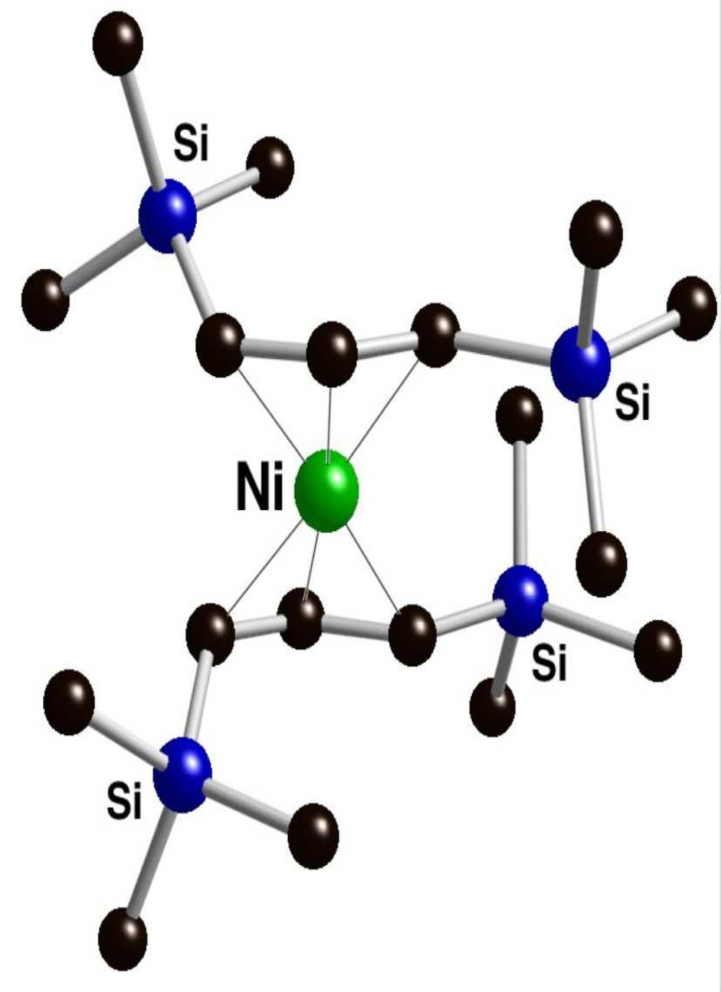
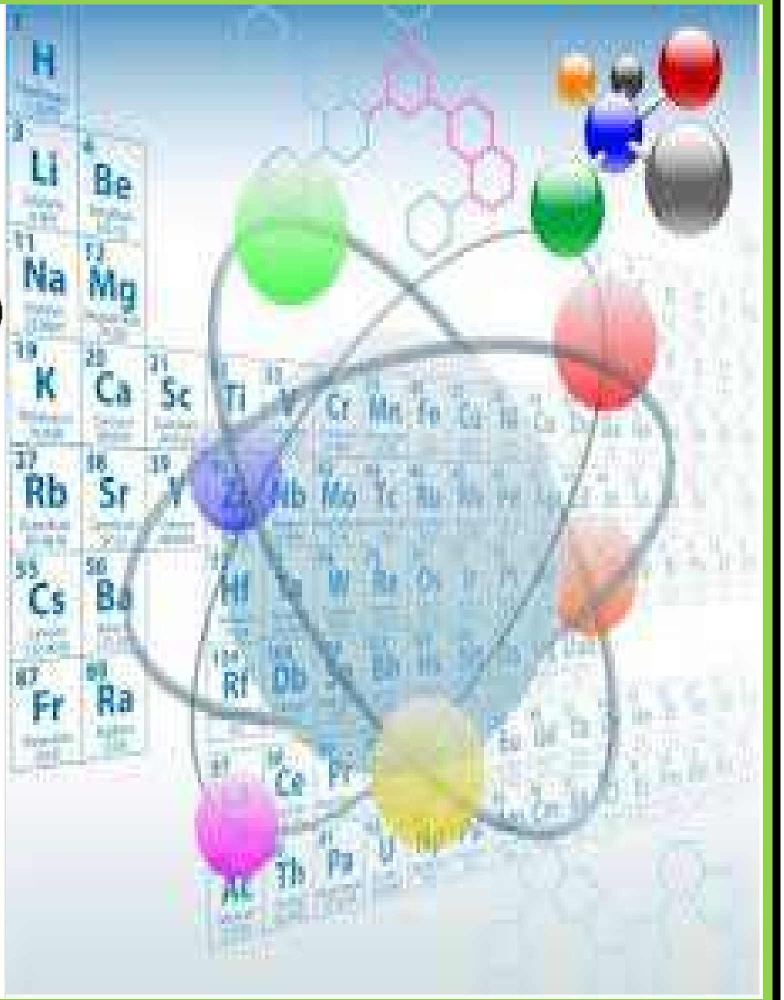
BSCCH- 301

B.Sc. III YEAR

INORGANIC CHEMISTRY-III





SCHOOL OF SCIENCES
DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY

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CONTENTS

BLOCK- 1

BLOCK-2

BLOCK-3

UNIT -1 HARD AND SOFT ACID AND BASE (HSAB)

CONTENTS:

1.1 OBJECTIVES

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

- To know the relationship between acid strength and the value of p*K*a.
- To understand the relationship between polarizability and the hardness or softness of an acid or base.
- To predict the stability of a chemical bond using the hard-soft acid base theory.
- To predict the relative acid or base strength of two organic compounds.
- To understand how the presence of a particular functional group affects the acid or base strength of another functional group.

1.2 INTRODUCTION

Lewis acid and base theory (also known as e^- donor-acceptor theory) is a broad, widely applicable approach to the classification of chemical substances and the analysis of chemical reactions. According to this theory, a base is an electron pair donor, and an acid is an electron pair acceptor. Donation of an electron pair from base to acid results in the combining of the acid and base with a covalent bond. The bonded acid-base species is called an adduct, a coordination compound, or a complex compound.

Since the strength of Lewis acids and bases is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength. Thus, from the above criteria, an acid base reaction should be a rapid reaction. The HSAB concept is a shortening for "hard and soft (Lewis) acids and bases". Also known as the Pearson acid base concept, HSAB is widely used in chemistry for explaining stability of compounds, reaction mechanisms and pathways. Soft Lewis base are those in which the donor atoms are easily polarized and have low electronegativity. While Hard Lewis base are those in which the donor atoms have low polarisabilities and high electronegativities. A hard Lewis acid, like hard base, is difficult to polarize, small size, high positive charge, having small size and a noble gas electronic configuration. While soft acid, like soft base, are readily polarized these have large size, low positive or zero charge and do not have a noble gas configuration.

Hard soft Acid Base Concept (HSAB Concept):

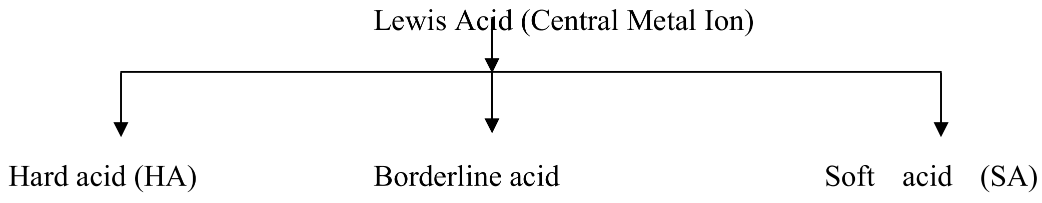
Experimentally, it was observed that certain ligands having a tendency to form the stable complexes with the lighter metal ion like Na^+, Li^+, Mg^{+2}, Sc^{+3}, Ti^{+4} etc. and certain other ligands having the tendency to form the stable complexes with the heavier metal ions like Ag^+, Cu^{+2}, Hg^{+2}, Cu^{+2} etc.

On the basis of this preferential bonding nature of ligand (Lewis base and Lewis acid), Pearson had categorised both the acid and bases into three different categories each, which are given in the next section.

1.3 CLASSIFICATION OF ACIDS AND BASES AS HARD AND SOFT

1.3.1 Classification of the Lewis's acid:

According to the Pearson, Lewis's acids can be of the three different types, which are given below:-



1. **Hard acid:-** All the Lewis acids having the following characteristic properties are known as hard acid:
    (i) Should exhibit the smaller size.
    (ii) Should have high + ve oxidation state.
    (iii) Polaris ability should be very low (on the basis of this property they are known as hard).
    (iv) Should have vacant d- orbital or approximate vacant d- orbital configuration (in the case of d – block elements)
2. **Soft acid:** All the Lewis acids having the following characteristic properties are known as soft acids:
    (i) Should exhibit larger size.
    (ii) Should have very low +ve oxidation state or zero oxidation state.
    (iii) Polaris ability should be very high (on the basis by this property they are known as soft).
    (iv) Should have filled d-orbital or approximate filed d-orbital configuration (in the case of d-black dements)

Borderline acids:- All the Lewis acids which exhibit the properties intermediate in between the hard & soft acids are known as borderline acids. Some of the samples of hard acid, soft acid & borderline acids are given in Table 1.1

Hard acids	**Soft acids**	**Borderline acids**
Li^+	Cu^+	Fe^{+2}
Na^+	Ag^+	Co^{+2}
K^+	Au^+	Ni^{+2}
Mg^{+2}	Hg^+	Cu^{+2}
Ca^{+2}	Pt^{+2}	Zn^{+2}
Al^{+3}	Hg^{+2}	Pb^{+2}
Ba^{+2}	Pd^{+2}	Sn^{+2}
Ga^{+3}	Ed^{+2}	SO_2
La^{+3}	BH_3	Bi^{+3}
Cr^{+3}	I^+	Sb^{+3}
Cr^{+6}	Br^+	NO^+

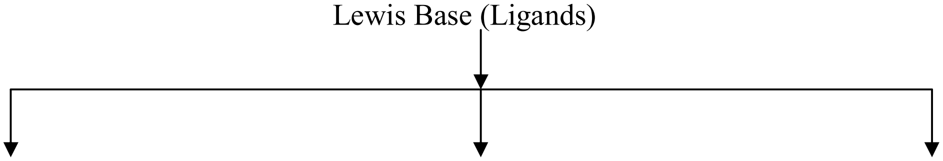
Co^{+3}	Metal atoms at zero oxidation states	GaH_3
Fe^{+3}		$B(CH_3)_3$
Si^{+4}		
Ti^{+4}		
Ce^{+3}		
Sn^{+4}		
SO_3		
BF_3, BCl_3, $B(OR)_3$, $Al(CH_3)_3$		
I^{+7}		
I^{+5}		
CO_2		

Table 1.1: *Examples of hard acid, soft acid & borderline acids*

1.3.2 Classification of the Lewis base

According to the Pearson concept, Lewis basis can be divided into 3 different types which are given below:-

Lewis Base (Ligands)



Hard Base (HB) Borderline Base Soft Base (SB)

1. **Hard base:** All the Lewis bases having the following characteristic properties are known as hard base:

   (i) Donor atom of the base should be highly electronegative like F, O, N & O.

   (ii) Polaris ability of the donor atom should be very high low.

2. **Soft base:** All the Lewis bases which have the following characteristic properties are known as soft bases:

   (i) Donor atom of the base should be less electronegative.

   (ii) Polaris ability of the donor atom should be very high.

3. **Borderline base:** All the Lewis bases which have the properties intermediate the soft & hard bases are known as borderline bases.

Some of the examples of hard bases, soft bases and borderline bases can be given as:-

Hard base: H_2O, OH^-, CH_3COO^-, PO_4^{-3}, SO_4^{-2}, CO_3^{-2}, ClO_4^- NO_3^-, ROH, R-O^-, R_2O (Doner O), NH_3, R-NH_2, N_2H_4 (doner N), F^-, Cl^-

Soft base: R_2S, R-SH, R-S^-, I^-, SON^- , S_2O_3, R_3P, $(RO)_3P$, CN^-, RNC, CO, C_2H_4, C_6H_6 , H^-, R^-, S^{-2}

Borderline base: C_6H_5-NH_2, C_5H_5N, Br^-, SO_3^{-2}, NO_2^-

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1.4 PEARSON'S HSAB CONCEPT: ACID BASE STRENGTH AND HARDNESS AND SOFTNESS

According to the Pearson HSAB concept, hard acid- hard base combination & soft acid-soft base combination give rise to the more stable compound or complexes in comparision to the hard acid–soft base & soft acid-hard base combination compound.

$$\text{Hard acid + hard base} \longrightarrow \text{more stable compound / complexes}$$

$$\text{Soft acid + soft base} \longrightarrow \text{more stable compound / complexes}$$

or

$$\left.\begin{array}{l}\text{Hard acid + soft base}\\ \\ \text{Soft acid + hard base}\end{array}\right\} \longrightarrow \text{Less stable complexes}$$

Explanation: Due to the very low polarise ability of hard acid and hard base their combination are ionic in nature while due to the very high polarize ability of soft acid and soft base their combinations are covalent in nature. Both these combinations of ionic and covalent nature have more stable combination due to which HSAB principle states the hard–hard and soft-soft combinations as a stable combination.

1.4.1 Applications of HSAB principle

1.4.1.1 Occurrence of metal ions on the earth

Lighter metal ions like Li^+, Na^+, Mg^{+2} , Ca^{+2} etc. exist in the form of there chlorides, carbonates, sulphates, phosphates (O^{-2}, CO_3^{-2} , SO_4^{-2}, PO_4^{-3}) on the earth crust but cannot exist in the form of their sulphides (S^{-2}) while on the other hand heavier metal ions like Ag^+, Hg^+, Cu^+ etc. exist in the form of their sulphides on the earth crust and cannot exist in the form of CO_3^{-2}, O^{-2} , SO_4^{-2} etc.

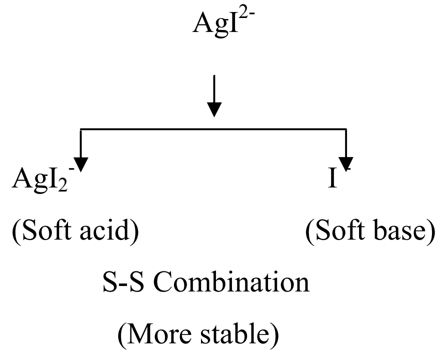
Explanation :- Lighter metal ions like Li^+, Na^+, K^+, Mg^{+2} , Al^{+3}, etc. form the stable hard – hard combination with the O^{-2} , CO_3^{-2}, SO_4^{-2}, PO_4^{-3} on the earth crust due to which they exist in the form of there oxides, carbonate, sulphates and phosphates while these lighter metal ion forms the less stable unstable hard soft combination with the sulphide ion due to which they connot exist in the form of there sulphides on the earth crust. Heavier metal ions like Ag^+, Hg^+, Cu^+ etc. form the stable soft –soft combination with the S^{-2} ion due to which they can exist in the form of their sulphides on the earth crust while on the other hand, the heavier metal ions like Ag^+, Hg^+, Cu^+ etc. form the unstable or less stable soft-hard combination with the O^{-2}, CO_3^{-2}, SO_4^{-2}, PO_4^{-3} etc. due to which they cannot exist in the form of there oxides, carbonates, sulphates and phosphates on the earth crust.

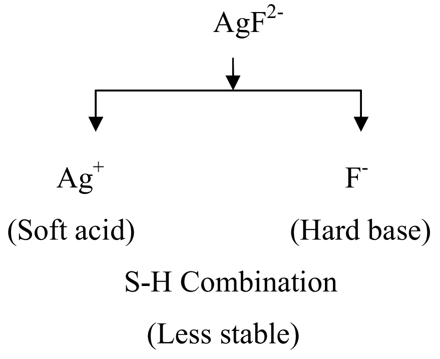
1.4.1.2 Stability of the compound/complexes

With the help of HSAB principle, we can compare the stability of various compounds or complexes.

(i) AgI_2^- is more stable than the AgF_2^-

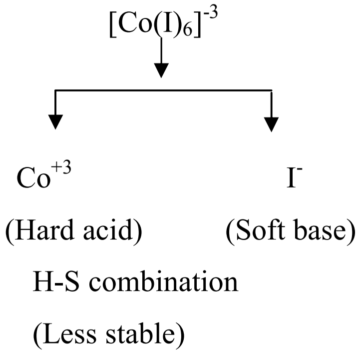
Explanation: AgI_2^- containing soft- soft combination due to which accoding to the HSAB principle, AgI_2^- well be more stable while AgF_2^- containing soft –hard combination, will be less stable or sometime cannot exist.

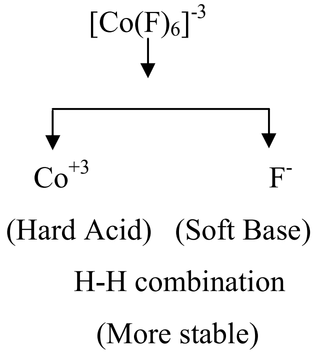




(ii) $[Co(F)_6]^{-3}$ is being more stable then $[Co(I)_6]^{-3}$ ion.

Explanation: $[Co(F)_6]^{-3}$ ion containing hard-hard (H-H) combination is more stable while on the other hand, $[Co(I)_6]^{-3}$ ion having hard-soft (H-S) combination, will be less stable.





1.4.1.3 Stability of the complexes containing different ligand

According to the Pearson principle, a complex containing more than one type of the ligands (hard or soft), then the complex will be more stable.

$[Co (N)_5(F)]^{-3}$ ion is less stable than $[Co(CN)_5(I)]^{-3}$ ion

Explanation: $[Co(N)_5(F)]^{-3}$ ion containing soft CN^- & Hard F^- ligands will be less stable while on the other hand $[Co(N)_5(I)]^{-3}$ ion containing both the soft ligands (CN^- and I^-) will be more stable.

1.4.1.4 Occurrence of the chemical reaction

With the help of HSAB principle we can give the idea about the occurrence of the chemical reaction. According to HSAB principle, if the reactants present in the chemical reaction have less stable H-S & S-H combinations, then they will have the tendency to react with each other to generate the more stable H-H & S-S combinations i.e. in such condition chemical reaction will be possible. If the reactants have more stable H-H & S-S combinations, then they will not have the tendency to convert into the less stable H-S & S-H combinations by the reaction i.e. in such condition reaction will not be possible.

$$\underset{(H-S)}{Li} + \underset{(S-H)}{CsF} \longrightarrow \underset{(H-H)}{LiF} + \underset{(S-S)}{CsI}$$

In the above reaction, both the reactants have less stable H-S & S-H combinations and the products have the more stable H-H & S-S combination so acc to HSAB principle the above Reaction will be possible.

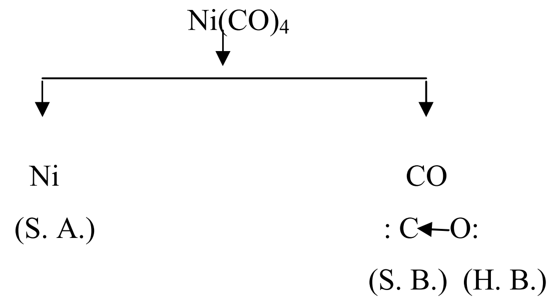
$$BeF_2 + HgI_2 \longrightarrow BeI_2 + HgF_2$$

(H-H) (S-S) (H-S) (S-H)

In the above reaction, both the reactants have more stable (H-H, S-S) combinations and products haveless stable H-S and S-H combinations. Hence, according to HSAB principle, this reaction will not be possible.

1.4.1.5 Nature of the doner site in the ambident ligand

With the help of HSAB principle, we can also give an idea about the actual doner site of an ambident ligand.

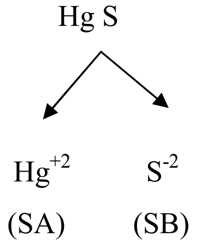


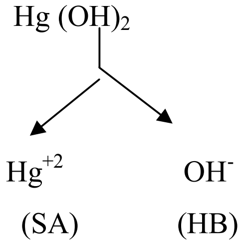
When the C atom of the CO behave as a doner site, then there occur the formation of more stable S-S combination with the central metal atom (Ni) while when the O atom of CO behaves as a doner site, then there occur the formation a less stable S-H combination with the central metal atom (Ni). Therefore, the actual doner site of CO will be carbon.

1.4.1.6 Solubility of the compounds

According to the HSAB concept, those compounds which have more stable H-H & S-S combinations, exhibit less solubility in the aqueous medium in compare to the compounds which have less stable H-S & S-H combinations.

Explanation: $Hg(OH)_2$ exhibits more solubility in the aqueous medium due to less stable H-S combination, while HgS exhibits less solubility in aqueous medium due to the more stable S-S- combination.





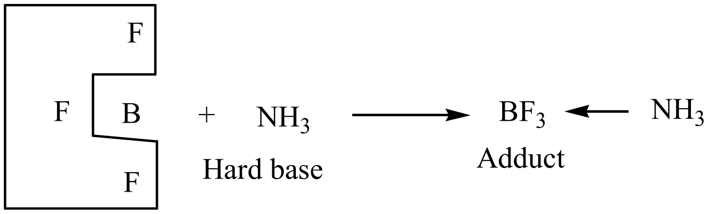
1.4.2 Limitation of HSAB principle

According to HSAB concept, chemical reactions have a tendency to occur in such direction which can generate the more stable H-H & S-S combination. But sometimes the chemical reactions can also occur in such direction which can generate the less stable S-H & H-S combination and this can not be explained by HSAB concept of Pearson.

1.5 SYMBIOSIS

In sense of biology, symbiosis may be defined as the dependency on each other i.e. when the two spices comes in the contact of each other then both are equally benefitted but in the sense of HSAB concept, symbiosis phenomena is different from the biological symbiosis. According to HSAB concept, attraction of the soft base toward the centre which is attached with the soft bases or attraction of the hard base toward the centre which is attached with the hard bases is known as symbiosis.

Explanation: NH_3 exhibit the symbiosis phenomena with the BF_3 because the hard base NH_3 having the tendency to attach with B centre which is already attached with hard bases F$^-$ ion.



1.6 THEORETICAL BASIS OF HARDNESS AND SOFTNESS

There are some theories that can explain the interactions in between the hard acids and hard bases and vice versa. No single theoy can explain this kind of interaction.

1.6.1 Electronegativity concept for the HSAB theory

According to the electronegativity theory, the interaction between HA and HB is ionic or electrostatic in nature. As hard acid and hard bases are small in size (HB is highly electronegative and HA is highly electropositive), the internuclear distance between them will be smaller. As a result, interaction between HA and HB will be highly stable.

1.6.2 Covalent concept for the HSAB theory (σ-bonding)

Soft acids have high polarising power and soft bases like I^- has high polarisability. Therefore, the interaction between SA and SB is covalent in nature.

1.6.3 Covalent concept for the HSAB theory (л-bonding)

Soft acids have fully filled d orbitals (low oxidation state) and soft bases are pi bonding ligands. Thus, SA has a good tendency to form π bonds with SB.

1.7 SUMMARY

The HSAB (Hard Soft Acid Base) theory categorizes chemical species as acids or bases and as "hard", "soft", or "borderline". It explains that soft acids or bases tend to be large and very polarizable, while hard acids or bases are small and non-polarizable. Since these categories are not absolute, there are species that are considered borderline, which lie in between hard and soft.

Hard acid – high positive charge, small size, not easily polarized
Soft acid – low positive charge, large size, easily oxidized, high polarizability
Hard base – low polarizability, high electronegativity, not easily oxidized
Soft base – high polarizability, diffuse donor orbital, low electronegativity, easily oxidized

HSAB provides a semi-quantitative method for understanding trends in acid-base reactivity: hard acids like hard bases and soft acids like soft bases.

1.8 TERMINAL QUESTIONS

1. Define soft base and give one example.
2. What is symbiosis?
3. How does HSAB principle govern the occurrence of minerals?
4. Define absolute hardness.
5. Give two examples of border line acids.
6. Which of the following is odd among the following:

Li^+, Ga^{3+}, Cd^{2+}, K^+

7. Why is pyridine a border line base while ammonia is a hard base?
8. What are the limitations of HSAB principle?
9. What are hard and soft acids and bases? Explain the HSAB principle with suitable examples.
10. Discuss the effect of substituent on hardness and softness of an acid.
11. How does HSAB principle explain the validity of the following reactions?
12. Discuss the contribution of π-bonding in soft-soft interactions.
13. Discuss giving examples, the applications of HSAB principle.
14. What are the theoretical justifications of HSAB principle?
15. Describe the origin of concept of hard and soft acids and bases.
16. Predict which way the following reactions will proceed:
17. Explain the following.
    a. What are the characteristics of a soft acid and a soft base?
    b. Exaplin HSAB principle. Discuss its applications.
    c. Explain clearly why hard acids co-ordinate with hard bases and soft acids co-ordinate with soft bases.

d. Hard-hard interaction is the major driving force for a reaction to proceed. Discuss

18. Explain the various limitations of HSAB principle.
19. What are hard acids and hard bases? Give their important characteristics.
20. What is HSAB principle? What are its uses?
21. How will you determine the relative strength of hard and soft acids and bases?
22. Why are hard-hard and soft-soft combinations preferred to hard-soft or soft-hard combination?
23. How does HSAB principle govern the occurrence of minerals?
24. What are hard acids and bases? Give their important characteristics.
25. How electronegativity can be used to explain hardness and softness of acids and bases?
26. Define HSAB principle. Discuss the applications of hard soft acid base principle.
27. State and explain HSAB principle.
28. Describe the contribution of π-bonding in soft-soft interactions.
29. What is symbiosis? Discuss theoretical basis of hardness and softness.

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UNIT- 2 METAL LIGAND BONDING IN TRANSITION METAL COMPLEXES

CONTENTS:

2.1 OBJECTIVES

This unit will help you to answer the following questions:

- What are the limitations of valence bond theory?
- What is the relative strength of a ligand?
- How can we compare the stability of complexes?
- What are the regions for colours associated with transition metal complexes?
- What are the basic premises of crystal field theory (CFT)?
- How molecular geometries associated with various d-orbital splitting patterns?
- How spectral and magnetic properties of transition metal complexes can be explained in terms of CFT concepts?

2.2 INTRODUCTION

Bonding in coordination chemistry has been described by many theories. In order to explain various properties exhibited by complexes, these theories were modified time to time.

The theory of Effective Atomic Number (EAN) rule was first used but found to be inadequate as behaviour of many complexes could not be explained by this method. The EAN rule states that stable compound should have electronic configuration of its nearest noble gas. There are many exceptions to this rule because it limits the coordination number possible for each metal. Octahedral complexes of many compounds show exception to this theory. However, the theory is sufficient to explain the bonding in metal complexes with metal in zero oxidation state.

Examples are [$Ni(CO)_4$] and [$Cr(CO)_6$] where the central metal has zero oxidation number and accommodates ligands sufficient enough to have the electronic configuration of their nearest noble gas. The theory cannot explain the reason for variation in coordination number, hence the need for another theory. Valence bond theory (VBT) is introduced to explain the reason for the variation in coordination number based on the number of hybridized orbitals of the metal used in bonding. It cannot explain fully the concept of colour and magnetic properties of complexes. Crystal Field Theory (CFT) is used to provide explanation for the spectra and magnetic properties of complexes.

2.3 LIMITATIONS OF VALENCE BOND THEORY

Valence Bond Theory (VBT) is a hybridization based theory proposed by the Pauling. According to them, metal- ligand bonding in a complex compound is of 100% covalent nature but there are certain limitations related to this theory which can be given as:

1. VBT cannot give the idea about the relative stabilities for different shapes and different coordination numbers in transition metal complexes, e.g. it cannot explain satisfactorily as to why Co^{+2} (d^7 configuration) forms both tetrahedral and octahedral complexes while Ni^{+2} (d^8 configuration) rarely form tetrahedral complexes.
2. VBT cannot explain why Cu^{+2} forms only distorted octahedral complexes even when all the six ligands are identical.
3. VBT cannot give the idea about the colour of the complexes.
4. VBT was failed to explain the strength of the ligands i.e. it cannot explain that which of the ligands will be called as stronger or weaker ligand.
5. According to the VBT magnetic moment of the complexes can determined by the following equation:

$$\mu_s = \sqrt{n(n+2)} \text{ B.M.}$$

But the actual value of magnetic moment is found to be slightly greater than as calculated by the above equation, which cannot be explained by VBT. In other word, we can say that VBT cannot give the idea about the orbital contribution in the magnetic moment of complexes.

6. This theory does not predict the magnetic behaviours of complexes. This theory only predicts the number of unpaired electrons and their correlation with stereochemistry is misleading. For example it was assumed that all the square planar complexes of Ni^{+2} (d^8 configuration) formed by dsp^2 hybridization, were diamagnetic in nature, while all tetrahedral complexes of Ni^{+2} formed by sp^3 hybridization were paramagnetic due to the presence of two unpaired electrons. By the X- ray analysis, it was observed that Ni^{+2} complexes have shown that one and the same complex can be obtained in both, paramagnetic form and diamagnetic form. VBT has no explanation for it.
7. According to VBT, inner orbital octahedral complexes with d^2sp^3 hybridization are covalent in nature and outer orbital octahedral complexes with sp^3d^2 hybridization are ionic in nature but there are certain complexes which have covalent character according to VBT but exhibit ionic property, which cannot be explained by VBT.
8. VBT cannot give any explanation for the order of reactivates of the inner orbital inert complexes of d^3, d^4, d^5 & d^6 ions and of the observed differences in the energies of activation in a series of similar complexes.
9. VBT was failed to explain the kinetics of the complexes.

2.4 AN ELEMENTARY IDEA OF CRYSTAL FIELD THEORY

In view of the above weaknesses, an alternative bonding model was applied to transition metal complexes. This is known as crystal field theory (CFT). Brethe and Van Vlick have been proposed a theory to explain the bonding in the ionic crystals, which is called as Crystal Field Theory (CFT). Initially this theory was propound for the ionic crystals but in 1952 Vage has been proposed this theory for the metal-ligand bonding in the complex compounds, which is known as CFT of the Coordination Chemistry.

