbitals on the iron atom are at a high energy and so these orbitals do not contribute much to bonding. The only orbitals that are well matched are  $e_{1g}$  ring and metal (3d) orbitals which form two strong  $\Pi$  bonds. These cp – Fe  $\Pi$  bonds are believed to supply most of the stabilization that holds the ferrocene molecule together.

In ferrocene, there are 18 valance electrons to be accommodated. Five  $\Pi$  electrons from each  $C_5H_5$  ring and eight valance electrons from Fe atom. There are 9 bonding or non – bonding molecular orbitals and ten antibonding molecular orbitals atom are shown in the right hand side of the diagram. The ring  $\Pi$  orbitals and the metal valance orbitals are linearly combined in the form of molecular orbitals shown in the centre of the diagram.

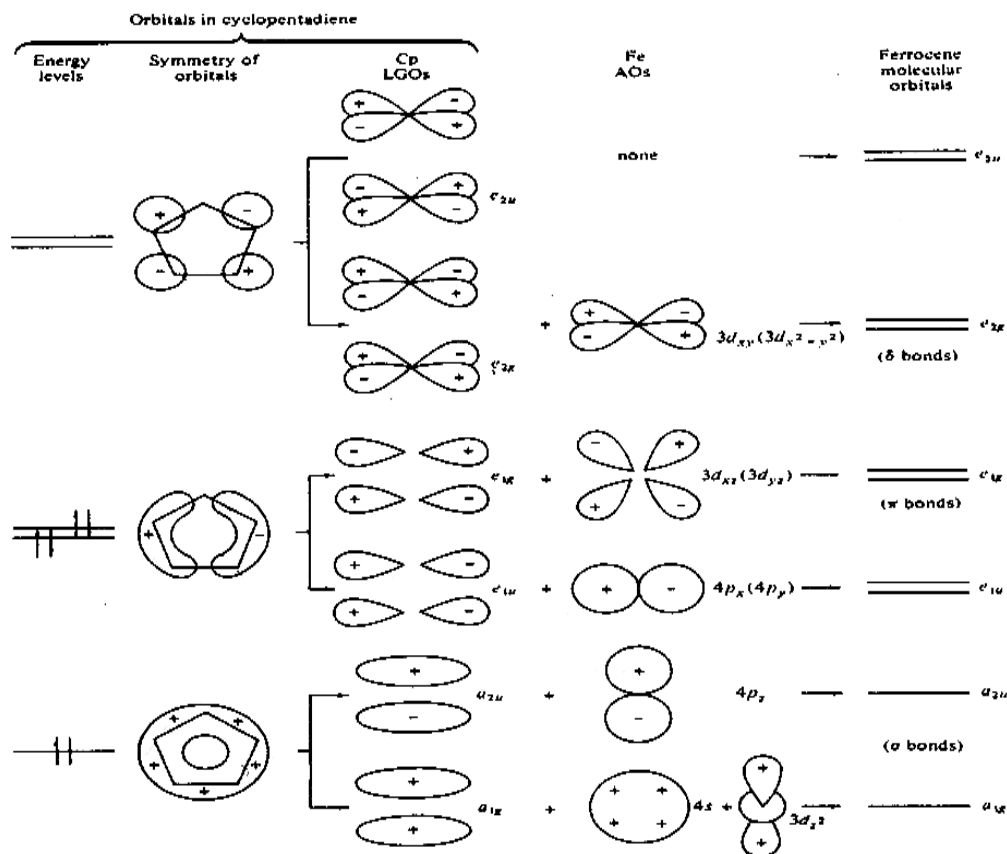
Metalloenes

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**Ligand group orbitals and matching atomic orbitals on iron for ferrocene**



NOTES

### Qualitative molecular orbital diagram for a metallocene

Hence the 18 electrons can just fill the bonding and non-bonding molecular orbitals giving a closed configuration.

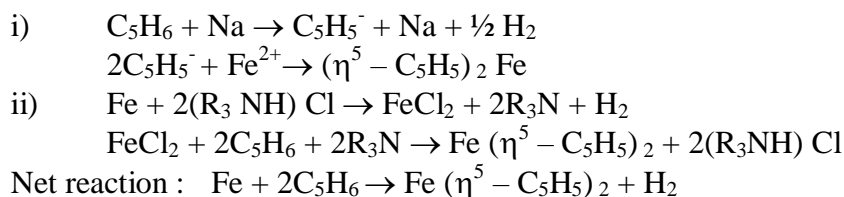
The 18-electron rule is a reflection of filling strongly stabilized molecular orbitals. In manganocene, chromocene and vanadocene are one, two and three electrons short of 18 while cobaltocene and nickelocene have one and two electrons in excess of 18. So all are paramagnetic except ferrocene.

The MO diagram is very much useful in understanding the rule violations and the magnetic properties.

The highest occupied molecular orbitals ( $e_{2g}$  and  $e_{1g}$ ) are only slightly bonding and therefore removing electrons from them does not greatly destabilize the complex. The  $e_{1g}$  LUMO is not significantly antibonding so when electrons are added to create 19-electron and 20-electron species the stability loss is minimal.

#### 9.4 preparation of Ferrocene ( $\eta^5\text{-C}_5\text{H}_5$ )<sub>2</sub>Fe

Bis (pentahaptocyclopentadienyl)Iron(II). Ferrocene has a sandwich structure, in which  $\text{Fe}^{2+}$  is sandwiched between two cyclopentadienyl ions. It is an orange red crystal with melting point  $174^\circ\text{C}$



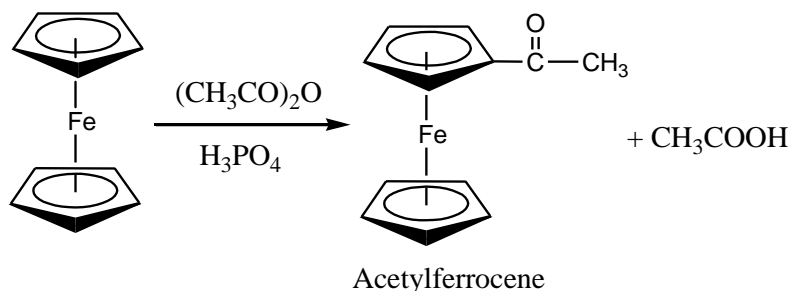
### 9.5 Properties of Ferrocene

The C–C bond orders in  $\eta^5\text{-C}_5\text{H}_5$  compounds resemble those of benzene. Ferrocene is stable and maintain the ligand metal bonds under harsh conditions, hence it is possible to carry out a variety of transformations on the cyclopentadienyl ligands. The cyclopentadienyl rings in ferrocene are aromatic and undergo many of the same reactions of benzene.

Ferrocene is more reactive than benzene towards electrophilic reagents, indicating that electrons are more readily available.

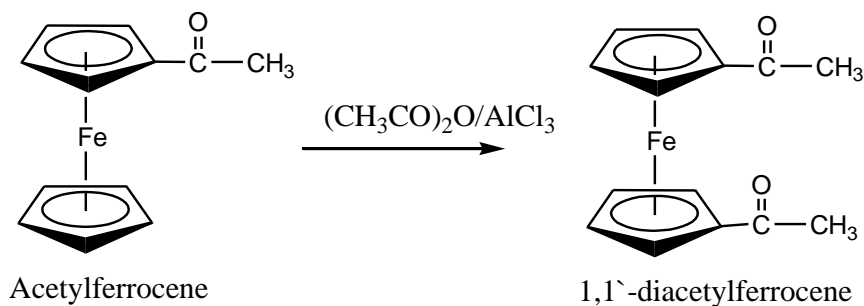
#### Acylation

Acylation of ferrocene by acetic anhydride containing phosphoric acid as catalyst gives the acetyl derivatives of ferrocene.



#### Acetylation of acetyl ferrocene

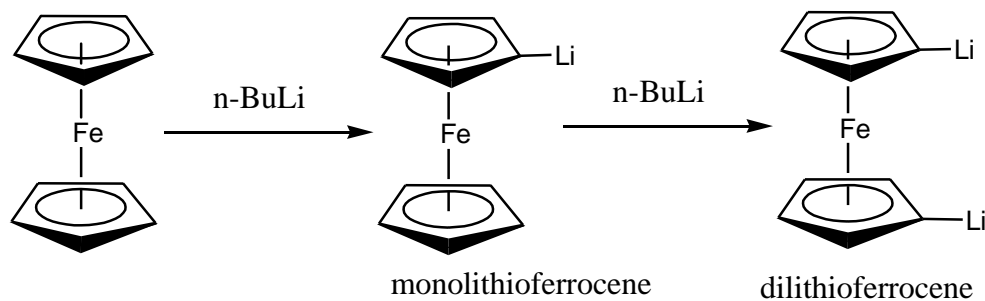
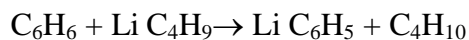
Acetylation of acetyl ferrocene deactivates the molecule. In order to obtain the diacetyl compound conditions similar to the usual acylation of aromatic rings are required.





**Metallation**

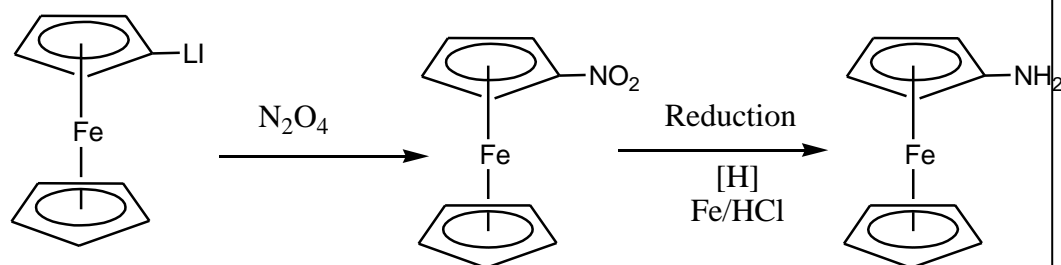
Ferrocene reacts with n – butyl lithium to give monolithio and dilithio derivative of ferrocene.



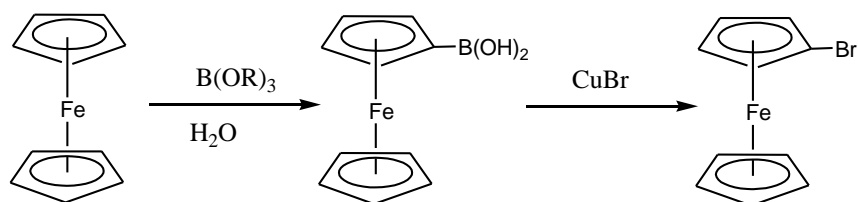
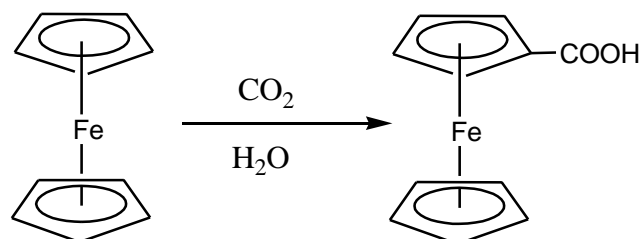
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**Nitration**

Direct nitration is not feasible as ferrocene is sensitive to oxidation. However the nitro derivative can be made indirectly.

**Carboxylation**

Ferrocene reacts with n  $\text{CO}_2/\text{H}_2\text{O}$  to ferrocene carboxylic acid



## 9.6 Fluxional Molecules

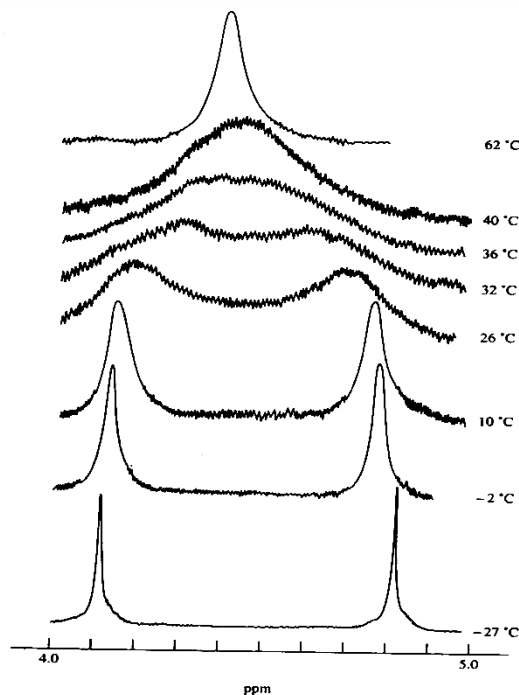
Fluxional Molecules possess more than a single configuration representing an energy minimum. Fluxionality is characteristic of certain classes of organometallic compounds. The phenomenon is seen characteristically in compounds containing conjugated cyclic polyolefins such as cyclopentadienyl, cycloheptadienyl or cyclooctatetraene, the three most common ones, attached to a metal atom through at least one but less than all of their carbon atoms.

Nuclear magnetic resonance techniques have proved to be particularly valuable in the study of fluxional molecules. If the interconversion process between them is slow on the NMR time scale, as might be the case at low temperature, two separate sets of equal intensity resonances, one for each configuration will be observed in the spectrum.

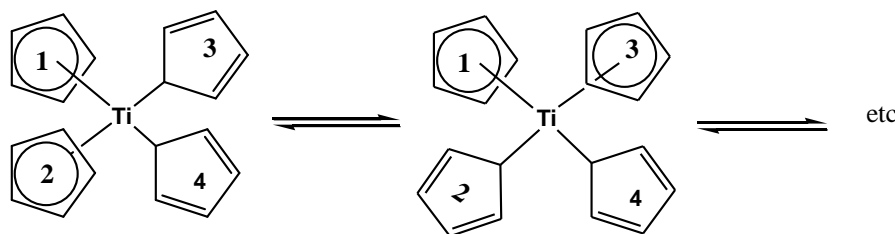
If we can raise the temperature of the sample sufficiently so that the process becomes rapid on the NMR time scale, the result will be a singlet and it will appear at the midpoint of the two sets observed at lower temperature. At this high temperature limit, the molecule is undergoing changes so rapidly that NMR cannot distinguish the two separate molecular configurations, only an average.

Consider  $(\eta^1-C_5H_5)_2(\eta^5-C_5H_5)_2Ti$ . The crystal structure of the molecule shows two monohapto and two pentahapto cyclopentadienyl rings.

At 62 °C, the  $^1H$ NMR spectrum consists of a single line, consistent with a dynamic process that renders the four ligands equivalent. As the temperature is lowered, the signal broadens and gradually splits into two lines which sharpen into equal intensity singlets at -27 °C. At this point, the process which interconverts mono and pentahapto ligands is occurring slowly enough that both configurations are observable in the spectrum.



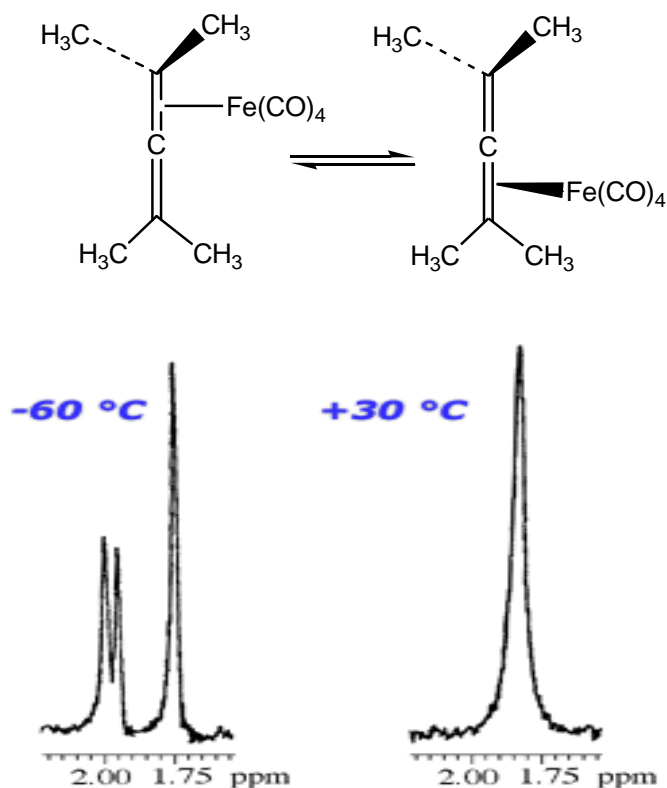
Proton NMR spectra of  $(\eta^1 - C_5H_5)_2 (\eta^5 - C_5H_5)_2Ti$  from  $-27$  to  $+62^\circ C$



Metallocenes

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$^1H$  NMR spectra of (tetramethylallene) $Fe(CO)_4$  at  $-60^\circ C$  and  $30^\circ C$  (tetramethylallene is  $Me_2C=C=CMe_2$ ) low temperature spectrum: the integrated ratios of the peaks are 1:1:2. it is not plausible for the allene to coordinate only via its central carbon atom because that carbon has no orbitals available to do this. The two of methyl groups (C) are chemically equivalent the other two (A and B) are not equivalent: one points at the metal and one away. At elevated temperature intramolecular process occur and the allene is "hopping" from one  $\pi$  face of the allene to another.



Migration of iron in tetracarbonyltetramethyl

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**9.7 Check your progress question**

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1. Define Metallocene
2. Write the equation for synthesis of ferrocene
3. Describe properties of ferrocene?
4. Explain Fluxional Molecules

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**9.8 Answers to check your progress questions**

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- A metallocene consists of a metal atom between two planar polyhapto rings and they are called sandwich compounds
- $C_5H_6 + Na \rightarrow C_5H_5^- + Na + \frac{1}{2} H_2$   
 $2C_5H_5^- + Fe^{2+} \rightarrow (\eta^5 - C_5H_5)_2 Fe$
- Acylation of ferrocene by acetic anhydride containing phosphoric acid as catalyst gives the acetyl derivatives of ferrocene. Ferrocene reacts with n – butyl lithium to give monolithio and dilithio derivative of ferrocene.
- Fluxional Molecules possess more than a single configuration representing an energy minimum. Fluxionality is characteristic of certain classes of organometallic compounds.

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**9.9 Summary**

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- A metallocene consists of a metal atom between two planar polyhapto rings and they are called sandwich compounds.
- Ferrocene was the first of many complexes which came to be known as metallocenes.
- Ferrocene is more reactive than benzene towards electrophilic reagents, indicating that electrons are more readily available.
- Fluxional molecules possess more than a single configuration representing an energy minimum. Fluxionality is characteristic of certain classes of organometallic compounds.

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**9.11 Self assessment question and exercise**

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1. What is meant by sandwich compound?
2. Explain the structure and bonding of ferrocene
3. Explain the dynamic behavior of organometallic compound?

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**9.12 Further Reading**

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1. **Inorganic Chemistry**,. G. S.Sodhi; 1<sup>st</sup>Edition, VB (P) Ltd, 2006.
2. **Inorganic Chemistry**, D. F. Shriver and P. W. Atkins, Oxford U.K., 1999.
3. **Modern aspects of Inorganic chemistry**, H.J. Emelius and Sharpe, Universal book Stall, New Delhi, 1989.
4. **Inorganic Chemistry- Principles of structure and reactivity**, J.E. Huheey, E.A. Keiter and R.L. Keiter, 4<sup>th</sup> edition, Pearson-Education, 2002.
5. **Advanced Inorganic Chemistry** - F.A. Cotton and G. Wilkinson, Wiley Eastern, 5<sup>th</sup>edition, 1998.
6. **Chemistry & Chemical Reactivity**, John C. Kotz, Paul M. Treichel, John Townsend, 8<sup>th</sup>ed., USA, 2012.

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## UNIT-10 METAL CARBONYL STRUCTURE

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- 10.0 Introduction
  - 10.1 Objectives
  - 10.2 Metal Carbonyls
    - 10.2.1 Classification
    - 10.2.2 Preparation and Properties of metal carbonyls
    - 10.2.3 Structure M-C bond
    - 10.2.4 Vibrational Spectra
  - 10.3 Metal Carbonylate Anions
  - 10.4 Metal Carbonyl Hydrides
  - 10.5 Metal nitrosyl complexes
  - 10.6 Check your progress questions
  - 10.7 Answers to check your progress questions
  - 10.8 Keywords
  - 10.9 Self-assessment questions and exercises
  - 10.10 Further readings
- 

### 10.0 Introduction

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The  $\pi$ -bonding in complexes was proposed for the first time, by Pauling (1924), in the form of back-bonding ( $M \rightarrow L$ ) to account for electro-neutrality of metal to ligand bond. According to him, if the ligand, linked with the metal ion through  $L \rightarrow M$ ,  $\sigma$ -bond, has vacant  $\pi$ -orbitals, it can accept lone pair of electrons from metal-ion (if present) to form  $M \rightarrow L$ ,  $\pi$ - bonds. This also accounts for the extra stability of metal complexes with unsaturated ligands. However the latest and the most successful theory of bonding for metal-complexes Ligand Field Theory (LFT), explained quantitatively while  $M \rightarrow \pi$ -bonding stabilizes, the complex,  $L \rightarrow M$   $\pi$ -bonding destabilize it. This also explains positions of  $CN^-$  and  $F^-$  ligands in the spectrochemical series.

Most transition metals form complexes with a wide variety of unsaturated molecules such as carbon monoxide, nitric oxide, dinitrogen, dioxygen etc. In many of these, the metal is in zero or another low oxidation state and, as we have already mentioned,  $\pi$ -bonding between the metal and the ligands is believed to play an important part in stabilizing these complexes. In this regard metal carbonyls are important as they involve both metal carbon  $\sigma$  and  $\pi$ -bonds. In this unit we shall consider the metal carbonyls, anions derived from them, some of their substitution product, and complexes formed by a few other ligands. Metal carbonyl compounds were first synthesized in 1868. Although many compounds were produced, they couldn't be fully characterized until the development of X-ray diffraction, and IR and NMR spectroscopy. Metal carbonyl compounds typically contain metals in the zero oxidation state. In general, these compounds obey the "18 electron rule." Although there are exceptions, this rule can be used to predict the structure of metal carbonyl cluster compounds, which contain metal-metal bonds. Many transition metal carbonyl compounds obey the 18-

electron rule. The reason for this can be readily seen from the molecular orbital diagram of  $\text{Cr}(\text{CO})_6$ . The  $\sigma$  donor and  $\pi$  acceptor nature of CO as a ligand results in an MO diagram with greatest stability at 18 electrons.

### 10.1 Objectives

The main aim of this unit is to study  $\pi$ -complexes of transition metals, with special reference to bonding and their structures. After going through this unit you should be able to:

- describe metal carbonyls, their classification, methods of preparation and reactions; with special reference to their structures,
- discuss how these complexes, almost without exception, conform to the effective atomic number rule and isolobal concept,
- explain bonding in these complexes in terms of IR spectra;
- describe preparation, properties and structures of metal nitrosyls,

### 10.2 Metal Carbonyls

The compounds formed by the combination of CO molecules with transition metals are known as metallic carbonyls. Carbon monoxide possesses a unique property of unsaturation by virtue of which it may combine with a large number of metals under suitable conditions. Such compounds of CO with metals are termed as metallic carbonyls. In carbonyls, a metal atom is directly linked to the carbon atom of a carbonyl group. Since the electrons forming  $\text{OC} \rightarrow \text{M}$  bond are supplied solely by CO molecule, metal atom in carbonyls is said to be in zero oxidation state. In metal carbonyls CO molecules act as neutral ligands. Metal carbonyls vary considerably in their properties ranging from volatile nonpolar to the nonvolatile electrovalent carbonyls. For example, nickel forms volatile nonpolar carbonyls, whereas alkali and alkaline earth metals form non-volatile electrovalent carbonyls.

The general formula of the carbonyls may be given as  $\text{M}_x(\text{CO})_y$  where M is a metal capable of forming carbonyl. Metal carbonyls may be regarded as parents of number of related compounds such as metal nitrosyl carbonyl,  $\text{M}(\text{NO})_y(\text{CO})_x$ , and metal carbonyl hydrides  $\text{H}_x\text{M}(\text{CO})_y$ .

#### 10.2.1 Classification

Carbonyls are classified into two distinct groups:

- 1) Mononuclear carbonyls: These carbonyls have the general formula  $\text{M}_x(\text{CO})_y$  which contain more than one metal atom per molecule.
- 2) However the carbonyls having 2 metal atoms are called binuclear carbonyls, and
- 3) those having more than two metal atoms as polynuclear carbonyls. Polynuclear carbonyls may be homonuclear e.g.  $[\text{Fe}_3(\text{CO})_{12}]$  or heteronuclear e.g.  $\text{MnCo}(\text{CO})_9$ ,  $\text{MnRe}(\text{CO})_{10}$

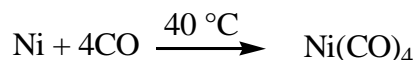
They have following characteristics:

- i. These are almost insoluble in organic solvents.
- ii. Many polynuclear carbonyls decompose at or below the melting point.

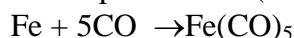
## 10.2.2 Preparation and Properties of metal carbonyls

### a. Direct synthesis

1. Nickel reacts with CO at room temperature and normal pressure;



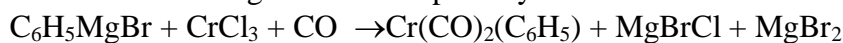
2. When CO is passed over reduced iron at 108°-220°C and pressure of 50 to 200 atm pressure. Fe(CO)<sub>5</sub> is formed;



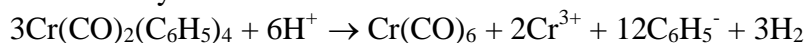
Rhenium, osmium and iridium carbonyls could not be prepared by direct reactions.

### b. Indirect synthesis involving the Grignard reagent:

Job prepared chromium hexacarbonyl by the action of CO on a mixture of grignard reagent and anhydrous chromium chloride in ether solution. According to Hiber the primary reaction is as follows:



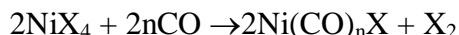
The unstable intermediate compound is composed with acid to yield the hexacarbonyl:



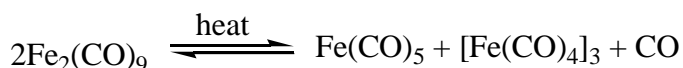
The reactions gives low yield which can be improved by using high carbon mono-oxide pressure.