Some of the postulates related to the CFT can be given as:

1. According to the CFT, central metal ion (CMI) of the complexes being surrounded by a number of ligands.

2. According to this theory, ligands can be of the two types which are given below:
   a. Negative ligandse.
   b. Neutral ligands also known as point dipole.
3. According to CFT, there does not occur any type of the overlapping between the orbitals of the ligand and CMI i.e. metal ligand bonding having zero % covalenay.
4. According to CFT, always there occur an electro static interaction between the +ve charge nucleus of the CMI and –ve charge of the ligand i.e. metal- ligand bonding having 100% ionic character. Complexes are thus presumed to be formed when CMI electrically attract ligand which may be either anions or dipolar molecules.

   If the complex contas neutral ligand, then the –ve pole of neutral ligand (point dipole) will be oriented towards the CMI.

2.4.1 CFT for the octahedral complexes

CFT of octahedral complexes can be defined in the following steps:-

Step I- Shape of 5- d orbital's of CMI

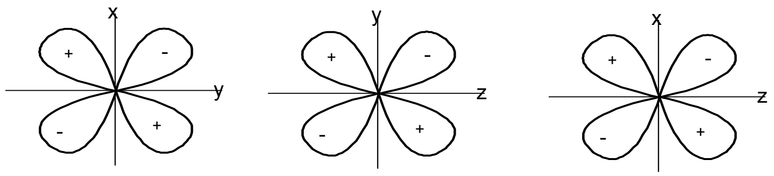
Five d- orbitals of the CMI can be divided into two different set of orbital's as given below:

a. t_{2g} set (Non-axial set of d-orbitals)

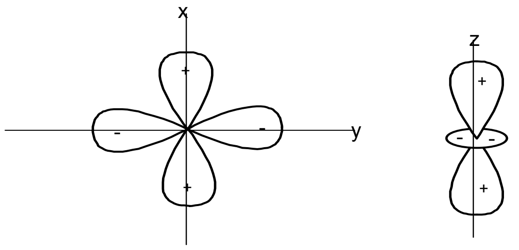
Three orbitals namely d_{xy} d_{yz} and d_{zx} orbitals are known as t_2g set of d orbitals. All these orbital being present between the axis due to which they are also known as Non-axial set of d- orbitals.

b. e_g set (Axial set of d- orbitals):

Two orbitals namely dx^2- y^2 and dz^2 are combindly known as e_g set of d orbitals. Both these orbitals being present over the axis due to which they are also known as axial set of d-orbitals (Figure 2.1).



t_2g orbitals (non axial)

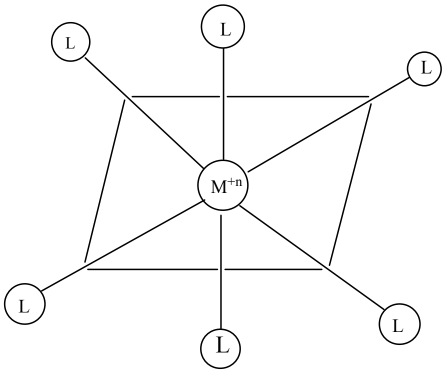


eg orbitals (axial)

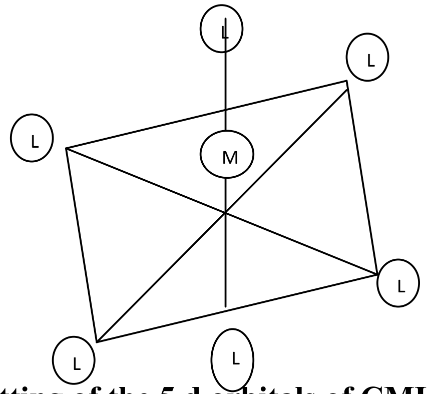
Figure 2.1: *Different types of d-orbitals*

Step II- Orientation of 6 ligands around the CMI in the octahedral complexes

In the octahedral complexes, all the six ligands being oriented toward the CMI from the six opposite corners of the three cartition axis, which can be represented as:



or



Step III- Crystal field splitting of the 5 d orbitals of CMI

When the CMI being present in the isolated form, then all the five d orbitals of the CMI have same energy and they are combindly known as degenerates of 5-d orbitals but if the ligand comes in the environment of CMI, the hypothetical energy of all the 5 d orbitals slightly increased due to the repulsion between the –ve charge of the ligand and 5 d orbitals. Finally, when the 6 ligands comes in the octahedral environment around the CMI to construct the octahedral complex, then 5 d orbitals of the CMI split into the lower energy t_{2g} set and higher energy e_g set of orbitals, which is called as crystal field splitting in the octahedral complexes. The energy difference between the spillited set of orbitals is known as crystal field splitting energy difference (Δ_o) (Figure 2.2).

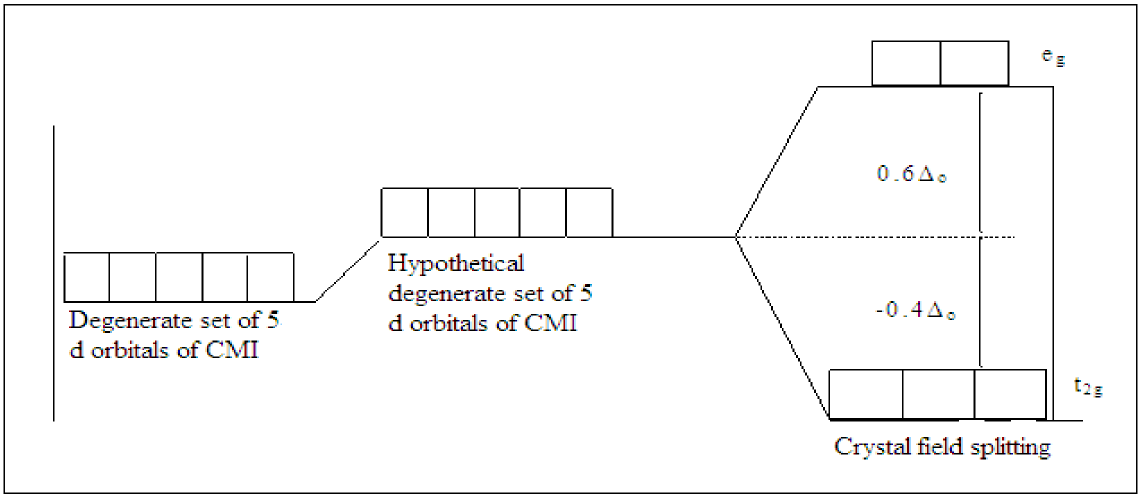


Figure 2.2: *Crystal field splitting of d orbitals in octahedral complex*

Step IV-Distribution of d^n configuration of the CMI in the splitted set of d-orbitals

To define the distribution of d^n configuration of CMI in the splitted set of d-orbitals, at first we have to define the strength of ligand i.e. spectro chemical series.

Spectrochemical Series: According to the concept of CFT, those ligands which have the more splitting power, are known as stronger ligands while on the other hand, those ligands which have the less spitting power, are known as weak ligands. After arranging the various ligands in order of their uncrossing or decreasing splitting power, the arrangement which is obtained is known as spectro chemical series.

Arrangement of certain ligands in order of their increasing splitting power according to spectrochemical series can be given as:

$I^- < Br^- < S^{-2} < SCN^- < Cl^- < NO_2^- < F^- < OH^- < H_2O < NCS^- < py < bipy < CN^- < CO$

The ligands interact weakly: - weak field ligands e.g. I^-, Br^-, S^{-2}, SCN^-, Cl^-

The ligands interact strongly: - strong field ligands e.g. NO,CN^- ,CO

Similarly, if metal ions are different with same ligand, Δ_o will be different. Metals with more positive charge and from 2nd and 3rd transition series interact more (higher splitting).

Now distribution of d^n configuration of the CMI can be given under the two conditions:-

(a) If Δ_o> P i.e. under the strong field octahedral condition

If the octahedral complex contains stronger ligand, than the value of Δ_o being greater than the mean pairing energy (p). Under such condition, distitution of the d^n configuration of CMI in the splitted set of d-orbitals can be given as shown in Figure 2.3.

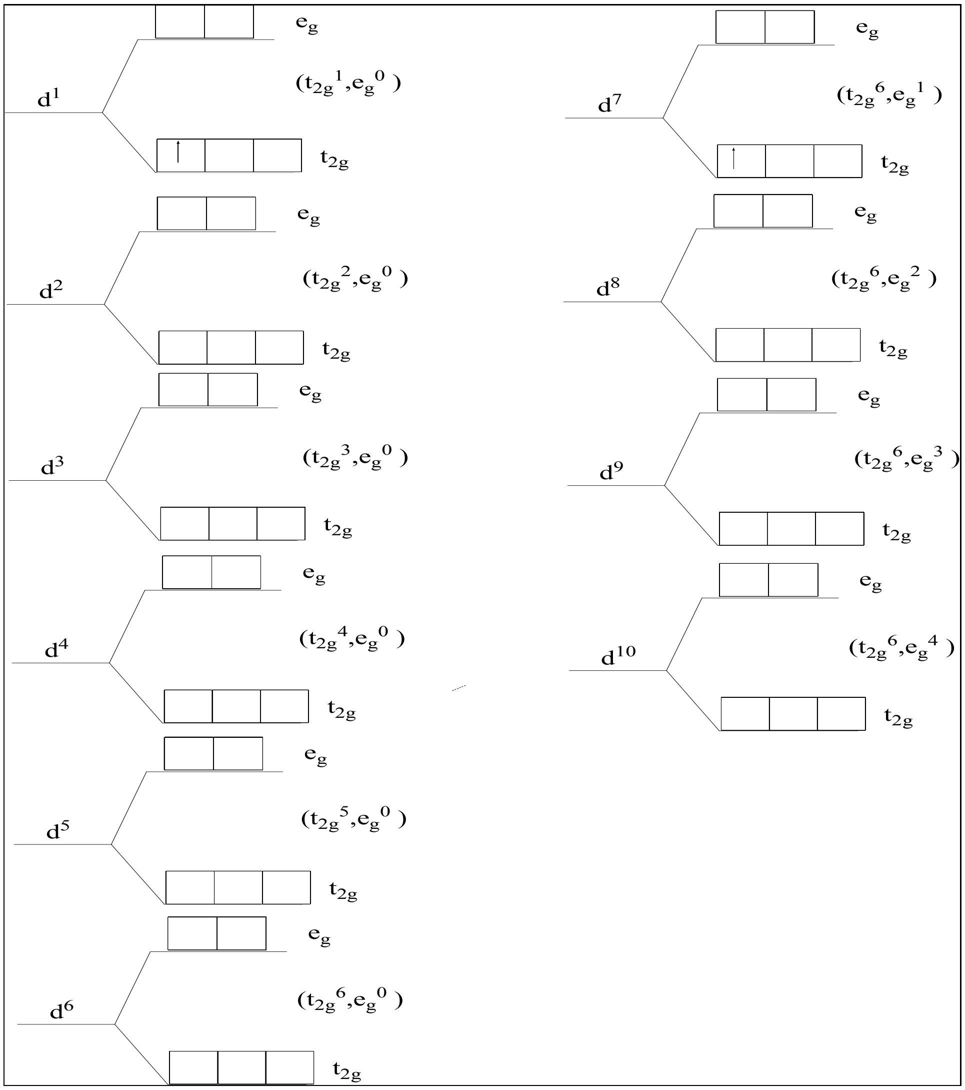


Figure 2.3: *Splitting of d^n configuration under the influence of strong field ligands*

(b) If Δ_o <P i.e. under the weak field octahedral condition

If the octahedral complex contains weak ligands, then the value of Δ_o being less than mean pairing energy (P). Under such condition, distribution of the d^n configuration of the CMI splits into set of d orbitals that can be given as shown in Figure 2.4.

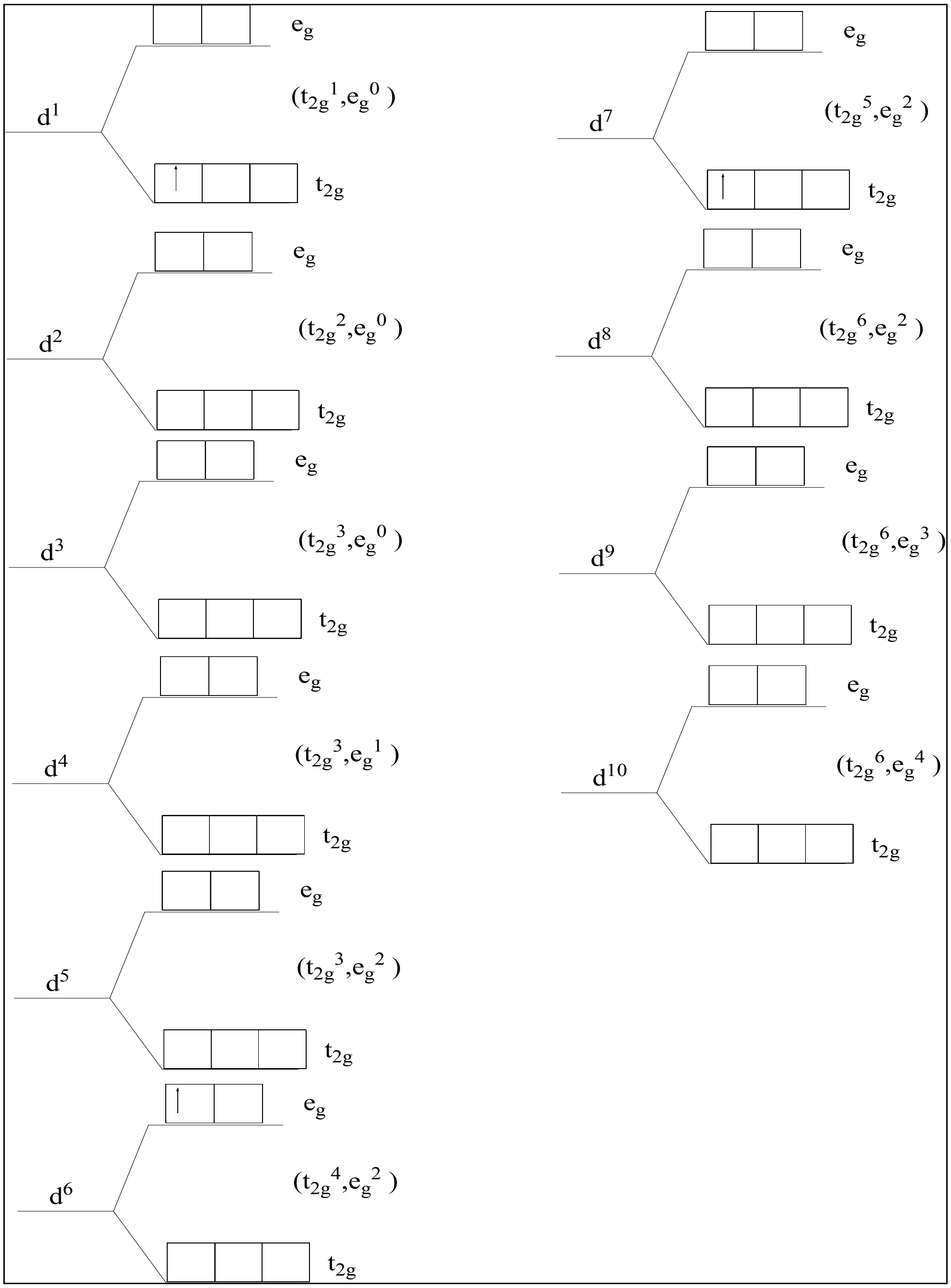
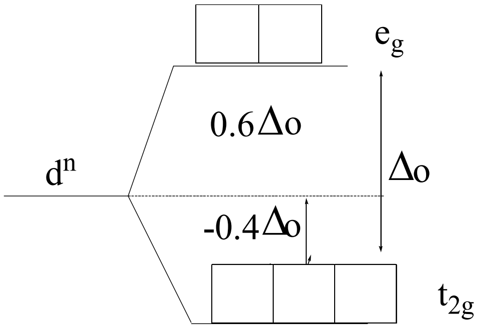


Figure 2.4: *Splitting of d^n configuration under the influence of weak field ligands in octahedral complex*

Step V: Crystal field stabilization energy in the octahedral complexes

Crystal field splitting of the d^n configuration in the octahedral complexes can be given as:



Suppose total number of electrons (e^-) in t_{2g} set = p (1 to 6)

Total no of e^- in e_g set = q (1to 4)

Than decrease in energy of d^n configuration by entrance of 1 e^- in t_{2g} set = $-0.4\ \Delta_o$

So, decrease in energy of d^n configuration by entrance of p e- in t_{2g} set = $(-4.\Delta_o)$ p

Increase in energy of d d^n configuration by entrance of 1e- in e_g set = $0.6\ \Delta_o$

So, increase in energy of d^n configuration by enterance of q e- in e_g set = $(0.6\Delta_o)$ q

Thus, total energy change of d^n configuration = $(-0.4\Delta_0)$ p + $(0.6\Delta_0)$ q

$$= (-0.4p + 6q)\ \Delta_0$$

This total amount of the energy change for the d^n configuration is known as crystal field stabilization energy (CFSE) for the d^n configuration of CMI in the octahedral complexe.

Thus,

$$\textbf{CFSE} = (-0.4p + 0.6q)\ \Lambda_0$$

If the value of mean pairing energy being P and number of pairs of electrons in the t_{2g} or e_g orbitals being n, then nP amount of energy will also increases the energy of d^n configuration.

Thus, the net energy will be

$$\boxed{\textbf{CFSE} = (-0.4\ p + 0.6q)\ \Delta_o\ + nP}$$

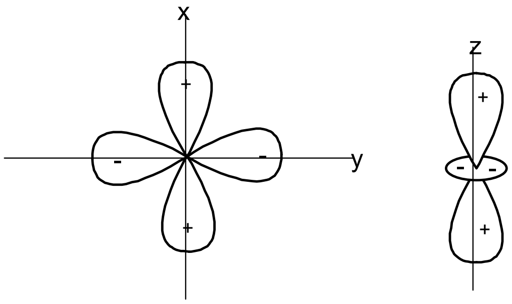
2.4.2. CFT for the tetrahedral complexes

CFT for tetrahedral complexes can be explained under the five different steps, which are given below:

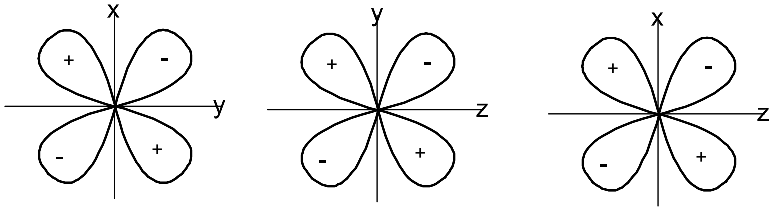
Step I Shape of 5- d orbitals: All the 5-d orbitals of the CMI can be devided into 2 different sets of orbitals, which are given below (Figure 2.5).

(a) 'e'- set: d_{x2-y2} and d_{z2} orbital are combindly known as 'e' set of axed set orbitals.

(b) t_2 set: d_{xy} , d_{yz} & d_{zx} orbitals are cmbindly known as '$t_2^{'}$ – set or non axial set of orbitals.



e orbitals (axial)

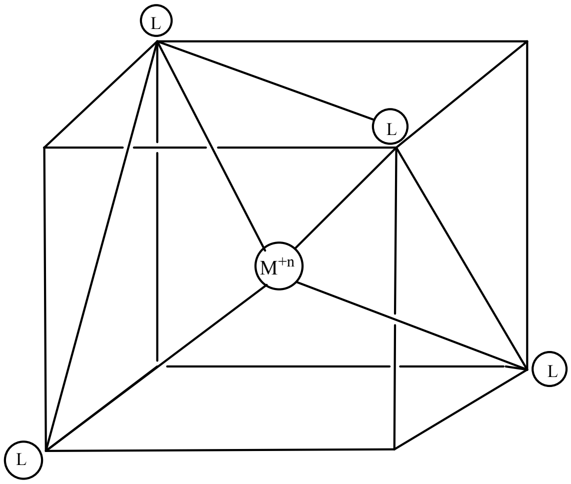


t_2 orbitals (non axial)

Figure 2.5: *Two Set of d orbitals in tetrahedral complex*

Step II- Orientation of 4 ligands around the CMI in the tetrahedral complexes

In the tetrahedral complexe, all the 4 ligands being oriented towards the CMI from the non axial position that can be represented as:



Step III- Crystal filed splitting of the 5 d orbitals of CMI in tetrahedral complexes

When the CMI being present in the isolated form, then all the 5 d orbitals of the CMI have same energy and they are combindly known as degenerate set of 5 d orbitals, but when the 4 ligands comes in the environment of CMI, then there occur the partial hypothetical repulsion between the –ve charge of the ligands and all the 5 d orbitals due to which energy of all the 5-d orbitals of CMI is slightly increased. Finally due to the tetrahedral environment from the non axial position, there occur the splitting of all the 5 d orbitals of CMI into lower energy e set and higher energy t_2 set and this is known as crystal field splitting in the tetrahedral complexes. The energy difference between the splitted set of d- orbitals is known as crystal field splitting energy difference of tetrahedral complex (Δ_t) (Figure 2.6).

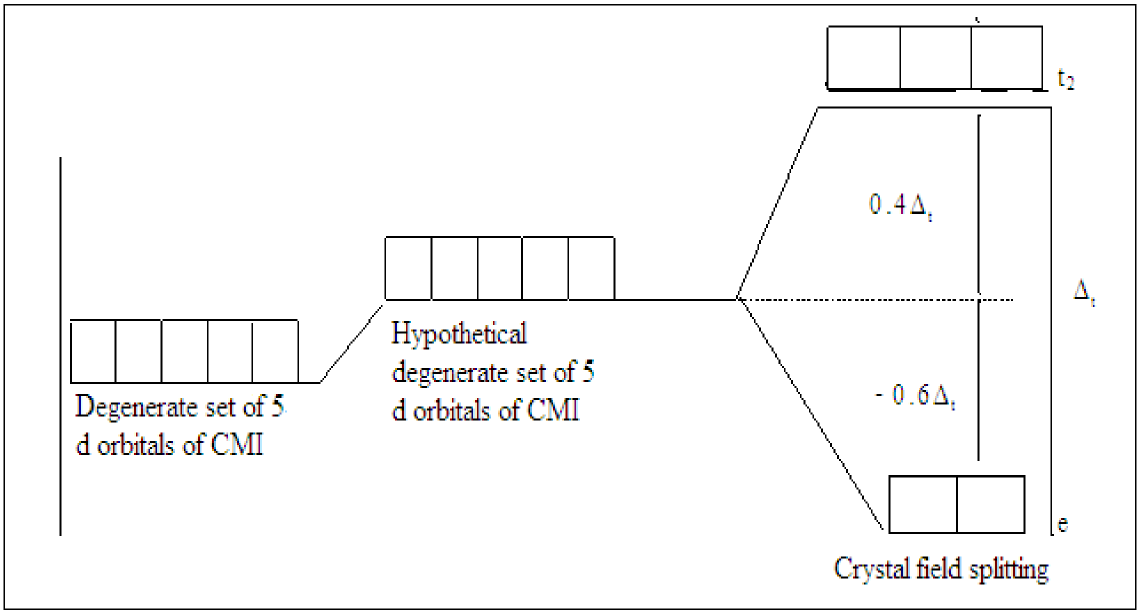


Figure 2.6: *Crystal field splitting in tetrahedral complexes*

Step IV- Distribution of d^n configuration of CMI in the tetrahedral complexes (Figure 2.7)

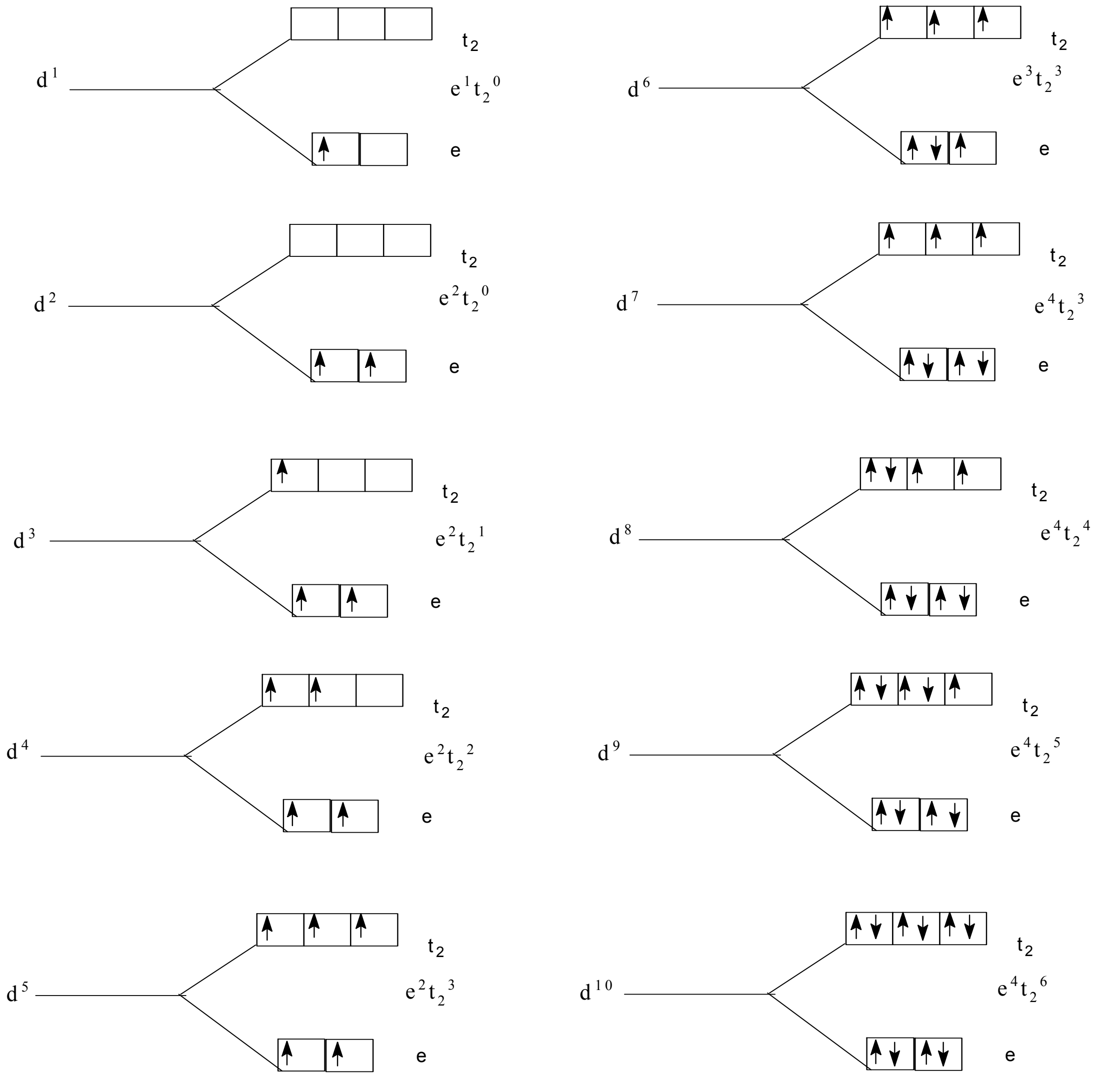
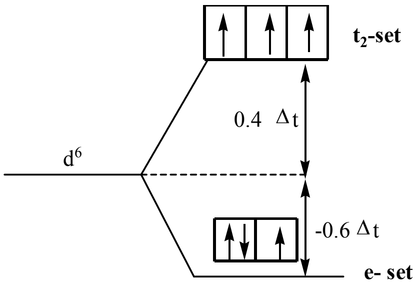


Figure 2.7: *Splitting of d^n configuration under the influence of weak field ligands in tetrahedral complex*

Step V- Crystal field stabilization energy in the tetrahedral complexes

Crystal field splitting diagram for the d^n configuration of CMI in the tetrahedral complexes can be represented as:



Suppose no. of e in e set = q (1to 4)

No. of e^- in t_2 set = p (1to 6)

Decrease in the energy of d^n configuration due to the entrance of one e^- in e set = $-0.6\ \Delta_t$

Decrease in energy of d^n configuration due to the entrance of qe^- in e set = $-0.6\ \Delta_t \times q$

Increase in energy of d^n configuration due to entrance of one e^- in t_2 set = $0.4\Delta_t$

So, increase in energy of d^n configuration due to entrance of p e- in t_2 set =$0.4\ \Delta_t \times p$

Net energy change of d^n configuration = $(-0.6\ \Delta_t \times q + 0.4\ \Delta_t \times p)$

$= (-0.6 \times q + 0.4 \times p)\ \Delta_t$

This net amount of the energy change for the d^n configuration is known as CFSE of the tetrahedral complexes.

i.e. $\boxed{\text{CFSE}= (-0.6q + 0.4P)\ \Delta_t}$

Suppose the value of mean pairing energy is denoted by the symbol P and total number of the pair in the splitted set of d orbitals denoted by the symbol n, then the nP amount of energy will also be involved in the CFSE formula.

Thus

$$\boxed{\text{CFSE}= (-.6q + .4P)\ \Delta_t + nP}$$

2.4.3 CFT for the square planar complexes

CFT of the square planar complexes is arises from the CFT of octahedral complexes. The crystal field splitting diagram for the square planer complexes originated from the splitting diagram of octahedral complexes in the two steps which can be represented as:

If the two trans ligands in an octahedral ML_6 complex (consider those along the z-axis) are moved either towards or away from the metal ion, the resulting structure is said to be tetragonally distorted. Ordinarily such distortions are not favored since they result in a net loss of bonding energy. In certain situations, however, such a distortion is favored because of a Jahn-Teller effect. A complex of general formula *trans*-Ma_2b_4 also will have tetragonal symmetry. For now, we will consider the limiting case of tetragonal elongation, a square planar ML_4 complex, for the purpose of deriving its d-orbital splitting pattern. The crystal field diagram for the tetragonally distorted complex and the square-planar complexes is shown below. Removal of ligands from z-direction completely leads to the square-planar geometry (Figure 2.8). This geometry is favoured by metal ions having a d^8 configuration in the presence of a strong field. This combination gives low-spin complexes where the first four orbitals are occupied and the high-energy d_{x2-y2} orbital is unoccupied.