**c. Indirect synthesis involving metal compounds:** Metal carbonyls can be prepared by the reaction of CO with certain metal compounds for example:

i. Nickel tetracarbonyl may be prepared by passing CO into a suspension of nickel cyanide, sulphide or mercaptide suspended in NaOH solution.



**Synthesis from other carbonyls:** when iron pentacarbonyl is exposed to UV light it loses CO and forms Fe<sub>2</sub>(CO)<sub>9</sub>. This compound undergoes thermal decomposition to yield iron pentacarbonyl and trimeric tetracarbonyl.



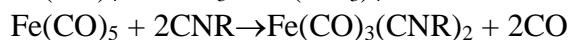
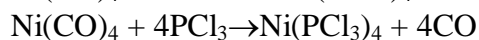
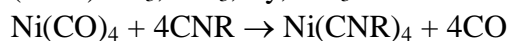
### NOTES

### Properties of Carbonyls

- The metal carbonyls are crystalline solids, except for nickel carbonyl and the pentacarbonyls of iron, ruthenium and osmium which are liquids.
- Many are coloured for example: Crystals of cobalt carbonyl are orange and iron pentacarbonyl is yellow oil and nickel carbonyl is colourless.
- Due to their covalent nature renders them insoluble in water, most of them are soluble in solvents like CCl<sub>4</sub>.
- Excepting V(CO)<sub>6</sub> all the carbonyls are diamagnetic. V(CO)<sub>6</sub> is paramagnetic and its paramagnetic property corresponds to the presence of one unpaired electron. The metal in carbonyls are in zero oxidation state.

### Chemical Properties

**1. Substitution Reactions:** Some or all CO groups present in carbonyls can be replaced by monodentate ligands such as alkyl or aryl isocyanide (CNR) PR<sub>3</sub>, PCl<sub>3</sub>, Py, CH<sub>3</sub>OH etc.

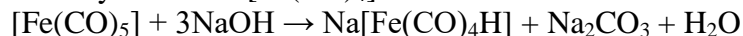


Substitution reactions of metal carbonyls frequently indicate differences in bonding characteristics of ligands. In the case of Mn(CO)<sub>5</sub>Br, radiochemical tracer studies have shown that only four CO groups undergo exchange with <sup>14</sup>CO.



The four CO molecules that undergo exchange reactions are those in the plane, which are all *trans* to each other. This indicates that the CO *trans* to Br is held more tightly because Br does not compete for π bonding electron density donated from Mn. In the case of the other four CO groups, competition between the groups, which are all good acceptors, causes the groups to be labilized

**2. Action of NaOH or Na metal:** Formation of carbonylate ion: Aqueous alcoholic solution of NaOH reacts with Fe(CO)<sub>5</sub> to form carbonylate anion [Fe(CO)<sub>4</sub>]<sup>-</sup>.

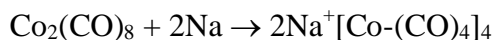


H-atom in [Fe(CO)<sub>4</sub>H]<sup>-</sup> ion is acidic which implies that Fe atom in this ion is in -2 oxidation state.

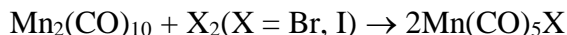
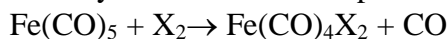
Na-metal in liquid NH<sub>3</sub> is able to convert Fe<sub>2</sub>(CO)<sub>9</sub>, Co<sub>2</sub>(CO)<sub>8</sub>, Fe<sub>3</sub>(CO)<sub>12</sub>, Cr(CO)<sub>6</sub>, Mn<sub>2</sub>(CO)<sub>10</sub> etc, into carbonylate anions and in this conversion these carbonyls are reduced.



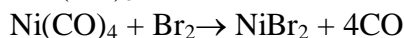
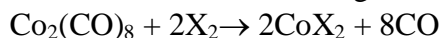




**3. Action of halogens:** Most of the carbonyls react with halogens to yield carbonyl halides. For example:

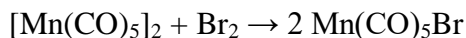


Both  $\text{Co}_2(\text{CO})_8$  and  $\text{Ni}(\text{CO})_4$  are decomposed into metallic halides and CO when treated with halogens.



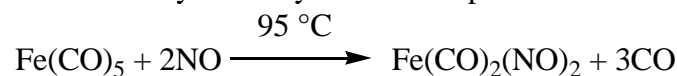
Reactions of metal carbonyls with halogens lead to the formation of carbonyl halide complexes by substitution reactions or breaking metal-metal bonds.

The reaction



involves the rupture of the Mn–Mn bond, and one Br is added to each Mn.

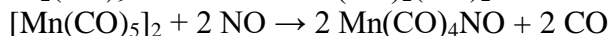
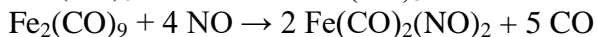
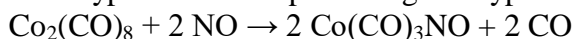
**4. Action of NO:** Many carbonyls react with nitric oxide (NO) to form metal carbonyl nitrosyls. For example:



The nitric oxide molecule has one unpaired electron residing in an antibonding  $\pi^*$  molecular orbital. When that electron is removed, the bond order increases from 2.5 to 3, so in coordinating to metals, NO usually behaves as though it donates three electrons. The result is formally the same as if one electron were lost to the metal,



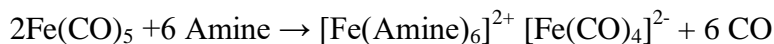
followed by coordination of  $\text{NO}^+$ , which is isoelectronic with CO and CN. Because  $\text{NO}^+$  is the nitrosyl ion, the products containing nitric oxide and carbon monoxide are called *carbonyl nitrosyls*. The following reactions are typical of those producing this type of compound:



It is interesting to note that the products of these reactions obey the 18-electron rule

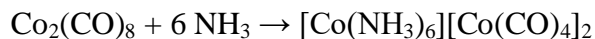
#### 4. Disproportionation

A number of metal carbonyls undergo disproportionation reactions in the presence of other coordinating ligands. For example, in the presence of amines,  $\text{Fe}(\text{CO})_5$  reacts as follows:



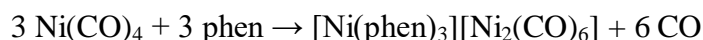
## NOTES

This reaction takes place because of the ease of formation of the carbonylate ions and the favorable coordination of the  $\text{Fe}^{2+}$  produced. The reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{NH}_3$  is similar.

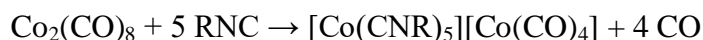


Formally, in each of these cases the disproportionation produces a positive metal ion and a metal ion in a negative oxidation state. The carbonyl ligands will be bound to the softer metal species, the anion; the nitrogen donor ligands (hard Lewis bases) will be bound to the harder metal species, the cation.

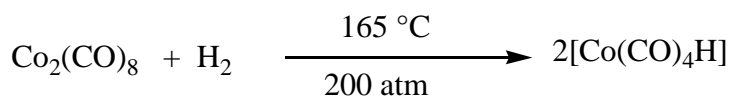
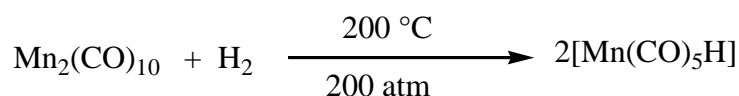
These disproportionation reactions are quite useful in the preparation of a variety of carbonylate complexes. For example, the  $[\text{Ni}_2(\text{CO})_6]_2$  ion can be prepared by the reaction



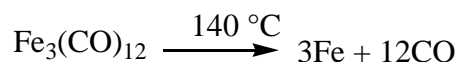
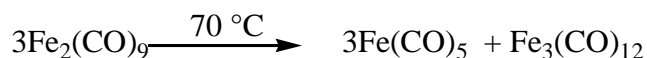
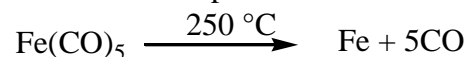
The range of coordinating agents that will cause disproportionation is rather wide and includes compounds such as isocyanides, RNC:



**5. Action of  $\text{H}_2$ :** Formation of carbonyl hydrides (reduction): when  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Co}_2(\text{CO})_8$  react with  $\text{H}_2$ , they get reduced to carbonyl hydrides,  $\text{Mn}(\text{CO})_5\text{H}$  and  $\text{Co}(\text{CO})_4\text{H}$  respectively.



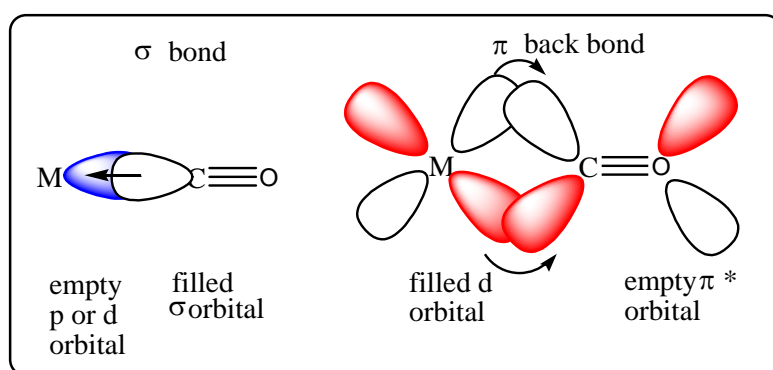
**6. Action of heat:** Different carbonyls yields different products when heated for example:



### 10.2.3 Structure M-C bond

According to MO theory, the bonding in metal carbonyl is overlap of the filled orbital of carbon and  $\sigma$  – type orbital of the metal atom to form a  $\sigma$  or dative bond. Electron flow in such a dative overlap increases the electron density of the metal atom. The metal therefore attempts to reduce this charge by pushing electrons back to the ligand. A second dative overlap of a filled d  $\pi$  or hybrid  $dp\pi$  metal orbital with an empty  $p \pi$  orbital or  $\pi g^*$  or  $2 \pi$  orbital on so.

This bonding mechanism is synergic. The drift of metal electrons referred to as back bonding into CO orbital increases the lewis basicity via the  $\sigma$  orbital of carbon. At the same time, the drift of electrons to the metal in the  $\sigma$  – bond tends to make the CO positive, thus enhancing the acceptor strength of the  $\Pi$  orbitals. Thus upto a point the effect of  $\sigma$  bond formation strengthen the  $\Pi$  bonding and vice versa.



#### 10.2.4 Vibrational Spectra

IR spectra give important information regarding nature of carbonyl groups present in metal carbonyl complexes. We can differentiate between the terminal carbonyl e.g. in  $Mn_2(CO)_{10}$  and bridging carbonyl groups, as in  $Co_2(CO)_8$ . Metal-carbon distances in  $Fe_2(CO)_9$  and  $Co_2(CO)_8$  fall into two groups, metal-bridging carbonyl distances being about 0-1 Å longer than metal-terminal carbonyl distances. Such a difference is compatible with the concept of two-electron donation by terminal carbonyls, and one electron donation (to each of two metal atoms) by bridging carbonyls, through the possible existence of  $\pi$  bonds of different strengths makes quantitative interpretation impossible. That the extent of  $\pi$  bonding to terminal and bridging carbonyls is different is clearly shown by carbonyl stretching frequencies. Carbon monoxide itself has stretching frequency of  $2143 \text{ cm}^{-1}$ ; neutral metal carbonyls known to have no bridging carbonyl groups have stretching frequencies in the range  $2125\text{-}2000 \text{ cm}^{-1}$ ; and  $Fe_2(CO)_9$  and  $Co_2(CO)_8$ , in addition to showing bands in this region, also show carbonyl absorption at  $1830$  and  $1860 \text{ cm}^{-1}$  respectively. In general, carbonyl absorption in the  $1900\text{-}1800 \text{ cm}^{-1}$  region is indicative of the presence of bridging carbonyl groups in

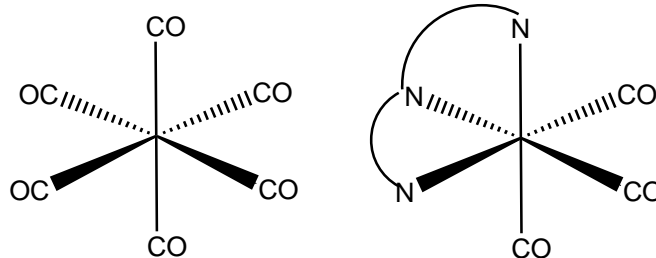
## NOTES

uncharged species, though the presence of other groups may result in the lowering of the stretching frequencies of terminal carbonyl groups into this region (in carbonylate anions such as  $[\text{Co}(\text{CO})_4]^-$  and  $[\text{Fe}(\text{CO})_4]^{2-}$  very low carbonyl stretching frequencies of 1883 and  $1788\text{ cm}^{-1}$  respectively result from the strong metal-carbon  $\pi$ -bonding which stabilizes the low oxidation state of the metal. In a few neutral species believed to contain carbonyl groups bonded to three metal atoms, stretching frequencies of  $1800\text{ cm}^{-1}$  or less are found.

Thus, in summary the terminal carbonyl absorption is obtained in the range of  $2125\text{--}2000\text{ cm}^{-1}$ , while bridging carbonyl frequency is obtained in the  $1900\text{--}1800\text{ cm}^{-1}$  region. While, the strong metal carbon  $\pi$  bonding is indicated by very low carbonyl stretching frequencies of 1883 and  $1788\text{ cm}^{-1}$  respectively.

**Evidences for back bonding.**

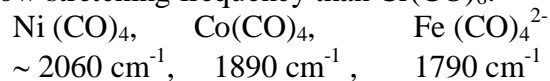
When there is back bonding  $\text{M}=\text{C}=\text{O}$ , the bond order is reduced to 2 and hence the stretching frequency decreased from  $2145\text{ cm}^{-1}$  (for  $\text{M}\equiv\text{O}$ ) to  $2125\text{--}1850\text{ cm}^{-1}$ .



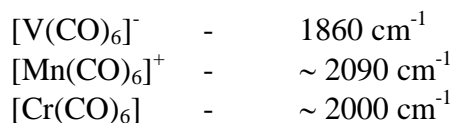
$2100, 2000, 1985\text{ cm}^{-1}$

$1900, 1760\text{ cm}^{-1}$

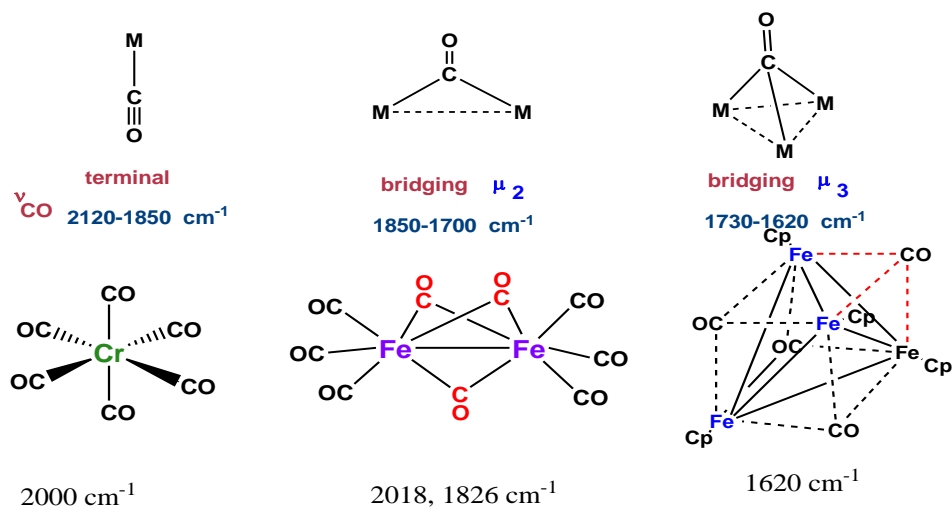
If we replace the CO (better  $\pi$  acceptor) by triamine (Poor  $\pi$  - acceptor), the CO ligands receive large electron density from the metal and the bond order increases. But the bond ( $\text{C}\equiv\text{O}$ ) order decreases and has a low stretching frequency than  $\text{Cr}(\text{CO})_6$ .



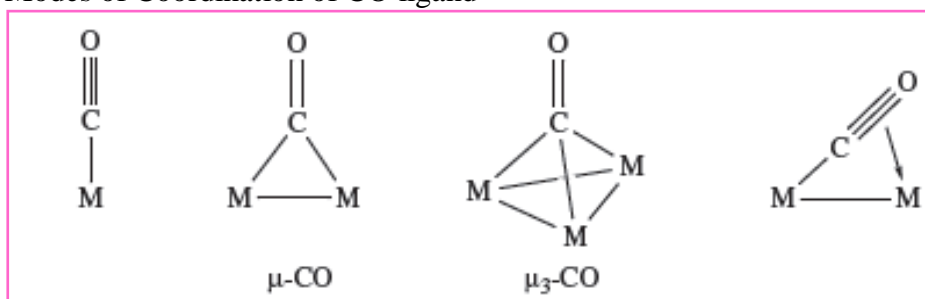
Because of the negative charge more and more electron density is taken away by carbon atom. In order to stabilize the valency of carbon, the carbon - oxygen bond order decreases and stretching frequency decreases.



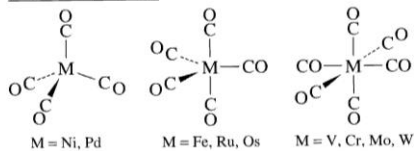
## Terminal versus bridging carbonyls



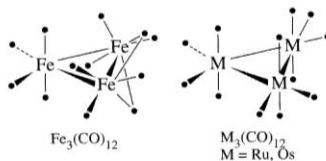
### Modes of Coordination of CO ligand



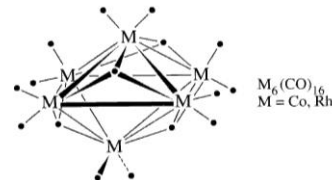
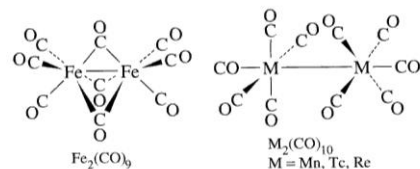
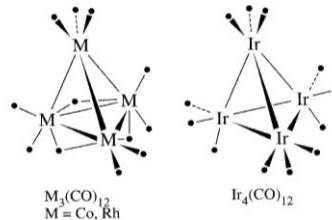
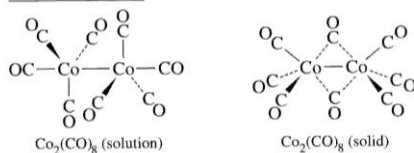
#### Mononuclear $[\text{M}(\text{CO})_x]$



#### Polynuclear (CO represented by • for clarity)



#### Binuclear $[\text{M}_2(\text{CO})_x]$



## NOTES

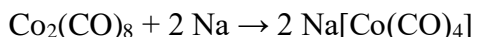
## NOTES

### 10.3 Carbonylate Anions

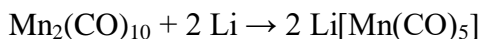
Several carbonylate anions such as  $\text{Co}(\text{CO})_4^-$ ,  $\text{Mn}(\text{CO})_5^-$ ,  $\text{V}(\text{CO})_6^-$ , and  $[\text{Fe}(\text{CO})_4]^{2-}$  obey the EAN rule.

One type of synthesis of these ions is that of reacting the metal carbonyl with a reagent that loses electrons readily, a strong reducing agent. Active metals are strong reducing agents, so the reactions of metal carbonyls with alkali metals should produce carbonylate ions.

The reaction of  $\text{Co}_2(\text{CO})_8$  with Na carried out in liquid ammonia at  $75^\circ\text{C}$  is one such reaction.



Similarly,



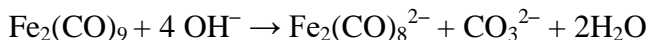
Although  $\text{Co}(\text{CO})_4$  and  $\text{Mn}(\text{CO})_5$  do not obey the 18-electron rule, the anions  $\text{Co}(\text{CO})_4^-$  and  $\text{Mn}(\text{CO})_5^-$  do

A second type of reaction leading to the formation of carbonylate anions is the reaction of metal carbonyls with strong bases.

For example,

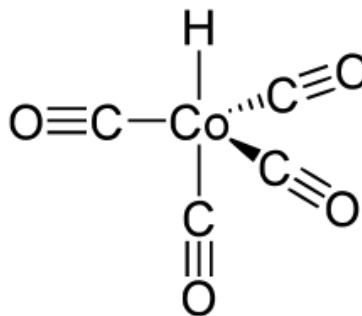
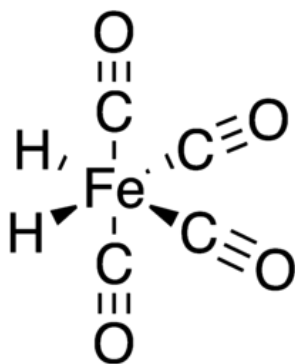


With  $\text{Fe}_2(\text{CO})_9$ , the reaction is



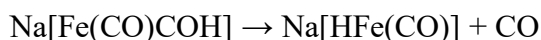
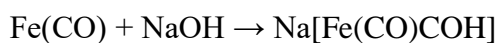
### 10.4 Metal Carbonyl Hydrides

Metal carbonyl hydrides are complexes of transition metals with carbon monoxide and hydride as ligands. These complexes are useful in organic synthesis as catalysts in homogeneous catalysis, such as hydroformylation.



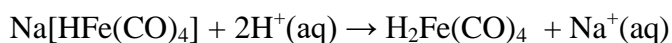
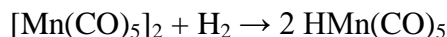
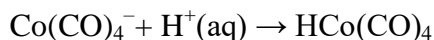
## Preparation

Walter Hieber prepared the first metal carbonyl hydride in 1931 by the so-called Hieber base reaction of metal carbonyls. In this reaction a hydroxide ion reacts with the carbon monoxide ligand of a metal carbonyl such as iron pentacarbonyl in a nucleophilic attack to form a metallacarboxylic acid. This intermediate releases of carbon dioxide in a second step, giving the iron tetracarbonyl hydride anion. The synthesis of cobalt tetracarbonyl hydride ( $\text{HCo}(\text{CO})$ ) proceeds in the same way.



A further synthetic route is the reaction of the metal carbonyl with hydrogen. The protonation of metal carbonyl anions, e.g.  $[\text{Co}(\text{CO})_4]^-$ , leads also to the formation of metal carbonyl hydrides.

Generally, carbonyl hydrides are obtained by acidifying solutions containing the corresponding carbonylate anion or by the reactions of metal carbonyls with hydrogen. The following reactions illustrate these processes:



## Properties

The neutral metal carbonyl hydrides are often volatile and can be quite acidic. The hydrogen atom is directly bounded to the metal. The metal-hydrogen bond length is for cobalt 114 pm, the metal-carbon bond length is for axial ligands 176 and 182 for the equatorial ligands.

Metal carbonyl hydrides are used as catalysts in the hydroformylation of olefins. Under industrial conditions the catalyst is usually formed in situ in a reaction of a metal salt precursor with the syngas. The hydroformylation starts with the generation of a coordinatively unsaturated 16-electron metal carbonyl hydride complex like  $\text{HCo}(\text{CO})$  or  $\text{HRh}(\text{CO})(\text{PPh})$  by dissociation of a ligand. Such complexes bind olefins in a first step via  $\pi$ -complexation. In a second step an alkyl complex is formed by insertion of the olefin into the metal-hydrogen bond, leading once again to a 16-electron species. This complex can bind another carbon monoxide, which can insert into the metal-carbon bond of the alkyl ligand to form an acyl complex. By

## NOTES

oxidative addition of hydrogen and elimination of the aldehyde the initial metal carbonyl hydride complex is regenerated.

The exact structure of the metal carbonyl hydrides has been determined by using neutron diffraction and nuclear magnetic resonance spectroscopy.

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### 10.5 Metal nitrosyl complexes

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Metal nitrosyl complexes, have gained significant interest in the past twenty years because of the important role nitric oxide displays as signaling molecule in biological systems. Metal nitrosyl complexes are complexes that contain nitric oxide, NO, bonded to a transition metal. Many kinds of nitrosyl complexes are known, which vary both in structure and coligand.

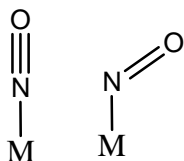
Most complexes containing the NO ligand can be viewed as derivatives of the nitrosyl cation,  $\text{NO}^+$ . The nitrosyl cation is isoelectronic with carbon monoxide, thus the bonding between a nitrosyl ligand and a metal follows the same principles as the bonding in carbonyl complexes. The nitrosyl cation serves as a two-electron donor to the metal and accepts electrons from the metal via back-bonding. The compounds  $\text{Co}(\text{NO})(\text{CO})_3$  and  $\text{Ni}(\text{CO})_4$  illustrate the analogy between  $\text{NO}^+$  and CO. In an electron-counting sense, two linear NO ligands are equivalent to three CO groups. This trend is illustrated by the isoelectronic pair  $\text{Fe}(\text{CO})_2(\text{NO})_2$  and  $[\text{Ni}(\text{CO})_4]$ . These complexes are isoelectronic and, incidentally, both obey the 18-electron rule. The formal description of nitric oxide as  $\text{NO}^+$  does not match certain measurable and calculated properties. In an alternative description, nitric oxide serves as a 3-electron donor, and the metal-nitrogen interaction is a triple bond.

#### Linear vs bent nitrosyl ligands

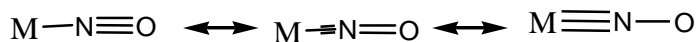
The M-N-O unit in nitrosyl complexes is usually linear, or no more than  $15^\circ$  from linear. In some complexes, however, especially when back-bonding is less important, the M-N-O angle can strongly deviate from  $180^\circ$ . The differing vibrational frequencies reflect the differing N-O bond orders for linear (triple bond) and bent NO (double bond).

The bent NO ligand is sometimes described as the anion,  $\text{NO}^-$ . Prototypes for such compounds are the organic nitroso compounds, such as nitrosobenzene. A complex with a bent NO ligand is *trans*- $[\text{Co}(\text{en})_2(\text{NO})\text{Cl}]^+$ .





Linear and bent M-NO bonds

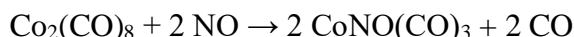


- Increasing strength of the p-back bond strengthens the M-N bond and weakens the N-O bond.
- If the backbonding effect is weak, the angle decreases significantly ( $\angle(\text{M-N-O}) \approx 120^\circ$ ) and the ligand can be described as “NO<sup>-</sup>”
- The Enemark-Feltham notation is used to describe the number of *d-type* electrons present in a given metal nitrosyl complex. Complexes with “ $d+\pi^*$ -electrons” in excess of six often tend to have bent NO ligands i.e.,  $\text{Co}(\text{NO})\text{dtc}_2$  (7 e,  $127^\circ$ ).
- Infrared spectroscopy and EPR spectroscopy can be used to distinguish between different bond modes.
- Linear M-N-O groups (N-O triple bond) absorb in the range  $1650\text{--}1900\text{ cm}^{-1}$  (i.e.,  $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ :  $1939\text{ cm}^{-1}$ ,  $[\text{Mn}(\text{CN})_5(\text{NO})]^{3-}$ :  $1700\text{ cm}^{-1}$ )
- Bent nitrosyl groups (N-O double bond) absorb in the range  $1525\text{--}1690\text{ cm}^{-1}$  (i.e.,  $[\text{Co}(\text{NH}_3)_5(\text{NO})]^{2+}$ :  $1620\text{ cm}^{-1}$ ).

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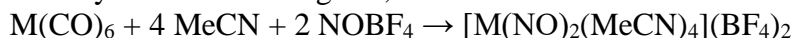
### Preparation

Nitrosyl complexes are typically prepared by treating reduced metal complexes with nitric oxide. The nitrosylation of cobalt carbonyl is illustrative



### From nitrosonium sources

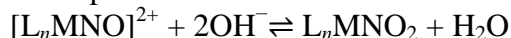
Replacement of ligands by the nitrosyl cation may be accomplished using nitrosyl tetrafluoroborate,  $[\text{NO}]\text{BF}_4$ . When applied to the hexacarbonyls of molybdenum and tungsten, the NO binds to the metal



Nitrosyl chloride and molybdenum hexacarbonyl react to give  $[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$ . Diazald is also used as an NO source.

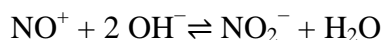
### Reactions

An important reaction is the acid/base equilibrium:

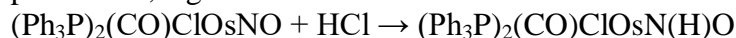


This equilibrium serves to confirm that the linear nitrosyl ligand is, formally,  $\text{NO}^+$ , with nitrogen in the oxidation state +3

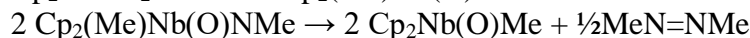
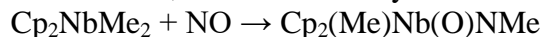
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Since nitrogen is more electronegative than carbon, metal-nitrosyl complexes tend to be more electrophilic than related metal carbonyl complexes. Nucleophiles often add to the nitrogen. The nitrogen atom in bent metal nitrosyls is basic, thus can be oxidized, alkylated, and protonated, e.g.:



In rare cases, NO is cleaved by metal centers:




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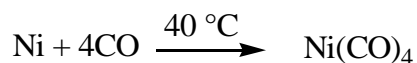
### 10.6 Check your progress questions

1. Explain  $\pi$ -back bonding
2. How will you prepare  $\text{Ni}(\text{CO})_4$
3. Describe physical properties of metal carbonyl
4. How IR vibration spectra used to predict the structure of Carbonyl complexes

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### 10.7 Answers to check your progress questions

if the ligand, linked with the metal ion through  $\text{L} \rightarrow \text{M}$ ,  $\sigma$ -bond, has vacant  $\pi$ -orbitals, it can accept lone pair of electrons from metal-ion (if present) to form  $\text{M} \rightarrow \text{L}$ ,  $\pi$ - bonds. This also accounts for the extra stability of metal complexes with unsaturated ligands.



- The metal carbonyls are crystalline solids, except for nickel carbonyl and the pentacarbonyls of iron, ruthenium and osmium which are liquids.
  - Many are coloured for example: Crystals of cobalt carbonyl are orange and iron pentacarbonyls is yellow oil and nickel carbonyl is colourless.
  - Due to their covalent nature renders them insoluble in water, most of them are soluble in solvents like  $\text{CCl}_4$ .
  - Excepting  $\text{V}(\text{CO})_6$  all the carbonyls are diamagnetic.  $\text{V}(\text{CO})_6$  is paramagnetic and its paramagnetic property corresponds to the presence of one unpaired electron. The metal in carbonyls are in zero oxidation state.
- The terminal carbonyl absorption is obtained in the range of  $2125\text{-}2000 \text{ cm}^{-1}$ , while bridging carbonyl frequency is obtained in the  $1900\text{-}1800 \text{ cm}^{-1}$  region. While, the strong metal carbon  $\pi$  bonding is indicated by very low carbonyl stretching frequencies of  $1883$  and  $1788 \text{ cm}^{-1}$  respectively.

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## 10.8 Keywords

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**Metal nitrosyl:** Metal nitrosyl complexes are complexes that contain nitric oxide, NO, bonded to a transition metal.

**Linear vs bent nitrosyl ligands:** The M-N-O unit in nitrosyl complexes is usually linear, or no more than  $15^\circ$  from linear. The bent NO ligand is sometimes described as the anion,  $\text{NO}^-$ .

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## 10.9 Self-assessment questions and exercises

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1. Give example for carbonylate anions
  2. Write the structure of metal carbonyl hydrate
  3. What is meant by  $\pi$ -back bonding
  4. Explain the structure of metal nitrosyl complexes
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## 10.10 Further reading

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- Hayton, T. W.; Legzdins, P.; Sharp, W. B. (2002). "Coordination and Organometallic Chemistry of Metal-NO Complexes". *Chem. Rev.* **102** (1): 935–991.
- Holleman, Arnold Frederik; Wiberg, Egon (2001), Wiberg, Nils (ed.), *Inorganic Chemistry*, translated by Eagleson, Mary; Brewer, William, San Diego/Berlin: Academic Press/De Gruyter, ISBN 0-12-352651-5
- W. Hieber, F. Leutert: Zur Kenntnis des koordinativ gebundenen Kohlenoxyds: Bildung von Eisencarbonylwasserstoff. *Die Naturwissenschaften*. volume 19, 1931, pp. 360–361,
- H. D. Kaesz, R. B. Saillant: Hydride Complexes of the Transition Metals" *Chem. Rev.*, 1972, volume 72, pp 231–281.
- Ralph G. Pearson The transition-metal-hydrogen bond. *Chemical Reviews*. volume 85, 1985, S. 41–49.
- E. A. McNeill, F. R. Scholer: Molecular structure of the gaseous metal carbonyl hydrides of manganese, iron, and cobalt. *Journal of the American Chemical Society*. volume 99, 1977, S. 6243–6249,
- F. A. Cotton: Structure and Bonding in Metal Carbonyls and Related Compounds. In: *Helvetica Chimica Acta*. 50, 1967, S. 117–130,

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# UNIT 11 CATALYSIS INVOLVING ORGANOMETALLICS

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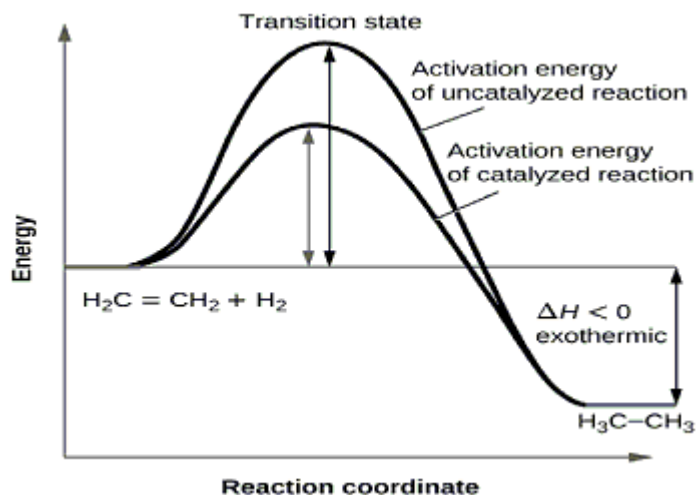
**Structure**

- 11.0 Introduction
  - 11.1 Objectives
  - 11.2 Oxidative addition
  - 11.3 Reductive elimination
  - 11.4 Hydrogenation
  - 11.5 Hydroformylation
  - 11.6 Monsanto process
  - 11.7 Ziegler Natta Polymerization
  - 11.8 Isomerisation
  - 11.9 Check your progress questions
  - 11.10 Answers to check your progress questions
  - 11.11 Summary
  - 11.12 Keywords
  - 11.13 self assessment question and exercise
  - 11.14 Further Reading
- 

**11. 0 Introduction**

A thermodynamically favorable reaction may be slow at modest temperatures and thus of little value for synthesis. Increased temperatures may help making it faster, but competing reactions may be accelerated as well. A more attractive approach to increase the rate of a reaction is to use catalysis.

Catalysts are the substances which increase the rate of the reaction which itself not consumed in the reaction. A catalyst typically increases the reaction rates by lowering the activation energy by opening up pathways with lower Gibbs free energies of activation ( $G$ ). Sometimes, the thermal reaction and the catalysed reaction give different products. This is because the catalyst has accelerated a reaction that is normally kinetically unfavourable. Generally, we will be interested in catalysts that increase the rate of reaction, but it should be noted that inhibitors which slow down certain reactions are also of great commercial and academic importance.



## NOTES

Catalytic efficiency of a catalyst is expressed in turn over number (N). In catalysis, the term turnover number has two meanings: the number of moles of substrate that a mole of catalyst can convert before becoming inactivated and is the amount of substrate converted per the amount of catalyst used. In theory, the Ideal catalyst would have an infinite turnover number and would never be consumed. In practice, turnover numbers begin at 100 and can go up to a million, more so in some cases. Further, the turn over number N is defined as the velocity of the reaction V divided by concentration of the catalyst [Q]. i.e.,  $N = V/[Q]$ . If N is high the catalyst is good, because for small concentration of the catalyst, the rate is high.

**Turnover Frequency (TOF)** A catalyst's turnover frequency number, or turnover number per time unit, characterizes its level of activity. So the TOF is the total number of moles transformed into the desired product by one mole of active site per hour. Larger the TOF, the more active the catalyst.

$$\text{TOF} = \text{TON}/\text{hour}$$

In catalysis by organometallic systems, the catalyst brings together substrates within the coordination sphere. This means that the catalyst must have a free coordination site, or at least be able to free-up a coordination site by ligand dissociation or isomerisation. The substrates are activated in some way by the process of coordination and a reaction takes place. Often the most difficult step is that of decomplexation of the transformed substrate. Indeed, although many "organic" processes can be mediated by organometallics, relatively few are truly catalytic. This is largely because the transformed fragment refuses to de-complex from the metal centre in order to free-up a coordination site for the next substrate molecule.

## NOTES

Thus the **Mode of Action of Transition-Metal Complexes in Catalysis.**

- The coordination of the reaction partners to a transition metal brings them into close proximity, thus promoting the reaction.
- Through coordination to a transition metal, a reaction partner can become activated for subsequent reactions.
- The coordination of an organic substrate to a transition metal can facilitate nucleophilic attack.
- Catalytically active systems therefore must possess vacant coordination sites or be able to generate them in a primary dissociation step.
- **Catalytic Cycles:** The essence of catalysis is a cycle of reactions that consumes the reactants, forms products and regenerates the catalytic species. The catalytic cycle operates in the principle of microscopic reversibility. i.e., If a certain series of steps constitutes the mechanism of a forward reaction, the mechanism of the reverse reaction is given by the same steps traversed backwards. (applies only to thermal reactions and not-photochemical reactions) The sequence of transition states and relative intermediates in the mechanism of a reversible reaction must be the same but in reverse order for the backward reaction as for the forward reaction

We will discuss the most well studied and/or useful examples of homogeneous catalysis: olefin hydrogenation (addition of hydrogen across C=C bond) olefin hydroformylation (addition of hydrogen and formyl HC(O) across C=C bond) olefin metathesis olefin polymerization carbonylation of methanol (Monsanto acetic acid process)Olefin hydrogenation. The following reaction is favorable but does not proceed at all at room temperature: In the beginning of the 20th century Paul Sabatier discovered that hydrogenation of olefins can be accelerated with finely dispersed Ni, Pt or Pd (heterogeneous catalysis).If hydrogenation of substrates with many functional groups in them is needed, heterogeneous catalysis is not a good choice because of the lack of selectivity:

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### 11.1 Objectives

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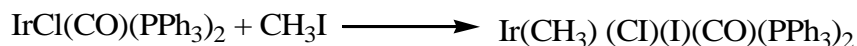
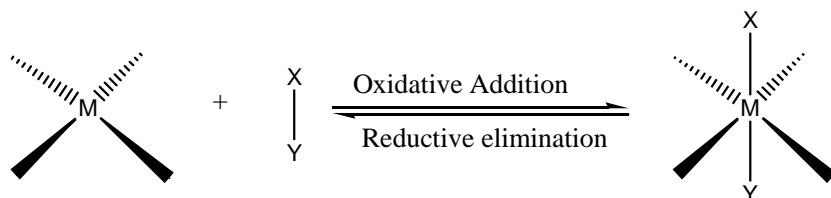
The main aim of this unit is to discuss the importance of organotransition metal complexes as catalysts in different industrially important reactions. After going through this unit you will be able to:

- Discuss the reactions taking part in the mechanism of catalytic reactions of organotransition metal complexes, such as oxidative addition reaction
- Describing hydrogenation, polymerization and Hydroformylation etc., reactions, can discuss the mechanism of catalytic part played by organotransition metal complexes in industrially important reactions
- Discuss the mechanisms of Zeiglar – Natta and Wacker process

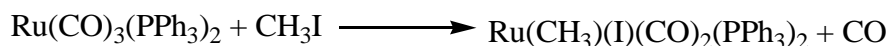
## 11.2 Oxidative addition

Oxidative addition (or oxad) reaction which are useful for establishment of new transition metal-carbon  $\sigma$ -bonds involve the oxidation (i.e., increase in the formal oxidation number), accompanied by an increase in the coordination number of the central metal atom. Complexes of metals in low spin  $d^7$ ,  $d^8$ , or  $d^9$  configurations generally undergo this type of reaction and in the process of enhancing their coordination number, the central metal tends to attain the stable closed-shell configuration corresponding to 18 valence electrons.

Coordinative unsaturated state of the central transition metal appears to facilitate an 'oxad' type of reaction. For example, in the following reaction, iridium (I) changes from 4-coordinate 16-electron to 18-electron iridium (III):



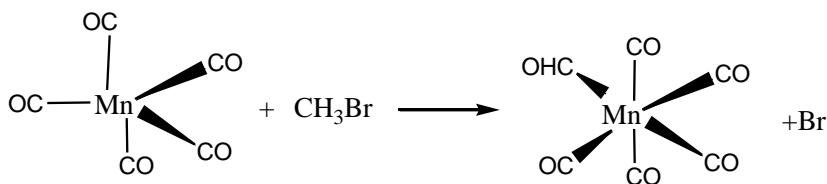
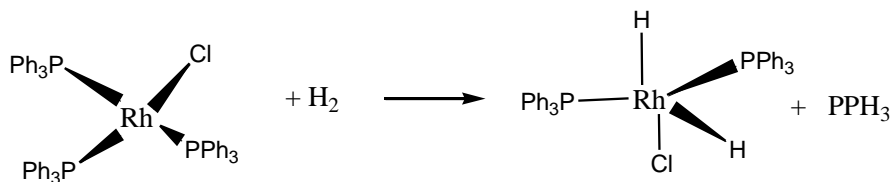
Similarly, in the following reaction, 5-coordinate 18-electron ruthenium(0) is converted into 6-coordinate 18-electron ruthenium (II), accompanied by the loss of a CO molecule:



To facilitate oxidative addition type of reactions, the metals should preferably be in low oxidation state. Unlike the main group metals (e.g. the formation of Grignard reagents from metallic magnesium and alkyl halides), the transition metals themselves are not generally reactive enough under ambient conditions and have to be in low oxidation state in the presence of coordinated ligands.

The oxidative addition reactions have assumed special importance in catalytic processes and this is generally the initiating step in a catalytic process and involves the formation of bonding of some kind ( $\sigma$ ,  $\pi$  other delocalized type) between the transition metal and the organic/inorganic substrate (through oxidative addition or coordination); this is generally a key step in the catalytic or / and stoichiometric process, e.g.:

## NOTES



The oxidative addition/ coordination reaction of a ligand is generally facilitated by the availability of vacant coordination site (s) on a metal complex in solution (homogeneous catalysis) or a metal surface (heterogeneous catalysis). The coordinative unsaturation may also arise from the dissociation of loosely held solvent molecules, giving rise to potentially vacant site(s). For example, a square planar  $d^8$  (4-coordinate) complex such as  $\text{RhCl(PPh}_3\text{)}_3$  (known as Wilkinson's catalyst) is coordinatively unsaturated and is one of the most active and versatile catalysts known so far. In this connection, it may be noted that coordinative unsaturation is generally guided by the 18-electron rule (or effective atomic number rule).

In view of the extensive applicability of oxidative addition reactions in catalysis, some of their essential features are indicated as follows:

**(A) Low Oxidation State of the Metal**

As oxidative addition reaction can be treated as a process undergoing loss of electrons from the electron rich metal centres, the same should be facilitated by the metal atom in the complex being in the lower oxidation state; in fact, any change in the metal complex which enhances the electron density at the central metal leads to an increase in reactivity. Although theoretically metal atoms in metallic (or zero oxidation) state could be expected to be better precursors for such reactions, yet these are of only very limited applicability on energetic grounds. However, the development of metal vapour and reactive metal production techniques have added new dimensions in this particular area.

**(B) Coordinative Unsaturation**

The oxidative addition reactions are generally accompanied by an increase in the coordination number of the central metal atom. It is, therefore, expected that organometallic precursors should be coordinatively unsaturated, e.g.  $\text{IrCl(CO)(PPh}_3\text{)}_2$ ;  $\text{(RhCl(PPh}_3\text{)}_3$ , etc. The coordinative unsaturation can be achieved either (i) by the generation of a

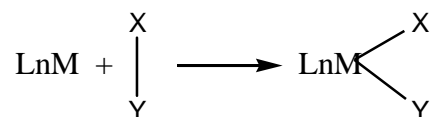


vacant coordination site or (ii) by the ability of a complex to exist in different coordination numbers.

### (C) Nature of the Metal

There are many indications that the lighter metals in a given sub-group are less basic or nucleophilic than the heavier elements. For example, while the complex  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  (Vaska's compound) reacts completely and irreversibly with  $\text{CH}_3\text{I}$ :

**Basic reaction:**



The new M-X and M-Y bonds are formed using:

- the electron pair of the X-Y bond
- one metal-centered lone pair

The metal goes up in oxidation state (+2)

X-Y formally gets reduced to  $\text{X}^-$ ,  $\text{Y}^-$

Common for transition metals, rare for main-group metals

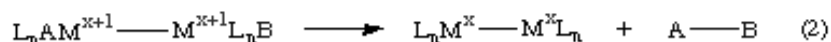
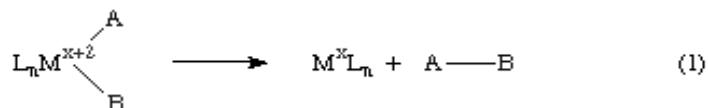
### 11.3 Reductive elimination

As the name implies reductive elimination involves the elimination or expulsion of a molecule from a transition metal complex.

In the process of this elimination, the metal center is reduced by two electrons.

In the simplest example below the metal goes from the  $x+2$  to the  $x$  oxidation state and a coordinatively unsaturated metal center is obtained.

In Equation 2 we see a case of a binuclear reductive elimination reaction:



Reductive elimination is formally the microscopic reverse of oxidative addition, and it is not surprising that a series of reactions involving an oxidative addition, a rearrangement and then a reductive elimination form the basis for a variety of industrially important catalytic cycles.

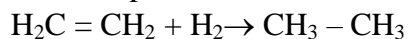
#### Factors which facilitate reductive elimination

- a high formal positive charge on the metal,
- the presence of bulky groups on the metal, and
- an electronically stable organic product.
- Cis orientation of the groups taking part in reductive elimination is a MUST Almost the exact reverse of Oxidative Addition

## NOTES

## 11.4 Hydrogenation

The addition of hydrogen gas to ethylene to form an alkane is thermodynamically favourable, but it does not take place at room temperature and pressure.



$$\Delta H^\circ = -136 \text{ KJ mol}^{-1}$$

$$\Delta H^\circ = -101 \text{ KJ mol}^{-1}$$

However this reaction is heterogeneously catalysed by metallic Ni, Cu, Pd or Pt, the reaction is fast and complete.

The first effective homogeneous catalyst discovered for hydrogenation of alkenes was the square – planar 16 – electron  $d^8$  complex, chlorotris (triphenylphosphine) Rhodium (I)  $[(\text{Ph}_3\text{P})_3 \text{Rh}^{\text{I}} \text{Cl}]$  which is known as Wilkinson's catalyst. In the catalyst  $[(\text{Ph}_3\text{P})_3 \text{Rh}^{\text{I}} \text{Cl}]$

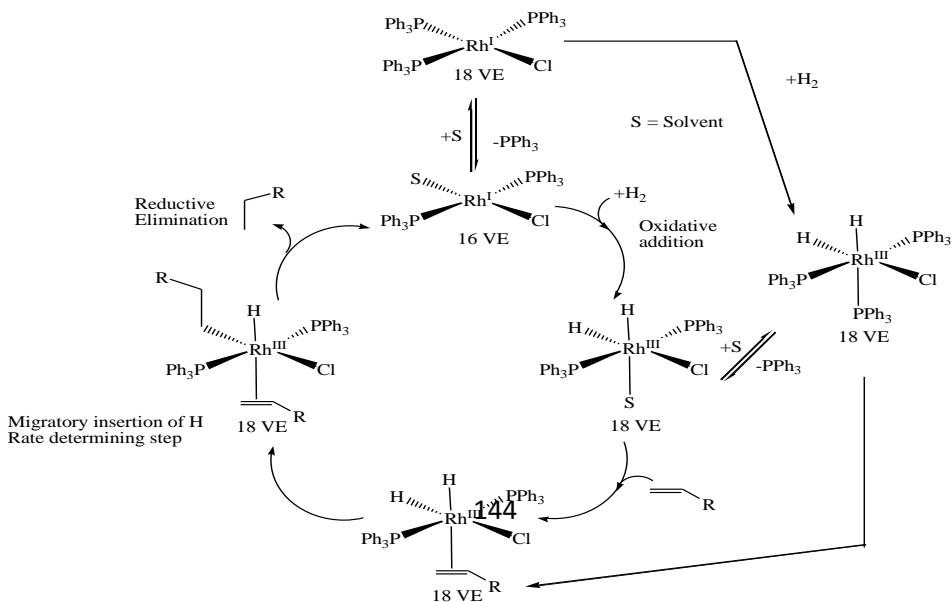
Electronic configuration =  $\text{Rh}^{\text{I}} \quad 4d^7 5s^1$

Rh	=	$8e^-$	So coordinatively unsaturated.
4 Ligands	=	$8e^-$	
$\Sigma$	=	$16e^-$	

Since  $\Sigma = 16$  which has two electrons short of 18 electrons and undergo oxidative addition and reductive elimination. So this complex becomes 5 coordinative through a simple addition of ligand or 6 coordinate through addition combined with oxidation.

In either case it achieves  $18e^-$  valence shell configuration Wilkinson's catalyst: The first example of an effective and rapid homogeneous catalyst for hydrogenation of alkenes, active at room temperature and atmospheric pressure.

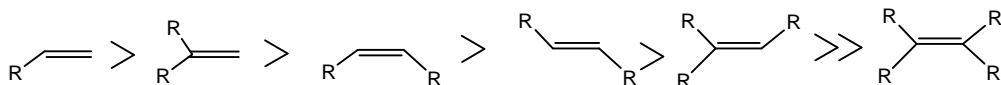
Wilkinson's catalyst is catalyst for hydrogenation of alkenes. Square planar 16 electron  $d^8$  complex  $(\text{Ph}_3\text{P})_3\text{RhCl}$ .



### Mechanism

- Wilkinson's catalyst catalyzes the hydrogenation of alkenes.
- Mechanism involves the initial dissociation of one or two triphenylphosphine ligands to give 14 or 12-electron complexes, respectively. In solution one of the phosphine ligands dissociates, leaving  $(\text{Ph}_3\text{P})_2\text{RhCl}$  the reaction can be represented as follows ( $\text{L} = \text{Ph}_3\text{P}$ ,  $\text{S} = \text{Solvent}$ ). Solvent must be an electron donor i.e., Lewis base.
- Followed by oxidative addition of  $\text{H}_2$  to the metal. The  $(\text{Ph}_3\text{P})_2\text{RhCl}$  molecule, possibly solvated undergoes oxidative addition of a  $\text{H}_2$  molecule.
- An alkene gets coordinated to the Rh metal atom displacing the solvent.
- The hydride ion ( $\text{H}^-$ ) migrates from the metal to a carbon in the coordinated alkene to form an alkyl group. This is often called an alkene insertion reaction.
- The solvent reenters and occupies the vacant site.
- Finally reductive elimination of ethylene and regeneration of catalyst takes place.
- The  $(\text{Ph}_3\text{P})\text{RhCl}$  formed in the dissociation step is tricoordinate, a very reactive complex and has not as yet isolated, but the closely related  $[\text{Ph}_3\text{P}]_3\text{Rh}^+$ , which could form from the dissociation of a chloride ion from Wilkinson catalyst has been studied and found to have T-shaped structure than triangular (3-coordinate).
- The reaction involving a catalyst can always be represented by a closed loop. The reaction 1 to 6 can be combined into a continuous cycle (closed loop) called 'TOLMAN CATALYTIC LOOP' in which various catalytic species formed in the main body of the loop the reactants and the products formed leaving at appropriate loop.
- Other applications of Wilkinson's catalyst include: catalytic hydroboration of alkenes and the selective 1,4-reduction of  $\alpha, \beta$ -unsaturated carbonyl compounds in concert with triethylsilane.

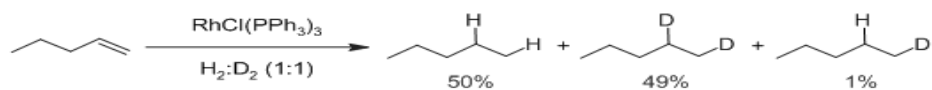
The rates of hydrogenations decrease with increase in the alkyl group substitution on double bond mirroring their relative binding affinities to the metal center. It is also partly due to steric factors.