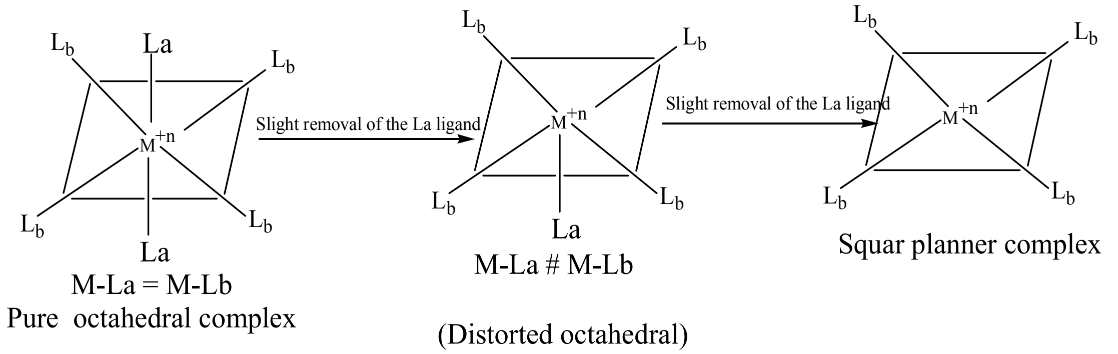


Figure 2.8. Formation of square planare complex from octahedral complex

Crystal Field splitting for square planar complex

Square planar complexes are similar to the octahedral complexes. The difference is that square planar complexes have two ligands missing in the z axis. There is a very large energy gap between the d_{x2-y2} orbital and the lower four orbitals. Square planar complexes are favored by metal ions with d^8 electron configurations. Since this configuration favours low-spin complexes in which the four lower-energy orbitals are filled and the high energy d_{x2-y2} orbital is empty. The crystal field splitting diagrame of square planar complex is given in Figure 2.9.

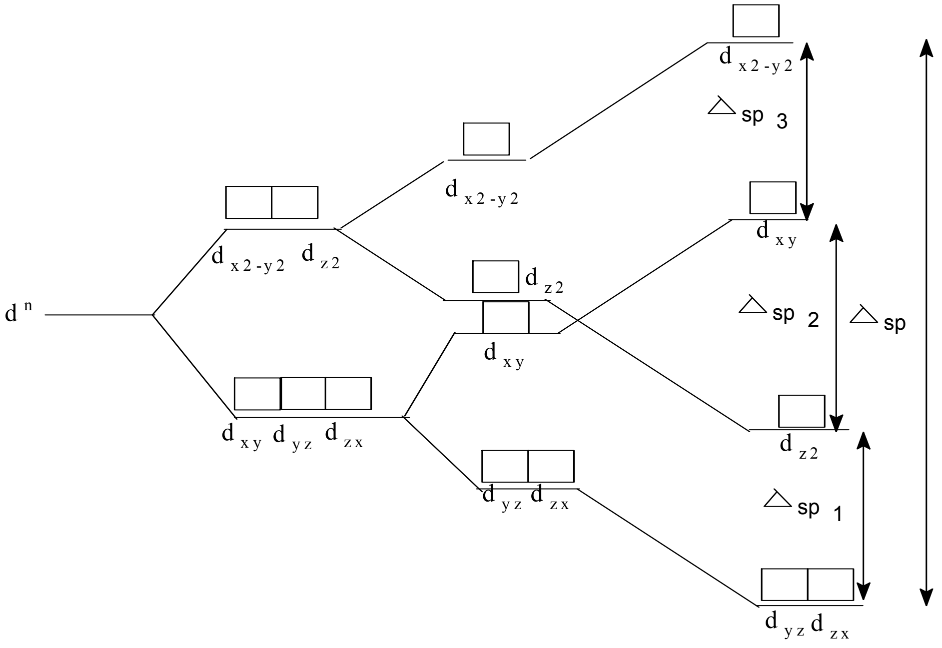


Figure 2.9. Crystal field splitting diagrame of square planar complex

2.5 FACTORS AFFECTING THE CRYSTAL FIELD PARAMETER

Some factors which can affect the value of Δ (Crystal field splitting energy difference) are given below:

2.5.1 Nature of ligands

With the increase in the strength of the ligands present in the complexes, the Δ value for the complexes is increases.

Explanation: With the increase in the strength of the ligand, the ability of the ligands to cause the closer approach with the central metal atom (CMA) increases by which the repulsion between the ligand and d orbitals as well as Δ value also increases.

Examples:

a. $[Fe(CN)_6]^{-4}$ ion contains the stronger CN^- ligands while $(Fe(Cl)_6]^{-4}$ ion contains the weak Cl^- ligands due to which the Δ value for $(Fe(CN)_6]^{-4}$ ion is found to be more than $(Fe(Cl)_6]^{-4}$ ion.

b. $[Co(F)_6]^{-3}$ ion contas the stronger F^- ligand while $[Co(Cl)_6]^{-3}$ ion contains the weak Cl^- ligand due to which the Δ value for $[Co(Cl)_6]^{-3}$ ion is found to be less than $[Co(F)_6]^{-3}$ ion.

2.5.2 Nature of central metal atom (CMA)

a. Same CMA with different charge

If the complexes containing same CMA with the different charge, then the complex with the higher +ve charge of the CMA will exhibit higher Δ value.

Explanation: In the complexes containing different charge on the CMA, the complex with the higher +ve charge of the CMA exhibit higher Δ value because the CMA with higher +ve charge can attract the ligand more closer toward itself by which the repulsion between the ligand and d- orbitals of CMA as well as Δ value is increases.

b. Different CMA with the different charge

If the complexes contain different charge, then the complex containing higher +ve charge on the CMA exhibit higher Δ value.

Explanation: If the complexes contain different CMA with the different charge, then the complex containing higher +ve charge on CMA exhibit the higher Δ value because the CMA with the higher +ve charge can attract the ligand more closer toward itself due to which the repulsion between the ligand and d- orbitals of CMA as well as Δ value are increases.

Examples: a. $[V(H_2O)_6]^{+2}$ complex ion contains lower +ve charge (+2) on the CMA while $[Cr(H_2O)_6]^{+3}$ ion contains higher + ve charge (+3) on the CMA due to which $[Cr(H_2O)_6]^{+3}$ ion will exhibit higher Δ value.

b. $[Fe(NH_3)_6]^{+3}$ ion contains higher + ve charge of the CMA (+3) while $[Fe(NH_3)_6]^{+2}$ ion contains lower + ve charge of the CMA (+2) due to which $[Fe(NH_3)_6]^{+3}$ ion will exhibit higher Δ value.

c. Different CMA with same charge

If the complexes contain different CMA with the same charge, then that complex containing lower d^n configuration of CMA will exhibit higher Δ value.

Explanation: This can be due to shielding effect.

Example: $[Fe(H_2O)_6]^{+2}$ ion has $3d^6$ configuration of CMA while $[Co(H_2O)_6]^{+2}$ ion contains the $3d^7$ configuration of CMA and both these complexes have same charge value, thus, the former complex ion with lower d^n configuration will exhibit high Δ value.

d. Principal quantum no of d^n configuration

With the increase in the Principal quantum number of d^n configuration of CMA, the value of Δ is increases. In other word the Δ value for the complexes of II-transition series elements being 30% greater than the Δ value for the complexes of I-transition series elements and the Δ value for the complexes of III- transition series element being greater than the II-transition series elements.

Example: $[Fe(CN)_6]^{-4}$ ion exhibits lower Δ value than the $[Ru(CN)_6]^{-4}$ ion because Ru have higher Principal quantum number of d^n configuration in comparison to Fe.

2.6 APPLICATIONS OF THE CFT

The following properties of transition metal complexes can be explained on the basis of CFT.

2.6.1. According the CFT, if the splitted set of d-orbitals of the CMI present in the complexes contains the unpaired e^- than the complex will be called as paramagnetic in napture while if the splitted set of d-orbitales of the CMI does not contain the unpaid e^-, then the complex will be called as diamagnetic in nature.

Example:

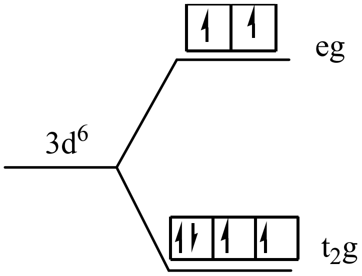
(I) $[(Co(F)_6]^{-3}$ ion

Configuration of Co = $3d^7, 4s^2$

Oxidation state of Co = +3

Configure of Co+3 = $3d^6$

According to CFT



The splitted set of d- orbitals contain 4 unpaired e^- due to which the complex ion $[Co(F)_6]^{-3}$ ion will be paramagnetic in nature according to CFT and its magnetic moment will be:

$$\mu = \sqrt{n\,(n+2)} \quad \text{B.M.}$$

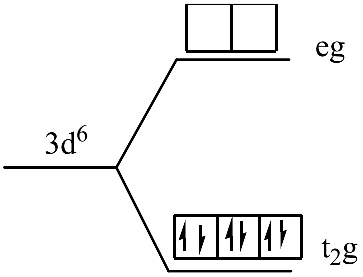
$$\mu = \sqrt{4\,(4+2)} = 4.9.\ \text{B.M.}$$

(II) $[Co(NH_3)_6]^{+3}$ ion

Configuration of Co = $3d^7\ 4S^2$

Oxidation State of Co = +3

Configuration of Co+3 = 3d6



According to CFT The splitted set of d- orbitals do not contain the unpaired e^- due to which the complex ion $[Co(NH_3)_6]^{+3}$ ion will be diamagnetic in nature.

2.6.2 Stability of the oxidation states

With the help of CFT we can compare the stability of the different oxidation states exhibited by a particular transition metal element under the strong field and weak field condition by using the CFSE concept.

Example: Co (III) is more stabilized than the Co (II) under strong filed condition while Co (II) is more stabilized than the Co (III) under the weak filed condition which can be explained by the CFSE concept of CFT.

Configuration of Co(III) under strong field condition = t_{2g}^6

CFSE =6 x -0.4 Δ_o + 3P (pairing energy) = -2.4 Δ_o + 3P

Configuration of Co(II) under strong field condition = $t_{2g}^6e_g^1$

CFSE = 6 x -0.4 Δ_o + 1 x 0.6 Δ_o + 3P (pairing energy) = -1.8 Δ_o + 3P

Configuration of Co(III) under weak field condition = $t_{2g}^4e_g^2$

CFSE =4 x -0.4 Δ_o + 2 x 0.6 Δ_o + 1P (pairing energy) = -0.4 Δ_o + 1P

Configuration of Co(II) under strong field condition = $t_{2g}^5e_g^2$

CFSE = 5 x -0.4 Δ_o + 2 x 0.6 Δ_o + 2P (pairing energy) = -0.8 Δ_o + 2P

Higher the value for CFSE, higher will be the stability of complex.

2.6.3 Colour of the complexes

To define the colour of the complexes formed by the d- block complex, at first, white light is passed from the solution of complex compound then,

(i.) If whole of the white light is transmitted by the sample, then the complex will be called as white in colour.

(ii.) If whole of the white light is absorbed by the sample, then the complex is called as black in colour.

(iii.) If some of the radiations of the white light are absorbed and some other radiations are transmitted, in such condition, the complex can be coloured only if the absorbed radiations belong to the visible range (4000A° – $7000\ \text{A}^{\circ}$)

When the complex absorbed the radiation of visible range, then the actual colour of the complex will depend on the wavelength of that particular radiation which is absorbed by the complex compound:-

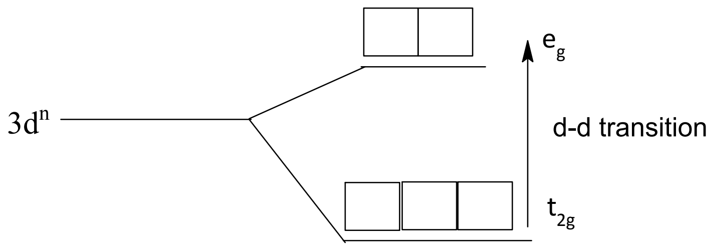
4000A^0 4350A^0 4800A^0 4900A^0 5000A^0 5600A^0 5800A^0 5900A^0 6050A^0 7000A^0

Colour of absorption	Voilet	Blue	Green blue	Blue Green	Green	Yellow green	Yellow	Orange	Red

Complementry colour	Yellow Green	Yellow	Orange	Red	Purple	Voilet	Blue	Green	Blow Green

The mechanism which is responsible for the colour in the complexes can be defined by d-d transition phenomena.

According to d-d transition phenomena, when the e^- present in the lower energy splitted set of d- orbitals of the CMI obsorbs the radiation of any particular wavelength, then there occur the transition of e^- to the higher energy splitted set of d- orbitals, which is known as d-d transition phenomena, that can be represented as:-



Color of the absorption as well as complementary colour corresponding to the d-d transition phenomena have already been discussed.Those complexes which containing the d^{10} or d^0 configuration of CMI being colourless because such complexes cannot exhibit the d-d transition phenomena.

Factor affecting the colour of the colour of the complexes

Colour of the complexes can be affected by the two different factors, which are given below:

(a) Nature of the ligands: With the change is the strength of the ligands present in the complexes, the value of crystal field splitting energy difference (Δ) between the splitting set of d- orbitals is changed by which the wavelength radiation for d-d transition phenomena as well as colour of the complex is changed.

(b) Nature of the CMI: With the change in the + ve oxidation state of CMI present in the complex, the value of Δ also changed by which the wavelength of radiation for d-d transition phenomena as well as colour of the complex will be changed.

2.6.4 Determination of the spinel structure

$Mg^{+2}\ Al_2^{+3}\ O_4$ is called as mineral spinel and accordingly all the mixed oxides having the general formula $A^{+2}\ B_2^{+3}O_4$ are known as spinals in which both the A^{+2} and B^{+3} cations can be same or different.

Oxide ion present in the spinel undergo cubic clossed packing to construct two types of void's known as tetrahedral void and octahedral void.

(i) If all the +2 cations are occupied in the tetrahedral voids and all the +3 cation occupied in the octahedral voids then the spinal is known as simple or normal spinel, which can be represented as:-

$$A^{+2}\ [B_2^{+3}]\ O_4$$

(ii) If all the +2 cations and half of the +3 cations are occupied in the octahedral voids while the remaining half of the +3 cations are occupied in the tetrahedral voids then the spinel is known as inverse spinel, which can be represented as:

$$B^{+3}\ [A^{+2}\ B^{+3}]\ O_4$$

Now the nature of spinels can be determined with the help of CFSE for the A^{+2} & B^{+3} cations under weak field octahedral and tetrahedral conditions.

2.6.4.1 Spinel Structure of Mn_3O_4

To determine the spinel structure of Mn_3O_4, at first we have to consider the Mn^{+2} and Mn^{+3} ions in the octahedral and tetrahedral voids to construct the weak field octahedral and tetrahedral complexes. Then after that we can calculate the CFSF value under weak field octahedral and tetrahedral conditions.

	$Mn^{+2}(3d^5)$	**$Mn^{+3}(3d^4)$**
CFSE under strong field octahedral condition	0	$-0.9\ \Delta_o$
CFSE under strong field tetrahedral condition	0	$-0.27\ \Delta_o$

Since, the value of CFSE for Mn^{+3} under weak field octahedral condition is more –ve, which indicates that Mn^{+3} will have the tendency to occupied in the octahedral voids i.e. the Mn_3O_4 will have simple spinel (Normal spinel) structure.

$$Mn_3O_4 \rightarrow Mn^{2+}[Mn_2^{3+}]O_4$$

2.6.4.2 Spinel structure of Fe_3O_4

Fe_3O_4 containing one of the Fe in the +2 oxidation states and 2Fe in the +3 oxidation state. To determine the spinel structure of Fe_3O_4, at first we have to consider the Fe^{+2} and Fe^{+3} in the octahedral and tetrahedral voids to construct the weak filed octahedral and tetrahedral complexes. Then after that we can determine the CFSE tetrahedral under the weak field octahedral and tetrahedral conditions.

	$Fe^{+2}(3d^6)$	**$Fe^{+3}(3d^5)$**
CFSE under strong field octahedral condition	$-0.4\ \Delta_o$	0
CFSE under strong field tetrahedral condition	$-0.27\ \Delta_o$	0

Since, the value of CFSE for the Fe^{+2} ion under weak field octahedral condition is more –ve, this indicates that the Fe^{+2} will have the tendency to occupied in the octahedral void i.e. the i.e. the Fe_2O_4 will have inverse spinal structure.

$$Fe_3O_4 \quad Fe^{+3}[Fe^{+2}Fe^{+3}]O_4$$

2.7 LIMITATIONS OF CFT

1. CFT considers the splitting of d- orbital but it does not consider the splitting of other orbitals in the ligand field environment.

2. CFT can’t explain that how certain ligands having more splitting power/ability while certain other ligands having very low splitting ability.

3. According to the CFT, metal ligand bond having 100% ionic character but from the various experiments, it was proved that metal ligand bonds have certain extent of covalence with the ionic character.

2.8 LIGAND FIELD THEORY AND MOLECULAR ORBITAL THEORY

The crystal field theory is modified to take into account the existence of some degree of covalence character in transition complexes based on the evidence from electron spin resonance spectra which shows that certain percentage of the electrons is diffused into the ligand orbitals. Consequently, the bond existing in the complexes is not purely electrostatic. The modification of CFT results into adjusted Crystal Field Theory also called Ligand Field theory (LFT). If the degree of diffusion or overlap is in excess, the LFT will not hold rather a pure covalent treatment will be suitable hence, the use of Molecular Orbital theory (MOT). The LFT can be considered as a mid-point between electrostatic and covalent description of bonding in metal complexes. The LFT is purely a parameter based model involving the uses of experimentally derived data or parameters like crystal field stabilization energy and Racah parameters which are derived from electronic spectra of complexes.

Molecular Orbital Theory is the result of overlap of bonding atomic orbital of the ligands and the hybridized orbital of the metal leading to formation of both bonding and antibonding molecular orbitals. In a molecular bonding scheme, the numbers of bonding and antibonding orbitals are equal but the antibonding orbitals canceled out the resultant effect of the bonding orbitals. Molecular Orbital Theory in an octahedral complex can be illustrated with complex $[Co(NH_3)_6]^{3+}$ in which metal–ligand σ-bonding is dominant. In the construction of a molecular orbital energy level diagram for such a complex, many approximations are made and the outcome is considered to be qualitatively accurate. Despite this, the results provide useful explanation on metal–ligand bonding.

Chromium ion (Cr^{3+}) is a first row metal ion, the valence shell atomic orbitals are 3d, 4s and 4p. In octahedral symmetry, the s orbital has a_{1g} symmetry, the p orbitals are degenerate with t_{1u} symmetry, and the d orbitals split into two sets with e_g (d_{z2} and d_{x2-y2}) and t_{2g} (d_{xy}, d_{yz} and d_{xz}) symmetries. Each ligand, NH_3, provides one orbital. Six orbitals from the ligands are assigned a_{1g}, t_{1u} and e_g symmetries. The nine valence orbitals of the metal are grouped into bonding and nonbonding orbitals the bonding orbitals are; 4s, $3p_x$, $3p_y$, $3p_z$, d_{x2-y2} and d_{z2} which are in the direction of the approaching, hence, suitable for overlapping. The t_{2g} set orbitals (d_{xy}, d_{xz}, d_{yz}) which are not exactly in the direction of the approaching ligands are considered as non-bonding. The diagram below shows the Molecular orbital arrangement for the complex $[Co(NH_3)_6]^{3+}$. The six ligand orbitals and six orbitals of the metal are grouped into six bonding molecular molecular orbitals (BMOs) and anti bonding molecular molecular orbitals (ABMO s). Electrons from the ligands are filled into the bonding MOs while the d electron(s) are filled into nonbonding t_{2g} orbitals and the Lowest Unoccupied Molecular Orbitals (LUMO) which are the antibonding MOs (Figure 2.10).

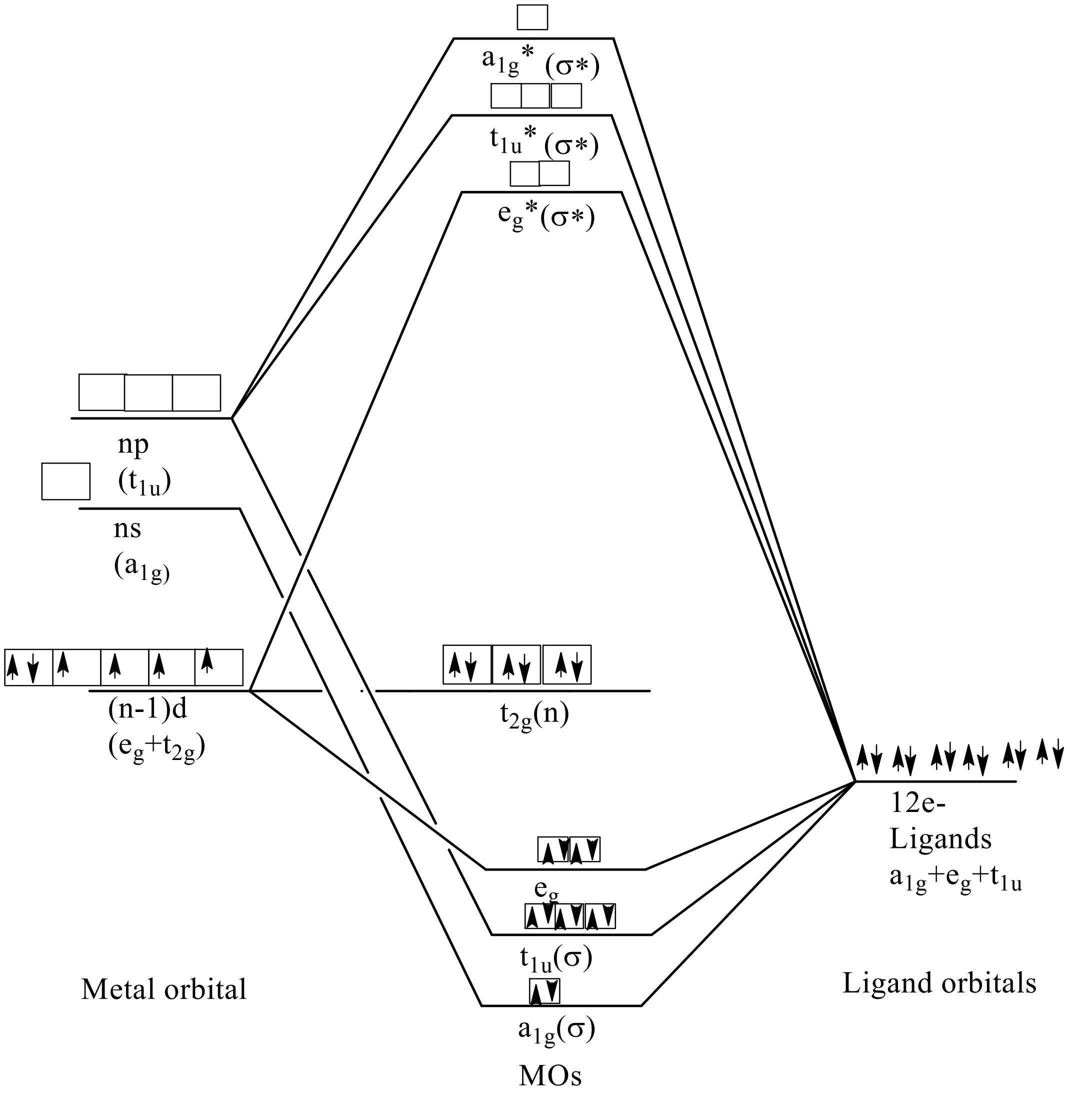


Figure 2.10. *Molecular orbital energy level diagram of* $[Co(NH_3)_6]^{3+}$

2.9 SUMMARY

From metal ligand bonding theories in transition metal complexes, the following deductions can be made:

- The shape of complex is determined by the coordination number of central metal atom or ion, hybridization and type of atomic orbitals of the metal hybridised.

- With concept of inner and outer orbital complexes, magnetic properties of low and high spin complexes can be predicted. Electrostatic treatment of bonding complexes provides information on colour and spectra of complexes.
- The Ligand Field and Molecular Orbital theories help to explain the concept of covalence observed in some complexes.

2.10 TERMINAL QUESTIONS

1. Give one example of an outer orbital complex.
2. Calculate CFSE for high spin octahedral complex.
3. Draw energy level diagram showing splitting of five d-orbitals ocatehdral field.
4. Calculate CFSE for tetrahedral complex.
5. Which of the two $[Co(H_2O)_6]^{+2}$ or $[Co(NH_3)_6]^{+3}$ has smaller Δ value?
6. What is the difference between low-spin and high-spin complexes?
7. What is meant by spectrochemical series?
8. Define crystal field stabilization enregy.
9. Explain how the orientation of d-orbitals in space leads to their splitting in a tetrahedral field of ligands.
10. Define CFSE and calculate its value for d^5 system in octahedral and tetrahedral field.
11. Explain crystal field splitting in square planar complexes.
12. How will you account for the purple colour of $[Ti(H_2O)_6]^{3+}$?
13. Explain how the orientation of d-orbitlas in space leads to the splitting in a tetrahedral field of lignads.
14. Define CFSE and calculate its value for system in octahedarl and tetrahedral fields.
15. (a) Give the salient features of crystal field theroy.
    (b) What is meant by spectrochemical series? Explain.
    (c) Explain the crystal field splitting in case of square planar complex.
16. (a) Define crystal field splitting energy and discuss the crystal field splitting of d-orbitlas in case of octahedral complexes..
    (b) Give reasons for the smaller value of crystal field splitting in tetrahedral than in octahedral complexes.
    (c) Discuss the bonding in and in terms of crystal field theory.

(a) Write electronic configuration and calculate CFSE for d^6 (high spin octahedral).

(b) Calculate the magnetic moment for the complex (spin only value).

18. Define crystal field stabilization energy. Calculate its value for low and high spin Octahedral complexes.

19. (a) Give a brief acoount of limitation of valence bond theory in transition metal complexes.

(b) Find out the number of unparied electrons in strong and weak octahedral complexes of cobalt.

(c) Explain why is purple in aqueous solution, while is colourless?

(d) Calculate the values of CFSE for the following systems:

(i) Tetrahedral (ii) Octahedral, high spin

20. (a) How are magnitude of crystal field splittig in octahedral and tetrahedral complexes realted?

(b) Calculate CFSE for weak field & strong field cobalt complexes.

(c) Discuss splitting of d-orbitals of metal atom or ion in octahedral field of ligands.

26. (a) Draw diagram showing splitting in square planar complexes.

(b) Using simple crystal field theory, explain why is colourless.

(c) Calculate the crystal field stabilization energy for octahedral complexes in a weak field and also in strong field. Calculate the spin-only magnetic moment for these complexes.

27. (a) Discuss the crystal field splitting of d-orbitlas in case of tetrahedral complexes.

(b) What is crystal field theory? How does this theory account for the fact that is paramagnetic but is diamagnetic though both are octahedral?

28. (a) Discuss the limitations of valance bond theory.

(b) Explain on the basis of CFT that $[Co(NH_3)_6]^{3+}$ is diamagnetic but $[Co(F)_6]^{3-}$ is paramagnetic.

(c) What are low and high spin complexes?

29. (a) The magnetic moment of $[Fe(H_2O)_6]^{3+}$ is 5.92 B.M. and that of $[Fe(CN)_6]^{3-}$ is 1.73 B.M. explain on the basis of CF theory.

(b) Explain why in tetrahedral complexes the subscript ‘g’ has been dropped from the orbital notation.

30. Calculate CFSE for the following:

(i) strong field octahedral (ii) tetrahedral

(iii) weak field octahedral (iv) tetrahedral

31. If the frequency of radiation absorb by a complex ion in the visible reason is 5.30 X 10^{14} sec^{-1}. What is the colour of the complex ion?

32. $[Fe(CN)_6]^{-4}$ ion is diamagnetic and $[Fe(CN)_6]^{-3}$ ion is paramagnetic although both the ions containing strong ligands explain it with the help of CFT?

33. For $[Cr(H_2O)_6]^{+2}$ ion, the mean paring energy P is found to be 23500cm^{-1} and the magnitude of Δ_o is 13900 cm^{-1}. Calculate the CFSE for this complex ion corresponding to strong field & weak field conditions.

34. Calculate the number of unpaired e^- and CFSE value in the following complexes:

a. $[Fe(NH_3)_6]^{+3}$ ion

b. $[Cr(NH_3)_6]^{+3}$ ion

c. $[Co(Cl)_4]^{3-}$ ion

35. Calculate the CFSE value for the following systems:

(a) d^1 octahedral

(b) d^1 tetrahedral

(c) d^5 low spin octahedral

(d) d^5 high spin octahedral

36. Explain why Co^{+3} is more stable under strong field condition in comparison to Co^{+2} while Co (II) is more stable in the weak filed $cond^n$ in compare to Co (III)?

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UNIT -3 MAGNETIC PROPERTIES IN TRANSITION METAL COMPLEXES

CONTENTS:

3.1 OBJECTIVES

By going through this unit, you will be to understand magnetic properties of transition etal complexes and the magnetic susceptibility of a paramagnetic sample by measuring the force exerted on the sample by a magnetic field gradient.

3.2 INTRODUCTION

By studying the magnetic properties of a substance, we can get an insight into the distribution of electrons in the constituent atoms or ions. We know that the magnetic properties like magnetic moment and magnetic susceptibility arise due to the presence of unpaired electrons. The distinction between high spin and low spin complexes can be made on the basis of their magnetic properties. We observe that most of the transition metals and their salts and complexes have unpaired electrons spins about its axis and therefore, shows magnetic properties. It acts as a tiny magnet. The molecules with paired electrons are diamagnetic. This is because the paired electrons have their spins in opposite direction and their magnetic moments cancel each other. The picture is different in the case of molecules having unpaired electrons. The magnetic moments produced by individual electrons in this case are not cancelled, rather they reinforce each other.