There is minimal scrambling of H/D in the product, when an equimolar mixture of  $\text{H}_2$  and  $\text{D}_2$  are used

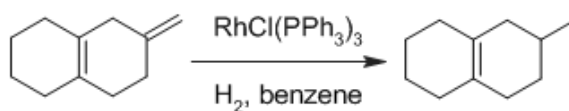
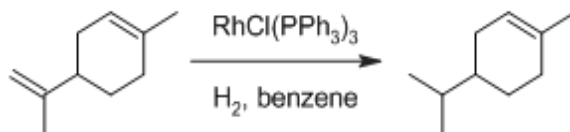
### NOTES

## NOTES

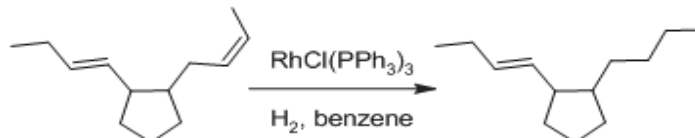


Wilkinson's catalyst can be used to achieve selective hydrogenations.

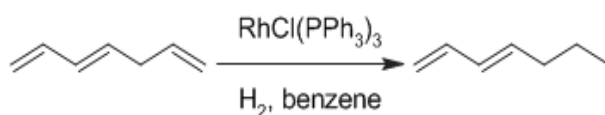
- Less substituted and sterically less hindered double bonds are selectively hydrogenated.
- Exocyclic double bonds are selectively hydrogenated over endocyclic double bonds.



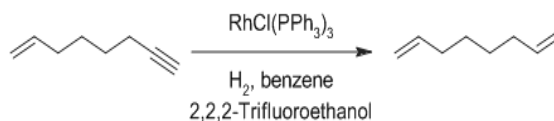
Cis alkenes are reduced rapidly than trans alkenes.



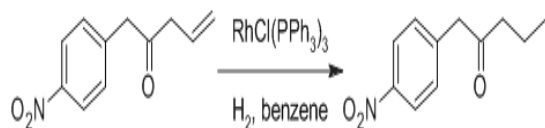
Isolated double bonds are rapidly hydrogenated over conjugated dienes.



Terminal alkynes are hydrogenated more rapidly than terminal alkenes. The selectivity can be enhanced by using acidic alcoholic co-solvents.



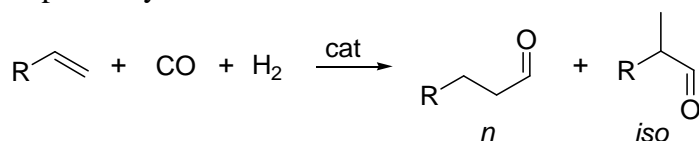
Functional groups like  $\text{C}=\text{O}$ ,  $\text{C}=\text{N}$ ,  $\text{NO}_2$ , Aryl,  $\text{CO}_2\text{R}$  etc., are unaffected. The compatibility of Wilkinson's catalyst with polar multiple bonds indicates the metal hydride bond is primarily covalent in character.



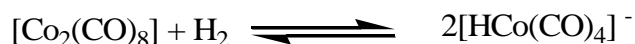
## 11.5 Hydroformylation

The reaction of an alkene with CO and H<sub>2</sub> catalysed by Co or Rh salts to form an aldehyde containing one more carbon atom than original alkene is called 'Hydroformylation' or 'Oxo process'.

The name hydroformylation arises from the fact that the H atom and formyl group are added across a double bond. The net result of the process is extension of carbon chain by one and introduction of the oxygen to the molecule. Main industrial application is in the production of butanal from propene. Further the products were generally mixtures of linear and branched-chain isomers in roughly 3 : 1 ratio. The formation of these is directed by anti-Markovnikov and Markovnikov additions respectively.



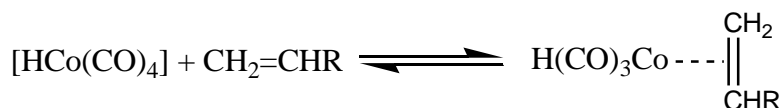
A pre equilibrium is established in which CO<sub>2</sub>(CO)<sub>8</sub> combines with H<sub>2</sub> at high pressure to yield the known tetra carbonyl hydride cobalt complex HCo(CO)<sub>4</sub>.



b) This complex loses CO to produce coordinately unsaturated complex HCo(CO)<sub>3</sub>



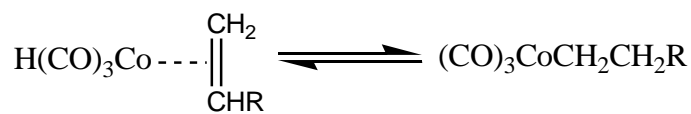
c) An alkene coordinates to HCo(CO)<sub>3</sub> producing 18e<sup>-</sup> complex.



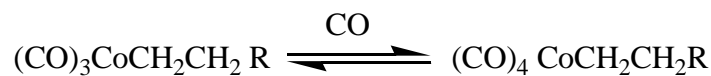
d) This 18 electron complex undergo migratory insertions of the olefin into Co – H bond thereby creating another 16 electron complex (acyl complex) and another.

### NOTES

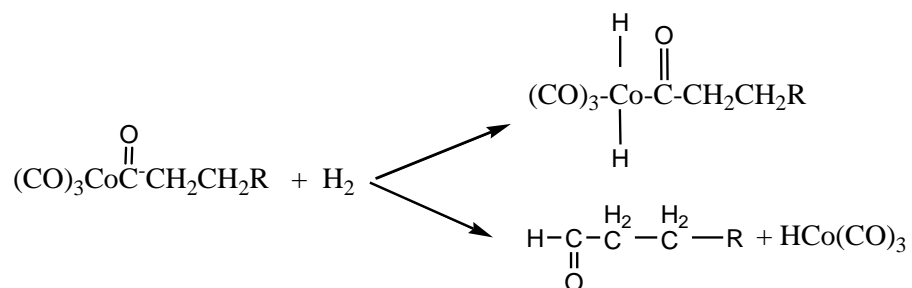
## NOTES



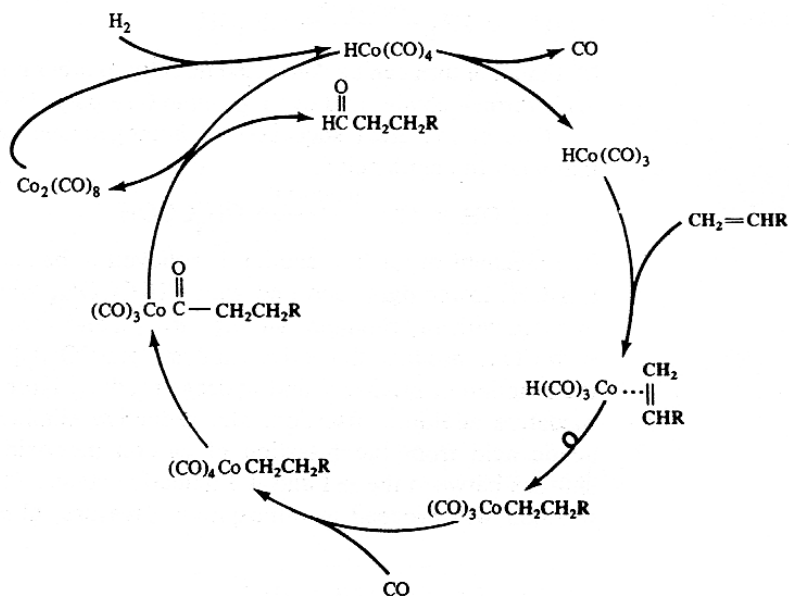
e) A CO of  $\text{RCH}_2\text{CH}_2\text{Co}(\text{CO})_4$  migrates to a position between the CO atom and alkyl group. This is the critical step in the formation of aldehyde.



f) Reaction with either  $\text{H}_2$  or  $[\text{HCo}(\text{CO})_4]$  releases the aldehyde and regenerates the catalytic Co complex.



This process may be carried out so that the aldehyde products are reduced to give alcohol such as 1-butanol or higher alcohols.



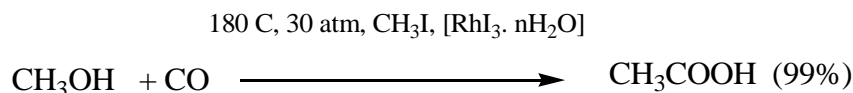
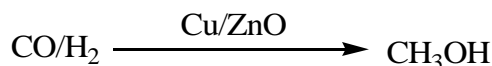

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## 11.6 Monsanto process

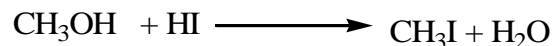
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Prior to 1970, acetic acid was made using cobalt catalysts (BASF process) In 1970 Monsanto commercialized a rhodium carbonyl iodide catalyst that is commonly called the Monsanto Acetic Acid Process. The Monsanto acetic acid process is the major commercial production method for acetic acid. Methanol, which can be generated from synthesis gas ("syn gas", a CO/H<sub>2</sub> mixture), is reacted with carbon monoxide in the presence of a catalyst to afford acetic acid. In essence, the reaction can be thought of as the insertion of carbon monoxide into the C-O bond of methanol, i.e. the carbonylation of methanol.

The catalyst system has two components, iodide and rhodium. Almost any source of Rh and I<sup>-</sup> will work in this reaction as they will be converted to the actual catalyst, [Rh(CO)<sub>2</sub>I<sub>2</sub>]<sup>-</sup> under the reaction conditions. Over 1,000,000 tons of acetic acid are produced every year using the Monsanto process.



The role of iodide is simply to promote the conversion of methanol to methyl iodide, the species which then undergoes reaction with the Rh metal catalyst



The catalytic cycle: Once methyl iodide has been generated, the catalytic cycle begins with the oxidative addition of methyl iodide to [Rh(CO)<sub>2</sub>I<sub>2</sub>]<sup>-</sup>. Coordination and insertion of carbon monoxide leads an intermediate 18-electron acyl complex which can then undergo reductive elimination to yield acetyl iodide and regenerate our catalyst.

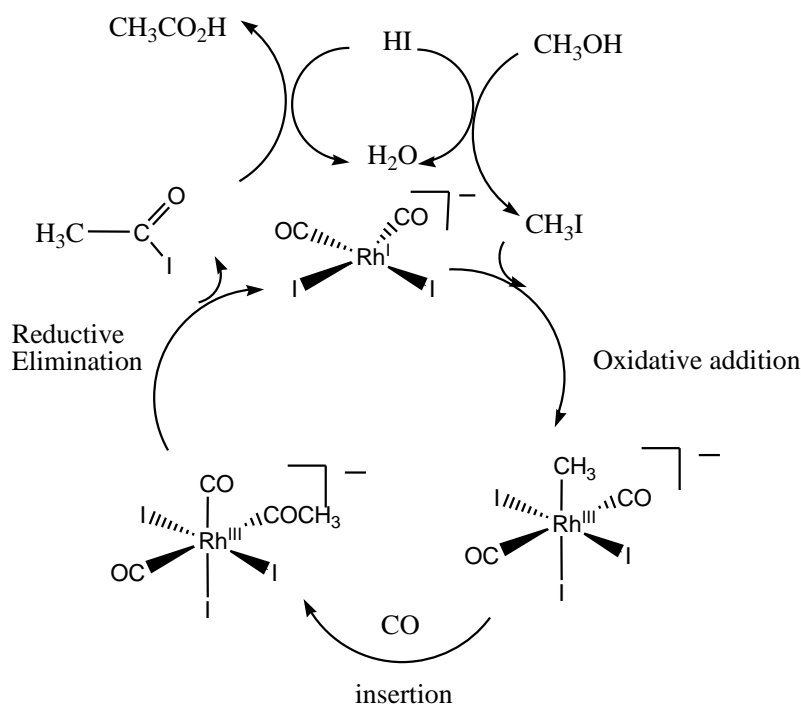
Notice that there are two catalytic cycles going in this reaction using metal and iodide. The acetyl iodide produced in the lower cycle is then hydrolyzed in the upper one to give acetic acid. This hydrolysis produces HI which can then convert more methanol to iodide and continue the cycle:

NOTES



In summary, the system is catalytic in both Rh and I.

## NOTES



### Benefits

- Uses a more efficient metal complex to synthesize a C-C bond
- Increased yield selectivity to > 99% based upon methanol
- Milder conditions needed for the synthesis (150-200 °C and 30-60 bar)
- Plant capacity: 500,000 tons annually

### Challenges

- Rhodium: expensive and precipitates under low water concentrations
- Large production of high boiling point by-products
- Replaced by an Iridium catalyst in the late 1990s by BP Chemicals

## 11.7 Ziegler Natta Polymerization

The German chemist Karl Ziegler (1898-1973) discovered in 1953 that when  $\text{TiCl}_3(\text{s})$  and  $\text{AlEt}_3$  are combined together they produced an



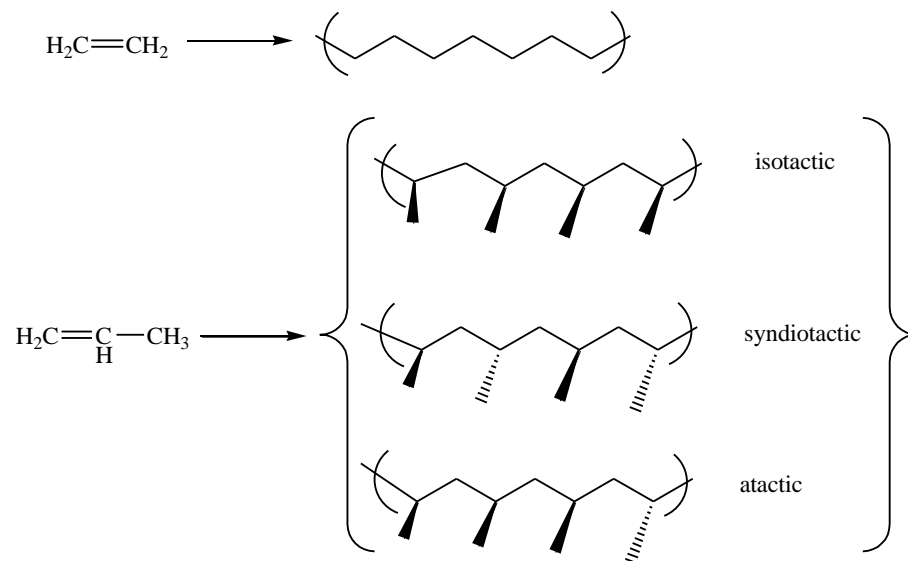
extremely active *heterogeneous* catalyst for the polymerization of ethylene at atmospheric pressure.

Giulio Natta (1903-1979), an Italian chemist, extended the method to other olefins like propylene and developed variations of the Ziegler catalyst based on his findings on the mechanism of the polymerization reaction. The Ziegler-Natta catalyst family includes halides of titanium, chromium, vanadium, and zirconium, typically activated by alkyl aluminum compounds. Ziegler and Natta received the Nobel Prize in Chemistry for their work in 1963.

Polyolefins are the most important products of organometallic catalysis (> 60 million Tons per year)

- Polyethylene (low, medium, high, ultrahigh density) used in packaging, containers, toys, and house ware items, wire insulators, bags, pipes.
- Polypropylene (food and beverage containers, medical tubing, bumpers, foot ware, thermal insulation, mats)

Ziegler-Natta process for polymerization of alkenes, it would be appropriate to point out that unsymmetrical alkenes can lead to different types of arrangements in the polymer. Catalysed polymerization of ethylene (ethene) produces a stereoregular polyethylene (polythene) Propylene, on the other hand, may form two stereoregular (either isotactic or syndiotactic) or a non-regular atactic polymer.

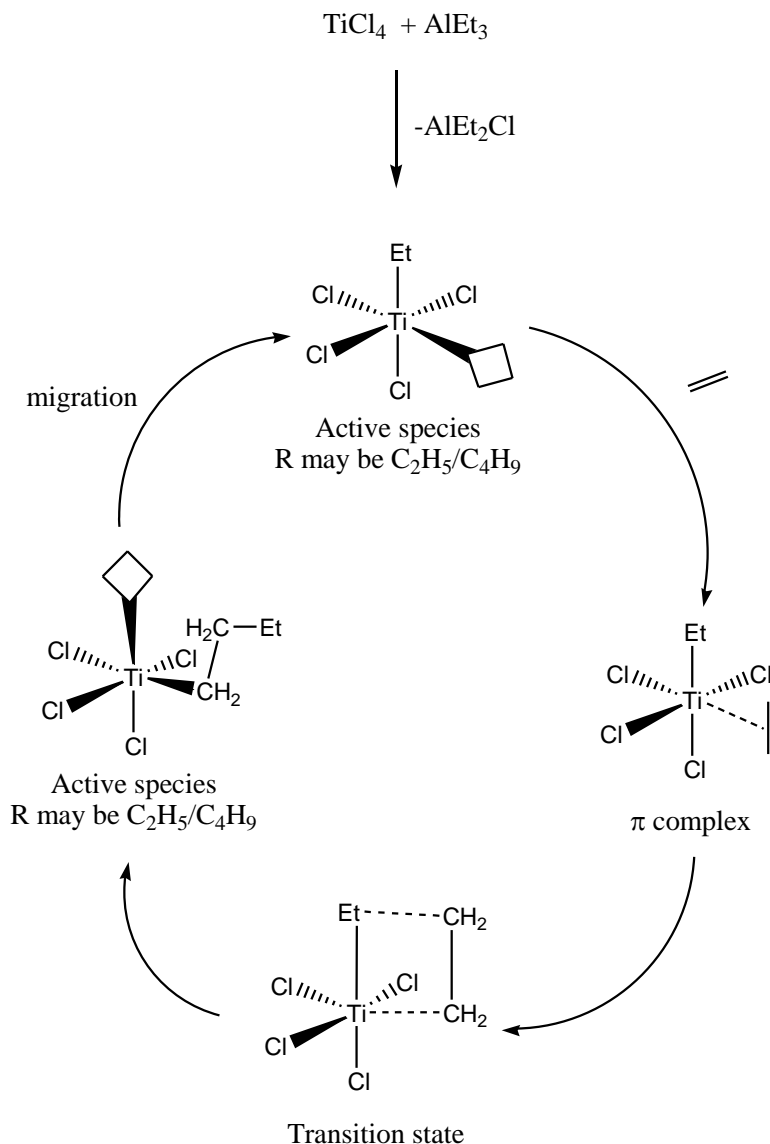


- Isotactic polymer: In this all methyl groups lie on the same side of the chain, which tends to adopt a helical shape so that the methyl groups do not sterically interfere with one another.

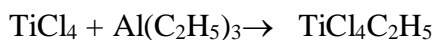
## NOTES

- Syndiotactic polymer: In this, there is a regular alternation of methyl groups along the chain.
- Atactic polymer: In this, there is no regularity in the configuration of methyl groups along the chain.

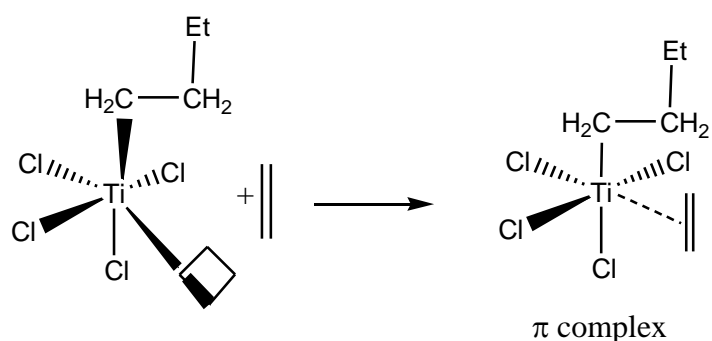
Zeigler – Natta Catalyst –  $\text{TiCl}_4 \text{ C}_2\text{H}_5$ . It is a Lewis acid. Accepts a pair of electron to form coordinate bond. It is coordinatively unsaturated.

**Mechanism**

- The  $\text{Al}(\text{C}_2\text{H}_5)_3$  alkylates the Ti – atom on the surface of the solid.



- An ethene molecule coordinates to the neighboring vacant site.
- The coordinated alkyl group undergoes a migratory insertion reaction. This is the propagation step for the polymerization.
- This migration opens up another neighbouring vacancy and so the next alkene molecule can coordinate and so the reaction can continue and the polymer chain can grow. This vacant site can be occupied by another ethene molecule and the insertion process is repeated and steps (2) and (3) continued until a chain termination process occurs by the severing of the titanium-alkyl bond



- The release of polymer from metal atom occur by  $\beta$  - hydrogen elimination and the chain is terminated.
- The stereoregularity of polypropylene was assumed to arise due to the nature of sterically controlled directing sites on the  $\text{TiCl}_3$  lattice.

### Applications

The Ziegler-Natta catalyst polymerisation is a beneficial and versatile reaction for producing polymers. Some of the most popular applications of this catalyst are;

They are used for the production of High and Low-Density Polyethylene. Production of thermoplastic polyolefins, polybutylene, crystalline polypropylene and carbon nanotubes nanocomposites.

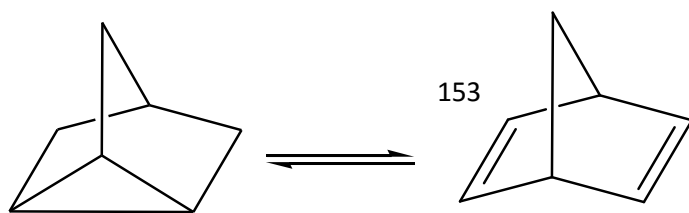
### Limitation of Ziegler-Natta Catalyst

Ziegler-Natta polymerisation has some limitations as it does not work for some monomers. Products like poly(vinyl chloride) cannot be generated by Ziegler-Natta polymerisation. Acrylates are also another example.

## 11.8 Isomerisation

### Valence isomerisation of strained hydrocarbons.

A number of complexes, notably of  $\text{Rh}^I$ ,  $\text{Pd}^0$  and  $\text{Ni}^0$  will induce valence isomerization of strained hydrocarbons. A typical example is the interconversion of norbornadiene and quadricyclane.

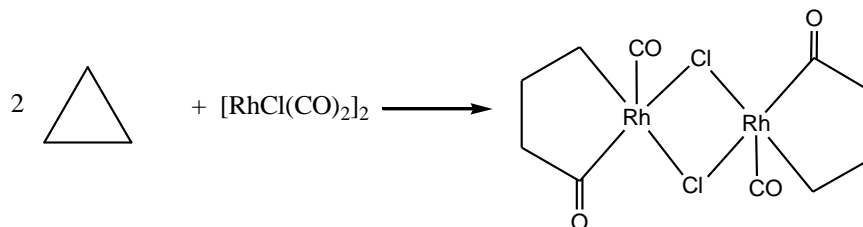


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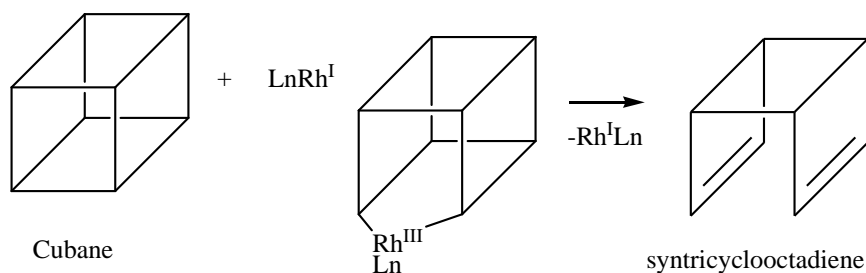
The reaction proceeds readily with metal ions such as  $\text{Fe}^{\text{I}}$  or  $\text{Cu}^{\text{I}}$  in the gas phase. The forward reaction is catalyzed for example, by  $\text{PdCl}_2$  (norbornadiene) while the norbornadiene  $\rightarrow$  quadricyclane photoisomerization is sensitized by an  $\text{Ir}^{\text{III}}$  ortho – metallated complex,  $[(\text{bipy})_2\text{Ir}(2, 2' - \text{bipyrid} - - \text{y}' - \text{C}^3, \text{N}') ]^{2+}$

## NOTES

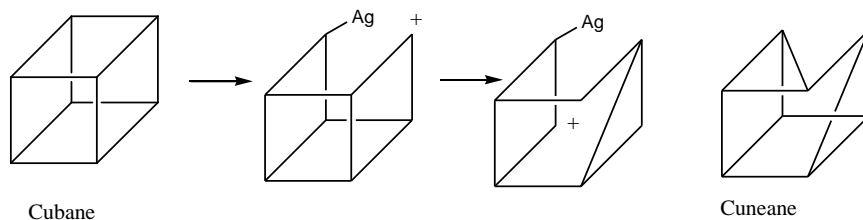
Most reactions of this type are considered to proceed by oxidative addition and cleavage of the C – C bond. For cyclopropane the reaction with  $[\text{RhCl}(\text{CO})_2]_2$  gives an isolable intermediate.



A few other intermediate have been isolated with non – carbonyl complexes eg  $\text{RhCl}(\text{PPh}_3)_3$ , the reaction is through to proceed as



The  $\text{Ag}^+$  ion also catalyses such isomerization, but these proceed by electrophilic cleavage of C – C bonds followed by carbonium ion rearrangements.



## 11.9 check your progress questions

1. Explain Turnover Frequency.
2. Describe Catalytic Cycles
3. What is meant by reductive elimination reaction?

4. Give molecular structure of Wilkinsons Catalyst
5. What is Hydroformylation reaction?
6. Describe Ziegler-Natta process

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### 11.10 Answers to check your progress questions

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- A catalyst's turnover frequency number, or turnover number per time unit, characterizes its level of activity. So the TOF is the total number of moles transformed into the desired product by one mole of active site per hour. Larger the TOF, the more active the catalyst.  $\text{TOF} = \text{TON}/\text{hour}$ .
- The essence of catalysis is a cycle of reactions that consumes the reactants, forms products and regenerates the catalytic species. The catalytic cycle operates in the principle of microscopic reversibility. i.e., If a certain series of steps constitutes the mechanism of a forward reaction, the mechanism of the reverse reaction is given by the same steps traversed backwards.
- reductive elimination involves the elimination or expulsion of a molecule from a transition metal complex.
- Square planar 16 electron  $d^8$  complex  $(\text{Ph}_3\text{P})_3\text{RhCl}$ .
- The reaction of an alkene with CO and  $\text{H}_2$  catalysed by Co or Rh salts to form an aldehyde containing one more carbon atom than original alkene is called 'Hydroformylation' or 'Oxo process'.
- Ziegler-Natta process for polymerization of alkenes, it would be appropriate to point out that unsymmetrical alkenes can lead to different types of arrangements in the polymer.

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### 11.11 Summary

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- The essence of catalysis is a cycle of reactions that consumes the reactants, forms products and regenerates the catalytic species.
- Catalytic efficiency of a catalyst is expressed in turn over number (N).
- Oxidative addition (or oxad) reaction which are useful for establishment of new transition metal-carbon  $\sigma$ -bonds involve the oxidation (i.e., increase in the formal oxidation number), accompanied by an increase in the coordination number of the central metal atom
- The first example of an effective and rapid homogeneous catalyst for hydrogenation of alkenes, active at room temperature and atmospheric pressure.
- During Oxo process the products were generally mixtures of linear and branched-chain isomers in roughly 3 : 1 ratio. The formation of these is directed by anti-Markovnikov and Markovnikov additions respectively.

## NOTES

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**11.12 Keywords**

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- **Oxo process:** The reaction of an alkene with CO and H<sub>2</sub> catalysed by Co or Rh salts to form an aldehyde containing one more carbon atom than original alkene is called 'Oxo process'.
- **Monsanto Acetic Acid Process:** Monsanto commercialized a rhodium carbonyl iodide catalyst that is commonly called the Monsanto Acetic Acid Process.
- **Zeigler – Natta Catalyst** – TiCl<sub>4</sub> C<sub>2</sub>H<sub>5</sub>. It is a Lewis acid. Accepts a pair of electron to form coordinate bond. It is coordinatively unsaturated.
- **isomerization:** Rh<sup>I</sup>, Pd<sup>0</sup> and Ni<sup>0</sup> complexes will induce valence isomerization of strained hydrocarbons.
- **Isotactic polymer:** In this all methyl groups lie on the same side of the chain, which tends to adopt a helical shape so that the methyl groups do not sterically interfere with one another.

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**11.13 Self assessment question and exercise**

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1. Write a note on hydrogenation of alkenes
2. Discuss the mechanism of Zeigler-Natta Catalyst
3. Write the advantages of Monsanto process.
4. What is oxidative addition?
5. What is TON?

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**11.14 Further Reading**

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7. **Modern aspects of Inorganic chemistry**, H.J. Emelius and Sharpe, Universal book Stall, New Delhi, 1989.
8. **Inorganic Chemistry- Principles of structure and reactivity**, J.E. Huheey, E.A. Keiter and R.L. Keiter, 4<sup>th</sup> edition, Pearson-Education, 2002.
9. **Advanced Inorganic Chemistry** - F.A. Cotton and G. Wilkinson, Wiley Eastern, 5<sup>th</sup> edition, 1998.
10. **Inorganic Chemistry**, D. F. Shriver and P. W. Atkins, Oxford U.K., 1999.
11. **Chemistry & Chemical Reactivity**, John C. Kotz, Paul M. Treichel, John Townsend, 8<sup>th</sup> ed., USA, 2012.
12. **Inorganic Chemistry**,. G. S.Sodhi; 1<sup>st</sup> Edition, VB (P) Ltd, 2006.

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# UNIT-12 METALLOPORPHYRINS AND METALLOENZYMES

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Metalloporphyrins and  
Metalloenzymes

## Structure

- 12.0 Introduction
- 12.1 Objectives
- 12.2 Chlorophyll
  - 12.2.1 Chemical structure of Chlorophyll
  - 12.2.2 Function of chlorophyll
  - 12.2.3 Mechanism of Photosynthesis
- 12.3 Structure and function of Hemoglobin (Hb) and myoglobin (Mb)
  - 12.3.1 Mode of Oxygen transport
  - 12.3.2 Mechanism of oxygenation in Hb and Mb
  - 12.3.3 Cooperativity
- 12.4 Cytochromes
- 12.5 Enzymes
  - 12.5.1 Enzyme action
  - 12.5.2 Inhibition
- 12.6 Vitamin B<sub>12</sub> and B<sub>12</sub> coenzymes
  - 12.6.1 Reactions of Vitamin B<sub>12</sub>
  - 12.6.2 Function
- 12.7 Carboxypeptidase – A
  - 12.7.1 Structure
  - 12.7.2 Mechanism of catalysis
- 12.8 Copper containing oxidases
  - 12.8.1 Structure
  - 12.8.2 Catalytic Mechanism
- 12.9 Answers to check your progress questions
- 12.10 Summary
- 12.11 Keywords
- 12.12 Self-assessment questions and exercises
- 12.13 Further readings

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## 12.0 Introduction

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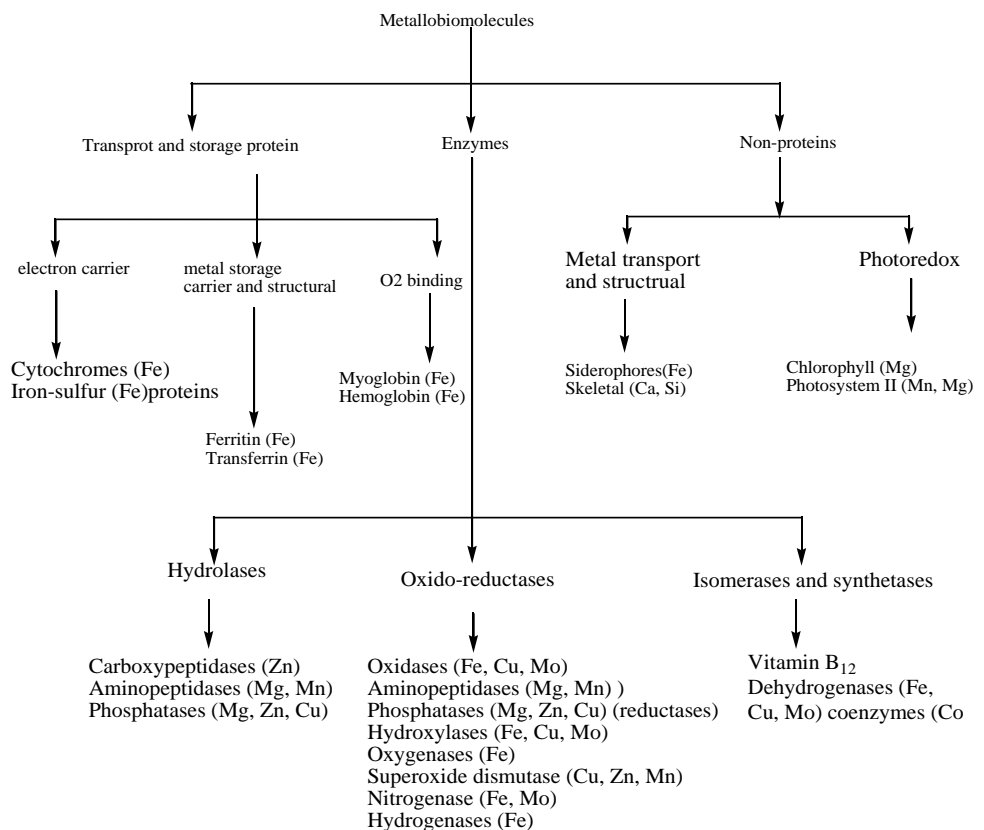
A cofactor is a non-protein chemical compound that is bound to a protein and is required for the protein's biological activity. These proteins are commonly enzymes. Cofactors are either organic or inorganic. They can also be classified depending on how tightly they bind to an enzyme, with loosely-bound or protein-free cofactors termed coenzymes and tightly-bound cofactors termed prosthetic groups. Over 25% of all enzymes contain tightly bound metal ions or require them for activity.

1. Metalloenzymes - contain definite quantity of functional metal ion that is retained throughout purification. Metal ions, most commonly transition metals, are Fe<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, or Co<sup>3+</sup>.

## NOTES

2. Metal-activated enzymes - loosely bind metal ions from solution, and require them for catalysis. Usually the presence of the alkali and alkaline earth metal ions is required:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , or  $\text{Ca}^{2+}$ .

The distinction between metalloenzymes and metal-activated enzymes thus rests on the affinity of a particular enzyme for its metal ion. The mechanism whereby metal ions perform their functions appear to be similar in metalloenzymes and metal-activated enzymes. The flowchart will explain the metallobiomolecules.



Porphyrins are tetradentate ligands which have the characteristic property of complexing with metal ions such as  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Co}^{3+}$ . The co-ordination compounds thus formed are metal chelates called metalloporphyrins. Metalloporphyrins are coloured compounds (organic pigments) found in living organisms. The iron porphyrin which constitutes the haem part of haemoglobin is a well known example of Metalloporphyrin.

## 12.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the structure and function of hemoglobin
- Explain the enzyme action
- Understand the mechanisms behind  $\text{B}_{12}$  and  $\text{B}_{12}$  coenzymes.
- Learn about the Copper containing oxidases
- Describe about Chlorophyll-



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## 12.2 Chlorophyll

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Chlorophyll is the molecule that absorbs sunlight and uses its energy to synthesise carbohydrates from CO<sub>2</sub> and water. This process is known as photosynthesis and is the basis for sustaining the life processes of all plants. Since animals and humans obtain their food supply by eating plants, photosynthesis can be said to be the source of our life also. Chlorophyll is the green colouring matter (pigment) of plant leaves.

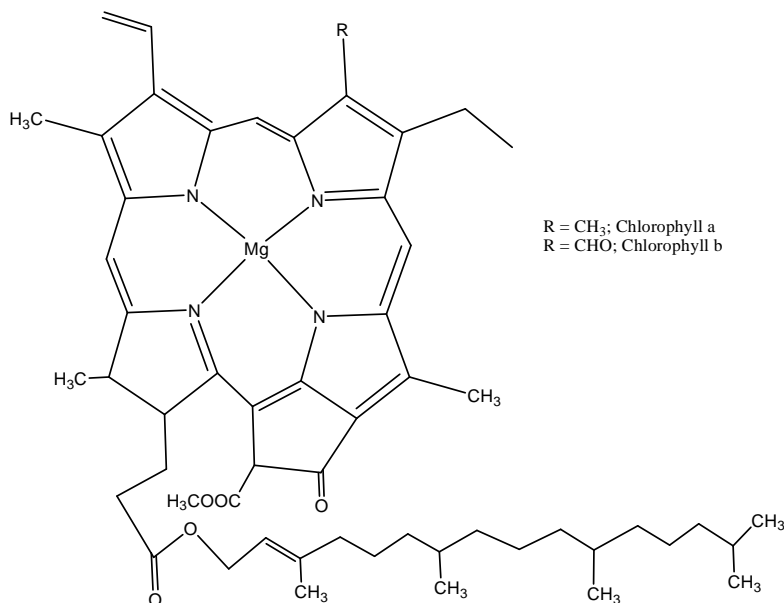
Natural chlorophyll is a 3:1 mixture of chlorophyll – a and chlorophyll – b. They differ only slightly, in the composition of a sidechain (in *a* it is -CH<sub>3</sub>, in *b* it is CHO). Both of these two chlorophylls are very effective photoreceptors because they contain a network of alternating single and double bonds, and the orbitals can delocalise stabilising the structure. Such delocalised polyenes have very strong absorption bands in the visible regions of the spectrum, allowing the plant to absorb the energy from sunlight. There is extensive conjugation of the porphyrin ring in chlorophyll. This lowers the energy of the electronic transitions and shifts the absorption maximum into the region of visible light. Conjugation also helps to make the ring rigid, and thus less energy is wasted in internal thermal degradation (via, molecular vibrations).

The chlorophyll ring system is a porphyrin in which a double bond in one of the pyrrole rings has been reduced.

### 12.2.1 Chemical structure of Chlorophyll

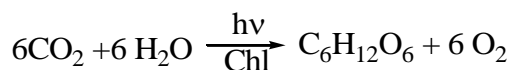
- ❖ Chlorophylls are numerous in types, but all are defined by the presence of a fifth ring beyond the four pyrrole-like rings.
- ❖ Most chlorophylls are classified as chlorins, which are reduced relatives to porphyrins (found in hemoglobin).
- ❖ The chlorin ring can have various side chains, usually including a long phytol chain.
- ❖ It is a magnesium porphyrin complex in which one of the pyrroles is partially reduced.
- ❖ A cyclopentanone ring is fused to the pyrrole ring C.
- ❖ Both the acid chains in chlorophyll are esterified – one is the methyl ester (COOMe) and the other is an ester of phytol (C<sub>20</sub>H<sub>39</sub>OH).

## NOTES



### 12.2.2 Function of chlorophyll

It is capable of channelling the energy of sunlight into chemical energy through the process of photosynthesis. In this process the energy absorbed by chlorophyll transforms carbon dioxide and water into carbohydrates and oxygen

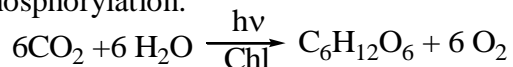


The chemical energy stored by photosynthesis in carbohydrates drives biochemical reactions in nearly all living organisms.

In the photosynthetic reaction electrons are transferred from water to carbon dioxide, i.e carbon dioxide is reduced by water. Chlorophyll assists this transfer as when chlorophyll absorbs light energy, an electron in chlorophyll is excited from a lower energy state to a higher energy state. In this higher energy state, this electron is more readily transferred to another molecule. This starts a chain of electron-transfer steps, which ends with an electron being transferred to carbon dioxide. Meanwhile, the chlorophyll which gave up an electron can accept an electron from another molecule. This is the end of a process which starts with the removal of an electron from water. Thus, chlorophyll is at the centre of the photosynthetic oxidation-reduction reaction between carbon dioxide and water.

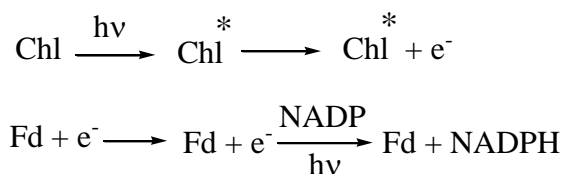
### 12.2.3 Mechanism of Photosynthesis

Photosynthesis is a light driven oxidation – reduction process. Water is oxidized to O<sub>2</sub> by a reaction in the presence of light. This is called light reaction. CO<sub>2</sub> is reduced to form glucose in a light independent reaction called dark reaction. In the light reaction causes oxidation of H<sub>2</sub>O to release O<sub>2</sub> and generation of ATP and NADPH (reductant) by a process called photophosphorylation.



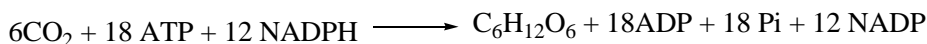
#### Light reaction

Chlorophyll absorbs light and gets excited. The excited chlorophyll molecule expels an electron which is rapidly transferred to electron carriers like ferridoxin and used to reduce NADP. The chlorophyll comes to the ground state by receiving an electron released by the decomposition of water by a Mn-containing complex via cytochromes. The electron translocation leads to ATP synthesis.



#### Dark reaction

CO<sub>2</sub> is reduced to hexose in the dark reaction which utilizes the NADPH and ATP generated by the light reaction (calvin cycle). Totally three ATP and two NADPH molecules are consumed by one molecule of CO<sub>2</sub>.



### 12.3 Structure and function of Hemoglobin (Hb) and myoglobin (Mb)

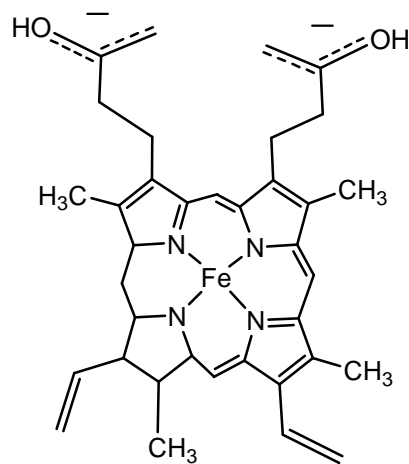
The function of both Hb and Mb is to bind oxygen, but their physiological roles are very different. Hemoglobin picks up oxygen in the lungs and carries it to tissues. Haemoglobin is an effective buffer for blood. The buffering capacity is due to the presence of ionisable groups in the imidazole side chain of histidine residues. Cellular oxygen is stored by Myoglobin, until it is required for metabolic action. Hemoglobin has an additional function of carrying CO<sub>2</sub> back to the lungs. Hb has the molecular weight 64,500 daltons. Each Hb molecule has four heme groups bound to the globin on its surface. In each heme unit of Hb the four square-planar coordination positions of Fe(II) are being occupied by the four nitrogens of the protoporphyrin ring the fifth coordination position of Fe(II) is occupied by the imidazole nitrogen of histidine residue of the protein chain i.e. globin chain, and the sixth

NOTES

coordination position of Fe(II) is occupied by O<sub>2</sub> on oxygenation. In a haem – proteins made of two parts . 1. Globin (96%) – protein part and Haem (4%) – prosthetic group.

Hb consists of a tetrahedral arrangement of four heme groups each surrounded by its polypeptide (globin) chain. Normal adults have two  $\alpha$  and two  $\beta$  type subunits and Hb can accordingly be represented as  $\alpha_2\beta_2$ . The  $\alpha$  and  $\beta$  forms are distinguished by their different amino-acid sequences  $\alpha$ -141,  $\beta$ -146.

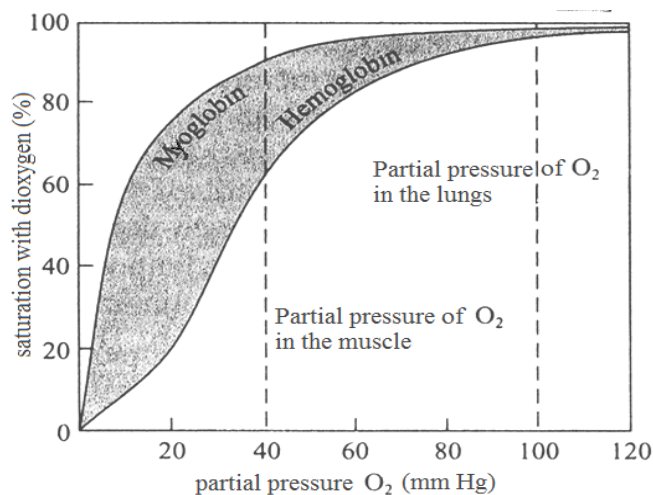
Myoglobin (Mb) (MW 17, 800) is a monomer having only one molecule of heme. The peptide chains in Hb and Mb have extensive helical structure. There are 7 helical segments in the  $\alpha$  chains and 8 in the  $\beta$  and myoglobin forms. These are linked by short non-helical segments. In free heme molecule there are two coordination positions above and below the plane of the porphyrin molecule. These two positions are occupied by water molecules.



Heme  
{Fe-protoporphyrin IX}

The iron (II) ion in heme is very sensitive to oxygen and it undergoes combination with it readily to form a labile Fe (II)-O<sub>2</sub> complex (Oxy-heme) which changes into the Fe(III) protoporphyrin called hematin or hemin. Hence free heme is not favored for oxygen transport. Hence an important function of the globin in hemoglobin, apart from the action as a carrier of heme, has been found to stabilize the heme-O<sub>2</sub> complex so that oxidation of iron of heme does not take place and it can act as an effective carrier of oxygen. As a protein chain is folded around the heme group, the position of the protein chain reduces the access of water to Fe<sup>2+</sup> and at the same time provides a hydrophobic surrounding. Thus the steric and chemical control permits the access of oxygen molecule but does

not permit the simultaneous presence of oxygen and one or more molecules of water which appears to be necessary for oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . The iron in Mb and Hb in +2 oxidation state. The oxidized forms containing iron(III) called met Mb and met Hb, will not bind oxygen.



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Typical curves of oxygenation vs. oxygen pressure ( $P_{O_2}$ ) under physiological condition for Hb and Mb. Curves for oxygenation of Mb is hyperbolic while that of Hb is sigmoidal in nature. It is the cooperativity of the four-heme groups that produces two types of the curves shown in figure. Figure shows that Hb is about as good an  $O_2$  binder as Mb at high  $O_2$  pressure. It is much poorer at the lower pressures prevailing in muscle and hence passes its oxygen on to Mb as required. Moreover, the need for  $O_2$  will be greatest in tissues where  $O_2$  is consumed followed by production of  $CO_2$ . The  $CO_2$  lowers the pH, thus causing the Hb to release even more oxygen to Mb. The pH-sensitivity (called the Bohr effect) as well as the progressive increase of  $O_2$  binding constants in Hb are due to the interaction between the subunits; Mb behaves more simply because it consists of only one unit. It is clear that each of the two is essential in the complete oxygen transport process. The oxygenation curve of Mb reflects a simple equilibrium



$$K_1 = \frac{[\text{MbO}_2]}{[\text{Mb}] [\text{O}_2]} \quad \text{-----} \quad 1$$

$$[\text{Mb}]_{\text{total}} = [\text{Mb}] + [\text{MbO}_2]$$

$$[\text{Mb}]_{\text{total}} = [\text{Mb}] + K_1[\text{Mb}][\text{O}_2] \text{ from equation 1 substituting the value of } [\text{MbO}_2]$$

$$[\text{Mb}]_{\text{total}} = [\text{Mb}] [1 + K_1[\text{O}_2]]$$

Substituting the value of  $[\text{Mb}]_{\text{total}}$  in equation - 2

NOTES

$$[\theta] = \frac{[\text{Mb}] K_1[\text{O}_2]}{[\text{Mb}] [1 + K_1[\text{O}_2]]}$$

Value of [MbO<sub>2</sub>] substituted from equation 1

$$[\theta] = \frac{K_1[\text{O}_2]}{[1 + K_1[\text{O}_2]]} \quad \text{-----} \quad 3$$

$$1 - \theta = \frac{1}{[1 + K_1[\text{O}_2]]} \quad \text{-----} \quad 4$$

Dividing equation 3 by equation 4

$$\frac{[\theta]}{1 - \theta} = K_1[\text{O}_2]$$

This equation is for Mb

Oxygenation curve of Hb may be approximated as

$$\frac{[\theta]}{1 - \theta} = K_1[\text{O}_2]^n \quad \text{with } n \sim 3$$

This equation is known as Hill equation and the exponent, n is called the Hill constant. In contrast to the hyperbolic curve obtained from the data for the monomeric heme (myoglobin), the data obtained by Hb shows "Sigmoidal" behavior, indicative of interaction between the subunits. The data obtained from Hb between 10 and 90% oxygenation can be fitted to the Hill equation to give values of n ~ 3 for normal Hb. The form of oxygenation curve and that the fact it fits n > 1 indicate that there is cooperative interaction between the subunits. The addition of oxygen to a subunit affects the oxygen affinities of other subunits, this is an example of Allosteric effect (Entatic effect) literally means "a stretched state or state of being under tension". n < 4 indicates that the cooperative interaction between heme units is rather moderate.

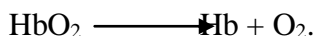
### 12.3.1 Mode of Oxygen transport

Hb binds with O<sub>2</sub> to form oxyhaemoglobin (an unstable complex) at high partial pressure (100 mm of Hg), in the lungs.



Since there are 4 haem units, fully saturated oxyhaemoglobin (96%) carries 4 O<sub>2</sub> molecules.

The oxyhaemoglobin dissociates into deoxyhaemoglobin at a low partial pressure (45mm of Hg), which prevails in tissues.



The oxygen thus released is bound by Myoglobin, as it has higher affinity for O<sub>2</sub> at low partial pressures.

### 12.3.2 Mechanism of oxygenation in Hb and Mb

Hb may be viewed as tetrameric of Mb. It has four heme groups bound to four protein chains. The differences between Hb and Mb in their behavior towards oxygen is related to the structure and movements of the four chains. It is found that, upon oxygenation of Hb, two of the heme groups move about 1 Å towards each other while two other separate by about 7 Å. These movements seem responsible for the cooperative effect observed. According to Perutz, changes in the coordination of the iron play a crucial role. DeoxyHb contains iron(II) in a high spin state, with two electrons occupying eg orbitals, the bonding radius of the iron is so large (0.78 Å) that it can not fit into the plane of four N atoms of the heme porphyrin. It therefore lies around 0.75 Å out of the plane. The iron is thus pentacoordinate with square pyramidal coordination provided by four porphyrin nitrogen atoms in the basal position and an imidazole nitrogen atom from histidine in the apical position. When an oxygen molecule is bound in the position opposite to this histidine, the iron atom goes in to a low spin state, eg orbitals are then empty and the radius of the iron decreases (by 0.17 Å) so much that it now fits in to the plane of the porphyrin system. Thus the iron atom moves down when deoxy Hb becomes oxygenated. Since it remains attached to the side chain of histidine this shift is transmitted to various parts of the subunits, causing particularly important movements of the entire helical section.

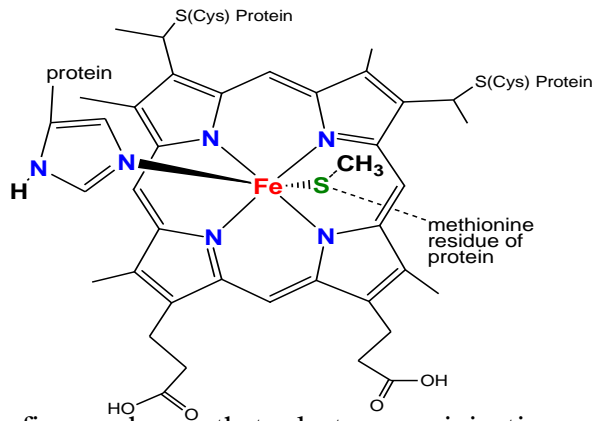
## 12.4 Cytochromes

**Cytochromes** are membrane-bound (i.e., inner mitochondrial membrane) heme proteins containing heme groups and are primarily responsible for the generation of ATP via electron transport and catalysis by reduction or oxidation of their heme iron. In the process of oxidative phosphorylation, a globular cytochrome c protein is involved in the electron transfer from the membrane-bound complex III to complex IV. It links the oxidation of substrates to the reduction of O<sub>2</sub>. Cytochromes are found in all aerobic forms of life. They are small molecules with a molecular weight ≈ 12,000. They operate by shuttling of the iron atom between Fe<sup>II</sup> and Fe<sup>III</sup>. They are found bound on the inner mitochondrial membrane either as monomeric proteins (e.g., cytochrome c) or as subunits of bigger enzymatic complexes that catalyze redox reactions.