3.3. TYPES OF MAGNETIC BEHAVIOUR

The salient features of various types of magnetic behaviours are as given below:

3.3.1 Paramagnetic substances

The substances which, when placed in magnetic field, allow the magnetic lines of force to pass through them rather than through vacuum, are called paramagnetic substances and the property due to which they show this behaviour is called paramagnetism.

Paramagnetism is subdivided in to (i) normal paramagnetism (ii) temperature independent and (iii) Pauli or free electron paramagnetism.

Origin of paramagnetism: Paramagnetism of a substance consisting of atoms, ions or molecules is caused by the presence of unpaired electrons in the substance. The greater the number of unpaired electrons, the greater will be paramagnetism shown by the substance. Paramagnetic molecules are free to orient themselves ideally in the gas phase, but in practice, also in solution and even in the solid state, if magnetically dilute (Figure 3.1).

3.3.2 Diamagnetic substances

Substances which do not possess unpaired electrons (their electrons are paired), do not show any magnetic moment. Such substances are repelled by external magnetic field. This is because, the magnetic fields produced by paired electrons are neutralized and no net magnetic field is produced by them .

Origin of dimagnetism: If two electrons with opposite spins are paired in the same orbital, the magnetic field produced by one electron is cancelled by that caused by the other electron, because each of the two electrons has equal and opposite magnetic moment. Thus, the substances having ony paired electrons give zero resultant magnetic moment and consequently are diamagnetic (Figure 3.1).

Dimagnetic property is temperature independent and is shown by all types of substances. Since diamagnetism is much weaker than paramagnetism (1 to 100 times weaker) and both act opposite to each other, it is difficult for the substances having unpaired electrons to show dimagnetism, i.e. the substances having unpaired electrons shows a net paramagnetism.

3.3.3 Ferromagnetism

In a normal paramagnetic material, the atoms containing the unpaired electrons are magnetically dilute, and so the unpaired electrons in one atom are not aligned with those in other atoms. However, in ferromagnetic materials, such as metallic iron, or iron oxides such as magnetite (Fe_3O_4), where the paramagnetic iron atoms are very close together, they can create an internal magnetic field strong enough that all the centers remain aligned (Figure 3.1).

3.3.4 Antiferromagnetism

The spins on the unpaired electrons become aligned in opposite directions so that the μ_{eff} approaches zero, in contrast to ferromagnetism, where μ_{eff} becomes very large. An example of anti- ferromagnetism is found in MnO (Figure 3.1).

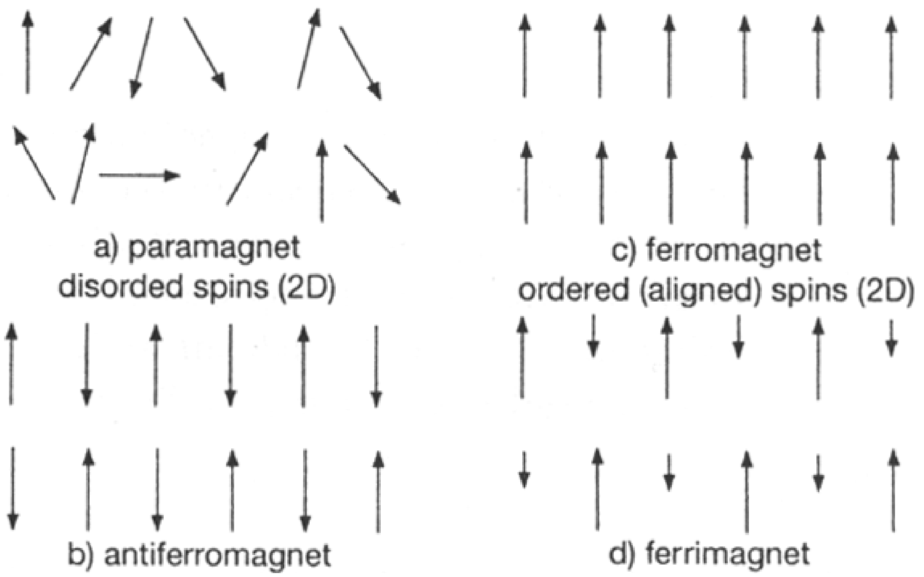

Figure. 3.1. *Types of magnetic behaviour in a substance*

3.4 METHODS OF DETERMINING MAGNETIC SUSCEPTIBILITY

Measurements of magnetic properties have been used to characterize a wide range of systems such as oxides, metallic alloys, solid state materials, and coordination complexes containing metals. Most of the organic and main group element compounds have all the electrons paired and these are diamagnetic molecules with very small magnetic moments. All of the transition metals have at least one oxidation state with an incomplete d sub shell. Magnetic measurements, particularly for the first row transition elements, give information about the number of unpaired electrons. The number of unpaired electrons provides information about the oxidation state and electron configuration. The determination of the magnetic properties of the second and third row transition elements is more complex.

The magnetic moment is calculated from the magnetic susceptibility, since the magnetic moment is not measured directly. There are several ways to express the degree to which a material acquires a magnetic moment in a field. The magnetic susceptibility per unit volume is defined by:

$$K = \frac{I}{H}$$

Where I is the intensity of the magnetization induced in the sample by the external magnetic field, H. The extent of the magnetic induction (I) depends on the sample. The induction may be visualized as an alignment of dipoles and/or by the formation of charge polarization in the sample. H is the strength of the external magnetic field in units of oversteds (Oe). The K is unit less.

Generally, it is more convenient to use mass units, therefore, the mass or gram susceptibility (χ_g) is defined as:

$$\chi_g = \frac{\kappa}{d}$$

Where d is the density of the solid. The molar susceptibility (χ_m) is the mass susceptibility multiplied by the formula weight (F.W.).

$$\chi_m = \chi_g \text{ (F.W. in g mol}^{-1}\text{)}$$

The terms κ, χ_g and χ_m are all measures of the magnetic moment of a substance in a magnetic field. There are various methods to measure magnetic susceptibility which are dicussed in the next section.

3.5. GOUY'S AND QUINCKE'S METHOD

3.5.1 Gouy's method

Gouy's balance named after the scientist who devised it generally to be used to measure paramagnetism. In this method, finely powdered substance or solution is taken in a pyrex cylindrical glass tube called Gouy tube the substance is weighed first without magnetic field and then in the presence of magnetic field (Figure 3.2). A paramagnetic substance will weigh more in the presence of a magnetic field than in its absence, the increase in weight gives a quantification of paramagnetism of the substance. More the number of unpaired electrons in a substance; greater will be the increase in its weight under a magnetic field. The magnetic susceptibility is measured from the difference in weight of the sample with and without magnetism.

Determination of magnetic moment

Measurement with standard substance

The apparatus can be calibrated by measuring the values of a substance whose susceptibility is accurately known. The standard substance commonly used for calibration is mercury tetrathiocynatocobaltate; Hg[Co(CNS)4]. Its magnetic susceptibility is $16.44\times 10^{-6} at\ 20^0C$.

I. Weigh the empty tube with and without magnetic field in gram

Weight of empty tube without magnetic field = A

Weight of empty tube with magnetic field = B

Difference in weights of emty tube = B-C

II. Weigh the tube filled with standard substance in presence and in absence of magnetic field in gram

Weight of tube filled with the standard in absence of magnetic field = D

Weight of tube filled with the standard in presence of magnetic field = E

Difference in weight of tube filled with standard = E-D

III. Difference in the weight of standard (Δw_s) = (E-D) – (B-A)

IV. Weight of standard in absence of magnetic field (w_s) = D-A

Measurement with unknown substance

I. Weigh the empty tube with and without magnetic field in gram

Weight of empty tube without magnetic field = F

Weight of empty tube with magnetic field = G

Difference in weights of emty tube = G-F

II. Weigh the tube filled with substance in presence and in absence of magnetic field in gram

Weight of tube filled with substance the in absence of magnetic field = H

Weight of tube filled with the substance in presence of magnetic field = I

Difference in weight of tube filled with substance = I-H

III. Difference in the weight of substance (Δw) = (I-H) – (G-F)

IV. Weight of substance in absence of magnetic field (w) = H-F

If magnetic susceptibility of the standard is χ_s then the magnetic susceptibility of the substance will be

$$\chi = \chi_s \frac{w_s}{\Delta w_s} \times \frac{\Delta w}{w}$$

$\chi_m = \chi$ x molecular weight of the substance

The Gouy method is a convenient method for measuring magnetic susceptibility. The sample is suspended (in a cylinder) in a non homogeneous magnetic field and the force exerted on the sample can be determined by weighing it. The force acting on the sample is

$$F = \frac{1}{2} A H^2 \kappa$$

Where A is the cross sectional area of the cyclinder; H is the intensity in the central homogenous part of the magnetic field and κ is volume susceptibility

The above equation is valid only when the measurements are taken in vacuum. However, if the sample is surrounded by air, then the air susceptibility (κ') must be subtracted from the measured susceptibility. Now the equation becomes:

$$F = \frac{1}{2} A H^2 (\kappa - \kappa')$$

Where κ' is the volume susceptibility of air

The Gouy tube itself produces a force which is always present. Therefore, actual force acting on the sample can be calculated by subtracting the force acting on the Gouy tube (δ) from the observed force. This force will be negative because of the diamagnetic material of the tube. Now the equation becomes:

$$F = \frac{1}{2} A H^2 (\kappa - \kappa') + \delta$$

For a sample with constant length and cross sectional area, the factor AH^2 will be constant. If the sample density is introduced, the above equation can be written as:

$$10^6\chi = \frac{\alpha + \beta F}{w}$$

Where α is a constant for the displaced air = 0.029 x specimen volume and expressed in mg; w is the weight of sample in gram; F is the force on the sample and β = tube calibration constant.

The apparatus can be calibrated by measuring the values of a substance whose susceptibility is accurately known. The standard substance commonly used for calibration is mercury tetrathiocynatocobaltate; Hg[Co(CNS)4]. Its magnetic susceptibility is 16.44$\times 10^{-6} at\ 20^0 C$. By taking measurements with this standard substance, the constant β is first calculated. By substuting the values of α, β, δ and F F on a sample of weight w, the susceptibility (χ) of the substance can be calculated

The forces are large because the amount of sample taken in the Gouy's tube is quite large and therefore, a chemical balance can also measure the changes in mass. The disadvantage of this method is that it requires perfect uniform packing of the substance in the Gouy's tube. Therefore, correct results can not be obtained if the Gouy's tube has not been packed uniformly.

3.5.2 Quinckes method

The Quincke's method is used to caluculate magnetic susceptibility of diamagnetic or paramagnetic substances in a liquid form. When an object is placed in a magnetic field, a magnetic moment is induced in it. Magnetic susceptibility of a magnetic substance is the ratio of the magnetization I (magnetic moment per unit volume) to the applied magnetizing field intensity H. The magnetic moment can be measured either by force methods or induction methods. The Quincke's method like the Gouy's method belongs to force method. The force f on the sample is negative of the gradient of the change in energy density when the sample is placed in magnetic field.

$$f = \frac{d}{dx}[\frac{1}{2}\mu_0(\mu_r - \mu_{ra})H^2] = \frac{1}{2}\mu_0(x - x_a)\frac{d}{dx}H^2 \ldots\ldots\ldots\ldots \quad (1)$$

Here, μ_0 is permeability of the free space and μ_r, χ and μ_{ra}, χ_a are relative permeability and susceptibility of the sample and the air respectively which the sample displaces. The force acting on an element of area A and length dx of the liquid column is fAdx. Therefore, the total force F on the liquid is

$$F = A\int f dx = \frac{A\mu_o}{2}(x - x_a)(H^2 - H_o{}^2) \ldots\ldots\ldots\ldots\ldots (2)$$

H is equal to the field at the liquid surface between the poles of the magnet and 0. The liquid of density r moves under the influence of this force until it is balanced by the pressure exerted over the area A due to a height difference of h between the liquid surfaces in the two arms of the U-tube. Therefore, the force will be

$$F = Ah(\int - \int a)g$$

Or

$$x = x_a + \frac{2}{\mu_o}g(\int - \int a)\frac{h}{(H^2 - H_0{}^2)} \ldots\ldots\ldots\ldots (3)$$

In actual practice χ_a, density of air ρ_a and H_0 are negligible and can be ignored and the above expression simplifies to

$$x = 2\int\frac{gh}{\mu_o H^2} \ldots\ldots\ldots\ldots\ldots (4)$$

This equation shows that by plotting h as a function of H^2, the susceptibilityc χ (called the volume susceptibility) can be determined directly from the slope of the straight line graph.

It is a dimensionless quantity. This expression is in S.I. units in which ρ, g, h and H are measured in kg/m^3, m/s^2, m and amp. turn/m respectively.

In C.G.S. units, equation (3) and (4) are

$$x = x_a + 2g(\rho - \rho_a)\frac{h}{(H^2 - Ho^2)} \ldots\ldots\ldots\ldots\ldots (5)$$

$$x = \frac{2\rho g h}{H^2} \ldots\ldots\ldots\ldots\ldots (6)$$

Where ρ, g, h and H are measured in g/cm^3, cm/s^2, cm and gauss respectively. The volume susceptibilities in the two systems of units are related as χ (SI units) = 4 χ (CGS units).

3.6. SPIN ONLY FORMULA

We begin the discussion of magnetochemistry with the so called spin-only formula, an approximation that has limited, but useful, applications. Paramagnetism arises from unpaired electrons. Each electron has a magnetic moment with one component associated with the spin angular momentum of the electron and (except when the quantum number l = 0) a second component associated with the orbital angular momentum. For many complexes of first row d-block metal ions we can ignore the second component and the magnetic moment, μ can be regarded as being determined by the number of unpaired electrons, n (equation 1 & 2) . The two equations are related because the total spin quantum number S = $\frac{n}{2}$.

$$\mu \text{ (spin only)} = \sqrt[2]{S\ (s+1)} \text{ .... } (1)$$

$$\mu \text{ (spin only)} = \sqrt{n\ \ (n+2)} \text{ .... } (2)$$

The effective magnetic moment, μ_{eff}, can be obtained from the experimentally measured molar magnetic susceptibility, χ_m and is expressed in Bohr magnetons (BM) where 1 BM = 9.27 x 10^{-24} Joule T^{-1}. Equation (3) gives the relationship between μ_{eff} and χ_m; using SI units for the constants, this expression reduces to equation (4) in which χ_m is in $cm^3\ mol^{-1}$.

$$\mu_{eff} = \sqrt{\frac{3k\chi m\ T}{L\ \mu_0\ \mu B^2}} \text{ ....} (3)$$

where k = Boltzmann constant; L = Avogadro number; μ_0 = vacuum permeability; T = temperature in Kelvin and χ_m is the molar suscptibility.

$$\mu_{eff} = 0.7977\sqrt{\chi_m\ T} \text{ ....} (4)$$

Spin-only values of μ_{eff} compared with approximate ranges of observed magnetic moments for high-spin complexes of first row d-block ions can be seen by Table 3.1.

Table 3.1. Comparison between the spin only and observed magnetic moments in high spin complexes of first row transition elements

Metal ion	**d^n configuration**	**S**	**μ_{eff} (spin only) BM**	**Observed values of μ_{eff} BM**
Sc^{+3}, Ti^{+4}	d^0	0	0	0

Ti^{+3}	d^1	½	1.73	1.7- 1.8
V^{+3}	d^2	1	2.83	2.8–3.1
V^{+2}, Cr^{+3}	d^3	3/2	2.87	3.7–3.9
Cr^{+2}, Mn^{+3}	d^4	2	4.90	4.8–4.9
Mn^{+2}, Fe^{+3}	d^5	5/2	5.92	5.7–6.0
Fe^{+2}, Co^{+3}	d^6	2	4.90	5.0–5.6
Co^{+2}	d^7	3/2	3.87	4.3–5.2
Ni^{+2}	d^8	1	2.83	2.9–3.9
Cu^{+2}	d^9	½	1.73	1.9–2.1
Zn^{+2}	d^{10}	0	0	0

3.7 SPIN AND ORBITAL CONTRIBUTION TO MAGNETIC MOMENTS

Various complexes of transition metals (mostly first transition series elements) give a magnetic moment much higher than μ_s. This is due to the orbital contributions to magnetic moment. The spin angular momentum of an electron is independent of its surroundings and therefore, the spin moment of unpaired electron remains, unaffected by changes in chemical bonding of the compound provided that there is no spin pairing because of bonding. On the conflicting, the orbital angular momentum of the electron depends upon the chemical environment. The orbital contribution of magnetic moment may get compensated or quenched. Thus, as a result, the observed magnetic moments are very close to spin only magnetic moment value.

The quenching of orbital angular momentum can be easily explained on the basis of Crystal Field Theory of bonding in transition metal complexes.

The unpaired electrons in a first transition series are present in the 3d orbitals. A transition metal ion has five 3d orbitals which are degenerate. An electron possesses as angular momentum along a given axis if it is possible to transform its orbital by rotation around this axis into another orbital which is equivalent to it in shape, axis and energy.

Thus, for orbital contribution to the magnetic moment, there must be two or more degenerate orbitals which can be inter converted by rotation about a suitable axis and these orbitals must be unequally occupied.

The orbital angular momentum along the given axis possessed by the electron in such an orbital is equal to the number of times the orbital gets transformed in to the equivalent orbital during a rotation of 90° around that axis. If the orbital degeneracy is lost by chemical bonding or crystal field effects, the orbital contribution to the total magnetic moment is partially or completely quenched.

Let us consider a free metal ion in which all the d orbitals are degenerate. An electron in d_{x2-y2} orbital will contribute to orbital angular momentum equal to 2 units of h/2π along z- axis because a rotation of d_{x2-y2} orbital by 45^0 around the z- axis takes it to equivalent d_{xy} orbital (Figure 3.2).

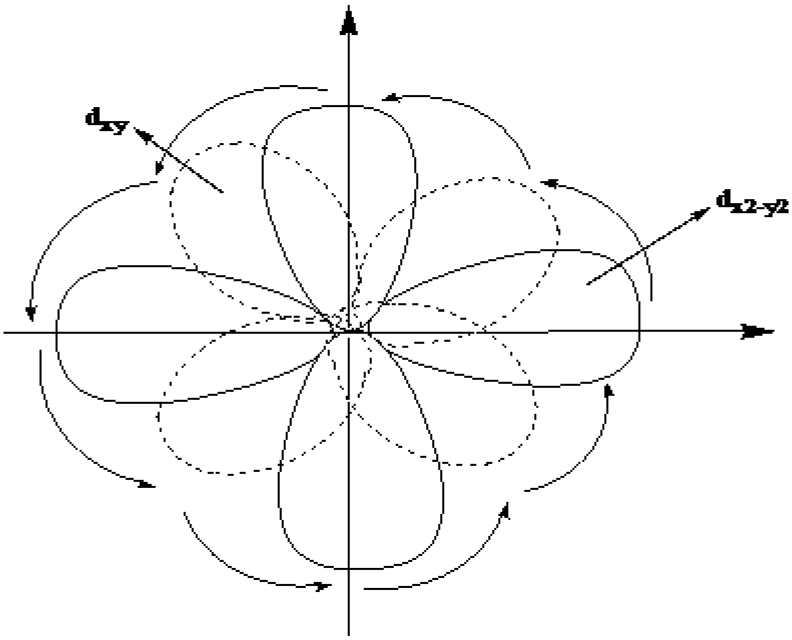

Figure 3.2. *Circulation of electron density about z axis in d_{xy} and d_{x2-y2} orbitals*

In the above discussion, it is clear that a rotation of d_{x2-y2} orbital by 90° around z- axis will carry this orbital in to d_{xy} orbital 2 times. Similarly, we can also say that an electron in d_{xy} orbital will contribute to orbital angular momentum of two in the units of h/2π along z- axis. Similarly, an electron in d_{xz} orbital will have an orbital angular momentum equal to 1 unit of h/2π along z- axis because d_{xz} orbital gets transformed into an equivalent d_{yz} orbital by rotating the d_{xz} orbital around x- axis by an angle of 90°.

When the metal ion is surrounded octahedrally by six ligands, the degeneracy of d-obritals gets disturbed. The d_{xy} and d_{x2-y2} orbitlas acquire different energies and therefore, are non-equivalent. As a result, an electron in d_{x2-y2} orbtial cannot be equated with an electron in d_{xy} orbital. In other words, the d_{x2-y2} orbital cannot be transformed into d_{xy} orbital and vice versa by rotation of the orbital along z-axis. Thus, the electron in d_{x2-y2} orbital will not cause to have orbital contribution along the z-axis.

3.8. SUMMARY

This chapter is concerning the magnetic properties of the transition metal complexes. It was realized that there was a diamagnetic criterion between magnetic properties and the nature of the metal ion in a complexes. In other word, the useful study of magnetic properties of transition metal complexes at low temperature is essential. Magnetic susceptibilities and specific heat are among the principal measurement that carries out on magnetic system.

3.9. TERMINAL QUESTIONS

1. Define the Magnetic susceptibility?
2. Explain why Cu (I) is diamagnetic where as Cu (II) is paramagnetic.
3. What is Magnetic susceptibility? How does it vary with temperature.
4. Calculate the spin magnetic moment of Cr^{+2} and V^{+3}.
5. What do you mean by the term diamagnetic correction?
6. Discuss the Gouy's method for the measurement of magnetic susceptibility.
7. What is the difference between ferromagnetism and antiferromagnetism.
8. Calculate spin only magnetic miment for Co^{+3} ion.
9. What is temperature independent paramagnetism?
10. Give a brief account of diamagnetism, paramagnetism, ferromagnetism and antiferromagnetism
11. Discuss the magnetic behaviour of first transition series metal compounds.
12. What is the calculated μ_s value for Fe^{+2} high spin ion.

13. Explain the phenomenon of orbital contribution of magnetic miment.

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UNIT -4 ELECTRON SPECTRA OF TRANSITION METAL-COMPLEXES

CONTENTS:

4.1. OBJECTIVES

In this unit, our concern will be with the electronic spectra of transition metal complexes, mainly those of the first transition series. The energy required for the promotion of an electron from one orbital to another, the excitation of a molecule from its ground state to an electronic excited state, corresponds to absorption of light in the near-infrared, visible or ultraviolet regions of the spectrum. By going through this unit, you will be able to understand:

- Electronic transitions
- Selection rules for electronic transitions
- Term symbol
- Spectrochemical series
- Orgel diagrams

4.2. INTRODUCTION

Transition metal compounds display a wide variety of colours. A compound is coloured if it absorbs part of the visible light. When a sample absorbs visible light, the colour observed by us is the sum of the remaining colours that are reflected or transmitted by the sample and strikes our eyes. The colour of these compounds is due to the electronic transitions generated by the incident light, causing absorption at certain wavelengths which depend on the structure and bonding in the molecule. Based on Crystal Field Theory (CFT), Uultraviolet (UV)–Visible spectroscopy is used to evaluate the absorption properties of the transition metal complexes.

The electronic transitions in the transition metal compounds can be categorized into three classes: charge transfer, d–d transition and f–f transitions. Charge transfer bands occur when the excited electrons move either from a metal orbital to a ligand orbital (metal–to–ligand charge transfer – MLCT) or from a ligand orbital to a metal orbital (ligand–to–metal charge transfer – LMCT). MLCT transitions are more common than LMCT. d–d transitions occur when the excited electron moves from one d orbital to another d orbital of the metal and f-f transition occur when the excited electron moves from f orbital to f orbital of the same metal centre . The d-d or f-f transitions can further be classified as spin–allowed transition where the spin quantum number in the ground and excited states are the same while in the spin–forbidden transition, the spin state changes during the excitation.

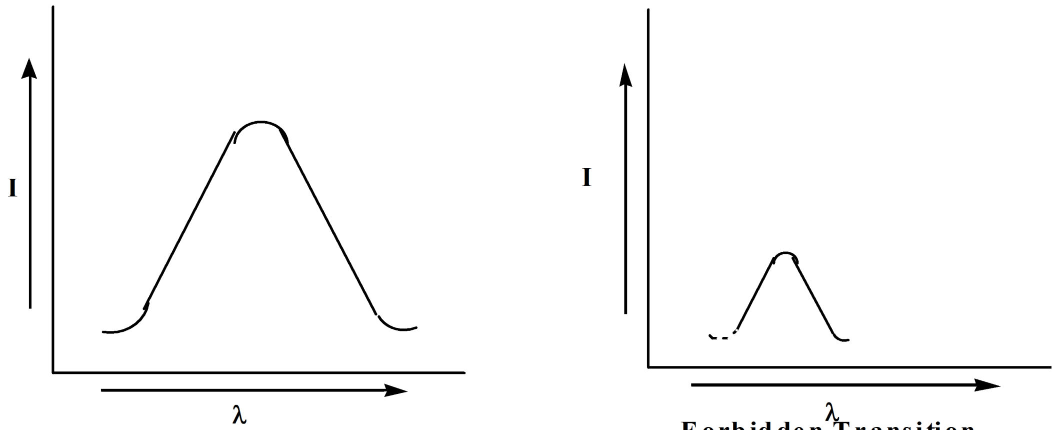
4.3. TYPES OF ELECTRONIC TRANSITIONS

When the Electromagnetic Radiation (EMR) is passed from the sample of the transition metal complexes, the transition of electron can occur by the absorption of certain EMR to give the electronic spectra.

Electronic transitions can be classified into two different types, which are given below (Figure 4.1):

1. **Allowed transitions:** The types of electronic transition which can generate the high intense spectra are known as allowed transitions.

2. **Forbidden transitions:** The types of electronic transition which can generate the low intense spectra are known as forbidden transitions.



Allowed Transition **Forbidden Transition**

Fig. 4.1 Types of d-d transition

4.4. SELECTION RULE FOR d-d TRANSITION

To define the allowed or forbidden nature of electronic transitions, 2 different selection rules can be used which are given below:

4.4.1. Spin selection rule

According to the spin selection rule, all the electronic transitions in the transition metal complexes which does not involve the change in the spin multiplicity are called as spin allowed transitions while on the other hand all the electronic transitions which can involve the change in the spin multiplicity are known as spin forbidden transitions. therefore,

$\Delta S = 0$ (Allowed transition)

$\Delta S \# 0$ (Forbidden transition)

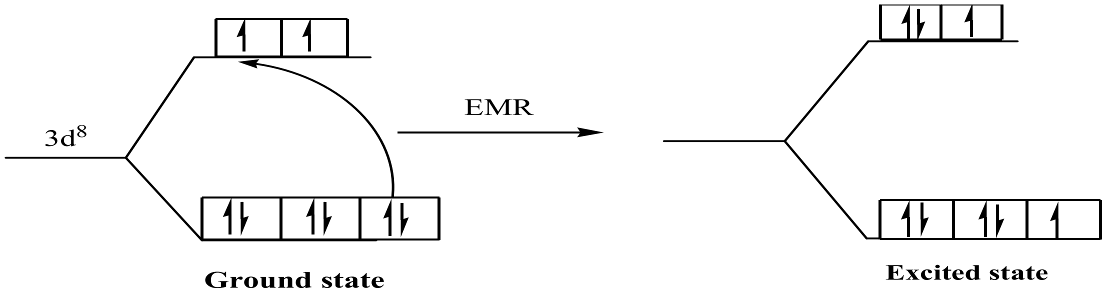
Example:

(i) $[Ni(H_2O)_6]^{+2}$ ion.

$Ni - 3d^8, 4s^2$

$Ni^{+2} - 3d^8, 4s^0$

According to CFT:



Spin multiplicity

Ground state Excited state

$$\underbrace{n + 1 = 3 \qquad\qquad (n + 1) = 3}_{\Delta S = 0}$$

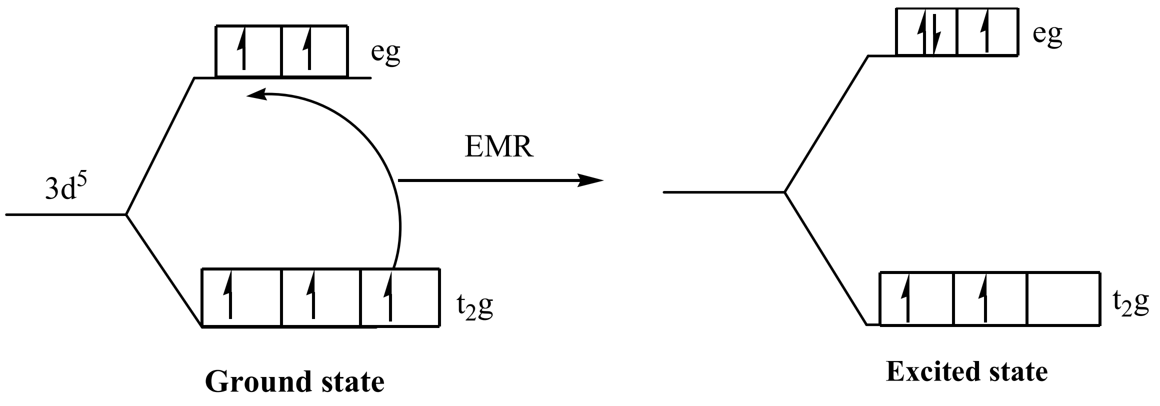
Allowed transition

(ii) $[Mn(H_2O)_6]^{+2}$ ion.

Mn - $3d^5, 4s^2$

Mn^{+2} - $4s^5, 4s^0$

According to CFT:



Spin multiplicity

Ground state Excited state

$$\underbrace{n + 1 = 6 \qquad\qquad (n + 1) = 4}_{\Delta S \# 0}$$

Forbidden transition

4.4.2. Laporte selection rule

According to the this rule, all the electronic transitions which occur from G (g) to U (u) (gerade to ungerade) or u to g orbitals, are known as Laporte allowed or symmetry allowed transitions while all the electronic transitions, which occur from g to g or u to u orbitals are known as Laporte forbidden transition or symmetry forbidden transition.

$$\left.\begin{array}{l} \mathrm{G} \longrightarrow \mathrm{U} \\ \mathrm{U} \longrightarrow \mathrm{G} \end{array}\right\}\text{Allowed} \qquad \left.\begin{array}{l} \mathrm{G} \longrightarrow \mathrm{G} \\ \mathrm{U} \longrightarrow \mathrm{U} \end{array}\right\}\text{Forbidden}$$

According to this selection rule all the d-d transition phenomena in the transition metal complexes bung forbidden.

Therefore, according to the Laporte selection rule, all the electronic transitions in which there does not occur any change in the orbital quantum no (l) value are known as Laporte forbidden transition while all the electronic transitions which involve certain change in the orbital quantum number are known as Laporte allowed transition.

$\Delta l = 0$ (Laporte forbidden transitions)

Δl # 0 (Laporte allowed transitions)

Thus, according to this selection rule, it is observed that all the d-d transitions (g-g transitions) are Laporte forbidden. There are certain relaxations in Laoprte selection rule due to the possibility of certain extent of d-p mixing.

4.5. TERM SYMBOL AND SPECTROSCOPIC GROUND STATE TERM

In quantum mechanics, the term symbol is the energy level of a single or multi-electron atom which is deduced from total angular momentam quantum number including orbital quantum number and spin quantum number. The atomic term symbols can be calculated from L-S coupling (Russell-Saunders coupling or Spin-Orbit coupling) and the ground state term symbol is predicted by Hund's rules.

Russell- Saunder coupling (Spin orbital or L-S coupling)

Russell and Saunder have proposed a coupling scheme i. e. Russell- Saunder coupling to calculate the term symbol for the various electronic configurations, which involve the following qauantum numbers:

(1) Total orbital momentum quantum number or L term

Vector summation of the l values of the differfent electrons present in a particular configuration is known as total orbital angular momentum quantum number (L term) for the configuration.

Different symbols for the different L value can be written as:

L	=	0	1	2	3	4	5	6	7
Symbol	=	S	P	D	F	G	H	I	J

(2) Total spin momentum quantum number or S term

Vector summation of spin angular momentum quantum number of all electrons present in any configuration (s values) is known as total spin angular momentum quantum number or S term.

$$S = \frac{n}{2}$$

Where n is the number of unpaired electrons

(3) Total angular quantum number or J term

Vector summation of L and S terms for a particular electronic configuration is known as total angular quantum number or J term which arises due to L-S coupling. The values of J are

$$J = L - S, L\text{-}S\text{-}1, L\text{-}S\text{-}2 \text{ ...... upto } L + S$$

For less than half filled configuration

$$J = L - S$$

For a configuration which is more than half filled

$$J = L + S$$

(4) Spin multiplicity or M term

Total number of the possible spin orientations of the unpaired electrons in a particular configuration is known as spin multiplicity or M term.

$$M = n + 1$$

$$= 2S+1$$

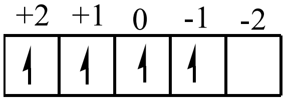
Where n = number of unpaired electrons

According to the above four different terms, term symbol for a particular configuration can be written as

$$^{M}L_{J}$$

For example for d^4 configuration

d^4 =



L = 2 (D)

$$S = \frac{n}{2} = \frac{4}{2} = 2$$

For an electronic configuration less than half filled

$$J = L – S = 0$$

$$M = 4 + 1 = 5$$

So, the term symbol for d^4 configuration is $^{M}L_{J}$ = $^{5}\mathbf{D_0}$

Term symbol for the various d^n configuration, P^n configuration, S^n configuration can also easily determined:-

Hund’s rule for ground state term

The calculation of term symbol for the ground state of an atom is relatively easy to using Hund's rules. Ground state term symbol corresponds to a state with maximum S and L values. Each electronic configuration except fully filled has large number of possible arrangements which are known as microstates which can be calculated as follow:

$$\text{Number of microstates} = \frac{n!}{r!\,(n-r)!}$$

Where n is maximum capacity (maximum number of electrons that can be accommodated in the orbital) of the particular configuration and r is number of electron in the configuration.

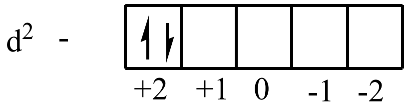
Out of the various possible electronic arrangements, one of the arrangement i.e. ground state electronic arrangement can be calculated with the help of different rule proposed by the Hund, which are given below:

Rule 1: According to the Hund's rule, out of the various electronic arrangements, the arrangement having the maximum value of spin multiplicity will be the ground state electronic arrangement.

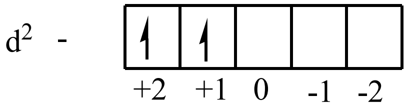
Rule 2: If more than one electronic arrangement have the same value of spin multiplicity, than the electronic arrangement with higher L value will be the ground state electronic arrangement.

Rule 3: Among various the ground state electronic arrangements with different J values, if the electronic configuration is less than half filled, than the ground state term will be withleast J value while if the configuration is more than half filled, than the ground state term will be the term with maximum J value.

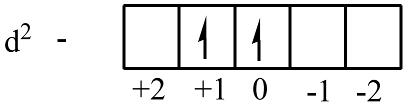
Example: Evaluation of ground state term symbol for d^2 configuration.



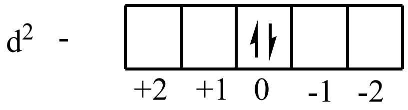
L = 4 (G)
S = 0
J = 4
M = 1



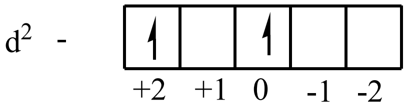
L = 3(F)
S = 1
J = 2,3,4
M = 3



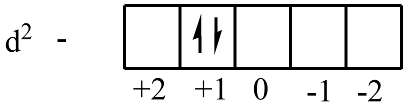
L = 1 (P)
S = 1
J = 0,1,2
M = 3



L = 0 (S)
S = 0
J = 0
M = 1



L = 2 (D)
S = 1
J = 1,2,3
M = 3



L = 2 (D)
S = 0
J = 2
M = 1

According to the Hund's rule, second arrangement will be the actual ground state electronic arrangement for d^2 configuration. Thus, the term symbol for d^2 configuration will be $^3F_2$.

4.6. SPECTROCHEMICAL SERIES

Order of ligands arranged according to the strength of ligand and arrangement of metal ions on the basis of oxidation number, group and its identity is called as spectrochemical series.

Accordung to crystal field theory, ligands can change the difference in energy between the two sets of d orbitals (Δ_o) called the ligand-field splitting parameter for ligands or the crystal-field splitting parameter, which can be the cause of differences in color of similar type of metal-ligand complexes.

The spectrochemical series was first given in 1938 and was based on the results of absorption spectra of cobalt complexes. Spectrochemical series of the ligands from smaller value of Δ_o to larger value of Δ_o is given below.

$O_2^{2-} < I^- < Br^- < S^{2-} < SCN^- < Cl^- < N^{3-} < F^- < NCO^- < OH^- < C_2O_4^{2-} \approx H_2O < NCS^- < CH_3CN$ < py (pyridine) < NH_3 < en (ethylenediamine) < bipy (2,2'-bipyridine) < phen (1,10-phenanthroline) < $NO2^-$ < PPh_3 < $CN^- \approx$ CO

Ligands present on the left end of this spectrochemical series are generally known as weaker ligands and cannot cause pairing of electrons within 3d level and thus, form outer orbital octahedral complexes and are called as high spin ligands. While, ligands present at the right end of the series are stronger ligands which can form inner orbital octahedral complexes after forcible pairing of electrons within 3d level and hence, are called as low spin ligands.

The strong ligands in the spectrochemical series are also called as л-acceptor ligands while weak ligands are known as σ-donor ligands.

4.7. ORGEL ENERGY LEVEL DIAGRAM FOR d^1 AND d^9 STATE

Orgel diagrams are the correlation diagrams that represent the relative energies of electronic terms in transition metal complexes.These diagrams are firstly drown by Leslie Orgel. Orgel diagrams are drawn for only weak field complexes (i.e. high spin). These are the diagrams drawn between Δ_o. These diagrams are qualitative and no energy calculations can be carried out from these diagrams. In Orgel diagrams, only symmetry states with the highest spin *multiplicity* are used instead of all possible terms. With the help of Orgel diagrams, we can deduce the number of spin allowed transitions. In these diagrams, the gtound state term (atomic term) (P, D, or F) is located at the center of the diagram in the absence of ligand field while in presence of ligand field, the atomic term splits into molecular Mulliken terms. On the basis of the above discussion, Orgel diagram for the various d^n configuration of transition metal complexes, are discussed in this section.

A. Orgel diagram for d^9 octahedral complexes

Orgel diagram of octahedral complexe with d^9 configuration can be drawn in the three different steps which are given below (Figure 4.2):

Step I:

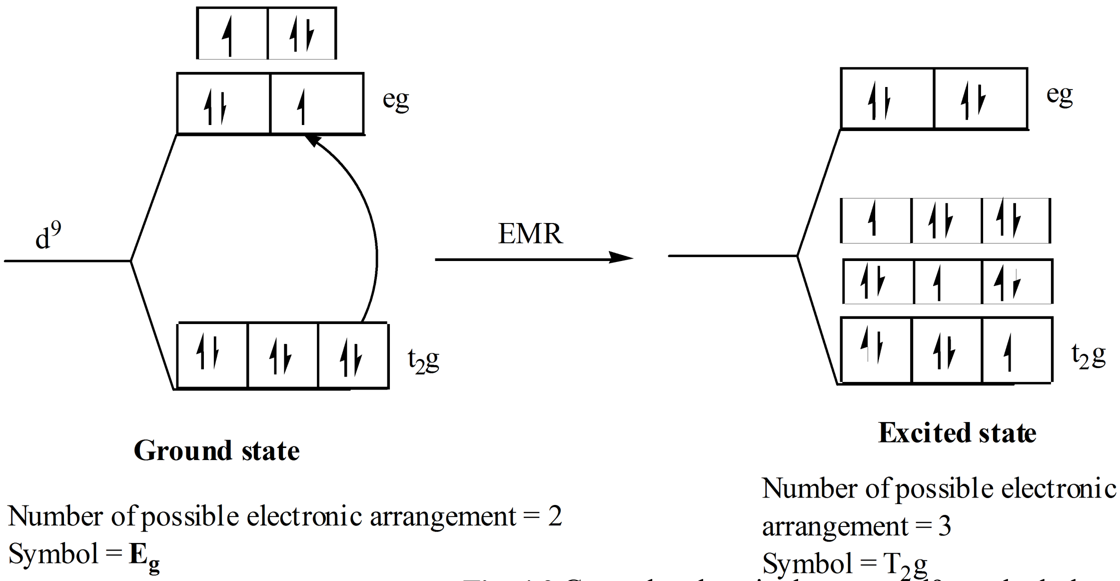
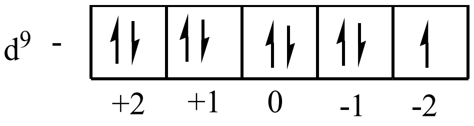


Fig. 4.2 Ground and excited states of d9 octahedral complex

Step II:



L = 2 (D)
S = 1/2
J = 5/2
M = 2

So, the term symbol for d^9 configuration = $^{2}\mathbf{D}_{5/2}$

Step III: Formation of Orgel diagram (Figure 4.3).

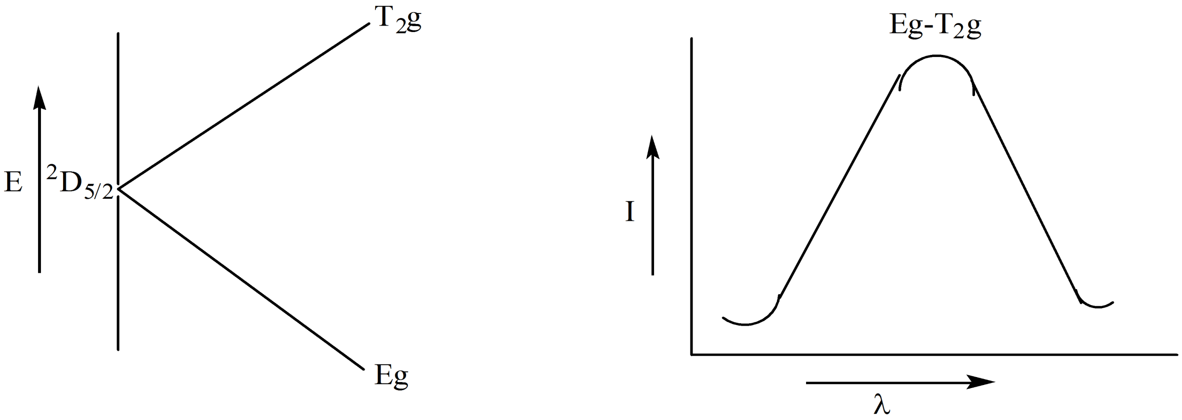
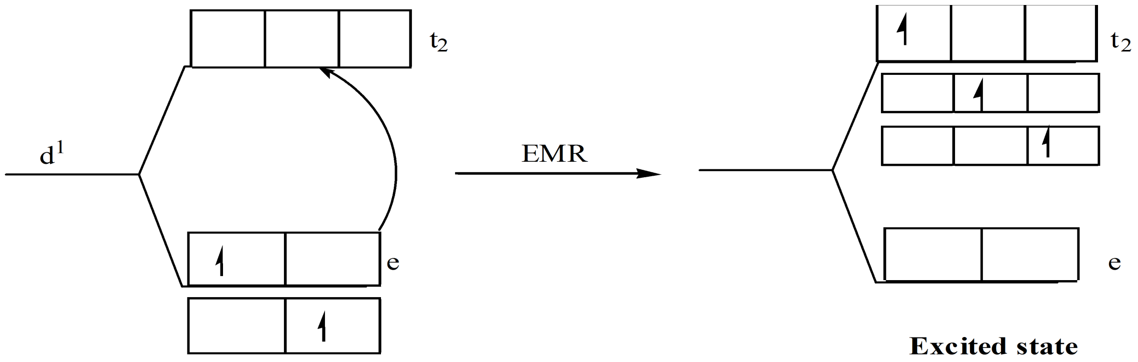


Fig. 4.3

Orgel diagram and absoption spectra of d9 octahedral complex

B. Orgel diagram for the d^1 tetrahedral complexes: Orgel diagram for the d^1 configuration of tetrahedral complexe can be explained in the three different steps, is are givenin Figure 4.4 and Figure 4.5.

Step I:



Excited state

Ground state

Number of possible electronic arrangement = 2

Symbol = **E**

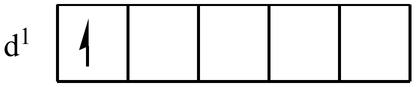
Number of possible electronic arrangement = 3

Symbol = $\mathbf{T_2}$

Fig. 4.4

Ground and excited states of d1 tetrahedral complex

Step II:



L = 2(D)
S = 1/2
J = 3/2
M = 2

So, the term symbol for d^1 configuration = $\mathbf{^2D_{3/2}}$

Step III:

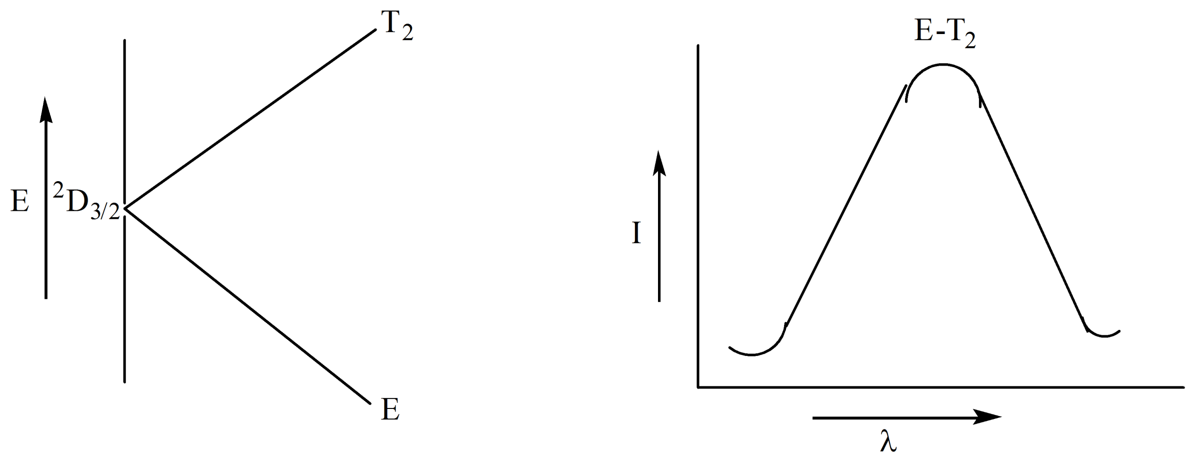


Fig. 4.5

Orgel diagram and absoption spectra of d1 tetraheral complex

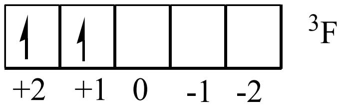
Thus, from the above, it can be concluded that d^n tetrahedral complexes and d^{10-n} octahedral complexes have same spectra while d^n tetrahedral complexes and d^{10-n} tetrahedral complexes or d^n octahedral complexes and d^{10-n} octahedral complexes have opposite spectra.

C. Orgel diagram for d^2 octahedral complexes

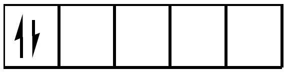
In the electronic spectra of d^2 configuration with octahedral ligand field, such as $[V(H_2O)_6]^{+3}$, it two peaks in the range of 1700cm^{-1} and 2100 cm^{-1} are obtained which indicates that the d^2 configuration with octahedral field ligands can exhibit two types of the electronic transitions.

According to Orgel, d^2 configuration has ground term symbol ^3F and various exited state term symbols like ^1S, ^1D, ^1G and ^3P. Out of these, only ^3P term (both having same multiplicity) symbol is used during the electronic transition because the electronic transitions from ground state to this excited state are allowed while the electron transitions from ground state to other excited states such as ^1S, ^1G and ^1D are spin forbidden. The Orgel diagram corresponding to this allowed transition for the d^2 configuration with octahedral field ligand can be given below.

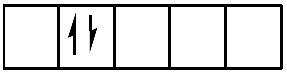
Ground state electronic arrangement for d^2 octahedral complexes is as follows:



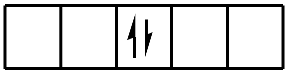
Exited state electronic arrangement for d^2 octahedral complexes is as follows:



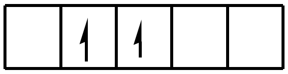
^1G



^1D



^1S



^3P

Thus, according to the above discussion, the Orgel energy level diagram and spectra for d^2 configuration with octahedral field ligand can be represented as shown in Figure 4.6.

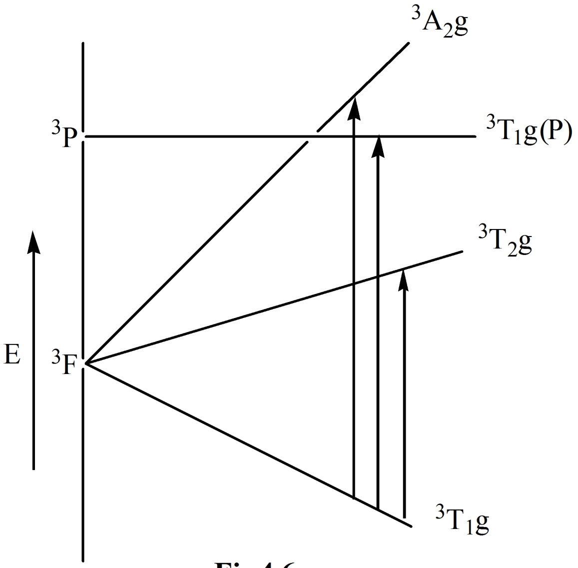


Fig.4.6

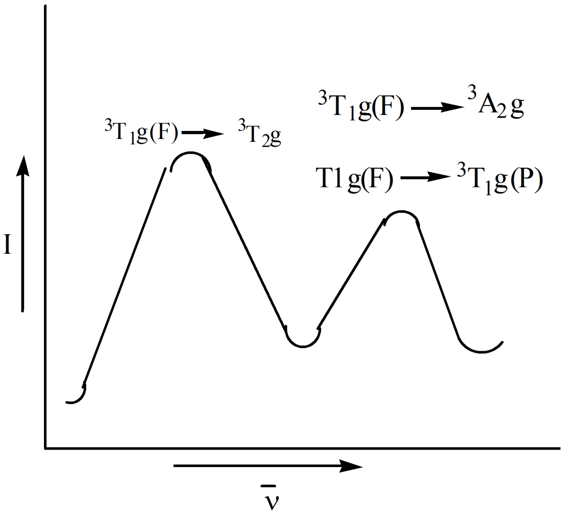


Fig.4.7

Orgel diagram and absoption spectra of d^2 octahedral complex

D. Orgel energy level diagram for d^8 octahedral complexes

The spectra of octahedral complexes with d^8 configurationcontains different peaks which indicates that octahedral complexes like $[Ni(H_2O)_6]^{+2}$, have different types of the transitions (Figure 4.7).

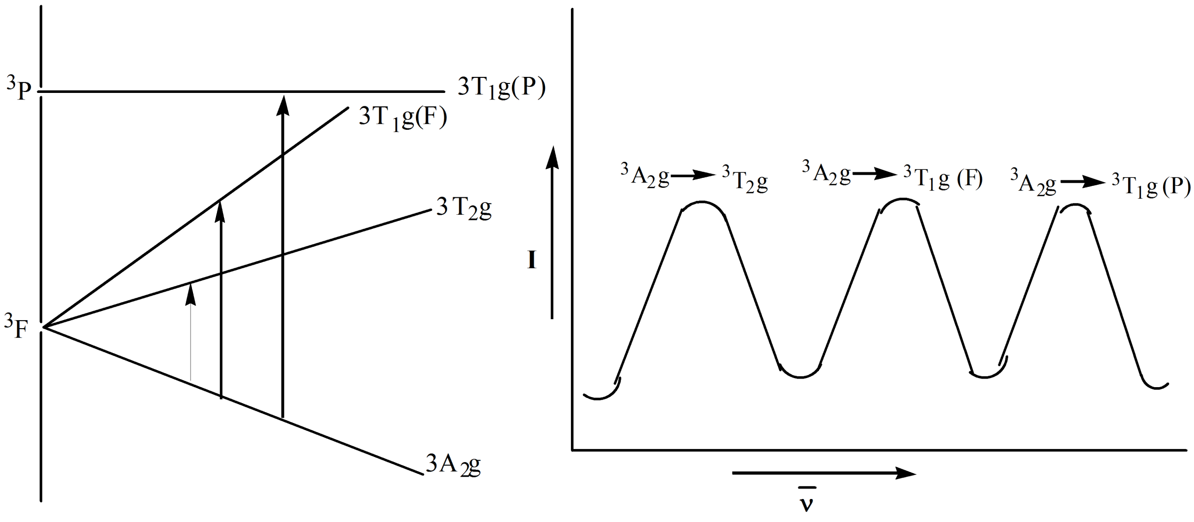


Fig.4.8 Fig.4.9

Orgel diagram and absoption spectra of d^8 octahedral complex

4.8. TYPES OF THE ELECTRONIC TRANSITION

Transition metal complexes can exhibit two types of the electronic transitions

1. d- d transition
2. Charge transfer transition

1. d-d transition: In a d–d transition, an electron in a d orbital on the metal is excited to another d orbital of higher energy by a photon. In complexes of the transition metals, the d orbitals do not all have the same energy. In centrosymmetric complexes, d-d transitions are forbidden by the Laporte rule. According to Laporte rule states that, if a molecule is centrosymmetric, transitions within a given set of p or d orbitals will be forbidden. However, forbidden transitions become allowed if the center of symmetry is disrupted. Transitions that occur as a result of an asymmetrical vibration of a molecule are called vibronic transitions. Through such asymmetric vibrations, transitions that should be theoretically forbidden, such as a d-d transition, are weakly allowed.

d-d- Transition is the phenomena of excitation of the electrons of the splitted lower energy set of d-orbitals into the higher energy splitted set of d- arbitals by the absorption of electromagnetic radiation is known as phenomena.

Example: In the d^1 configuration containing octahedral complex i. E. $[Ti(H_2O)_6]^{+3}$ ion, the d-d transition phenomena is representedin Figure 4.8.

$[Ti(H_2O)_6]^{+3}$ ion

Ti = $3d^2, 4s^2$
Oxidation state of Ti = +3
$Ti^{+3} = 3d^1$

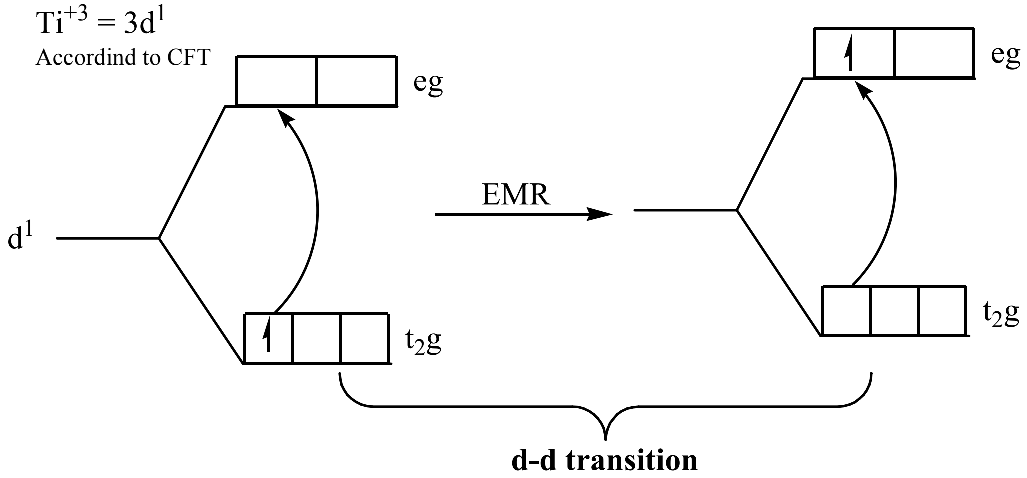


Figure 4.10. d-d Transition in $[Ti(H_2O)_6]^{+3}$

2. Charge transfer transition: In inorganic compounds, most of the charge-transfer complexes involve electron transfer between metal atoms and ligands. The charge-transfer bands of transition metal complexes result from shift of charge density between molecular orbitals (MO) that are predominantly metal like nature and those that are predominantly ligand like nature. If the transfer occurs from the MO with ligand character to the MO with metal-like charcater, the complex is called a ligand-to-metal charge-transfer (LMCT) complex and the transfer is LMCT. If the electronic charge shifts from the MO with metal character to the MO with ligand character, the complex is called a metal-to-ligand charge-transfer (MLCT) complex. Thus, oxidation of the metal center occurs as a result of MLCT, whereas a LMCT results in the reduction of the metal center.

Depending on the direction of charge transfer, these are classified as either ligand-to-metal (LM) or metal-to-ligand (ML) charge transfer

(a) Ligand-to-metal charge transfer (LMCT)

LMCT complexes arise from the transfer of electrons from MO having ligand character to those having metal character. This type of transfer occurs when complexes have ligands with relatively high-energy lone pairs and if the metal has low-lying empty orbitals. In such complexes, metals have higher uncommon oxidation states or less number of d-electrons (even d^0). These conditions suggest that the acceptor metal level is available which is of low energy.

Consider a d^6 octahedral complex, such as $IrBr_6^{3-}$, whose t_{2g} orbitals are filled. As a result, an intense absorption peak is observed around 250 nm corresponding to a transition from ligand like σ MO to the empty e_g MO of metal like character. However, in case of $IrBr_6^{2-}$, a d^5 complex, two absorption peaks, one near 600 nm and another near 270 nm, are observed. This is because two transitions are possible, one to t_{2g} (that can now accommodate one more electron) and another to e_g. The 600 nm band corresponds to transition of electron from ligand orbital to the t_{2g} MO of metal and the 270 nm band correspond to transfer of electron from ligand MO to the e_g MO of the metal.

Charge transfer bands may also arise from transfer of electrons from nonbonding orbitals of the ligand to the e_g MO of metal.

Examples:

MnO_4^-: The permanganate ion with tetrahedral geometry is intensely purple coloured due to strong absorption involving charge transfer from MO of filled oxygen p orbitals to empty MO of manganese (VII).

CdS: The yellow color of cadmium sulphide is due to the transition of electrons from Cd^{2+} (5s) ← S^{2-} (π).

HgS: It is red due to Hg^{2+} (6s) ← S^{2-} (π) electronic transition.

(b) Metal-to-ligand charge transfer

Metal-to-ligand charge-transfer (MLCT) complexes arise as a result of transfer of electrons from MO with metal-like character to those with ligand-like character. These transitions are most common in complexes with ligands having low-lying π* orbitals, especially aromatic ligands. For these trasitions to occur, metal should have low oxidation state with sufficient number of electrons and should be relatively high in energy.

Examples:

i. **Tris (2,2'-bipyridyl)ruthenium(II):** This is a orange-colour complex due to MLCT.

ii. $W(CO)_4(phen)$

iii. $Fe(CO)_3(bipy)$

4.9. DISCUSSION OF THE ELECTRONIC SPECTRUM OF [Ti $(H_2O)_6]^{+3}$ COMPLEX ION

In $[Ti(H_2O)_6]^{+3}$ complex, Ti (III) has d^1 configuration and in an octahedral field, the configuration is t_{2g}^1. The t_{2g} level is triply degenerated due to the presence of single electron in the excited state (configuration being e_g^1), Jahn Teller distortion was observed in the abnsorption spectra of $[Ti(H_2O)_6]^{+3}$ ion (Figure 4.10). Due to tetragonal distortion, the ion was compressed along the z axis. The CFSE will be $2/3\delta_2$ larger than it would have been in a regular octahedron. The excited state (t_{2g}^0 e_g^1) splits due to Jahn Teller distortion. Therefore, the spectrum of the complex ion shows a shoulder as a result of this splitting (Figure 4.11) and seems to be comprised of two peaks: one from the ground state to the lower e_g level and the other to the upper e_g level (Figure 4.12).