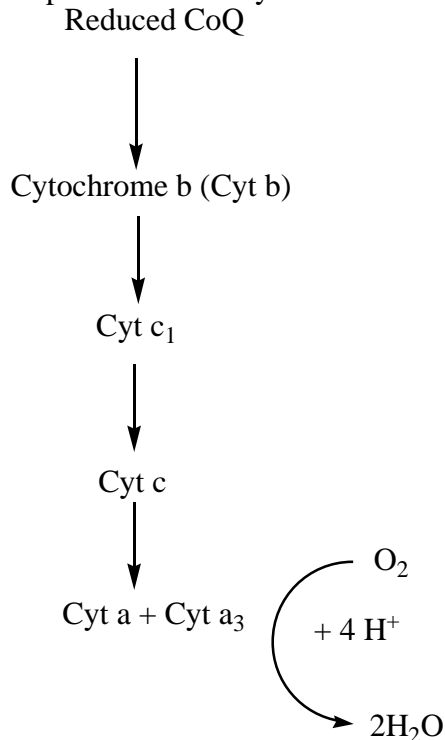
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These heme proteins are classified on the basis of the position of their lowest energy absorption band in the reduced state, as cytochromes *a* (605 nm), *b* (~565 nm), and *c* (550 nm). A view of the structure of a typical cytochrome *c*, is shown below. The iron – porphyrin unit is seen edge-locked in a pocket created by the folding of the peptide chain. The iron atom is ligated on both sides of the porphyrin plane by the CH<sub>2</sub>CH<sub>2</sub>SCH<sub>3</sub> side chain of a methionine and a nitrogen atom of a histidine. The rest of the pocket is lined by hydrophobic side chains and only a small part of the rim of the porphyrin ring is at or near the exposed surface of the molecule.



The following figure shows that electrons originating with reduced coenzyme Q (CoQ) are accepted by a cytochrome *b* and proceed through a series of intermediate cytochromes, until at the end, four electrons are delivered at an appropriate potential to carry out the reduction of O<sub>2</sub> to water.





The redox potentials of the intervening cytochromes gradually increase to cover the gap stepwise between that for the oxidation of reduced CoQ and that for reduction of dioxygen.

To do this, the cytochromes have distinctive structures and properties.

In cyt b, cyt  $c_1$  and cyt c the heme group is the same as that in haemoglobin and myoglobin. In Cyt b, the haem is not covalently attached to the protein, but is held only by ligation to the iron atom. In cyt  $c_1$  and cyt c, the haem is covalently connected by thioether linkages and the iron atom is coordinated by protein side chains.

Cytochromes a and cyt  $a_3$  exist together as a complex, sometimes called cytochrome oxidase, and they contain a heme with several different substituents on the periphery of the porphyrin ring. Cyt  $a_3$  also contains copper, which goes from CuII to CuI and thus transfers an electron from the haem of Cyt  $a_3$  to the dioxygen molecule. In general, the processes are outer-sphere reactions that can be accounted for by the Marcus theory.

Cytochromes C seems to be one of the most ancient of biomolecules, having evolved in essentially its present form, more than 1.5 billion years ago, even though it is present in all animals and plants, including those that have appeared more recently. It has been found that the cytochrome C of any eukaryotic species will reach with the cytochrome oxidase of any other species, thus confirming that this electron transfer chain has resisted evolutionary change for a very long time.

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## 12.5 Enzymes

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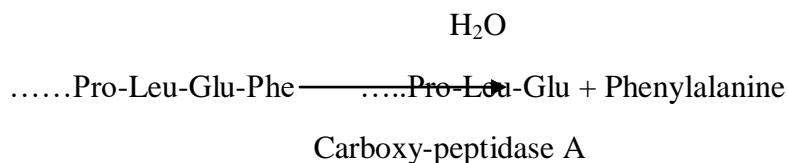
- Enzymes are biologically active proteins that accelerate the breakdown of food that is eaten.
- Enzymes are biological catalysts. They accelerate reactions, but are not consumed or changed in reactions. They not only control the rate of reactions, but can lower the activation energy for the formation of one product rather than another.
- Enzymes are named by adding the suffix -ase to the name of the substrate on which it acts. For example, Lipase enzyme is substrate of Lipid, and Amylase enzyme is substrate of Amylum.
- Enzymes are highly specific in their action, and are capable of bringing out only one or a small group of reactions. Thus, specificity is an important criterion for an enzyme.

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### 12.5.1 Enzyme action

To illustrate the structure of an enzyme and its relation to function, consider carboxy peptidase A. This is a pancreatic enzyme, which cleaves the carboxyl terminal amino acid from a peptide chain by hydrolyzing the amide linkage.



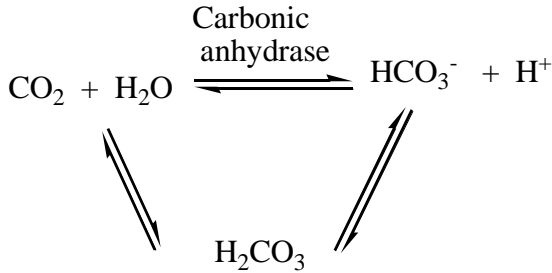
The enzyme consists of a protein chain of 307 amino acid residues plus one  $\text{Zn}^{2+}$  ion to give a molecular weight of about 34,600. The molecule is roughly egg-shaped. There is a cleft on one side, that contains  $\text{Zn}^{2+}$  ion, which is the active site. The metal is coordinated tetrahedrally to two N atoms and an oxygen atom from three amino acids, in the protein chain. The above example illustrates the basic key and lock theory first proposed by Emil Fischer in which the enzyme and substrate fit each other sterically. There is evidence that the enzyme also encourages the reaction by placing a strain on the bond to be broken. The substitution of a different metal into an enzyme provides a very useful method for studying the immediate environment of the metal site.

### 12.5.2 Inhibition

Ligands that can coordinate to an active center in an enzyme and prevent coordination by the substrate will tend to inhibit the action of that enzyme. Carbonic anhydrase inhibitors are a class of pharmaceuticals that suppress the activity of carbonic anhydrase. Their clinical use has been established as anti-glaucoma agents, diuretics, antiepileptics, in the management of mountain sickness, gastric and duodenal ulcers, idiopathic intracranial hypertension, neurological disorders, or osteoporosis.

1. An example is that of carbonic anhydrase which catalyses the interconversion of  $\text{CO}_2$  and carbonates, i.e., that drives the hydration of carbon dioxide and dehydration of bicarbonate. It is found in Parietal Cells in Stomach, Pancreatic duct cells, Red blood cells and found in ciliary process, cornea, iris, and retina. Like carboxypeptidase, carbonic anhydrase has one zinc atom per molecule (with a molecular weight of 30,000) and coordinated to 3 histidine residues (His 94, His 96, His 119) and a water molecule of hydroxide ion. The active site contains other amino acids that may function through hydrogen bonding, proton transfer etc. The relative bonding power of Zn ion towards halide ions is reversed in the enzyme ( $\text{I} > \text{Br} > \text{Cl} > \text{F}$ ). This reversal maybe due to the

'softening' effect on Zn by the apoenzyme. Also  $\text{NO}_3^-$ ,  $\text{CNO}^-$  and  $\text{N}_3^-$  are bound with exceptional strength. This can be explained by the structure of the enzyme to form a pocket about 450 pm long next to the  $\text{Zn}^{2+}$  ion, an additional positive center to stabilize ions of appropriate size.



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**Mechanism of Action**

The zinc atom is thought to be more acidic in carbonic anhydrase than in carboxypeptidase A. The substitution of a third, neutral and less basic histidine in place of the glutamate anion contributes to the greater acidity.

This polarises an attached water molecule, perhaps to the point of loss of a hydrogen ion to form a coordinated hydroxo group. The mechanism of the reversible hydration of  $\text{CO}_2$  to carbonic acid, follows the pathway given below.

Inhibitor binds to active site, blocking interactions of water bound to zinc and inhibiting enzymatic activity. The water bound to the zinc ion is broken down to proton and hydroxyl ion. Zinc (since positive) stabilizes negatively charge hydroxyl so it can attack carbon dioxide.

CAH2 inhibitor helps block the enzyme shifts the fluid balance, reducing the pressure. Inhibitors are mostly sulfanomides. Acetazolamide, dorzolamide (All compounds are sulfonamides). Inhibition of membrane-bound carbonic anhydrase (CA) in the cells of proximal tubule which leads to blockade of the reaction  $\text{H}_2\text{CO}_3 = \text{H}_2\text{O} + \text{CO}_2$  that normally occurs in the proximal tubule lumen. Inhibition of cytoplasmic CA in the cells of proximal tubule which leads to blockade of the reaction:  $\text{H}_2\text{O} + \text{CO}_2 = \text{H}_2\text{CO}_3$  that normally occurs in the cytoplasm The final effect is a nearly complete abolition of  $\text{NaHCO}_3$  reabsorption in the proximal tubule (but  $\text{NaHCO}_3$  reabsorption by mechanisms independent from carbonic anhydrase still occur in other parts of the nephron).

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2. Inhibition may also be effected by metal ions. Coordination of the apoenzyme to a heavier metal ion may destroy the enzymatic activity. Metal ions such as  $\text{Hg}_2\text{Cl}_2$  are poisonous.  $\text{Hg}^{2+}$  has a special affinity for S and tends to form extremely stable complexes such as cysteine, and methionine.

The affinity of S and Hg are attributed for the poisonous effects of Hg in biological system. Often these effects are reversed by addition of sulphur – containing compounds such as cysteine or glutathionine. Another sulphur donor, 2, 3 – dimercaptopropanol has proved to be extremely useful as an antidote for Arsenic, Cadmium and Mercury poisoning.

3. Uric acid is the chief end product of purine metabolism in primates, birds, lizards and snakes. Due to metabolic errors in humans, there is an increase in uric acid levels and its deposition as crystals in joints. This condition (gout) may be treated by the drug allopurinol, which is oxidised by Xanthine oxidase to alloxanthine. However, alloxanthine binds so tightly to the Mo, that the enzyme is inactivated, the catalytic cycle is broken and uric acid formation is inhibited. The extra stability of the alloxanthine complex may be a result of N-H.....H hydrogen bonding by the N in the 8<sup>th</sup> position.

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## 12.6 Vitamin B<sub>12</sub> and B<sub>12</sub>coenzymes

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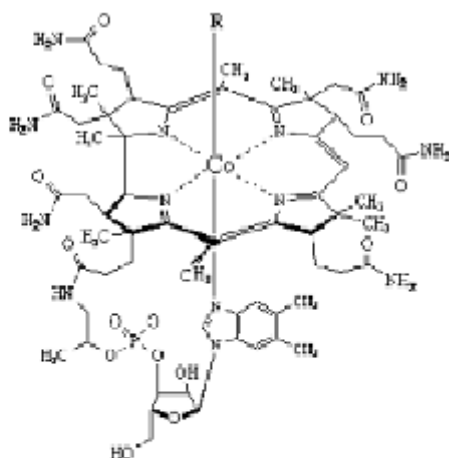
### Chemical structure of Vitamin B<sub>12</sub>

Vitamin B<sub>12</sub> is the only known essential biomolecule with a stable metal-carbon bond, that is, it is an organometallic compound. Vitamin B<sub>12</sub> is the only, metal-containing vitamin –it is also a water-soluble vitamin that is stored in the liver and must come from the diet. Vitamin B<sub>12</sub> (cobalamin) only synthesized by bacteria and micro-organisms.

- ❖ The core of the molecule is a corrin ring with various attached side groups.
- ❖ The ring consists of 4 pyrrole subunits, joined on opposite sides by a C-CH<sub>3</sub> methylene link, on one side by a C-H methylene link, and with the two of the pyrroles joined directly. It is thus like a porphyrin, but with one of the bridging methylene groups removed.
- ❖ The nitrogen of each pyrrole is coordinated to the central cobalt atom.
- ❖ The cobalt can link to: 1. a methyl group - as in methylcobalamin.  
2. 5'-deoxyadenosine at the the 5' positon - as in

adenosylcobalamin (coenzyme B<sub>12</sub>). 3. a cyanide group - as in Vitamin B<sub>12</sub>.

- ❖ The center-piece in the structure is of course the cobalt(III), the octahedral coordination to five nitrogens and a carbon is common to all three cobalamins,
- ❖ The sixth ligand below the ring is a nitrogen of a 5,6-dimethylbenzimidazole. The other nitrogen of the 5,6-dimethylbenzimidazole is linked to a five-carbon sugar, which in turn connects to a phosphate group, and back onto the corrin ring via one of the seven amide groups attached to the periphery of the corrin ring.



**Where**

**R = OH (Hydroxocobalamin)**

**R = CN (Vitamin B<sub>12</sub>)**

**R = Adenosyl (Adenosylcobalamin, AdoCbl, Coenzyme B<sub>12</sub>)**

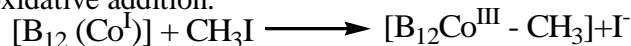
**R = Me (Methylcobalamin, MeCbl)**

- ❖ The base ligand thus forms a 'strap' back onto the corrin ring. An important aspect of the corrin ring, when compared to the porphyrin, is the relative flexibility of the corrin system, the corrin ring is also less flat when viewed from the side than is a porphyrin ring.
- ❖ This adds up to some considerable differences between the chemistry of a cobalt porphyrin and a cobalt corrin.
- ❖ In addition, the corrin only has a conjugated chain around part of the ring system, whereas a porphyrin is delocalised around the whole four pyrole rings.

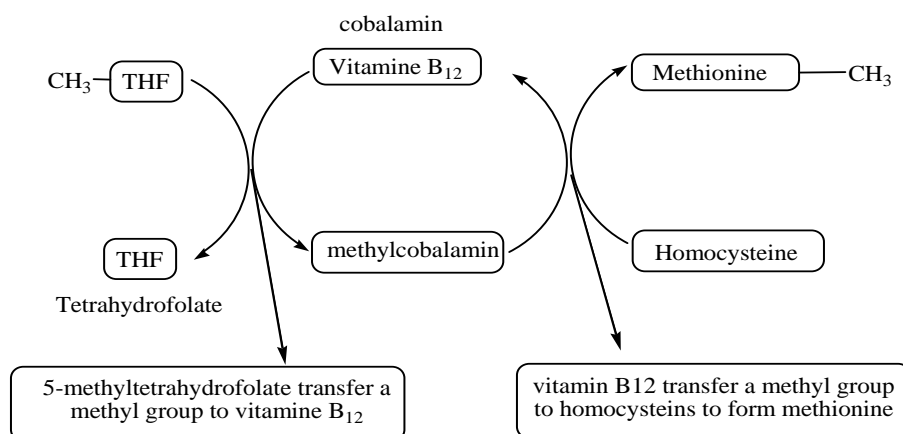
## 12.6.1 Reactions of Vitamin B<sub>12</sub>

Vitamin B<sub>12</sub> may be reduced by one electron (Vitamin B<sub>12r</sub>) or two electron (vitamin B<sub>12s</sub>) to form the Co(II) and Co(I) complexes, respectively.

The latter is strongly nucleophilic and readily undergoes alkylation via oxidative addition.



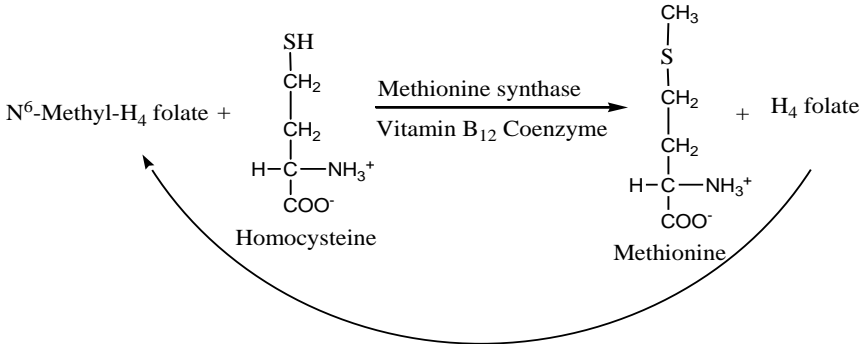
In biological systems the two – electron reduction may be accomplished by NADH and flavin adenine dinucleotide (FAD). The methyl donor is N<sup>5</sup>-methyltetrahydrofolate (CH<sub>3</sub>-THF). The Co (III) corrinoid (methyl cobalamin) can then takepart in biomethylation reactions.



## 12.6.2 Function

- ❖ Vitamin B<sub>12</sub> is important for the normal functioning of the brain and nervous system and for the formation of blood. It controls the production of blood platelets and red and white blood cells.
- ❖ It is involved in the metabolism of every cell of the body, especially affecting DNA synthesis and regulation but also fatty acid synthesis and energy production. Both vitamin B<sub>12</sub> and the vitamin folate are essential for the production of DNA and RNA.
- ❖ Cyanocobalamin promotes normal growth and development; treats pernicious anaemia. This is a disease caused by inability to absorb vitamin B<sub>12</sub> through the gut wall. It is due to the increase in excretion of methylmalonic acid, as the body fails to convert it to succinic acid.
- ❖ Vitamin B12 helps in the maintenance of the central nervous system
- ❖ B12 plays a vital role in the metabolism of fatty acids essential for the maintenance of myelin.

Adenosylcobalamin (B<sub>12</sub>) is a coenzyme in the reaction involved in methionine metabolism using methionine synthase reductase (MSR) – that is further reactions after methionine has been formed. In the MS reaction below – CH<sub>3</sub>-cobalamin is the cofactor.

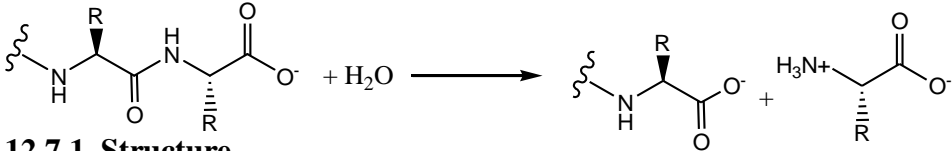


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H<sub>4</sub>folate is converted to N<sup>5</sup>-methyl-H<sub>4</sub>folate in a number of different reactions as it accepts methyl groups. The methyl group can only be removed and the H<sub>4</sub>folate regenerated by the above reaction.

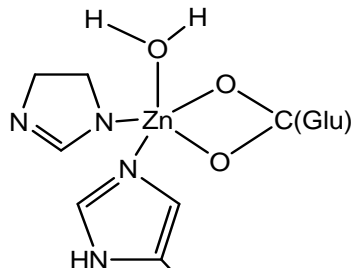
**12.7 Carboxypeptidase – A**

Carboxypeptidases are mammalian digestive Zinc enzymes, with a molecular weight of 34,600. It catalyses the hydrolysis of the terminal peptide bond at the carboxyl end of proteins and other peptide chains. It is also effective toward correspondingly placed ester linkages. It is a compact globular protein and is a metalloenzyme, having a tightly bound zinc ion that is essential for its activity. There is a marked preference for peptide bonds in which the side chain of the terminal residue is aromatic or a branched aliphatic chain. Carboxypeptidase A have been found in the pancreas of many mammals including man, but studies were carried out in the bovine enzyme. The three-dimensional structure of carboxypeptidase A was elucidated by William Lipscomb at Harvard in 1967. It has a single polypeptide chain of 307 amino acid residues



**12.7.1 Structure**

The active site of the enzyme contain Zn(II) ion as the central atom. The Zn(II) center is in distorted square pyramidal geometry. The central atom is surrounded by two nitrogen atoms from two histidine imidazole residues, two oxygen atoms from a glutamic acid moiety, and one water molecule situated at the axial position. The enzyme has a preference towards the substrates possessing large hydrophobic C-terminal side chain, e.g., phenylalanine. Here, hydrophobic pocket creating phenyl ring situated close to the active site. The Presence of arginine, and tyrosine residue close to the active site, facilitate substrate binding.



### 12.7.2 Mechanism of catalysis

The carbonyl oxygen atom of the peptide or ester link that is to undergo hydrolysis becomes coordinated to the Zn atom. This polarizes it in the  $O-C^+$  sense, thus making the carbon atom more prone to nucleophilic attack.

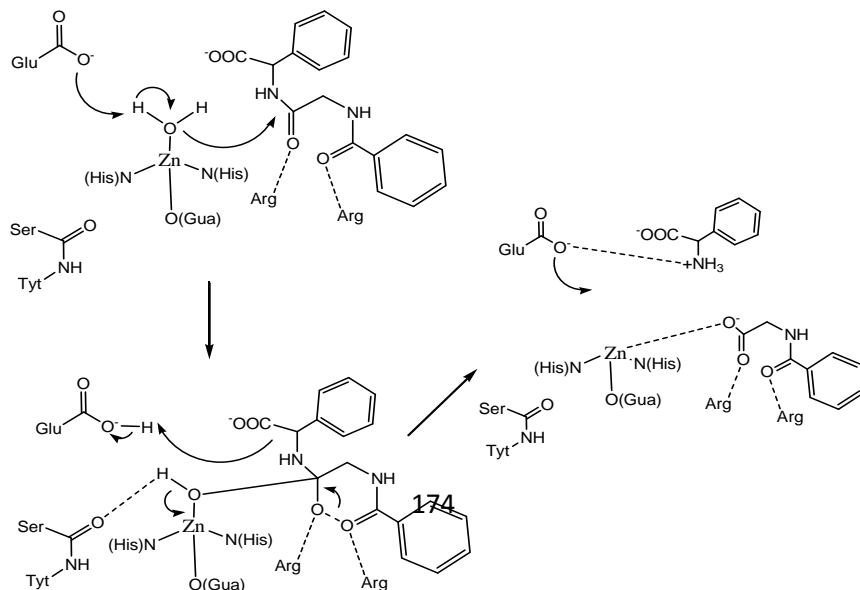
The arginine – 145 residue forms a strong hydrogen – bonded linkage to the terminal carboxyl group.

This accounts for the specificity of the enzyme for catalyzing hydrolysis of the terminal residue at the carboxyl end of the peptide. It is also results in a good fit of a large nonpolar side chain on the terminal residue into an available hydrophobic pocket.

At this point, so – called Michaelis – complex has been formed. Controversy on bond scission and generation of products, exists. This concept accounts for the fact that Michaelis complex (a metastable complex / intermediate) is formed, and only then is the product complex formed, from which the products promptly dissociate, leaving the enzyme ready for the next cycle.

This second complex must be one of the species in which there is an intermediate anhydride involving the carboxyl group of Glu – 270.

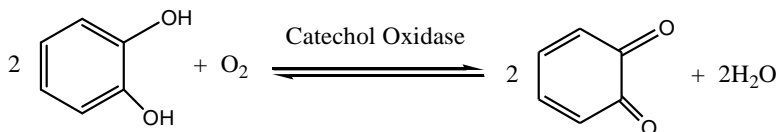
Another key mechanism is the generation of Zn-OH group, which is responsible directly for the attack on the carbonyl carbon atom. The Zn ion thus serves twice as a lewis acid: once in binding and polarizing the carboxyl group and again in enhancing the acidity of the bound water molecule so that it can become the necessary OH nucleophile. There is indirect evidence for the occurrence of this Zn-OH attack on the mixed anhydride intermediate from study of model systems.





## 12.8 Copper containing oxidases

Catechol oxidase is a copper oxidase that contains a type III di-copper cofactor and catalyzes the oxidation of ortho-diphenols into ortho-quinones coupled with the reduction of molecular oxygen to water.



It is present in a variety of species of plants and fungi including sweet potato and tea leaf. Metalloenzymes with type 3 copper centers are characterized by their ability to reversibly bind dioxygen at ambient conditions.

In plants, catechol oxidase plays a key role in enzymatic browning by catalyzing the oxidation of catechol to o-quinone in the presence of oxygen, which can rapidly polymerize to form the melanin that grants damaged fruits their dark brown coloration.

### 12.8.1 Structure

- ❖ It is a globular, single domain monomeric enzyme.
- ❖ The active site of catechol oxidase is di-copper center,
- ❖ A phenylalanine side-chain (Phe261) is above one of the copper centers and prevents the substrate from coordinating with both copper ions in the active site.
- ❖ The nitrogens on the imidazole side chains of His88, His109, and His118 coordinate with the first catalytic copper while the nitrogens on the imidazole side chains on His240, His244 and His274 coordinate with the second catalytic copper ion.
- ❖ In the oxidized Cu(II)-Cu(II) state, each copper ion possesses a four coordinate trigonal pyramidal geometry, with the three histidine residues and a bridging hydroxide molecule forming the four ligands on each copper ion.
- ❖ In the oxidized Cu(II)-Cu(II) state, the Cu-Cu distance is 3.3 Å while in the reduced Cu(I)-Cu(I) state, the distance increases to 4.4 Å.

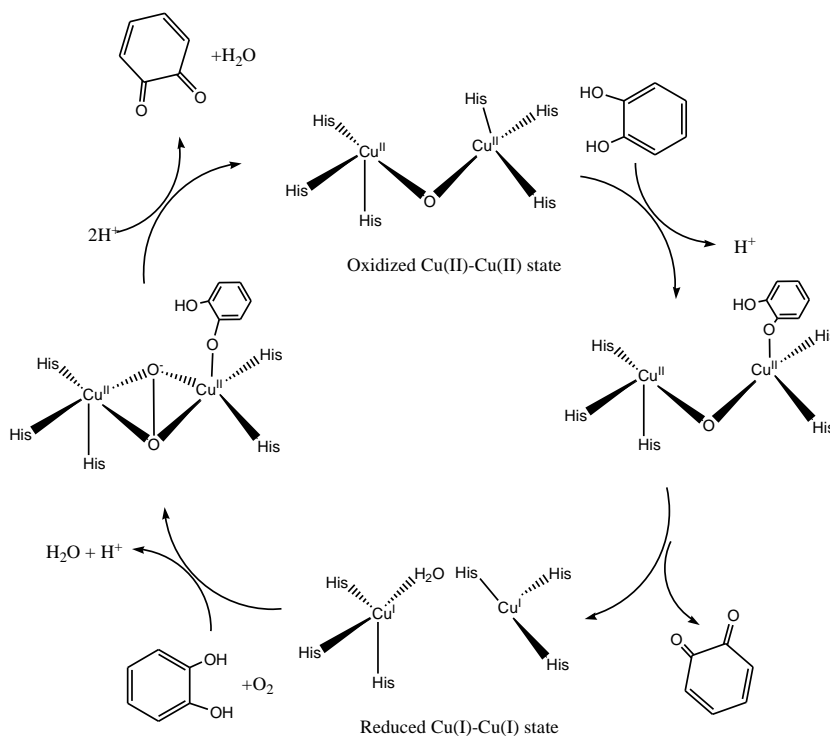
### 12.8.2 Catalytic Mechanism

- The catalytic cycle begins with the catechol oxidase in its native oxidized Cu(II)-Cu(II) state with a coordinated hydroxide ion bridging the two copper centers.
- As catechol enters the active site, a proton is abstracted from one of the alcohols.
- The catechol coordinates with a Cu(II) center in a monodentate fashion, displacing one of the coordinating histidine residues.
- The coordinated hydroxide ion abstracts another proton from catechol to form water, and the catechol is oxidized to o-quinone.