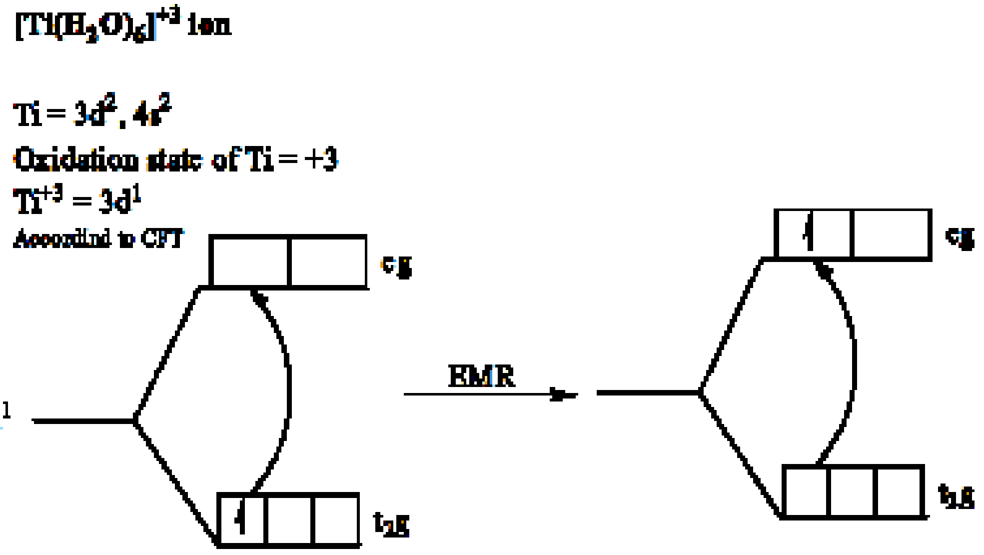


Fig. 4.11 d-d transition in [Ti(H2O)6]+3

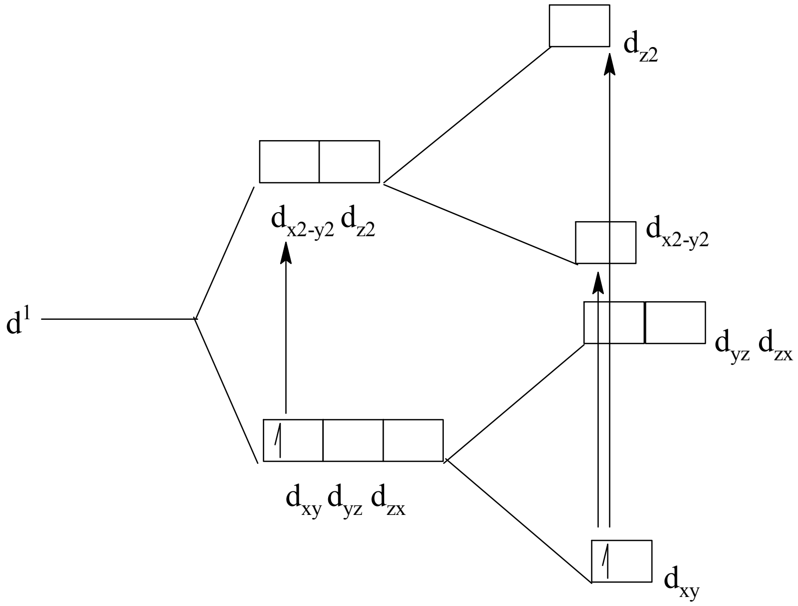


Figure 4.12. *Transtitions in d^1 configuration due to Jahn Teller distortion*

4.10. SUMMARY

Electronic spectra of transition metal complexes help us to understand the structure and bonding in these complexes. A very special characteristic of transition metal complexes is that they exhibit colours of varying intensity of the visible region.

It has been established that colour of the complex compounds is because of d-d transition. The electrons excite from lower energy set of d orbital to high energy set of d orbitals. Energy from the visible range is absorbed by the transition metal complexes and the energy of complementary colour is transmitted. It is the transmitted radiation that from the colour of the substance.

4.11. TERMINAL QUESTIONS

A. Short Answer Type Questions

1. Why metal complexes are having colors?

2. If the transition is between one set of d-orbital to another set of d-orbital, only one color should be there for a complex. However, different colors are seen for different complexes. Why?
3. Why d-d transitions are weak as compared to CT transitions?
4. Calculate the term symbol for d^9 octahedral complex.
5. Differentiate between LS coupling and JJ coupling.
6. Why do tetrahedral complexes of an element give much more intense d-d spectra than its octahedral complexes?
7. Discuss the electronic spectra of $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ complexes.
8. What are spin multiplicity forbidden and Laporte forbidden transitions?
9. What are selection rules for electronic spectra?
10. Discuss the spectral features of Mn(II) in octahedral complexes of weak ligand fields.
11. Write briefly about L-S coupling.
12. Discuss the absorption spectra for Co(II) octahedral and Co (II) tetrahedral complexes.
13. Calculate the ground state terms with spin multiplicity for the following octahedral ions: Vi^{3+}, Ni^{2+}, Cu^{2+}
14. Discuss the Orgel diagram and absorption spectra for a d^8 ion.
15. Determine the ground state term symbol of anion with d^1 configuration.
16. Draw the energy level diagram for d^2 configuartion in tetrahedral and octahedral fields showing three possible transitions.
17. How does Hund's rule help to arrange the different spectroscopic terms in order of their increasing energies? How does it help to find the terms in ground state?
18. Discuss Russel-Saunders states for d^2 configurations.
19. Discuss the special features of electronic spectra of $[Ni(H_20)_6]^{2+}$ ion.
20. Discuss special features of electronic spectra of Cr(III) octahedral and Mn(II) octahedral complex ions.
21. Arrange the different spectroscopic terms of titanium with the help of Hund's rules.
22. State and explain the Laporte selection rule.
23. What are the two important limitations of Orgel diagrams?
24. Draw combined Orgel diagram for d^1 and d^9 octahedral complexes.
25. What are Orgel diagrams? What information is conveyed by these diagrams?

26. Give a detailed account of the selection rules of electronic spectra.
27. State and explain Hunds rule for assigning ground state spectroscopic term with suitable examples.
28. Why do tetrahedral complexes give much more intense d-d transition than octahedral complexes?
29. Calculate the term symbol for ground state of Cr.

B. OBJECTIVE TYPE QUESTIONS

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1. Which metal complex ion is expected to be subject to a Jahn-Teller distortion?
   a. $[Cr(H_2O)_6]^{+3}$
   b. $[Cr(NH_3)_6]^{+2}$
   c. $[Cr(CN)_6]^{-3}$
   d. $[Cr(bpy)_3]$
2. A d^1 electron configuration corresponds to which of the following terms?
   a. ^2D
   b. ^1D
   c. ^2P
   d. ^3P
3. How many microstates are possible for a d^2 configuration, including both weak and strong field limits?
   a. 15
   b. 45
   c. 10
   d. 90
4. The‘d-d’ transitions in an octahedral $[NiX_6]^{2+}$ complexes are:
   a. Laporte forbidden but spin allowed
   b. Laporte forbidden and spin forbidden
   c. Laporte allowed and spin allowed
   d. Laporte allowed but spin forbidden

5. Why does the absorption spectrum of aqueous $[Ti(OH_2)_6]^{3+}$ exhibit a broad band with a shoulder?

   a. The ground state of $[Ti(H_2O)_6]^{3+}$ is Jahn-Teller distorted
   b. The excited state of $[Ti(H_2O)_6]^{3+}$ undergoes a Jahn-Teller distortion
   c. $[Ti(H_2O)_6]^{3+}$ is a d^2 ion and therefore there are two absorptions
   d. $[Ti(H_2O)_6]^{3+}$ is partly reduced to $[Ti(H_2O)_6]^{2+}$ in aqueous solution and two absorptions which are close in energy are observed, one for each species

6. Ground state term for d^2 configuration is:

   a. ^3F b. ^3P c. ^1G d. ^1S

7. For Laporte forbidden transitions,

   a. $\Delta l = 0$ b. $\Delta S = 0$ c. $\Delta l = -1$ d. $\Delta l = \pm 1$

8. Mullikin symbol for spectroscopic term P in octahedral field is:

   a. A_{1g} b. T_{1g} c. T_{2g} d. E_g

9. The ground state for $2p^3$ is:

   a. $^4S_3$ b. $^3P_4$ c. $^4S_{3/2}$ d. $^2P_1$

10. The ground state term for p^6 is same for

   a. d^{10} b. d^6 c. p^3 d. d^5

4.12. ANSWERS

1. a **2.** a **3.** b **4.** c **5.** b **6.** a **7.** a **8.** b **9.** c **10.** a

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UNIT-5 THERMODYNAMIC AND KINETIC ASPECTS OF METAL COMPLEXES

CONTENTS:

5.1. OBJECTIVES

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

- The fundamental difference between reaction thermodynamic and kinetics.
- Chemical equilibrium expression and determine step-wise stability constant and overall stability constant of complexes.
- Estimatimation and interpretation of the entropy and free energy of complexes

- Reaction mechanism in transition metal complexes

5.2 INTRODUCTION

Thermodynamic stability and reaction kinetics of coordination compounds is a very important aspect of coordination chemistry and find its application to all disciplines including; catalyst deign in production industries, pharmaceutical studies of drug design, chemical analysis and biochemical studies of drug metabolism. This is because the stability study and reaction mechanism of complexes determine their behaviour in different environments that may include change in temperature or change in pH of reaction medium. Kinetic and thermodynamic stability of complexes are entirely different. Thermodynamic stability is a function of the equilibrium constant. Higher equilibrium constant indicates greater stability of a complex. However, kinetic stability is a function of the rate constant. The reaction with high rate constant is expected to proceed fast.

5.3 A BRIEF OUTLINE OF THERMODYNAMIC AND KINETIC STABILITY OF METAL COMPLEXES

To define the stability of the complex compound formed in the solution, two types of the stability concept can be used which are given below:

5.3.1. Thermodynamic stability concept of the complexes

When the stability of the complexes formed in the solution is defined by the thermodynamic parameters like bond energy, stability constant or formation constant then such type of the stability concept is called as thermodynamic stability concept of the complexes. According to the thermodynamic stability concept, complex compound can be deluded into 2 different types which are given below:

1. **Stable complexes:** Those complexes which exhibit very high formation constant in the solution are known as stable complexes.

2. **Unstable complexes:** Those complexes which exhibit low formation constant in the solution are known as unstable complexes.

5.3.2. Kinetic stability concept of the complexes

When the stability of the complexes formed in the solution is defined by the kinetic parameter then the stability concept is called as kinetic stability concept of the complexes. According to the kinetic stability concept, complex compounds in the solution can be divided into two types:

1. **Inert Complex:** Those complexes which exhibit very low or negligible rate of replacement reaction in the solution are known as inert complexes.
2. **Labile Complex:** Those complexes which exhibit very high rate of replacement reaction in the solution are known as labile complexes.

Relationship between thermodynamic and kinetic stability concept

$[Hg(CN)_4]^{-2}$ ion having very high formation constant (10^{42}) in the solution but it can easily undergos replacement reaction in the solution. Therefore, this complex is thermodynamically stable but kinetically labile.

$$[Hg\ (CN)_4]^{-2} + 4\ CN^{14-} \longrightarrow [Hg\ (CN14)_4]^{-2} + 4CN^-$$

Similarly $[CO(NH_3)_6]^{+3}$ ion is kinetically inert but thermodynamically unstable. Thus, from the above discussion, it is proved that there is no relationship between thermodynamic and kinetic stability concept.

Stepwise formation of the complexes and stepwise formation constant

According to the J. Bjerrum, the solution proceeds by the stepwise addition of the ligands to the CMI. Thus, the formation of complex ML_n by the stepwise formation method can be given as:

$$M + L_1 \longrightarrow ML_1 \quad K_1 = \frac{[ML_1]}{[M][L_1]}$$

$$ML_1 + L \longrightarrow ML_2 \quad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML2 + L \longrightarrow ML3 \quad K3 = \frac{[ML3]}{[ML_2][L]}$$

$$MLn + L \longrightarrow MLn \quad Kn = \frac{[MLn]}{[MLn - 1][L]}$$

Where K_1, K_2, K_3,- - - K_n are stepwise formation or stability constant for the complexes formed in the corresponding steps.

The formation of complex ML_n may also proceed in a single step which can be given as:

$$M + nL \longrightarrow MLn \qquad \beta_n = \frac{[MLn]}{[M]\ [L]^n}$$

Where β_n = overall formation constant for ML_n complex

Relationship between stepwise formation constant and overall formation constant

To give the relationship between stepwise formation constants and overall formation constant, let us consider the formation of ML_3 complex by the stepwise formation method and overall formation method.

According to stepwise formation method

$$M + L \longrightarrow ML \quad K1 = \frac{[ML]}{[M]\,[L]} \quad ---- (1)$$

$$ML + L \longrightarrow ML2 \quad K2 = \frac{[ML_2]}{[ML]\,[L]} \quad - --- (2)$$

$$ML2 + L \longrightarrow ML3 \quad K3 = \frac{[ML_3]}{[ML_2]\,[L]} \quad ---- (3)$$

According to overall formation method

$$M + 3L \longrightarrow ML_3 \quad \beta_3 = \frac{[ML_3]}{[M]\,[L]^3} \quad --- (4)$$

Dividing and multiplying the equation (4) by $[ML_2]$ $[ML]$

$$\beta_n = \frac{[ML_3]}{[M]\,[L]^3}\;\frac{[ML_2]}{[ML2]}\;\frac{[ML]}{[ML]}$$

or

$\beta_3 = \frac{[ML_3]}{[ML_2]\,[L]}\;\frac{[ML_2]}{[ML]\,[L]}\;\frac{[ML]}{[M]\,[L]}$ - - - - (5)From eq, (1), (2), (3) & (5)

$$\boxed{\beta_3 = K_3 \times K_2 \times K_1}$$

Thus, from the above equation, it is observed that the product of stepwise formation constant is always equal to the overall formation constant for any particular complex.

5.4 FACTORS AFFECTING THE STABILITY OF THE COMPLEXES

There are two different factors which can affect the stability of complexes formed in the solution given as below:

5.4.1. Nature of the central metal ion (CMI)
5.4.2. Nature of the ligands

5.4.1. Nature of central metal atom (CMA)

Some of the factors related with the CMA which can affect the stability of complexes are given below:

(i) Charge on the CMA: Metal ion having high charge density forms stable complexes. Charge density means ratio of the charge to the radius of the ion. Thus, smaller the size and higher the charge of the metal ion, complexes are more stable. This is because a smaller, more highly charged ion allows closer and faster approach of the ligands and greater force of attraction results in to stable complex. In general, greater the charge on the central metal ion, greater is the stability of the complex.

Stability α +ve oxidation state of CMI

(ii) Size of CMA: As the size of metal ion decreases, the stability of complex increases. If we consider the divalent metal ions, then the stability of their complexes increases with decrease in the ionic radius of the central metal as given below:

Ion	Mn^{+2},	Fe^{+2},	Co^{+2},	Ni^{+2},	Cu^{+2},	Zn^{+2}
Ionic radius (pm)	91	83	82	78	69	74

Therefore, the order of the stability is:

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

This is again because the charge density increases from left to right. This order is called natural order of stability of Irving William's order. Complexe compounds formed by the Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2} & Zn^{+2} ions with any particular ligand having the following stability order-

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

The stability order of these metal ions is called as Irving William order, which is due to the regular decrease in size from Mn^{+2} to Cu^{+2} and increase in size from Cu^{+2} to Zn^{+2} ion.

(iii) Electronegativity: This is another factor which determines stability of a complex. We can classify the metal ions in to two types:

Class 'a' metals: These are electropositive metals and include the alkali metals, alkaline earth metals, most of the non-transition metals and those transition metals having only a few d-valence electrons (such as Sc, Ti, V). Such metals have relatively few electrons beyond an inert gas core.

Class 'b' metals: These are less electropositive heavy metals such as Rh, Pd, Ag, Ir, Pt, Au, Hg, Pb, etc. These have relatively large number of d electrons.

Class 'a' metals, which attract electrons weakly, form most stable complexes with the ligands having electronegative atom such as nitrogen, oxygen and fluorine.

Class 'b' metals form most stable complexes with π acceptor ligands containing P, S, As, Br and I. Stability of the complexes is increases with the increase in the electronegativity of CMA.

Stability α *Electronegativity*

(iv) Polarising power: With the increases in the polarising power of CMA, stability of complexes also increases.

Stability α Polarising power of CMA

5.4.2. Nature of ligand

Some of the factors related with the nature of ligand which can affect the stability of complexes are given below:

(i) Size and charge of the ligands: In general Ligands with less charge and more size are less stable and form less stable coordination compounds. Ligands with higher charge have small size and form more stable compounds.

With the increase in the – ve charge value of the ligand stability of complexes is increase i.e.

Stability α –ve charge at the ligand

For example: F^- forms more stable complexes with Fe^{+3} than Cl^-, Br^- or I^-. Thus, a small fluoride F^- ion forms more stable Fe^{+3} complex as compared to the large Cl^- ion. This is due to easy approach of the ligand towards metal ion.

Similarly, a small dinegative anion O^{2-} forms more stable complexes than does the large S^{-2} ion.

(ii) Basis character: Higher the basic character or strength of the ligand, higher will be the stability of coordination compounds. It is defined that a strong base or higher basic strength of the ligand means it forms more stable compounds or its donating tendency of electrons to central metal ion is higher.

Stability α Basis character of ligand

For example: Aromatic diamines form unstable coordination compounds while aliphatic diamines form stable coordination compounds. Ligands like NH_3, CN- etc. have more basic character and thus, they form more stable compounds.

(iii) Chelate effect: The term chelate effect is used to describe special stability associated with complexes containing chelate ring when compared to the stability of related complexes with monodentate ligands. The chelate effect can be seen by comparing the reaction of a chelating ligand and a metal ion with the corresponding reaction involving comparable monodentate ligands.

We observed that complexes formed by chelating ligands such as ethylene diamine (en), ethylene diamine tetra acetic acid (EDTA), etc. are more stable than those formed by monodentate ligands such as H_2O or NH_3. This enhanced stability of complexes containing chelating ligands is called chelate effect.

The complex formation of Ni^{2+} with ammonia or 1, 2-diaminoethane, can be expressed by the following equations:

$$[Ni(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+} + 6H_2O \quad \beta_6 = 10^{8.76}$$

$$[Ni(H_2O)_6]^{2+} + 3en \longrightarrow [Ni(en)_3]^{2+} + 6H_2O \quad \beta 6 = 10^{18.28}$$

The overall stability constant value for the Ni^{2+} complex with three chelate rings (en) is about 10^{10} greater than that formed with six monodentate ligands (NH_3). Major factors responsible for the special stability of chelate can be attributed to increase in entropy as the reaction leading to the formation of the chelate results in increase in population of product species when compared to reactant species. However, with monodentate ligand, the reaction results in no change in population.

(iv) Steric effect: Complexes containing less sterically hindered ligands have more stability than the complexes having satirically hindered ligand (this factor remains dominated over the basic character of the ligand concept).

For example, $NH_2CH_2CH_2NH_2$ ethylene diamine (en) forms more stable complexes than its substituted derivative $(CH_3)_2N\ CH_2CH_2\ (CH_3)_2N$.

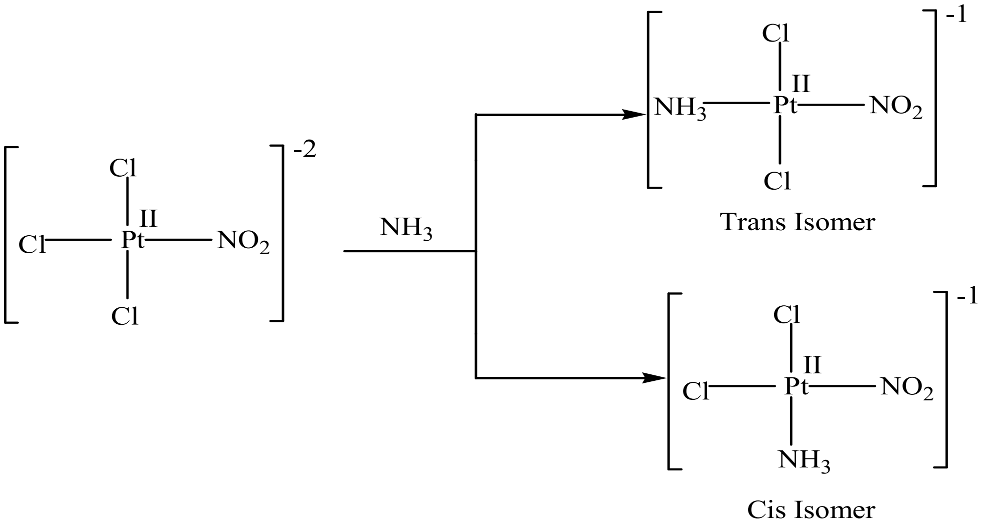
5.5 TRANS EFFECT IN THE SQUARE PLANAR COMPLEXES

Ability of any particular ligand to replace the ligand present in the trans position by any other ligand in the Pt (II) square planar complexes is known as it's trans effecting ability or power and this type of the replacement phenomena is called as trans effect.

Different ligands having the different trans effecting power. When we arrange the various ligands in order of their increasing trans effecting power, then the arrangement which is obtained is called as trans effecting series. Arrangement of certain ligands in order of their increasing trans effecting power in trans effecting series can be given as:

CN^-, NO, CO, $C_2H_4 > PR_3 > NH_2–CO–NH_2 > NO_2^-$, I^-, $SCN^- > Br^- > Cl^- > F^- > Py$, $NH_3 > H_2O$, OH^-

Example: When $[Pt(Cl)_3(NO_2)]^{-2}$ complexes ion react with NH_3 ligand, then two types of the isomeric forms of $[Pt(Cl)_2(NO_2)]^{-1}$ can be expected which are given below:



But experimentally, it was observed that only trans isomer is formed which can be due to the more trans effecting power of NO_2 than the Cl^- ion.

Theories of the trans effect phenomena: Trans effect phenomena in the Pt (II) square planar complexes can be explained by the two different types of the concepts:

1. Polarisability concept: According to the polarisability concept, if the Pt(II) square planar complexes contain two different ligands in the trans position, then the ligand with the high polorisability exhibits more trans effecting power because this ligand due to its more polarbility, increases the strength of bond with the CMA and removal of trans ligand become easier.

2. π-bonding concept: If the square planar complexes have non π-bonding and π-bonding ligands in trans position with each other, then the π-bonding ligand exhibits more trans effecting power because the π-bonding ligand increases the strength of bonding with the CMA and thus, removal of the non π-bonding ligand present trans to it become easier.

5.6 NUCLEOPHILIC SUBSTITUTION REACTIONS OF SQUARE PLANAR COMPLEXES

Before starting the study on mechanism of ligand substitution reactions in coordination compounds the following terms should be defined.

5.6.1 Transition state or activated complex

Let us consider the energy changes occurring during the course of the reaction.

$$\underbrace{X\text{—}Y\text{—}Z}_{\text{Reactants}} \longrightarrow \underbrace{X\text{—}Y + Z}_{\text{Product}}$$

Initially, both X and Y-Z posses certain amount of potential energy represented by the point (a) on the curve, increase in the potential energy occur until a critical energy state (in which Y-Z bond is weakened at point b) and ultimately the products, X-Y and Z are formed as shown at point (c) (Figure 5.1). In this process, the potential energy of the system is again changed into kinetic energy and then into heat or any other form of energy. Figure 5.1 (a) illustrates that for an exothermic reaction, the reactants originally posses more potential energy than the products and excess energy (+ΔH) is liberated as heat. Figure 5.1 (b) shows that for an endothermic reaction, the reactants have less potential energy than the products and, therefore, the reactants absorb heat equal to H from the surroundings during their change into products. The energy difference between the reactants and the products is ΔH and is called reaction energy.

The reaction,

$$X + Y\text{—}Z \longrightarrow X\text{—}Y + Z$$

The above reaction can take place by the following steps:

The molecule X approaches Y-Z from a direction remote from Z. While X draws nearer to Y,Z starts being repelled from Y until a stage is reached in which X and Z are rather loosely attached to Y and approximately equidistant from it. In this stage, the species X...Y...Z is formed. This species is called the transition state or activated complex which has the following characteristics.

1) In this X to Y and Y to Z distances are slightly greater than the normal bond lengths.

2) It is not a true molecule as the bonds are partial. Thus, it is of a transitory nature and refers to an imaginary molecule and hence cannot be isolated.

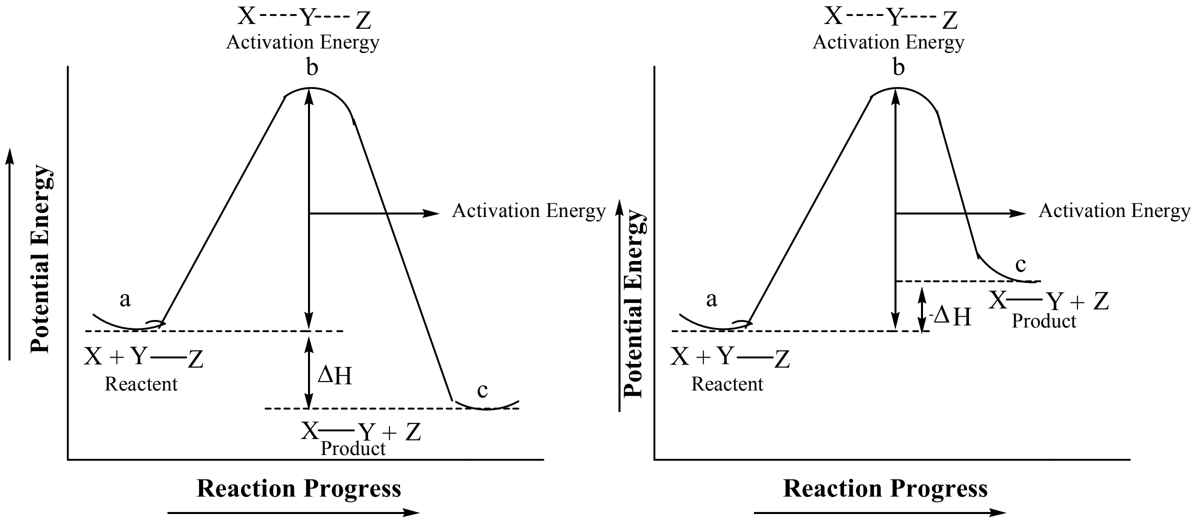
3) It has the maximum energy and hence, is the most unstable and has very-very short life time. The activated complex which is the most unstable state, changes to give the products X-Y and Z. The various steps responsible for the reaction are:

$$\underset{\text{Reactents}}{X + Y\text{—}Z} \longrightarrow \underset{\text{Activated complex}}{X\text{------}Y\text{-----}Z} \longrightarrow \underset{\text{Product}}{X\text{—}Y + Z}$$

The difference in energy between the reactants and the activated complex is called activation energy:

5.6.2 Energy changes in exothermic and endothermic reactions

The energy changes in exothermic and endothermic reactions are represented in Figure 5.1.



a. Energy change in an exothermic reaction **b. Energy change in an endothermic reaction**

Figure 5.1. Energy profile diagram of substitution reaction

Some terminologies related to substitution reaction s are as follows

Substrate:

A substrate may be defined as the reactant in which some bonds are broken and some new bonds are formed as a result of the attack of a reagent.

Attacking reagents:

We have mentioned above that a reaction proceeds when a reagent attacks on a substrate. These reagents are called attacking reagents and are of two types:

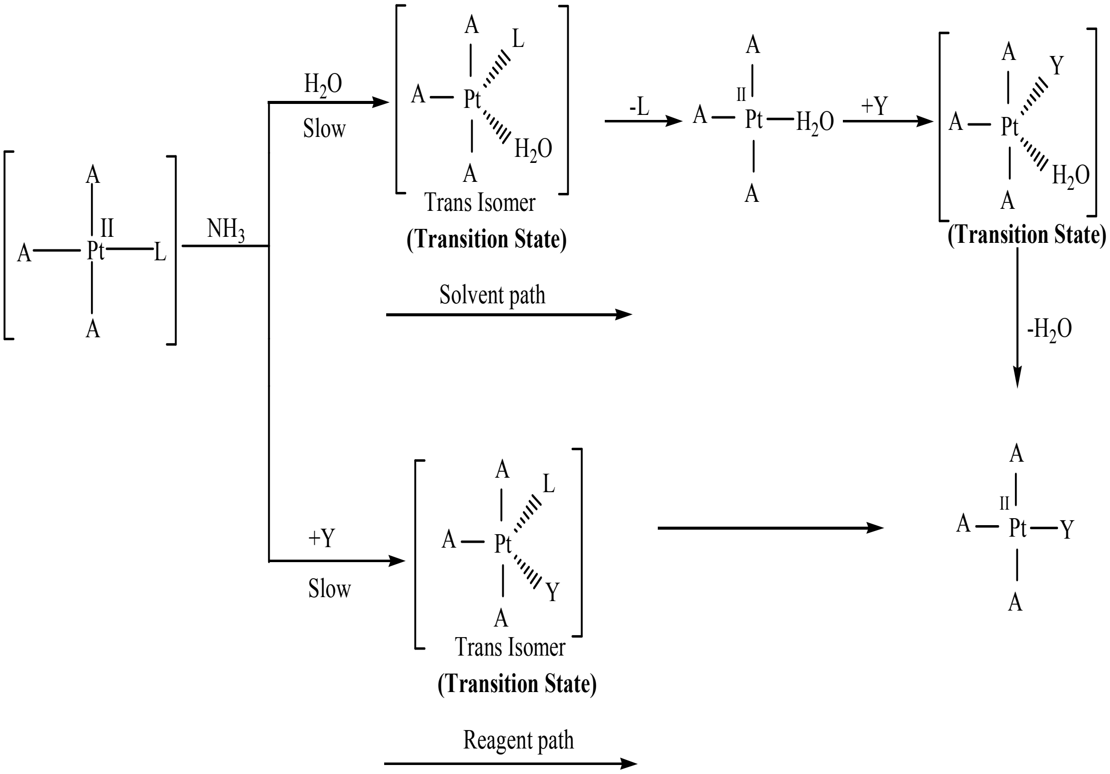
1) Electrophilic reagents
2) Nucleophilic reagents

1) **Electrophilic reagents:** These are also called electrophiles (electro means electron, philic means loving). These are electron loving (electron-seeking) or electron pair acceptor, since these are deficient by two electrons. Thus these are Lewis acids. These may be positively charged ions like carbonium ion, bromonium ion (Br^+), nitronium ion (NO_2^+), nitrosonium ion (NO^+), diozonium ion ($C_6H_5N_2^+$), bisulphonium ion (SO_2OH^+), proton (H^+), hydronium (H_3O^+) or neutral molecules such as BF_3, $AlCl_3$, SO_3, $FeCl_3$ etc.
2) **Nucleophilic reagents:** These are also called nucleophiles (nucleo means nucleus, philic means loving these reagents are nucleus-loving; nucleus-seeker). Since, the nucleus is electrically positive, the nucleophiles are electrically negative ions like carbanion, chloride

ion (Cl^-), hydroixdie ion(OH^-), cyanide ion (CN^-), bisulphide ion (SH-), hydride ion (H^-) or electron-rich neural molecules such as NH_3, H_2O. Since, these have unshared pair of electrons; these are called as Lewis bases (i.e., electron pair donor). In coordination chemistry, the central metal ion is an electrophile, since, it accepts an electron pair while the ligands are nucleophiles because these donate electron pairs.

5.6.3 Nucleoplhilic substitution reactions (S_N2) in square planar complexes

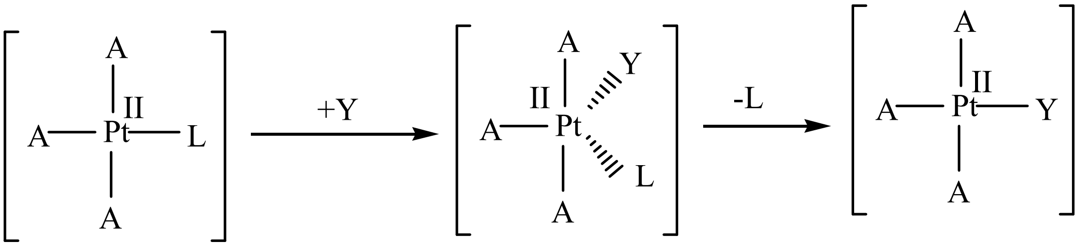
When the Pt (II) square planar complexes undergo nucleophilic substitution reaction with the various ligands, then the reaction occurs by the S_N2 mechanism through two different paths, which are known as solvent path and reagent path. Nucleophlic substitution reaction in the $[Pt^{II}A_3L]$ square planar complex by the $S_N2$mechanism takes place through both the solvent path & reagent path which can be represented as:



5.6.4 Factors affecting the S_N2 reaction of square planar complexes

Some of the factors which can affect the rate of the S_N2 reaction in the square planar complexes are given below:

1. **Trans Effect:** In the Pt(II) square planar complexes, with the increase in the trans effecting power of ligand (A) present in the trans position of leaving ligand (L), the rate of $S_N2$reaction increases.



Where A = C_2H_4 , NO^{2-}, Br^-, Cl^-

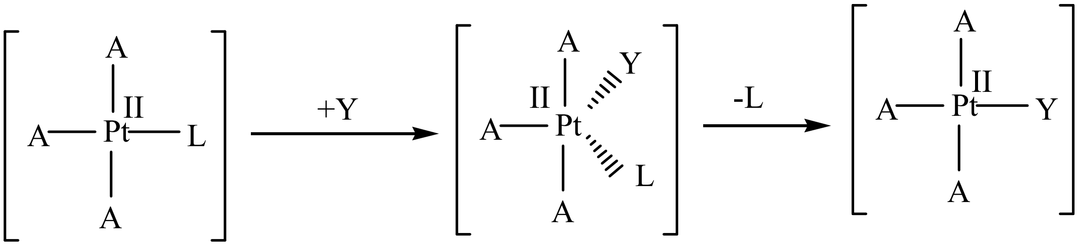
L = F^-

Trans effecting power of A = $C_2H_4 > NO^{2-} > Br^- > Cl^-$

Rate of SN_2 reaction = $C_2H_4 > NO^{2-} > Br^- > Cl^-$

2. **Nature of leaving ligand (L):** With the increase the trans effecting power of leaving ligand (L), it's bonding with CMA become more and more stable by which it's rate of replacement decreases.

Example:



Where A = $C_2 H_4$

L = PR_3 , NO_2^-, Br^-, Cl^-, F^-

Trans effecting power of L = $PR_3 > NO_2^- > Br^- > Ci^- > F^-$

Rate of $S_N2$reaction = $PR_3 > NO_2^- > Br^- > Cl^- > F^-$

3. Solvent Effect: According to the kinetic evidence of $S_N2$reaction, it was observed that $S_N2$reaction can also be affected by the solvent.

5.7 SUMMARY

- Thermodynamic stability of a complex is related to the thermodynamic parameters like bond energy, stability constant or formation constant.
- The complexes with high formation constant are stable and with low formation constant are unstable complexes.
- Kinetic stability of a complex is related to the kinetic parameters like rate of reaction. The complexes with low or negligible rate of replacement reaction in the solution are known as inert complexes amd the complexes with high rate of replacement reaction in the solution are known as labile complexes.
- Stability of a complex depends upon charge on the CMA, size of CMA, electronegativity of CMA, polarising power of CMA, size and charge of the ligands, basic character of ligands, chelate effect and steric effect.
- Chelate effect is the special stability associated with complexes containing chelate ring. It depends upon ring formation and ring sizes effects. Tran's effect is the ability of a particular ligand to replace a ligand present at the trans position to any other ligand in a square planar complex.
- Kinetic studies of complexes show that reactions of complexes are only approximate to $S_N1$and $S_N2$and that the reactions mechanisms are influenced by solvent, ion-pair formation and pH.

5.8 TERMINAL QUESTIONS

1. What are labile complexes?
2. What is chelate effect?

3. Name the type of mechanism commonly observed in square planar substitution reactions.
4. What is thermodynamic stability of a complex?
5. Define stepwise stability constant and overall stability constant.
6. Name two metal ions which generally form square planar complexes.
7. Define trans effect.
8. What do you mean by inert complexes?
9. What do you understand by the stability of a chelate ring?
10. What do you mean by labile complexes and inert complexes? Explain.
11. How does the presence of ring structure affect the stability of complexes?
12. Write short notes on: (i) Labile and inert complexes (ii) Stepwise and overall stability constants.
13. What is trans effect? Discuss the theories for trans effect.
14. How does the central metal ion affect the stability of a complex?
15. Define trans-effect and ligands with trans-directing effect. Explain these with an example.
16. Explain the term associative and interchange associative in the reaction.
17. How does the following factor affect the stability of complexes?
    (i) Naute of central metal ion
    (ii) Nature of lignad
19. What do you understand and by the stability of a chelate ring?
20. What are labile and inert complexes? Do they convey same meaning as unstable and stable complexes?
21. Which theory of trans effect explains larger trans effect of CO as compared to pyridine?
22. Explain the difference between thermodynamic stability and kinetic stability of the complexes.
23. Name the factors affecting the stability of metal complexes. Discuss any one example which is thermodynamically stable but kinetically labile? 24. Derive relationship between stepwise and overall stability constants.
25. How does nature of the central metal ion affect the stability of the complex?
26. What is meant by the terms: inert and labile complexes? Show that inertness of a complex is different from its thermodynamic stability.

27. What are the possible pathways in which a lignad may replace another lignad in square planar complexes?
28. Discuss mechanism of substitution reactions in square planar complexes.
29. Discuss mechanism of nucleophilic substitution reactions in square planar complexes.
30. How do you explain the aceleration of substitution reactions in square planar complexes?
31. How does nature of the ligand affect the stability of the complexes?
32. What are the factors that affect the stability of complexes?
33. Define trans effect and ligands with trans direction effect. Why should trans effect be controlled kinetically?
34. (a) What do you mean by labile and inert complexes?
    (b) How chelation increases the stablity constants?
    (c) What are stapwise and overall stability constants?
35. Discuss steric and chelate effect to describe the stability of complexes.
36. (a) Define stepwise stability constant and overall stability constant giving one example each.

(b) What is trans effect? Explain the theories for it.

(c) How do the natures of central metal ion as well as lignad affect the stability of the complexes?

37. Out of the following pair of complexes which one is more stable? Also give the reason for your answer?
    1. $K_4 [Fe(CN)_6]$ & $K_3 [Fe(CN)_6]$
    2. $[Co(H_2O)_6]^{+2}$ & $[Co(NH_3)_6]Cl_2$
    3. $[Cu(en)_2] Cl_2$ & $[Cu(NH_3)_4]^{2+}$–
    4. $[Co(NO_2)_6]^{-4}$ & $[Co(NO_2)_6]^{-3}$
    5. $[Mn(F)_6]^{4-}$ & $[Mn(I)_6]^{4-}$
38. Explain why stability constant value varies in the following order:

$$[Cu(NH_3)_4]^{+2} < [Cu(en)_2]^{+2} < [Cu(trine)]^{+2}$$

39. Represent the stepwise formation and overall formation of the $[Ni(NH_3)_6]^{+2}$ ion in the aqueous solution of Ni^{+2} ion.

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UNIT-6 METAL CARBONYL AND ORGANO METALIC CHEMISTRY

CONTENTS:

6.1 OBJECTIVES

In this unit, you will learn the following:

- Introduction about metal carbonyls.
- Classification of metal carbonyls.
- Principal synthetic routes of metal carbonyls.
- Understand static and dynamic structures of mono- and di-nuclear carbonyls.
- Understand and apply reactions of coordinated CO.
- Synthesis, characterization and reactivity of the metal carbonyl compounds.
- CO ligand and its binding ability to metal.
- Synergism between the ligand to metal forward σ-donation and metal to ligand backward π-donation in a metal-CO interaction.
- Classification of organometallic compounds.
- Understand and apply the 18-electron rule for mono- and poly-nuclear examples.
- Organometallic reactions useful in organic synthesis.

6.2 INTRODUCTION

Organometallic Chemistry is the study of chemical compounds containing at least one bond between a carbon atom of an organic compound and a metal, including alkali metal, alkaline earth metal, transition metal, and other cases. Moreover, some related compounds such as transition metal hydrides and metal phosphine complexes are often included in discussions of organometallic compounds. Metal carbonyls of transition elements is an another important class of organometallic compounds. The field of organometallic chemistry combines aspects of traditional Inorganic and Organic Chemistry.

π- Acid ligand and acid complexes

All the ligands having the ability to denote the electron pair as well as empty π orbitals to accept the electron pair are known as π acid lgands or π acceptor ligands or π bonding ligands.

Example: CO, CN^-, NO^+ etc.

These ligands combine with the transition metals at very low or zero oxidation state to form the complexes called as π acid complexes. **π** Acid complexes contain two types of the bonds known as L→M σ-bond & M→L-**π** bond.

6.3 DEFINITION OF METAL CARBONYLS

Metal carbonyls are **c**ompounds which are formed by the combination of carbonyl ligand with the transition metal atom in the low or zero oxidation state.

6.4 NOMENCLATURE OF METAL CARBONYLS

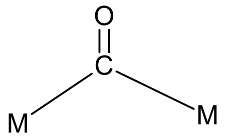
The nomenclature of the metal carbonyls depends on the number and type of central metal atoms (CMA), the charge of the complex, the number and type of ligands and their binding modes.

- The metal carbonyls can occur as positively charged metal carbonyl cations or as negatively charged metal carbonylates or as neutral complexes.
- The carbon monoxide ligand may be bound as terminal (bind to a single metal atom) or bridging (bind to two or more metal atoms).
- These metal carbonyls may be homoleptic, containing only CO ligands, such as ($Ni(CO)_4$ or $Fe(CO)_5$ or metal carbonyls are heteroleptic that contain a mixture of ligands.
- The metal carbonyls containing only one metal, are called as mononuclear metal carbonyls. Chromium, iron, nickel, Os etc. form neutral mononuclear complexes.
- Polynuclear metal carbonyls contain more then one metal atom center such as $Fe_2(CO)_5$, $Fe_3(CO)_{12}$ etc.
- The number of carbon monoxide ligands in metal carbonyls is described by a Greek numeral value, followed by the word carbonyl.
- Carbon monoxide (carbonyl) has different types of binding modes in metal carbonyls. They differ in the hapticity and bridging mode. The hapticity can be defind as the number of carbon atoms, which are directly bonded to the central atom. The denomination of hepticity can be done by letter η^n, which is used as a prefix to the name of the complex (n is the number of directly bonded carbon atoms ligands to the metal). The monohapto coordination

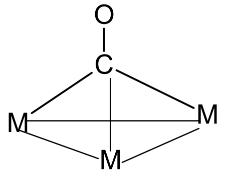
is usually not separately designated. If metal atom in a metal carbonyl is bonded to two atoms of ligands, it will be referred to as dihapto coordinated η^2.

- If CO in the metal carbonyls are present as bridges between metal atoms, they can be nominated as:

  Between two metal atoms = μ^2-CO



  Between three metal atoms = μ^3-CO

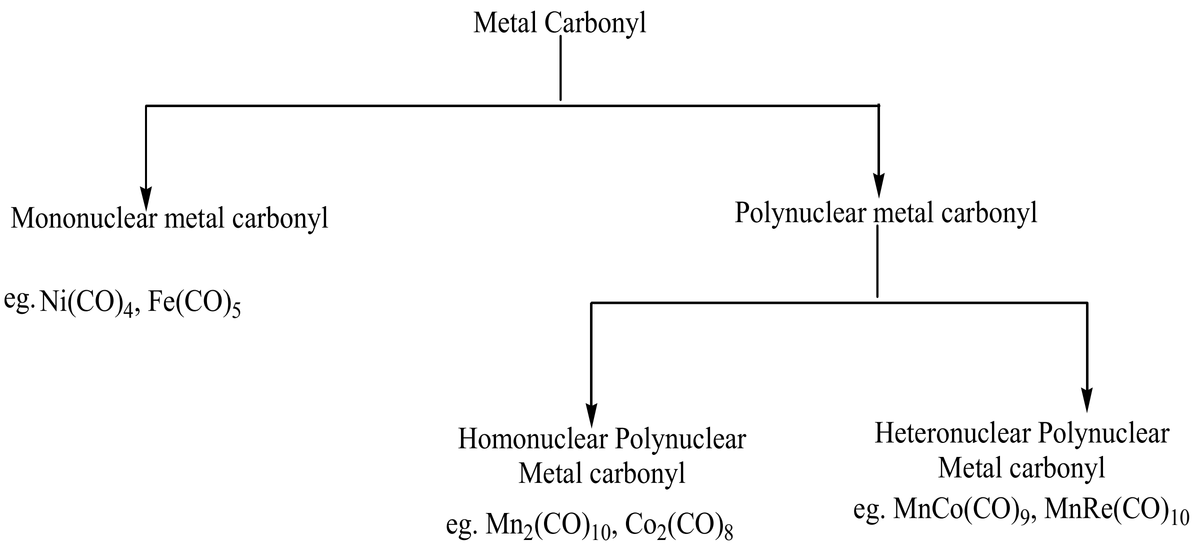


6.5 CLASSIFICATION OF METAL CARBONYLS

Two types of the classification are used to define the metal carbonyls which is given below:

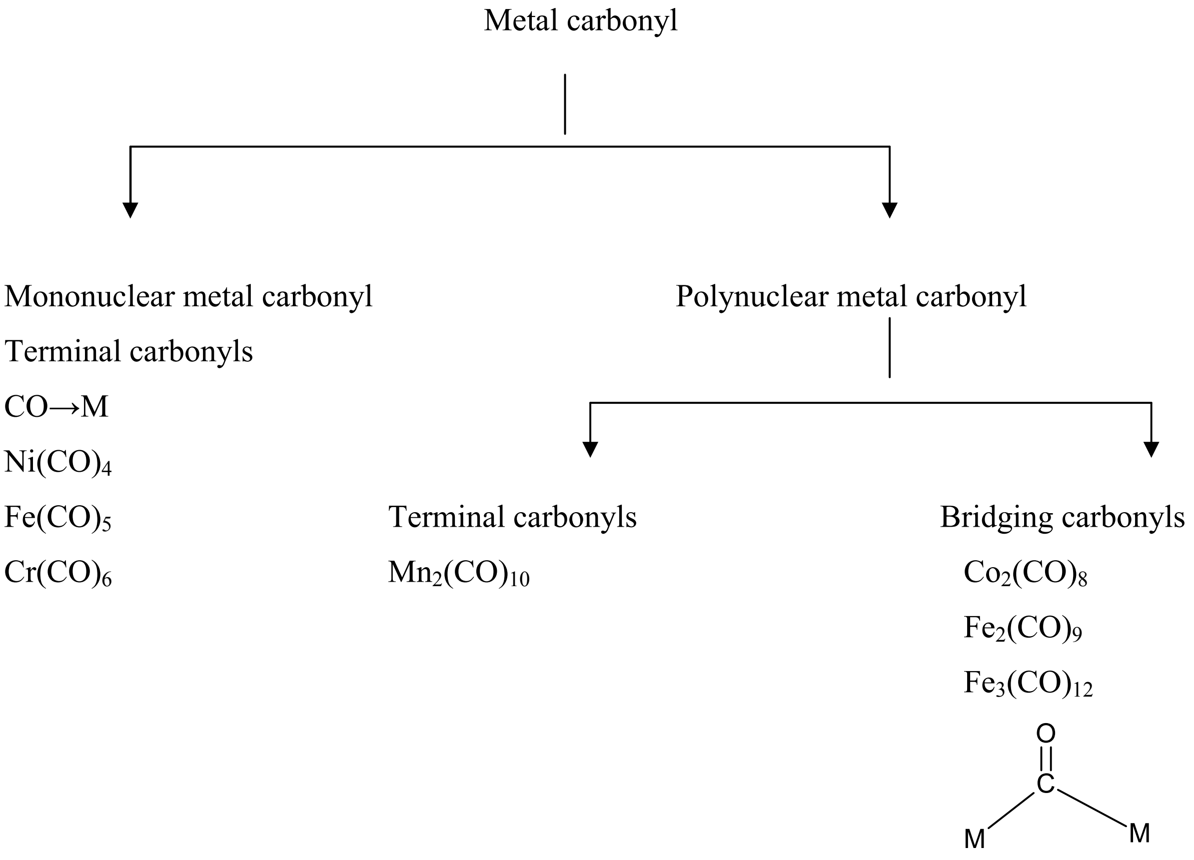
6.5.1 Classification I (based on the number of metal atom)

This classification explains the following types of carbonyls:



6.5.2 Classification II (based on the nature of bonding)

This classification explains the following types of carbonyls.



6.6 GENERAL METHODS OF PREPARATION

Some of the methods for the preparation of metal carbonyls can be given as:

1. **By the direct synthesis:** When the metal atoms (already reduced) react with the carbonyl ligand under the particular condition of temperature and pressure, then there can occur the formation of metal carbonyl.

$$\mathrm{Ni + 4CO \xrightarrow[1\ atm]{25°C} Ni(CO)_4}$$

$$\mathrm{Fe + 5CO \xrightarrow[10\ atm]{200°C} Fe(CO)_5}$$

2. **Reduction:** In this method, the metal salts like halides, oxides etc. are reduced in the presence of CO gives metal carbonyls.

$$\mathrm{CrCl_3 + Al + 6CO \xrightarrow[C_6H_6]{AlCl_3} Cr(CO)_6 + AlCl_3}$$

$$\mathrm{WCl_6 + 3Zn + 6CO \xrightarrow{AlCl_3/120^0C} W(CO)_6 + 3ZnCl_2}$$

$$\mathrm{OsO4 + 9CO \xrightarrow{250^0C,\ 350\ atm} Os(CO)_a + 4CO_2}$$

3. **Photolysis or thermolysis:** Higher carbonyls such as $Fe_2(CO)_9$ and $Os_3(CO)_{12}$ can be synthesised by photolysis or thermolysis of lower metal carbonyls.

$$2Fe(CO)_5 \xrightarrow{hv} Fe_2(CO)_9 + CO$$

$$3Os(CO)_5 \xrightarrow{hv} Os_3(CO)_{12} + 3CO$$

4. By the substitution reaction: Some carbonyls can be prepared by substitution reactions of metal halides with carbonyl.

$$VCl_3 + 6CO \overset{Na}{\rightarrow} V(CO)_6 + 3NaCl$$

$$CrCl_3 + 6CO \overset{(C_2H_4)_3Al}{\rightarrow} Cr(CO)_6 + 3AlCl_3$$

$$MoCl_6 + 6CO \overset{Na}{\rightarrow} Mo(CO)_6 + 6NaCl$$

5. By the reaction of CO with oxides: Some carbonyls can be prepared by the reaction between carbonyl and metal oxides.

$$OsO_4 + 9CO \rightarrow Os(CO)_5 + 4CO_2$$

6.7 PROPERTIES OF METAL CARBONYLS

6.7.1 Physical properties

a. **Physical state:** Most of the metallic carbonyls are either liquids or volatile solids.

b. **Colour:** Majority of the mononuclear carbonyls are colourless to pale yellow except $V(CO)_6$, which is a bluish-black solid. Polynuclear carbonyls exhibit dark colour.

c. **Solubility:** Metal carbonyls are soluble in organic solvents like diethyl ether, glacial acetic acid, benzene, carbon tetrachloride and acetone.

d. **Magnetic Property:** All the metal carbonyls except $V(CO)_6$, are diamagnetic. The metals with even atomic number have a tendency to form mononuclear carbonyls. Therefore, all the electrons in the metal carbonyls are paired. While, in case of dinuclear metal carbonyls, the unpaired odd electrons present in the metal atom, are utilized in the formation of metal-metal bonds.

e. **Thermal Stability:** Most of the metal carbonyls melt or decompose at low temperatures and therefore, they are very toxic in nature.

6.7.2 Chemical properties

The metal carbonyls show a variety of chemical reactions which are given as:

a. **Ligand substitution reactions:** Substitution of carbon monoxide ligand can be carried out by various monodentate and bidentate ligands using thermal and photochemical reactions. Monodentate ligands such as phosphine (PR_3), cyanide (CN^-), isocyanides (CNR) and ethers can completely or partially replace the carbonyl group (CO).

$$Fe(CO)_5 + 2CNR \longrightarrow Fe(CO)_3(CNR)_2 + 2CO$$

$$Ni(CO)4 + 2CNR \longrightarrow Ni(CNR)_4 + 4CO$$

$$Fe(CO)_5 + 2Ph_3P \longrightarrow Fe(CO)_3(PPh_3)_2 + 2CO$$

b. **Reaction with sodium metal:** Sodium metal and its amalgam (NaHg) can be used to reduce the metal carbonyls.

$$Cr(CO)_6 + 2Na \longrightarrow Na_2[Cr(CO)_5] + CO$$

$$Mn_2(CO)_{10} + 2Na \longrightarrow 2Na[Mn(CO)_5] + CO$$

c. **Reaction with sodium hydroxide:** On reaction with sodium hydroxide, metal carbonyls form metal carboxylic acid complex by nucleophilic attack of hydroxide ion.

$$Fe(CO)_5 + NaOH \longrightarrow Na[Fe(CO)_4COOH]$$

$$Na[Fe(CO)_4COOH] + NaOH \longrightarrow Na[HFe(CO)_4] + NaHCO_3$$

$$Na[HFe(CO)_4] + H^+ \longrightarrow H_2Fe(CO)_4 + Na^+$$

The above reaction is known as Heiber base reaction.

d. Reaction with hydrogen: Some of the metal carbonyls react with hydrogen to give carbonyl hydrides.

$$Co_2(CO)_8 + H_2 \xrightarrow{165^0C/200atm} 2[Co(CO)_4H]$$

6.8 MONONUCLEAR CARBONYLS

The methods of preparation, properties and structure of some mononuclear metal carbonyls are given below:

$Ni(CO)_4$,Nickel tetracarbonyl

Preparation

It can be prepared by passing carbon monoxide over nickel in the temperature range of 60-100°C.

$$Ni + 4CO \xrightarrow{60^0C} Ni(CO)4$$

It can also be prepared by passing CO through alkaline suspensions of nickel cyanate or nickel sulphide .

$$NiS + 4CO \longrightarrow Ni(CO)_4 + S$$

$$Ni(CN)_2 + 4CO \longrightarrow Ni(CO)_4 + C_2N_2$$

Properties

A. Physical Properties:

It is a colourless liquid with a melting point -25°C, boiling point 43°C and decomposition temperature in the range of 180–200°C. It is insoluble in water but dissolves in organic solvents.

B. Chemical Properties

1. It reacts with concentrated sulphuric acid along to form nickel sulphate, hydrogen and carbon monoxide.

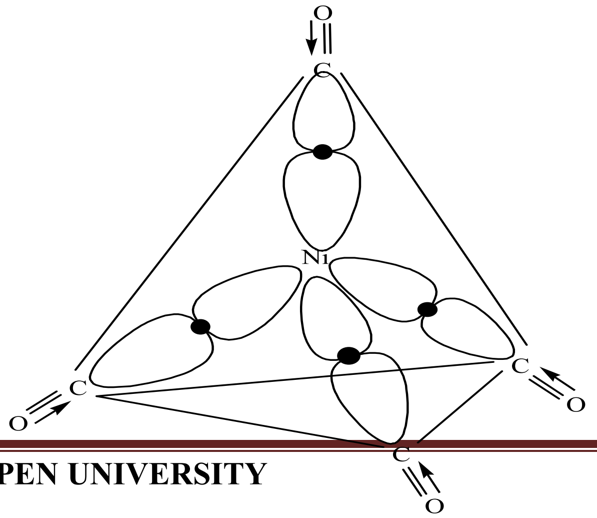
$$Ni(CO)_4 + H_2SO_4 \longrightarrow NiSO_4 + H_2 + 4CO$$

2. It reacts with moist nitric oxide to form deep blue coloured compound.

$$2Ni(CO)_4 + 2NO + 2H_2O \longrightarrow 2Ni(NO)(OH) + 8OH^- + H_2$$

Uses

1. $Ni(CO)_4$, on heating, decomposes to nickel metal and hence, it is used in the production of nickel by Mond's process.
2. It is used for nickel plating on the other metals.
3. It is used as a catalyst during the synthesis of acrylic monomers in plastic industries.



Tetrahedral structure of nickel tetracarbonyl

$Fe(CO)_5$, Iron pentacarbonyl

Preparation

1. **$Fe(CO)_5$**can be prepared by passing carbon monoxide over iron powder at high temperature and pressure.

$$Fe + 5CO \xrightarrow{200^0C,\ 100\ atm} Fe(CO)_5$$

2. It can also be prepared by carbonylation of ferrous iodide / sulphide in presence of Cu-metal, which acts as a reducing agent.

$$2FeS + 10CO + 2Cu \xrightarrow{200^0C,\ 200\ atm} Fe(CO)_5 + Cu_2S$$

Properties

A. Physical properties

1. It is a pale yellow liquid having melting point -20°C, boiling point 103°C and decomposition temperature around 250°C.
2. It is insoluble in water but soluble in methanol, acetone, glacial acetic acid, diethyl ether and benzene.
3. It is readily hydrolysed by acids and water.

B. Chemical Properties

1. Cold solution of penta carbonyl iron in glacial acetic acid undergoes dimerization in ultra-violet light.

$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

2. It reacts with sodium metal in liquid ammonia to give carbonylate anion.

$$Fe(CO)_5 \ + \ \xrightarrow{\text{liquid } NH_3} Na_2Na[Fe(CO)_4] \ + \ CO$$

3. It reacts with halogens in non-aqueous solvents to form stable tetracarbonyl halides.

$$Fe(CO)_5 \ + \ X \longrightarrow Fe(CO)_4X \ + \ CO$$

6.9 STRUCTURE AND BONDING IN METAL CARBONYLS

6.9.1 Molecular orbital diagram of carbonyl

Mode of attachment of carbonyl ligand in metal carbonyl may be of the two types: terminal carbonyl ligand and bridging carbonyl ligand. To determine the structure of metal carbonyls, at first we have to study the structure of both the terminal and bridging carbonyl ligand.