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The two resulting electrons reduce both copper centers to their Cu(I)-Cu(I) state.

- Dioxygen then binds one copper center, displacing the coordinated water molecule, and another molecule of catechol binds to the other copper center, displacing another histidine residue.
- This forms a complex in which one copper center has a tetragonal planar coordination with His240, His244 and the dioxygen molecule. The other copper center retains its initial tetragonal pyramidal geometry with dioxygen, His88 and His118 in the equatorial positions, and His109 in an axial position.
- In this state, the enzyme active site is in a ternary catechol oxidase-O<sub>2</sub><sup>2-</sup>-catechol complex. Two electrons are transferred from the substrate to the dioxygen, followed by cleavage of the O-O bond.
- Water is released, and the second o-quinone product is formed together with the restoration of the initial Cu(II)-Cu(II) state to complete the catalytic cycle.



### Check Your Progress

1. What is carbonic anhydrase?
2. What are vitamin B<sub>12</sub> and vitamin B<sub>12</sub> coenzyme?
3. What is the function of catechol oxidase in plant tissues?

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## 12.9 Answers to check your progress questions

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- An enzyme present in red blood cells, carbonic anhydrase, aids in the conversion of carbon dioxide to carbonic acid and bicarbonate ions. When red blood cells reach the **lungs**, the same enzyme helps to convert the bicarbonate ions back to carbon dioxide, which we breathe out.
- vitamin B<sub>12</sub> (cobalamin) is the coenzyme that affects the cellular metabolism and works together with the vitamin B<sub>9</sub> folate to synthesize nucleic acids, helps to maintain healthy blood cells, maintains the nervous system, and helps prevent types of anemia.
- In plants, catechol oxidase plays a key role in enzymatic browning by catalyzing the oxidation of catechol to o-quinone in the presence of oxygen, which can rapidly polymerize to form the melanin that grants damaged fruits their dark brown coloration.

## NOTES

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### 12.10 Summary

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- Metalloenzymes - contain definite quantity of functional metal ion that is retained throughout purification.
- Chlorophyll is the molecule that absorbs sunlight and uses its energy to synthesise carbohydrates from CO<sub>2</sub> and water.
- Haemoglobin is an effective buffer for blood. The buffering capacity is due to the presence of ionisable groups in the imidazole side chain of histidine residues. Cellular oxygen is stored by Myoglobin, until it is required for metabolic action.
- **Cytochromes** are membrane-bound (i.e., inner mitochondrial membrane) heme proteins containing heme groups and are primarily responsible for the generation of ATP via electron transport and catalysis by reduction or oxidation of their heme iron. Enzymes are biologically active proteins that accelerate the breakdown of food that is eaten. Enzymes are biological catalysts.
- Coenzyme B<sub>12</sub> is based on the Co(III)-corrin ring with a 5'-deoxyadenosyl group bound to the Co(III).
- Coenzymes bind to an apo-enzyme to form a holoenzyme that is biologically active. The Co changes between Co(I), Co(II), and Co(III) in its reactions.
- Carboxypeptidases are mammalian digestive Zinc enzymes,
- Catechol oxidase is a copper oxidase that contains a type III di-copper cofactor and catalyzes the oxidation of ortho-diphenols into ortho-quinones coupled with the reduction of molecular oxygen to water.

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### 12.11 Keywords

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- **Chlorophyll:** Chlorophyll is the molecule that absorbs sunlight and uses its energy to synthesise carbohydrates from CO<sub>2</sub> and water.

- **The Bohr effect:** The pH-sensitivity as well as the progressive increase of O<sub>2</sub> binding constants in Hb are due to the interaction between the subunits
- **Vitamin B<sub>12</sub>** is the only known essential biomolecule with a stable metal-carbon bond, that is, it is an organometallic compound
- **Catechol oxidase** is a copper oxidase that catalyzes the oxidation of ortho-diphenols into ortho-quinones coupled with the reduction of molecular oxygen to water.

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### 12.12 Self-assessment questions and exercises

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1. What is the function of chlorophyll
2. Write short notes on structure of Haemoglobin
3. Differentiate metalloenzyme and metalloprotein
4. Describe the biological activity of zinc containing enzyme

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### 12.13 Further Readings

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1. Gerdemann C, Eicken C, Krebs B (March 2002). "The crystal structure of catechol oxidase: new insight into the function of type-3 copper proteins". *Accounts of Chemical Research*. 35 (3): 183–91.
2. G. S.Sodhi. *Inorganic Chemistry*,.1stEdition, VB (P) Ltd, 2006.
3. John C. Kotz, Paul M. Treichel, John Townsend , *Chemistry & Chemical Reactivity*,, 8<sup>th</sup> ed. Cengage Learning, USA, 2012.

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# UNIT-13 NON-HEME IRON PROTEINS

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## Structure

- 13.0 Introduction
- 13.1 Objective
- 13.2 Structural motifs
  - 13.2.1 Rubredoxins [**1Fe-0S**] proteins
  - 13.2.2 Two-Iron Ferredoxins [**2Fe-2S**] proteins
  - 13.2.3 3Fe-4S clusters
  - 13.2.4 4Fe-4S clusters
- 13.3 Nitrogen Fixation
  - 13.3.1 In Vivo Nitrogen fixation
- 13.4. Check your progress question
- 13.5 Answers to check your progress questions
- 13.6 Keywords
- 13.7 Summary
- 13.8 Self-assessment questions and exercises
- 13.9 Further Reading

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## 13.0 Introduction

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**Non-heme iron proteins:** Rubredoxins, ferredoxins, hemerythrin, aconitase, and high-potential iron proteins are Non-heme iron proteins, which contain strongly bound functional iron atoms attached to sulfur, but they do not contain porphyrins. Heme iron is typically absorbed at a higher rate than non-heme iron, which means that the body more easily absorbs iron from animal products than iron derived from plant foods.

Iron-sulfur proteins are proteins characterized by the presence of iron-sulfur clusters containing sulfide-linked di-, tri-, and tetrairon centers in variable oxidation states. The iron-sulfur proteins occurs extensively in all living organisms and take part in a wide range of electron-transfer processes, either as redox centers (*e. g.* ferredoxins, rubredoxins) or as catalysts (*e.g.* hydrogenase, nitrogenase, etc). Iron-sulfur clusters are found in a variety of metalloproteins, such as the ferredoxins, as well as NADH dehydrogenase, hydrogenases, coenzyme Q – cytochrome c reductase, succinate – coenzyme Q reductase and nitrogenase. Additionally, some Fe-S proteins regulate gene expression. Fe-S proteins are vulnerable to attack by biogenic nitric oxide, forming dinitrosyl iron complexes. In most Fe-S proteins, the terminal ligands on Fe are thiolate, but exceptions exist.

Iron sulfur proteins are found to be of low molecular weight (6000-20,000) and contain iron, cysteinyl sulfurs (coming from the amino acid cysteine in the protein chain) and 'inorganic sulfur', the so called non-cysteinyl sulfur atoms. The sulfur ligands are arranged tetrahedrally about the iron atoms. The presence of inorganic sulfur is indicated through the release of H<sub>2</sub>S gas when these proteins are treated with a mineral acid. The cluster of iron and inorganic sulfur atoms in the form  $Fe_nS_n$ , or  $(nFe-n'S)$  where  $n$  and  $n'$  are 1,0; 2,2; 3,4; 4,4

## NOTES

respectively constitutes the core group in these proteins and are their redox centres. These redox centres are wrapped in the protein chain with the cysteinyl sulfurs of the protein coordinating to theirons of the core group. These proteins may be categorised into five accepted classes of Fe-S centres, according to the numbers of iron and inorganic sulfur atoms in the cluster.

### 13.1 Objective

After going through the unit you will be able to

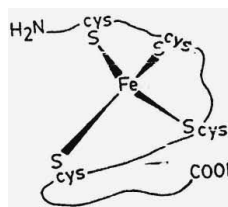
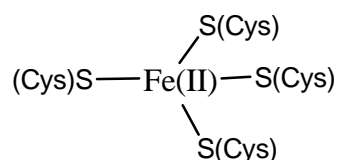
- Understand the structural motifs of iron-sulfur proteins
- Relate the mechanism of iron-sulfur proteins
- Value the role and importance of nitrogenase enzyme

### 13.2 Structural motifs

In almost all Fe-S proteins, the Fe centers are tetrahedral and the terminal ligands are thiolato sulfur centers from cysteinyl residues. The sulfide groups are either two- or three-coordinated.

#### 13.2.1 Rubredoxins [1Fe-0S] proteins

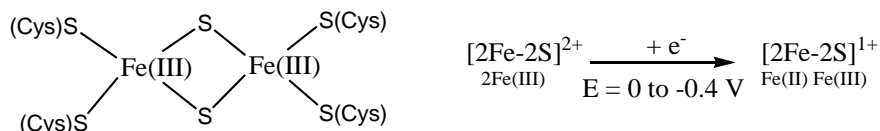
Iron-sulfur proteins with no bridging sulfur (0S) or sulfide atom is known as rubredoxins. It is mainly found in bacteria and acts as one electron donor-acceptor. The arrangement around the iron center is tetrahedral and the Fe(II) center is surrounded by four sulfur atoms from four cystine (Cys) residues present in the protein chain of 55 amino acids. The redox centre is made up of only high spin Fe(III) and there are no inorganic sulfur atoms in the core group. The Fe-S distances range from 2.24 to 2.33 Å and the S-Fe-S angles from 104 to 114°. When the Fe(III) is reduced to Fe(II) there is a slight (0.05 Å) increase in the Fe-S distances but the essentially tetrahedron coordination is maintained. Mossbauer spectroscopy has shown that the iron is in the high spin condition in both oxidation complexes, to understand the properties of rubredoxins.



#### 13.2.2 Two-Iron Ferredoxins [2Fe-2S] proteins

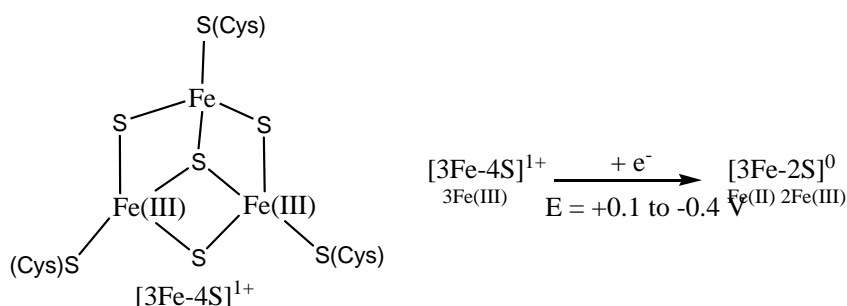
Ferredoxins are most important family of iron-sulfur proteins. Three major categories of ferredoxins are, [2Fe-2S], [3Fe-4S], and [4Fe-4S]. The [4Fe-4S] is most important. Ferredoxins and high potential iron proteins are also relatively small proteins of molecular weight 6000 – 12,000. Isolated from mammals, plants, and bacteria. Both the iron centers are in tetrahedral coordination environment and linked by two inorganic sulfide bridges. Both Fe(III) centers are antiferromagnetically coupled to each other. Hence, a diamagnetic ground state results. After accepting a electron one center becomes Fe(II) and the other is Fe(III).

After antiferromagnetic coupling between the  $S = \frac{1}{2}$  ground state appeared. The oxidized proteins contain two  $\text{Fe}^{3+}$  ions, whereas the reduced proteins contain one  $\text{Fe}^{3+}$  and one  $\text{Fe}^{2+}$  ion. These species exist in two oxidation states,  $(\text{Fe}^{\text{III}})_2$  and  $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}$ . Spectroscopic evidence shows that in  $[2\text{Fe}-2\text{S}]^+$  cluster, the added electron is localized on one iron atom, so that one  $\text{Fe}^{\text{II}}$  and one  $\text{Fe}^{\text{III}}$  are present. In the  $[2\text{Fe}-2\text{S}]^{2+}$  cluster, the Fe to Fe distance is only  $2.72\text{\AA}$  and the two high spin ( $d^5$ ) Fe atoms have their magnetic moments so strongly coupled antiferromagnetically that the cluster is diamagnetic.



### 13.2.3 3Fe-4S clusters

Proteins are also known to contain  $[\text{Fe}_3\text{S}_4]$  centres, which feature one iron less than the more common  $[\text{Fe}_4\text{S}_4]$  cores. The structure is a distorted cubic core. Three sulfide ions bridge two iron ions each, while the fourth sulfide bridges three iron ions. All the iron centers are tetrahedral. Their formal oxidation states may vary from  $[\text{Fe}_3\text{S}_4]^+$  (all- $\text{Fe}^{3+}$  form) to  $[\text{Fe}_3\text{S}_4]^{2-}$  (all- $\text{Fe}^{2+}$  form). In a number of iron-sulfur proteins, the  $[\text{Fe}_4\text{S}_4]$  cluster can be reversibly converted by oxidation and loss of one iron ion to a  $[\text{Fe}_3\text{S}_4]$  cluster. E.g., the inactive form of aconitase possesses an  $[\text{Fe}_3\text{S}_4]$  and is activated by addition of  $\text{Fe}^{2+}$  and reductant. It is found in several iron containing metalloenzymes like nitrogenase, hydrogenase, etc..and also in pig heart. All the iron centers are in tetrahedral coordination environment and linked with each other by two inorganic sulfide bridges.



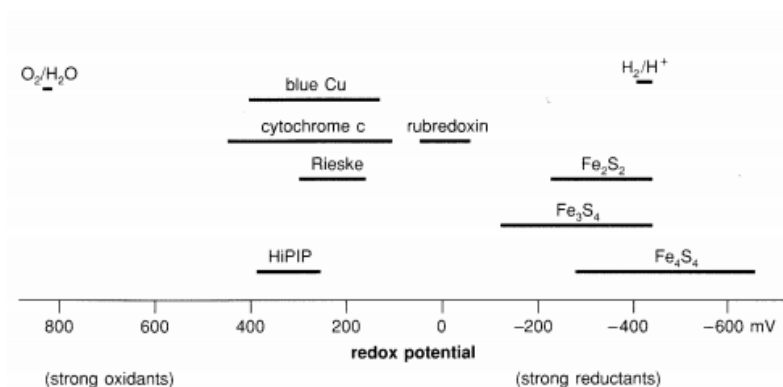
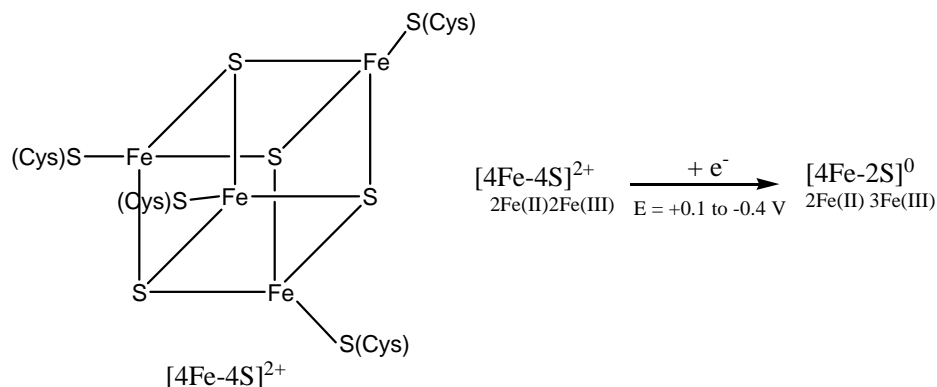
### 13.2.4 4Fe-4S clusters

A common motif features a four iron ions and four sulfide ions placed at the vertices of a cubane-type cluster. The Fe centers are typically further coordinated by cysteinyl ligands. The  $[\text{Fe}_4\text{S}_4]$  electron-transfer proteins ( $[\text{Fe}_4\text{S}_4]$  ferredoxins) may be further subdivided into low-potential (bacterial-type) and high-potential (HiPIP) ferredoxins. Low- and high-potential ferredoxins are

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related by the redox scheme. In HiPIP, the cluster shuttles between  $[2\text{Fe}^{3+}, 2\text{Fe}^{2+}]$  ( $\text{Fe}_4\text{S}_4^{2+}$ ) and  $[3\text{Fe}^{3+}, \text{Fe}^{2+}]$  ( $\text{Fe}_4\text{S}_4^{3+}$ ). The potentials for this redox couple range from 0.4 to 0.1 V. In the bacterial ferredoxins, the pair of oxidation states are  $[\text{Fe}^{3+}, 3\text{Fe}^{2+}]$  ( $\text{Fe}_4\text{S}_4^{4+}$ ) and  $[2\text{Fe}^{3+}, 2\text{Fe}^{2+}]$  ( $\text{Fe}_4\text{S}_4^{2+}$ ). The potentials for this redox couple range from  $-0.3$  to  $-0.7$  V. The two families of  $4\text{Fe}-4\text{S}$  clusters share the  $\text{Fe}_4\text{S}_4^{2+}$  oxidation state. The difference in the redox couples is attributed to the degree of hydrogen bonding, which strongly modifies the basicity of the cysteinyl thiolate ligands. A further redox couple, which is still more reducing than the bacterial ferredoxins is implicated in the nitrogenase.



*A schematic diagram of the redox potential of the various FeS centers in comparison with other known redox centers.*

### 13.3 Nitrogen Fixation

Nitrogen fixation is a process by which nitrogen in the air is converted into ammonia ( $\text{NH}_3$ ) or related nitrogenous compounds. Atmospheric nitrogen is molecular dinitrogen, a relatively nonreactive molecule that is metabolically useless to all but a few microorganisms. Biological nitrogen fixation converts  $\text{N}_2$  into ammonia, which is



metabolized by most organisms. Nitrogen fixation is essential to life because fixed inorganic nitrogen compounds are required for the biosynthesis of all nitrogen-containing organic compounds, such as amino acids and proteins, nucleoside triphosphates and nucleic acids. As part of the nitrogen cycle, it is essential for agriculture and the manufacture of fertilizer. It is also, indirectly, relevant to the manufacture of all chemical compounds that contain nitrogen, which includes explosives, most pharmaceuticals, and dyes.

Nitrogen fixation is carried out naturally in the soil by a wide range of microorganisms termed diazotrophs that include bacteria such as *Azotobacter*, and archaea. Some nitrogen-fixing bacteria have symbiotic relationships with some plant groups, especially legumes. Looser non-symbiotic relationships between diazotrophs and plants are often referred to as associative, as seen in nitrogen fixation on rice roots. Nitrogen fixation also occurs between some termites and fungi. It also occurs naturally in the air by means of NO<sub>x</sub> production by lightning.

All biological nitrogen fixation is effected by enzymes called nitrogenases. These enzymes contain iron, often with a second metal, usually molybdenum but sometimes vanadium. Molecular nitrogen (N<sub>2</sub>) is so unresponsive to ordinary chemical reactions that it has been characterized as 'almost as inert as a noble gas'. The very large triple bond energy (945KJ/mol) tends to make the activation energy prohibitively large. The common Haber process requires about 20 MPa pressure and 500 °C temperature to proceed, even in the presence of the best Haber catalyst. But the fixation of atmospheric dinitrogen occurs readily in various bacteria, blue green algae, yeasts and in symbiotic bacteria – legume associations under mild conditions.

### 13.3.1 In Vivo Nitrogen fixation

There are several bacteria and blue – green algae that can fix molecular nitrogen in vivo. Both free living species and symbiotic species are involved the strictly anaerobic *Clostridium pasteurianum*, aerobes like *Klebsiella pneumoniae* and strict aerobes like *Azotobacter vinlandii*. Even in the aerobic forms it appears that the nitrogen fixation takes place under essentially anaerobic conditions.

The most important nitrogen – fixing species are the mutualistic species of *Rhizobium* living in root nodules of various species of legumes (clover, alfalfa, beans, peas, etc).

The active enzyme in nitrogen fixation is nitrogenase. Two proteins are involved. The smaller has a molecular weight of 57,000 – 73,000. It contains an Fe<sub>4</sub>S<sub>4</sub> cluster. The larger protein is an α<sub>2</sub>β<sub>2</sub> tetramer with a molecular weight of 220,000 – 240,000 containing two molybdenum atoms, about 30 iron atoms and about 30 labile sulfide ions. The iron – sulfur clusters probably act as redox centers. It is possible to isolate a soluble protein – free cofactor containing molybdenum and iron.

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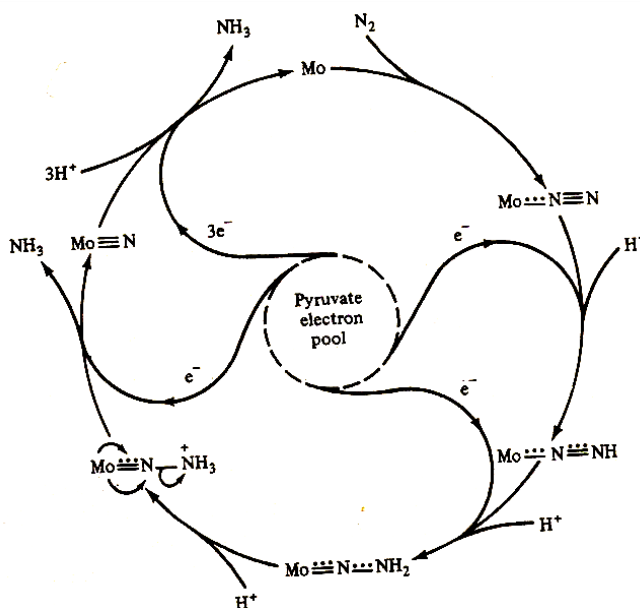
## NOTES

Recombination of the cofactor with inactive nitrogenase restores the activity.

It seems likely that the active site for dinitrogen binding involves the molybdenum atom. It has been established by EXAFS that the coordination sphere consists of several sulphur atoms at distances of about 235pm. An Mo=O double bond, so common in complexes of Mo(IV) and Mo(VI), is not present. There are other heavy atoms, perhaps iron, nearby (~270pm).

The ultimate source of reductive capacity is pyruvate, and the electrons are transferred via ferredoxin to nitrogenase. There is some evidence, not strong, that Mo(III) is involved. Two Mo(III) atoms cycling through Mo(VI) would provide the six electrons necessary for reduction of dinitrogen.

Alternatively, since the enzyme is rich in ferredoxin – type clusters, there should be a ready flow of electrons, and the molybdenum may stay in the one or two oxidation states that most readily bind dinitrogen and its intermediate reductants. The overall catalytic cycle may be represented as,



### 13.4 Check your progress question

1. Compare the different types of iron sulfur protein
2. What is meant by nitrogen fixation?

### 13.5 Answers to check your progress questions

1. Iron–sulfur proteins are proteins characterized by the presence of iron–sulfur clusters containing sulfide-linked di-, tri-, and tetrairon centers in variable oxidation states. The iron–sulfur proteins occur extensively in all living organisms and take part in a wide range of electron-transfer processes, either as redox centers (*e. g.* ferredoxins, rubredoxins) or as catalysts (*e. g.* hydrogenase, nitrogenase, etc).

2. **Nitrogen fixation** is a process by which nitrogen in the air is converted into ammonia (NH<sub>3</sub>) or related nitrogenous compounds.

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### 13.6 Keywords

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**Rubredoxins [1Fe-0S] proteins:** Iron-sulfur proteins with no bridging sulfur (0S) or sulfide atom is known as rubredoxins.

**Ferredoxins** are most important family of iron-sulfur proteins. Three major categories of ferredoxins are, [2Fe-2S], [3Fe-4S], and [4Fe-4S].

**Nitrogen fixation** is a process by which nitrogen in the air is converted into ammonia (NH<sub>3</sub>) or related nitrogenous compounds.

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### 13.7 Summary

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In this unit we discuss about iron-sulfur cluster and nitrogen fixation. The fact that iron-sulfur clusters occur as an integral component of electron transfer proteins is an exciting area of bioinorganic chemistry. Now, more than about thirty years after their initial discovery, Fe-S proteins are being understood to a certain extent and with more refined techniques and many more years of work, the exact nature of the ways in which they operate may be understood. This will result in many openings in biochemistry, not least of which are the exact nature of nitrogen fixation and chloroplast function and the implications which will follow if these are initiated in the laboratory.

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### 13.8 Self-assessment questions and exercises

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1. Explain Non-heme iron proteins
  2. Draw the structure of Rubredoxins
  3. Describe the function of High potential iron protein
  4. What is the advantages of nitrogen fixation.
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### 13.9 Further Reading

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- R H Holm, S Ciurli and J A Weigel. *Progress in Inorganic Chemistry*.38.1, 1990.
- P J Stephens, DR Jollie and A Warshel, *Chemical Review*, 96. 2491, 1996.

# UNIT-14: METAL IONS IN BIOLOGY

## STRUCTURE

- 14.0 Introduction
- 14.1 Objective
- 14.2 Alkali and Alkaline earth metals in biology
  - 14.2.1 Biological importance of Sodium
  - 14.2.2 Biological Importance of Magnesium
  - 14.2.3 Biological Importance of Potassium
  - 14.2.4 Biological Importance of Calcium
- 14.3 Sodium ion pump
  - 14.3.1 Steps involved in the Sodium-Potassium Pump (Na<sup>+</sup>-K<sup>+</sup> pump)
  - 14.3.2 Details of mechanism
- 14.4 Metal Ion Poisoning
  - 14.4.1 Industrial Sources
  - 14.4.2 Metallotherapy
  - 14.4.3 Automobile Engines
  - 14.4.4 Foods and Plants
- 14.5 Chelating agents in medicine
  - 14.5.1 Synergistic Chelation Therapy
  - 14.5.2 Mixed Ligand Chelation Therapy
  - 14.5.3 Chelate Therapy
- 14.6 Check your progress questions
- 14.7 Answers to check your progress questions
- 14.8 Summary
- 14.9 Keywords
- 14.10 self assessment question and exercise
- 14.11 Further Reading

## 14.0 Introduction

Twenty five elements are known to be essential for living organisms, and several more may be biochemically significant. After the major constituents of organic substances (C, O, H), several groups of elements may be distinguished.

### Classification of minerals found in the human body:

- macroelements (minerals), required in amounts greater than > 100 mg/day

C, H, O, N, S, P, Ca, Mg, Na, K, Cl

- microelements (trace elements), required in amounts less than < 100 mg/day

- essential: Co, Cr, Cu, F, Fe, J, Mn, Mo, Se, Zn
- probably essential: Ni, Si, Sn, V
- nonessential: As, B, Cd, Hg, Pb, Sb ...

### Functions of metal ions in biological systems

- catalytic (metalloenzymes, metal-activated enzymes)
- Structural (hydroxyapatite)

- in hormone action (calcium, iodine)
- in antioxidants (copper, zinc, manganese, selenium)
- as drug components (gold, lithium, platinum)

The alkali metals sodium, potassium (Group IA in the Periodic Table) are essential for a number of processes, including ion transport, electrical signaling, and electrolyte balance. The alkaline earths calcium and magnesium (Group IIA) play different roles. Mg is critically linked to phosphate biochemistry, as it binds to ATP and kinases, enzymes which control ATP activity. It is also important in many enzymes, and plays the central photo-capture role in chlorophyll. Calcium is important for cell wall structure, the contraction of muscle (and other) fibers, and the acquisition and transport of phosphate. It is involved in cell division and other reproductive processes. Ca is a main component of common biomineralization structures including oxalates (in the worst case, kidney stones), phosphates (such as bone and teeth) and calcium carbonate shells.

## NOTES

### 14.1 Objective

After going through this unit you will be able to

- ❖ Understand the biological importance of Alkali and Alkaline earth metals
- ❖ Explain the concept and mechanism of sodium-potassium pump
- ❖ Discuss about metal ion poison
- ❖ Describe about chelating agent in medicine

### 14.2 Alkali and Alkaline earth metals in biology

Among the ‘metals of life’ (ie, biometals), four metals form an ‘island’ in the periodic table. These are Sodium, Magnesium, Potassium and Calcium. These four biometals are also called the ‘main group metals’. These inorganic elements, especially at trace quantities play a vital role at the molecular level in a living system. The metals of the main group are specially involved in maintaining the osmotic balance and producing skeleton. Some of them may participate in enzymatic processes.

Sodium and calcium are the main cations outside the cells while potassium and magnesium are the main ones within the cells and there is an ion-pump mechanism for driving the ions in the required direction for maintaining some biological functions such as nerve-impulse transmission, muscle contraction etc.,

Alkali metal salts are generally soluble but sometimes their insoluble salts may create some problems, like – insoluble sodium salt of uric acid causes gout. Similarly, the insoluble salts of calcium as carbonate, fluoride, oxalate and phosphate sometimes produces troubles such as clogging of blood streams.

#### 14.2.1 Biological importance of Sodium

It is one of the most abundant cations in the extracellular part of mammalian tissues. It is important in nerve impulse transmission and

maintenance of osmotic pressure. It is also an essential cation for electro neutrality. It is moderately toxic when injected intravenously. Sodium regulates blood volume, blood pressure, neuron function, osmotic equilibrium &  $P^H$ . Higher levels of sodium can prevent kidney failure, loss of fluids, hypothyroidism, heart failure, liver cirrhosis etc. Sodium plays an important role in the body because it deals with maintaining water balance, transmitting nerve impulses and regulating muscle contraction & relaxation. Iodized salt is essential for the body as it helps in the production of thyroid hormones which affects growth & metabolic rates

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#### **14.2.2 Biological Importance of Magnesium**

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It is required in photosynthesis. In chlorophyll, Mg is present in the cavity of a porphyrin. Such metallation makes chlorophyll phosphorescent, but the free porphyrin gives fluorescence emission. This phosphorescent behaviour is biologically very important, without which the light energy absorbed will be lost and will not be available for chemical transformation. For phosphorescence to occur, there must be a suitable excited state of finite life time so that it has sufficient energy to transfer the energy for chemical reaction. Probably, through the spin-orbit coupling phenomenon, mixing of the excited singlet and triplet state is the source of phosphorescence and of the energy required for photosynthetic chemical reaction.

- Activity of enzymes: Mg plays a crucial role in the biochemical reactions occurring in our body. The main role of this ion in the body is to regulate the functions of enzymes which in turn are responsible for various chemical reactions. Magnesium as an enzyme co-factor plays an important role in the breakage of glucose and fat molecules, in the production of enzymes, proteins and regulation of cholesterol.
- Acts as fuel source: It plays an important role in the production of energy within the cells. Without the sufficient supply of this ion nutrients cannot be converted into usable energy or ATP (adenosine triphosphate) which is the fundamental unit of energy in human body. Production of ATP is significant to perform various actions such as cell reproduction, protein synthesis etc.
- Protector of human DNA: DNA synthesis is not possible without the sufficient supply of this ion. It is responsible for the stability and proper functioning of DNA.
- To maintain an electrolyte balance: It is one of the most important mineral in order to maintain a healthy electrolytic balance in our body. Deficiency of this ion leads to the improper functioning of sodium-potassium pump.

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#### **14.2.3 Biological Importance of Potassium**

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It is one of the most abundant cations occurring in the intracellular fluids in mammalian systems. It is important for electrolytic and osmotic balance. Its proper concentration gradient across the membrane is extremely useful in the creation and transmission of nerve

impulses and in muscle contraction. It is also important in maintaining proper rhythm of the heart beat.  $K^+$  participates as a cofactor in a number of internal enzymes. It activates pyruvate kinase which is required for glycolysis. It is also required in high concentration for the biosynthesis of proteins by ribosomes. In taking higher levels of potassium can reduce the risk of hyper tension, stroke and potassium deficiency as well as reduce bone turnover in people. Potassium bromated is used to improve dough strength and rise height. Potassium helps move nutrients into cells and waste products out of cells. Potassium is needed for muscle growth, nervous system and brain function. Measuring the amount of potassium by blood test can identify the presence of kidney disease, diabetes, and vomiting problem in the body. Consumption of foods rich in potassium plays a role to prevent osteoporosis.

## NOTES

#### **14. 2. 4 Biological Importance of calcium**

Like Magnesium, it is also important in controlling different electrochemical processes such as nerve impulse conduction. Calcium is mainly found in the bones and teeth of the living beings. It is used in the construction of cell walls, bones, teeth etc.  $Ca^{2+}$  can antagonize the potentiating effect of  $Mg^{2+}$  in enzymic processes and hence very important in the enzyme control mechanism. Blood is a large tank of this mineral. It participates in the formation of casein from milk and formation of fibrin from fibrinogen during blood clotting. Deficiency of calcium increases the blood clotting time. It is also important for the correct rhythm of heart beat and in lactation. Calcium supports muscle contraction. The deficiency of this metal leads to disorder of nerves. It plays a significant role in the metabolism of nitrogen in plants. Absence of this mineral in the plants affects the size and number of chloroplasts.

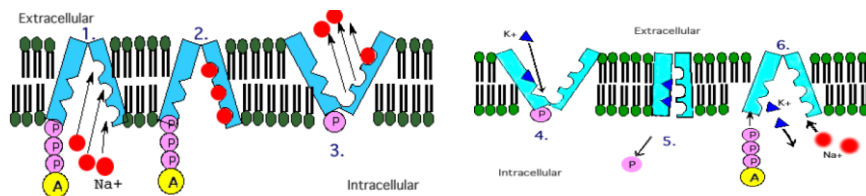
#### **14.3 Sodium ion pump**

A molecular mechanism by which sodium ions are transferred across a cell membrane by active transport especially one that is controlled by a specialized plasma membrane protein by which a high concentration of potassium ions and a low concentration of sodium ions are maintained within a cell. The process of moving sodium and potassium ions across the cell membrane is an active transport process involving the hydrolysis of ATP to provide the necessary energy. It involves an enzyme referred to as  $Na^+/K^+$ -ATPase. The sodium-potassium pump is an antiporter transport protein. This pump is responsible for the usage of almost 30 % of the body's ATP, this is due to 1 molecule of ATP being hydrolysed as three molecules of  $Na^+$  are pumped out of the cell and two molecules of  $K^+$  are pumped into the cell. The sodium-potassium pump is a very important protein in our cell membranes. The pump can be used to generate ATP when supplies are low by working in the opposite way. The pump is also used to control the osmolarity of the cell, by pumping the  $Na^+$  out that have diffused into the cell down their high electrochemical gradient the cell can be kept at

osmotic equilibrium. The pump plays a large role in nerve cells and initiating action potentials. The main function of the  $\text{Na}^+/\text{K}^+$  ATPase pump is to maintain resting potential so that the cells will be keeping in a state of a low concentration of sodium ions and high levels of potassium ions within the cell. Action potentials could not occur without these cells. They initiate the first part of the depolarisation before the voltage-gated channels come into play. The sodium-potassium pumps also recover the axon to its resting state of  $-60\text{mV}$  after an action potential has passed.

### 14.3.1 Steps involved in the Sodium-Potassium Pump ( $\text{Na}^+/\text{K}^+$ pump)

- 3  $\text{Na}^+$  ions from inside the cell bind to the  $\text{Na}^+/\text{K}^+$  pump
- The pump changes shape, transporting the 3  $\text{Na}^+$  ions across the cell membrane and releases them on the outside of the cell membrane.
- The pump is now exposed to the outside surface of the cell. 2  $\text{K}^+$  ions from outside the cell bind to the pump and the pump changes shape again.
- $\text{K}^+$  ions are transported across the cell membrane and are released inside the cell
- During this process, ATP is split into ADP and inorganic phosphate. The breaking of this bond releases energy to power the pump.
- Overall, because 3 positively charged ions left the cell and only 2 positively charged ions entered the cell, a charge gradient develops across the cell membrane such that the outside of the cell has more positive charge and the inside of the cell has more negative charge.



### 14.3.2 Details of mechanism

- A molecule of adenosine triphosphate (ATP, a source of chemical energy) binds to a site on the intracellular side of the  $\text{Na}^+/\text{K}^+$  pump protein.
- Three sodium ions (3  $\text{Na}^+$ , shown as red balls) from the cytoplasm bind to “lock and key” sites on the  $\text{Na}^+/\text{K}^+$  pump.
- The bound ATP is then split into ADP and inorganic phosphate (the ADP is released back into the cytoplasm, while the inorganic phosphate, P, remains bound to the pump). The breaking of this bond releases energy that powers a change in the shape of the



- $\text{Na}^+\text{-K}^+$  pump protein, releasing the three sodium ions ( $3 \text{Na}^+$ ) outside the cell.
- Two potassium ions ( $2 \text{K}^+$ ) from outside the cell bind to “lock and key sites” on the protein of the  $\text{Na}^+\text{-K}^+$  pump.
  - The protein of the  $\text{Na}^+\text{-K}^+$  pump changes shape again as the remaining inorganic phosphate group leaves the protein's active site.
  - The two potassium ions ( $2 \text{K}^+$ ) are released into the cytoplasm, as another ATP molecule binds to the active site on the  $\text{Na}^+\text{-K}^+$  pump protein and the process starts over.
  - When this process repeats many times, an imbalance of charge forms across the membrane. There will be more positive charged ions outside the membrane than inside. This creates a chemical potential energy which can be used by the cell to later generate lots more ATP, for generating electrical impulses, or for muscle contractions.
  - Neurons communicate with one another when this charge difference is used to generate an “**action potential**” along the axon of a neuron.

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#### 14.4 Metal Ion Poisoning

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A **toxic heavy metal** is any relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts. Heavy metals are found naturally in the earth, and become concentrated as a result of human activities, or, in some cases geochemical processes, such as accumulation in peat soils that are then released when drained for agriculture. Common sources are mining and industrial wastes; vehicle emissions; lead-acid batteries; fertilisers; paints; treated woods; aging water supply infrastructure, and microplastics floating in the world's oceans. Heavy metals "can bind to vital cellular components, such as structural proteins, enzymes, and nucleic acids, and interfere with their functioning". Symptoms and effects can vary according to the metal or metal compound, and the dose involved. Broadly, long-term exposure to toxic heavy metals can have carcinogenic, central and peripheral nervous system and circulatory effects.

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##### 14.4.1 Industrial Sources

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For the industrial purposes many mining metals such as Co, Cu, Zn, Pu, Be, Cd, etc., are being accumulated in our ecosystem during their winning, smelting and roasting processes. Mercury is extensively used as a catalyst in different industries. It is often used as an electrode in the manufacture of caustic soda, chlorine and in many other electrochemical processes. It has been proposed that the mercury discharged from different sources in to the sea undergoes methylation to form methyl mercury cation ( $\text{CH}_3\text{Hg}^+$ ). The toxicity of  $\text{CH}_3\text{Hg}^+$  is much more severe due to the facts,

- i) The organic moiety gives it a lipophilic character so that it can easily pass through the biological lipid membrane.

ii) The Mercury is tightly bound to carbon so that the molecule is not easily degraded and it may maintain its toxicity for a long time.

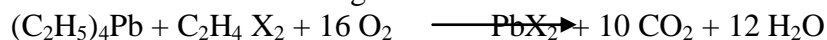
#### 14.4.2 Metallotherapy

Different metallic compounds are used in human diseases and from such treatments, different toxic metals may be accumulated in our body

For examples gold from gold therapy for arthritis, Platinum from platinum complexes used against cancer, iron from iron containing pills, arsenic and antimony from the use of organic arsenicals and antimony based organic compounds for bacterial infections.

#### 14.4.3 Automobile Engines

Lead alkyls are used extensively to increase the octane number of gasoline in automobile engines. Ethylene dihalides are used to promote the formation of lead halides rather than the non – volatile compounds that would foul the engine.



This becomes a potential source of lead poisoning and it is a world wide problem.

#### 14.4.4 Foods and Plants

Industrial food processing is becoming a potential source of metal poisoning. For an example – abrasions on equipments can lead the processed foods to be contaminated with As, Pb, Cu, Zn, Ni, Hg and Sb. Use of Nickel as catalyst in the hydrogenation of oils is also worth mentioning. There are the main sources of metal poisoning.

#### 14.5 Chelating agents in medicine.

**Chelating agents** are chemical compounds that react with metal ions to form a stable, water-soluble complex. They are also known as chelants, chelators, or sequestering **agents**. Chelating agents have a ring-like center which forms at least two bonds with the metal ion allowing it to be excreted. Chelation therapy is the preferred medical treatment for metal poisoning, including acute mercury, iron, arsenic, lead, uranium, plutonium and other forms of toxic metal poisoning. The chelating agent may be administered intravenously, intramuscularly, or orally, depending on the agent and the type of poisoning.

There are two types of chelation therapy based on the number of different types of ligands administered.

1. Single Ligand Therapy, 2. Double Ligand Therapy

##### 1. Single Ligand Therapy

To remove a particular toxic metal one selective chelating drug is administered in this method.

##### 2. Double Ligand Therapy

In this method, two different ligands are simultaneously administered for a particular toxic metal. Based on their mechanism of action in vivo, it be classified into -.

a. Synergistic chelation Therapy, b. Mixed Ligand Chelation Therapy.

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### 14.5.1 Synergistic Chelation Therapy

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Synergistic Chelation Therapy (P.M. May and D.R. Williams, 1979) occurs when one drug mobilizes the metal, while the other traps it in plasma to be excreted in the urine.

For an example, 'puchel' and 'dtpa' act synergistically (D.R. Williams et al, 1984) in a chronic plutonium intoxication. Puchel being more lipophilic, can mobilize the radionuclides from the sites of Pu – deposition and transfer it into the plasma where dtpa can trap the plutonium to excrete in the urine. It is worth mentioning that the thermodynamic affinity of dtpa towards plutonium is greater than that of puchel. Such beneficial combinations of chelating drugs acting synergistically have been reported.

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### 14.5.2 Mixed Ligand Chelation Therapy

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In this process, two different ligands are introduced in 1:1 molar ratio, the ligands form ternary complexes with the toxic metal (J. Schubert and S.K. Deer, 1979). Due to the formation of ternary complexes, the thermodynamic stabilities are enormously increased due to many factors such as statistical factors, charge neutralization, intramolecular electrostatic interactions, cooperative electronic effects, particularly with the aromatic secondary ligands etc.,

Moreover, due to the formation of a ternary complex, the pharmacokinetic properties are also significantly changed depending on the total dentateness of the chelants and the ligancy of the metal. When the total dentateness is less or greater than the ligancy of the metal ion, the metal chelates are hydrophilic and they are lipophilic when the total dentateness is equal to the ligancy of the metal ion. thus, Pu (edta), Pu (SA), Pu (dtpa) (SA) are hydrophilic and Pu (dtpa), Pu (edta) (SA) are lipophilic. (SA = Salicylate).

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### 14.5.3 Chelate Therapy

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Chelating agents can be used therapeutically to treat problems caused by the presence of toxic elements. An essential element can be toxic if present in too great a quantity.

#### i) Removal of excess of Copper

Wilson's disease is a genetic disease involving the buildup of excessive quantities of copper in the body. Many chelating agents have been used to remove the excess copper, but one of the best is D – Penicillamine, HSC (CH<sub>3</sub>)<sub>2</sub> COOH. This chelating agent forms a complex with copper ions that is coloured an intense purple and surprisingly has a molecular weight of 2600.

Another surprising fact is that the complex will not form unless chloride or bromide ions are present and the isolated complex always contains a small amount of halide.

These puzzling facts were explained by X – ray crystallographic studies. The structure consists of a central halide ion surrounded by eight Cu(I) atoms bridged by sulfur ligands. These are in turn coordinated to

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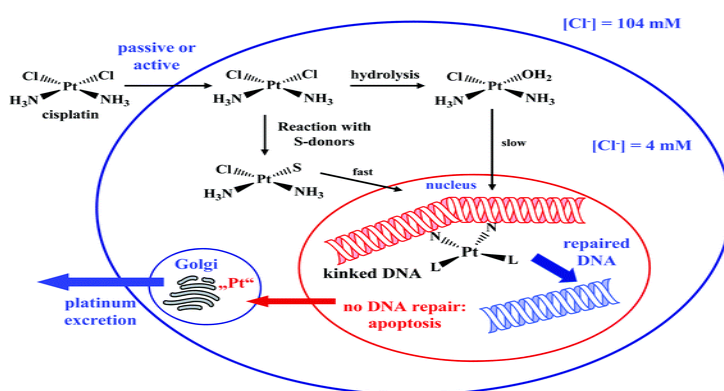
## NOTES

six Cu(II) atoms. Finally, the chelating amino groups of the penicillamine complete the coordination sphere of the copper (II) atoms.

ii) An excessive intake of iron causes various problems known as siderosis. Chelating agents are used to treat the excessive buildup of iron. In many cases the chelates resemble or are identical to the analogous compounds used by bacteria to chelate iron. Thus desferroxamine B is the drug of choice for African siderosis. The ideal chelating agent will be specific for the metal to be detoxified. Since a more general chelating agent is apt to cause problems by altering the balance of other essential metals. The concepts of hard and soft metal ions and ligands can be used to aid in this process of designing therapeutic chelators.

iii) A slightly different mode of therapy involves the use of cis – diamminedichloro platinum (II),  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  and related bis (amine) complexes in the treatment of cancer.

The exact action of the drug is not known, but only the cis-isomer is active at low concentrations, not the trans isomer. It is thought that the platinum binds to DNA, with the chloride ions first being replaced by water molecules and then by DNA base such as guanine. Studies in vitro with nucleotide bases as well as theoretical calculations indicate that the N7 position of guanine is the favoured site for platinum coordination. The cis-diamine moiety can bind to groups about 280 pm apart. The most important interaction is interstrand linking of two adjacent guanine bases on the DNA chain by the platinum atom. The binding of cisplatin to DNA would seriously interfere with the ability of the guanine bases to undergo Watson – Crick base pairing. Thus, when a self complementary oligomer (a portion of the DNA Chain) reacts with the cis – isomer, two adjacent guanines are bound and Watson – Crick base pairing is disrupted.



For cis – diammine dichloroplatinum (II) to work according to the proposed mechanism, it must hydrolyse in the chromosomes and not in blood. Fortunately, the blood is approximately 0.1 M in chloride ion, inhibiting its hydrolysis in blood. In the cytoplasm, the chloride ion

concentration is only 4 mM. Thus, hydrolysis and subsequent reactions with the appropriate biological targets can readily take place.

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#### 14.6 Check your progress questions

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1. Write the functions of metal ions in biological systems
  2. Give Biological importance of Sodium
  3. Describe Metal Ion Poisoning
  4. Explain the mechanism of Sodium ion pump
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#### 14.7 Answers to check your progress questions

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1. catalytic (metalloenzymes, metal-activated enzymes)  
Structural (hydroxyapatite)  
in hormone action (calcium, iodine)  
in antioxidants (copper, zinc, manganese, selenium)  
as drug components (gold, lithium, platinum).
  2. It is one of the most abundant cations in the extracellular part of mammalian tissues. It is important in nerve impulse transmission and maintenance of osmotic pressure. It is also an essential cation for electro neutrality.
  3. A **toxic heavy metal** is any relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts.
  4. A molecular mechanism by which sodium ions are transferred across a cell membrane by active transport especially one that is controlled by a specialized plasma membrane protein by which a high concentration of potassium ions and a low concentration of sodium ions are maintained within a cell. The process of moving sodium and potassium ions across the cell membrane is an active transport process involving the hydrolysis of ATP to provide the necessary energy.
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#### 14.8 SUMMARY

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- ❖ Among the 'metals of life' (ie, biometals), four metals form an 'island' in the periodic table. These are Sodium, Magnesium, Potassium and Calcium.
- ❖ Higher levels of sodium can prevent kidney failure, loss of fluids, hypothyroidism, heart failure, liver cirrhosis etc.,
- ❖ In chlorophyll, Mg is present in the cavity of a porphyrin. Such metallation makes chlorophyll phosphorescent and it is one of the most important mineral in order to maintain a healthy electrolytic balance in our body.
- ❖ Potassium is one of the most abundant cations occurring in the intracellular fluids in mammalian systems. It is also important in maintaining proper rhythm of the heart beat.  $K^+$  participates as a cofactor in a number of internal enzymes.
- ❖ The process of moving sodium and potassium ions across the cell membrane is an active transport process involving the hydrolysis of ATP to provide the necessary energy. It involves an enzyme referred to as  $Na^+/K^+$ -ATPase.

- ❖ A **toxic heavy metal** is any relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts.
- ❖ Chelating agents have a ring-like center which forms at least two bonds with the metal ion allowing it to be excreted. Chelation therapy is the preferred medical treatment for metal poisoning, including acute mercury, iron, arsenic, lead, uranium, plutonium and other forms of toxic metal poisoning.
- ❖ cis – diamminedichloro platinum(II),  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  and related bis (amine) complexes used for the treatment of cancer.

#### 14.9 Keywords

**Sodium ion pump:** A molecular mechanism by which sodium ions are transferred across a cell membrane by active transport especially one that is controlled by a specialized plasma membrane protein by which a high concentration of potassium ions and a low concentration of sodium ions are maintained within a cell.

**Heavy metal:** A **toxic heavy metal** is any relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts.

**Chelating agents:** **Chelating agents** are chemical compounds that react with metal ions to form a stable, water-soluble complex. They are also known as chelants, chelators, or sequestering **agents**.

**Cis platin:** cis – diamminedichloro platinum (II),  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$

#### 14.10 Self Assessment Question and Exercise

##### Short answer question

1. How many  $\text{Na}^+$  ions are being pumped out?
2. Is more sodium inside the cell?
3. Define heavy metals
4. What is meant by chelation

##### Long answer question

1. Discuss detail about biological importance of Alkali and Alkaline earth metals
2. Describe briefly about sodium-potassium ion pump
3. Explain about chelating agent in medicine

#### 14.11 Further Reading

1. Frausto da Silva and Willams, The Biological Chemistry of the Elements, 1991.
2. Alberts B, Johnson A, Lewis J, Raff M, Roberts K, Walter P Molecular Biology of the Cell. Garland Science, Fifth Edition 2008.
3. Beauge, L. A., Gadsby, D. C., and Garrahan, P. J. *Na/K-ATPase and Related Transport ATPases: Structure, Mechanism and Regulation* (eds. Annals New York Academy Sci., New York, 834, 1997.
4. Jorgensen, P. L. in *Molecular Aspects of Transport Proteins* (ed. De Pont, J. J. H. M. M.) Elsevier Service Publisher B.V., 1,1992.

Time: Three hours Maximum: **75 marks**

**SECTION A Answer All Questions**

(10 X2 = 20)

1. Explain chelate effect
2. Describe stability constant of coordination complexes
3. Give one example for hydrolysis in octahedral complexes
4. Explain electron transfer reaction
5. What is meant by two electron transfer reaction
6. Explain term symbol
7. What is spinel?
8. Define cluster?
9. How will you synthesis metal alkyene complexes ?
10. Explain Metallocene

**SECTION B Answer ALL questions, choosing either (a) or (b)**

(5 × 5 = 25)

11. (a) What are inner sphere and outer sphere complexes? Explain them with suitable mechanisms.  
(or)  
(b) What are anation reactions? Give the mechanism.
12. (a) What are complementary and non-complementary electro transfer reactions?  
(or)  
(b) What are labile and inert complexes? Give one example each.
13. (a) Give the role of group vibrational frequencies of ligands in the study of metal complexes.  
(or)  
(b) Discuss the bonding in acetylene complexes with suitable examples.
14. (a) Describe the mechanism of hydroformylation reactions?  
(or)  
(b) Explain the reactivity of ferrocene.
15. (a) Discuss in detail about Non-heme iron proteins  
(or)  
(b) Discuss briefly the working of sodium ion pump.

**SECTION C Answer any THREE questions**

(3 × 10 = 30)

16. What is stability constant? How is it determined by pH metric and spectrophotometric methods?
17. (a) Describe the mechanism of Ziegler-Natta polymerisation.  
(b) Discuss briefly on metal-olefin complexes.
18. Discuss briefly the structure and functions of hemoglobin and myoglobin.
19. (a) Construct the Orgel diagram for a  $d^9$  configuration and explain  
(b) Give the significance of Racah parameters.
20. Explain the following
  - a. Wade's rule
  - b. Trans effect
  - c. Vitamin B12.