A. Structure of terminal CO ligand

According to the Valence Bond Theory, both the C and O atoms undergo sp hybridization. After that there corresponding orbitals undergo overlapping with each other to construct the stricture of terminal CO ligand which can be given as:

$C \longrightarrow 2S^2, 2Px^1, 2Py^1, 2Pz^0$

$C_{Sp} \longrightarrow (Sp_C)^2, (Sp_C)^1, 2Py^1, 2Pz^0$

$O \longrightarrow (Sp_O)^2, (Sp_O)^1, 2Py^1, 2Pz^2$

$O_{Sp} \longrightarrow 2S^2, 2Px^1, 2Py^1, 2Pz^2$

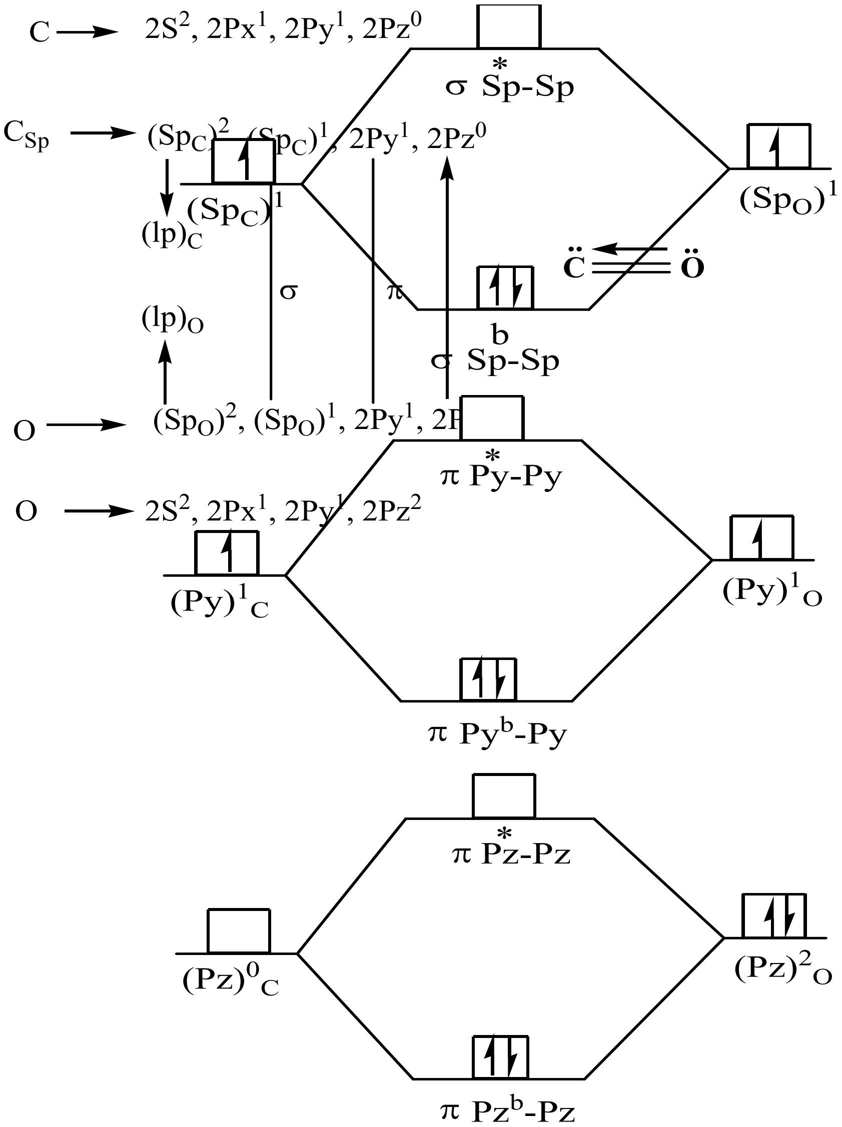


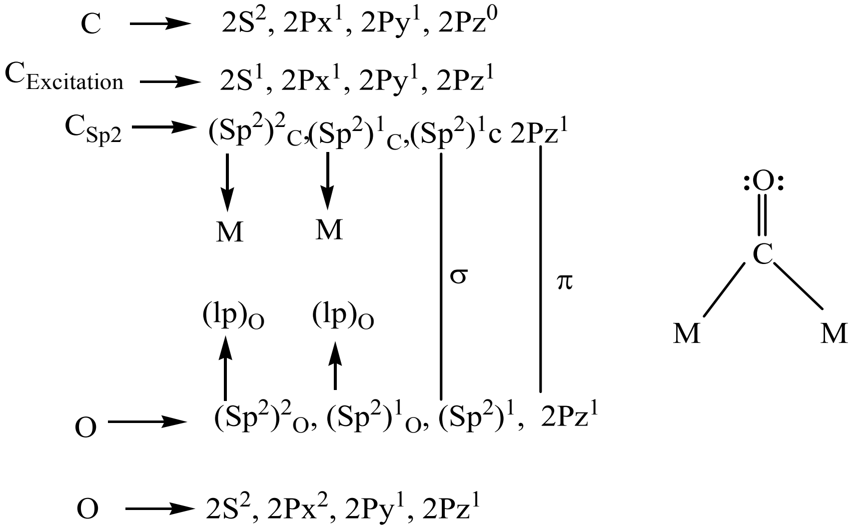
Figure 6.1: *Molecular orbital diagram of carbonyl*

B. Structure of terminal CO ligand according to Molecular Orbital Theory (MOT)

According to MOT, at first both the carbon and oxygen atoms undergo sp hybridization and after that the corresponding orbitals of C and O undergo Molecular Orbital (MO) formation to give the different types of the molecular orbitals as given in Figure 6.1.

C. Structure of bridging CO ligand

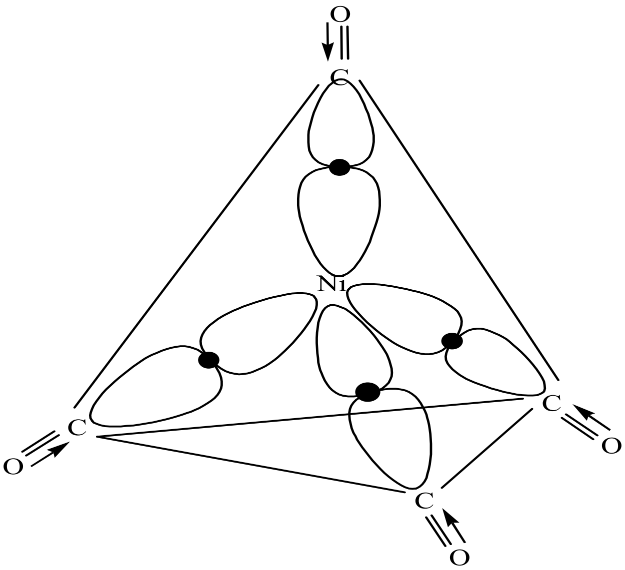
In case of bridging CO ligands, at first both the C and O atom undergo sp^2 hybridization and after than corresponding orbitals of the C and O atoms undergo overlapping with each other to construct the structure of CO ligand, which can be given as:



6.9.2 Sigma bonding (Mononuclear metal carbonyls)

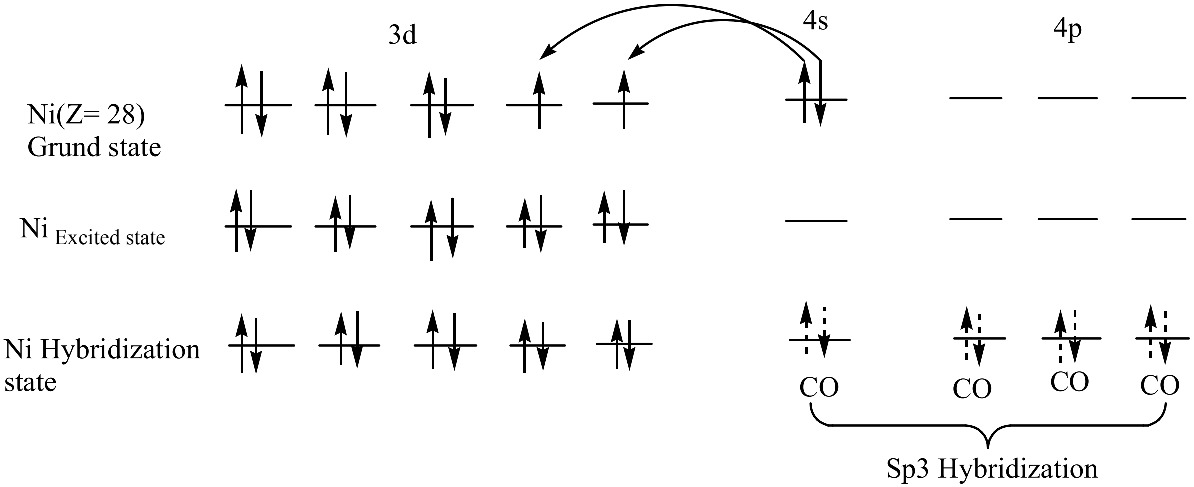
Nickel tetracarbonyl

Nickel tetracarbonyl has a tetrahedral geometry with Ni-C bond lengths of 1.5 Å (Figure 6.2). Nickel atom in $Ni(CO)_4$ is sp^3 hybridized. All the ten electrons present in the valence shell of Ni atom (Ni = $3d^8\ 4s^2$) get paired in 3d orbitals due to strong field CO ligand and the valence shell configuration of Ni atom in $Ni(CO)_4$ molecule becomes $3d^{10}\ 4s^0$ (Figure 6.3). The OC→Ni back bond results from the overlapping of empty sp^3 hybrid orbital of Ni atom and the HOMO of C atom in CO molecule.



Tetrahedral structure of nickel tetracarbonyl

Figure 6.2: *Tetrahedral geometry of nickel tetracarbonyl*



sp3 hybridization of nickel atom in nickel tetracarbonyl

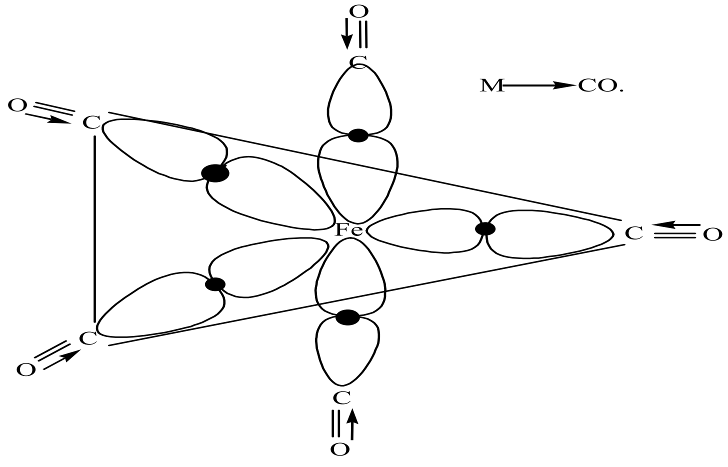
Figure 6.3 *sp^3 hybridization of nickel atom in nickel tetracarbonyl*

Electron density on nickel atom increased due to acceptance of four electron pairs by nickel in zero oxidation state. To reduce this electron density on the electropositive metal centre, nickel atom donates back some electron density to the lowest unoccupied molecular orbital (LUMO) orbitals of CO molecule resulting in the formation of a double bond. i.e. $M \longrightarrow CO$.

Iron pentacarbonyl

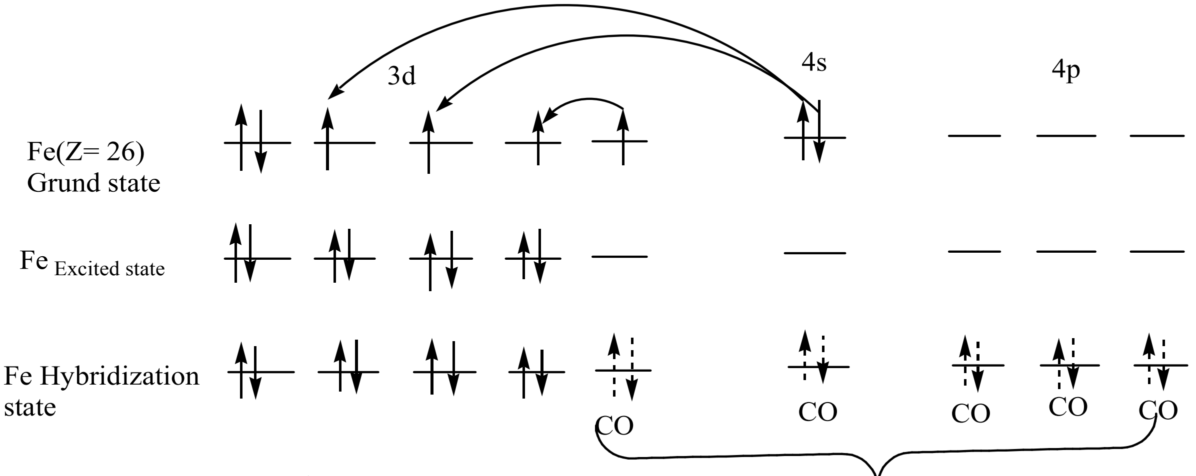
The geometry of iron pentacarbonyl is trigonal bipyramidal (Figure 6.4). The Fe-C bond lenth is 1.80 Å and 1.84 Å for axial and equatorial bonds respectively. The molecule is diamagnetic.

The central iron atom is dsp^3 hybridized. All the eight electrons present in the valence shell of Fe atom (Fe-3d^{6}4s^2) get paired in four 3d orbitals due to strong field CO. Thus, the valence shell configuration of Fe in Fe(CO)$_5$ becomes 3d^{8}4s^0. The OC→Fe bond results by the overlap between the empty dsp^3 hybrid orbitals on Fe atom and the highest occupied molecular orbitals (HOMO) of C atom in CO molecule as shown Figure 6.5.



Trigonal bipyramidal structure

Figure 6.4: *Trigonal bipyramidal geometry of iron pentacarbonyl*

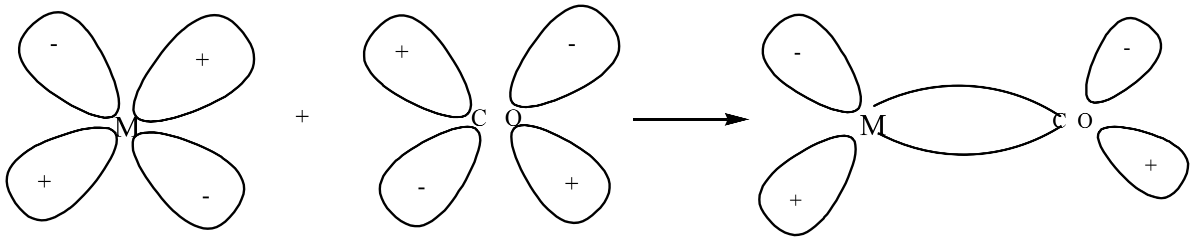


dsp^3 hybridization in iron pentacarbonyl

Figure 6.5: *dsp^3 hybridization of iron atom in iron pentacarbonyl*

6.9.3 Pi bonding (Polynuclear metal carbonyls)

After the formation of normal $M \rightarrow CO$ σ bond in the metal carbonyl, accumulation of a large amount of the –ve charge occur at the central metal atom (CMA) due to which there can occur repulsion and to minimize this repulsion or this extra accumulated –ve charge, the filled d-orbitals of CMA undergo lateral (sidewise) overlapping with the empty π* p_z- p_z molecular orbital of CO ligand to construct the M←CO π bond or back bond that can be represented as follows (Figure 6.6).



Filled d orbital of CMA (donar orbital)

Vacant π Pz*- Pz MO Acceptor orbital

Figure 6.6: Pi bond formation in metal carbonyls

Briginging metal carbonyls

Polynuculear metal carbonyls containing bridging CO, terminal CO and M—M bond are known as bridging metal carbonyls (Figure 6.7), Structures of the bridging metal carbonyls can be analysed on the basis of Infra Red (IR) spectra. The terminal CO bands appear in the orange of 1900- 2050cm^{-1} while the bridging CO absorption bands appear in the range of 1800-1900cm^{-1}.

$Fe_2(CO)_9$

Fe = $3d^6, 4s^2$, 4p0,$4d^0$

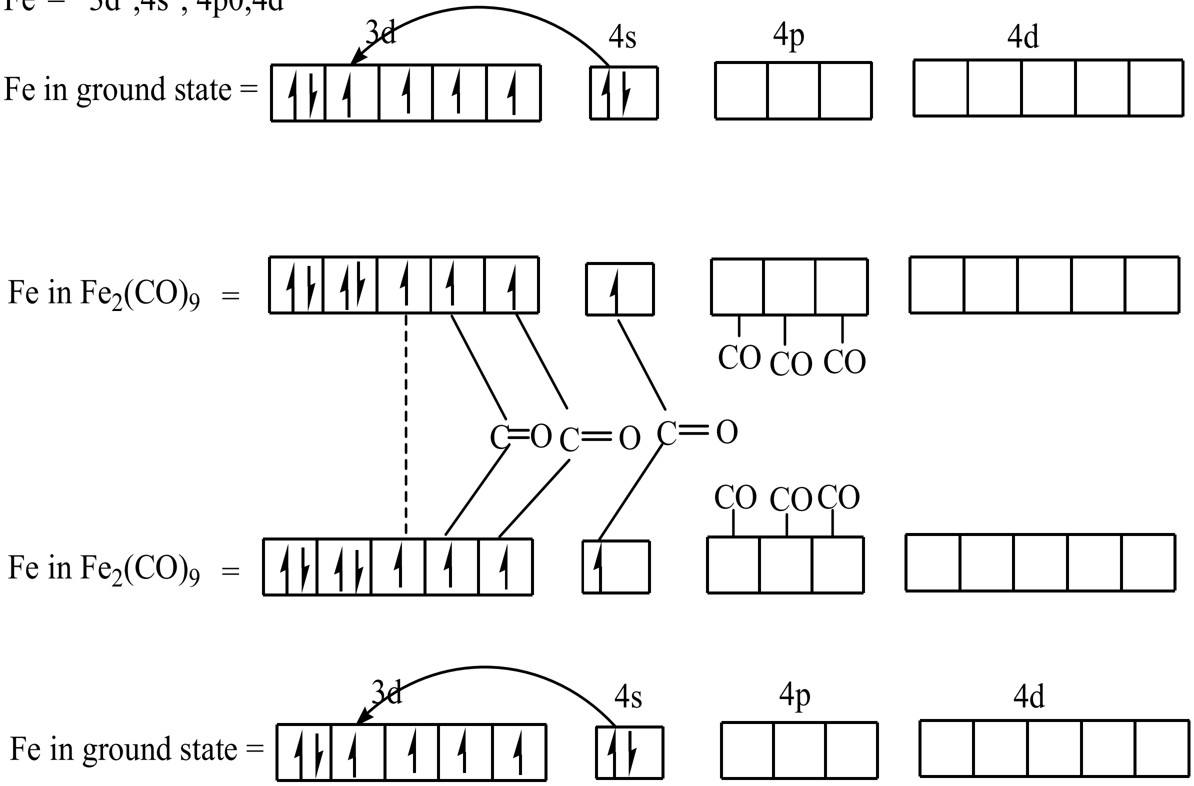


Figure 6.7: Bonding in bridging metal carbonyls

Effective Atomic Number (EAN) rule

Effective Atomic Number (EAN) is the total number of electrons surrounding the a metal atom/ion in a complex compound. This rule is given by Sidwick and is also known as inert gas rule. The EAN of a metal atom/iom in a stable complex is equal to the atomic number of a noble gas present in the same period of the periodic table. Most of the organometallic compounds along with carbonyls and nitrosyls obey the EAN rule.

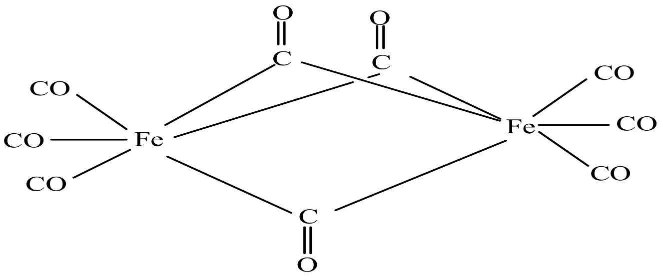
Calculation of EAN

Effective Atomic Number of the central metal atom/ion in a metal carbonyl can be determined with the help of following general formula:

$$\textbf{EAN} = \left[\begin{matrix}\textbf{No of electrons at CMA}\\ \textbf{in its oxidation state}\end{matrix}\right] + 2\left[\textbf{No of terminal CO Ligand}\right] + 1\left[\textbf{No of bridge by CO ligand}\right] + 1\left[\textbf{No. of M- M bond}\right]$$

If the EAN value for the central metal atom/ion in the metal carbonyl comes equal to the atomic number of the next inert gas, then the complex will said to follow the EAN rule.

Example :- (i) $Fe_2(CO)_9$



No. of e^- at CMA (Fe) = 26

No. of e^- donated by 3 terminal CO = 6

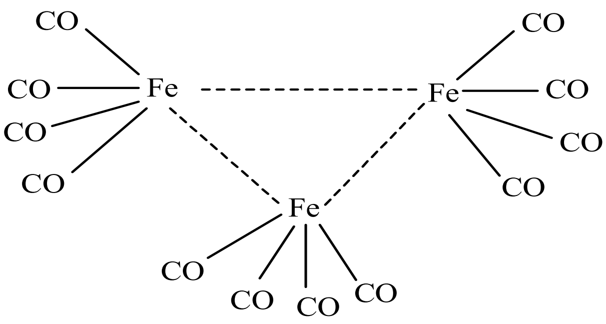
No. of e^- donated by 3 bridging CO = 3

No. of e^- demoted by 1 M –M bond = 1

So, EAN of Fe in $Fe_2(CO)_9$ = 36

Thus, this complex is said to follow the EAN rule.

(ii) $Fe_3(CO)_{12}$



No. of electrons at CMA (Fe) = 26

No. of electrons donated by 4 terminal CO = 8

No. of electrons donated by 3 bridging CO = 3

No. of electrons donated by 2 M –M bond = 2

So, EAN of Fe = 36 and the complex will follow EAN rule.Table 6.1 is presenting calculation for EAN in some metal carbonyls.

Table 6.1: Calculation of effective atomic number (EAN) in some metal carbonyls

Metal Carbonyls	**Atomic number of iron atom**	**terminal carbonyl groups**	**No. of bridges**	**M-M bonds**	**EAN**
$Ni(CO)_4$	28	4 x 2 = 8	0	0	36 [Kr]
$Fe(CO)_5$	26	5 x 2 = 10	0	0	36 [Kr]
$Ru(CO)_5$	44	5 x 2 = 10	0	0	54 [Xe]
$Os(CO)_5$	76	5 x 2 = 10	0	0	86 [Rn]
$Cr(CO)_6$	24	6 x 2 = 12	0	0	36[Kr]
$Mo(CO)_6$	42	6 x 2 = 12	0	0	54 [Xe]
$W(CO)_6$	74	6 x 2 = 12	0	0	86 [Rn]
$Fe_2(CO)_9$	26	3 x 2 = 6	3 x 1 = 3	1 x 1 = 1	36[Kr]
$Co_2(CO)_8$ (bridged)	27	3 x 2 = 6	2 x 1 = 2	1 x 1 = 1	36[Kr]

18-Electron rule

If a metal carbonyl contains a total of 18 electrons which is the sum of valance electrons of central metal atom/ion, electrons donated by terminal CO ligands, electrons donated by M-M bond then the metal carbonyl will said to fallow the 18 e^- rule.

Example:

i. **Fe_2 $(CO)_9$**

Total valance electrons of Fe = 8

Electrons donated by 3 terminal CO = 6

Electrons donated by 3 bridging CO = 3

Electrons donated by M-M bond = 1

Total = 18

The complex will follow 18 e^- rule.

ii. [Mo $(CO)_3$ (η^6 C_7H_8)]

Total valance electrons of Mo = 6

Electrons donated by 3 terminal CO = 6

Electrons donated by $\eta^6C_7H_8$ = 6

Total = 18

This complex will follow 18 e^- rule.

iii. V $(CO)_6$

Total valance electrons of V = 5

Electrons donated by 6 terminal Co = 12

Total = 17

This complex will not follow the 18 e^- rule.

6.10 OREGANOMETALLIC COMPOUNDS

Organometallic compounds are organic compounds of metals in which metal is directly attached to carbon and metal-carbon bond is present. These compounds can have ionic or covalent, localised or delocalised bonding between one or more carbon atoms of organic group or molecule and transition metal, lanthanide, actinide or main group metal-atom. In these compounds, one or more hydrocarbon radical(s) are directly linked with metal atom. Metal-carbides, metal carbonates, metal cyanides and metal carboxylates are not organometallic compounds. Metal carbonates and metal carboxylates are not organometallic compounds, as they do not have metal-carbon bond. Whereas, although metal-carbides and metal-cyanides have metal-carbon bond, they are not organic compounds. All the compounds in which metal atom is attached to the organic part such as alkyl group, aryl group, allylic group, vinylic groups etc. are known as organometallic compounds.

6.10. 1 Classification of organametallic compounds

Two types of the classifications have been used to define the organometallic compounds which can be given as:

1. Classification I- Classification based on the nature of atoms or groups

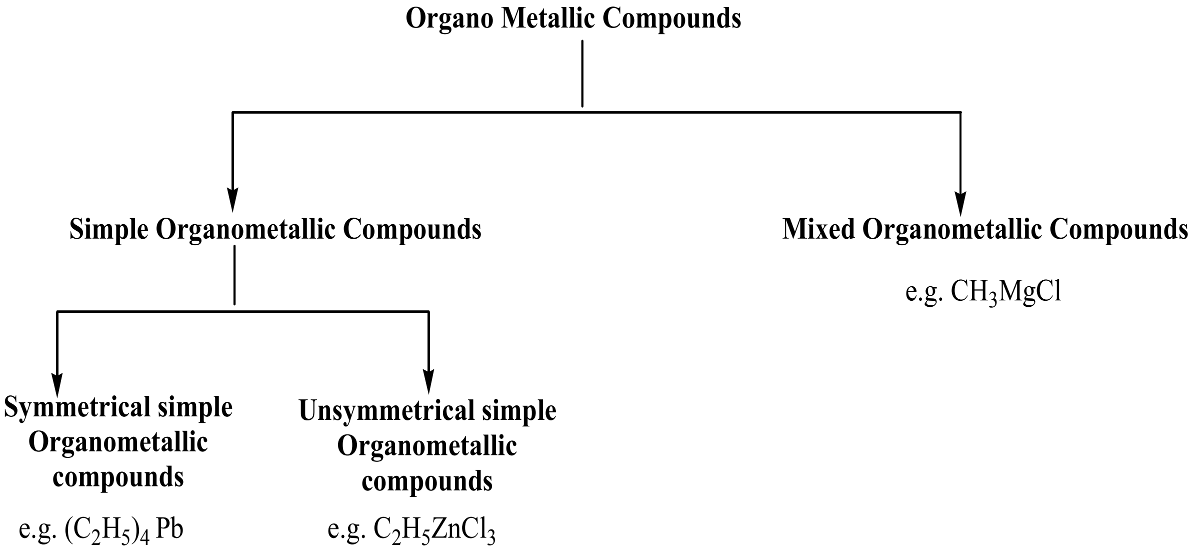
On the basis of the nature of atoms or groups attached to the metal atom, organometallic compounds can be classified into two different groups, which are given below:

(a) Simple organometallic compounds: In these organmetallic compounds, metal atom is attached with the organic part or attached with the organic part as well as H atom are known as simple organometallic compounds.

Simple organometallic compounds can be divided into two different types, which are given below:

(i) Symmetrical simple organometallic compounds.
(ii) Unsymmetrical simple organometallic compounds.

(b) Mixed organometallic compounds: In this type of the organometallic compounds, metal atom is attached with the organic part as well as some other atoms or groups other than H, are known as mixed organometallic compounds.



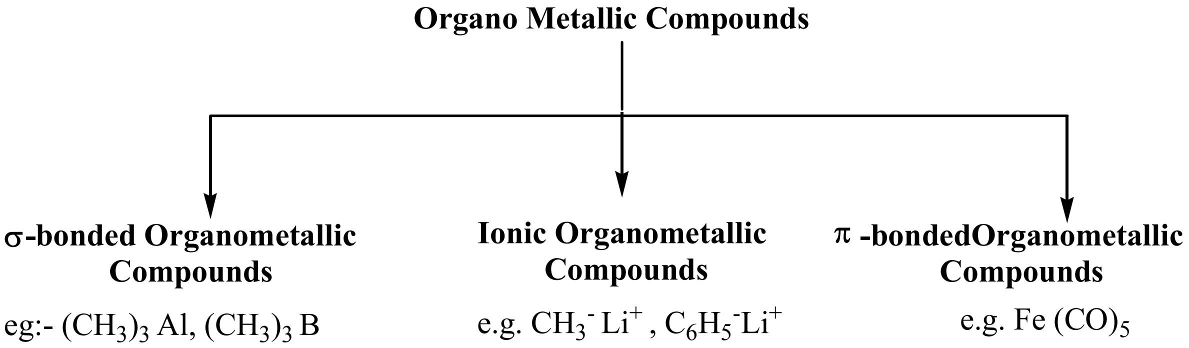
2. Classification II- Classification based on the nature of bonding

On the basis of the nature of bonding between the metal atoms and organic groups, organometallic compound can be divided into three different classes which are given below:

(a) σ-Bonded organometallic compounds: In such types of organometallic compounds, σ covalent bonding between the metal atom and carbon atom of organic part occur. This type of the organometallic compounds are mostly formed by the p- block elements because the electronegativity difference between the carbon atom of organic part and p-block elements is very small.

(b) Ionic organometallic compounds: In such type of the organometallic compounds, ionic bonding occur between the metal atom and carbon atoms of organic part. In these type of the organometallic compounds, there occur a large electronegativity difference between the s- block elements and carbon atom of organic part.

(c) π-Bonded organometallic compound: In such type of the organometallic compounds, normal σ bonding as well as π-bonding (back bonding) occur between the metal atom and carbon atom of organic part.



6.10.2 PREPARATIONS OF ORGANOMETALLIC COMPOUNDS

Some of the methods by which organometallic compound can be formed are given in this section.

i. By free radical reaction

$$(C_2H_5)_4\,Pb + Sn \xrightarrow{hv} Pb + (C_2H_5)_4\,Sn$$

Mechanism:

$$(C_2H_5)_4\,Pb \xrightarrow{hv} Pb + 4C_2\dot{H}_5$$

$$4C_2\dot{H}_5 + Sn \xrightarrow{hv} (C_2H_5)_4\,Sn$$

ii. By the reaction of metal with olefins

$$CH_2{=}CH_2 + 2Na \longrightarrow \overset{Na^+}{\bar{C}H_2}-\overset{Na^+}{\bar{C}H_2}$$

iii. By the reaction of metal with CO ligand

$$Ni + 4CO \longrightarrow Ni\,(CO)_4$$

$$Fe + 5CO \longrightarrow Fe\,(CO)_5$$

iii. By the reaction of alkyl halide with metal

$CH_3 \overset{\curvearrowright}{-} I \quad + \quad 2Li \qquad\qquad CH_3Li \quad + \quad LiI$

$2CH_3 \overset{\curvearrowright}{-} I \quad + \quad Zn \qquad\qquad (CH_3)_2Zn \quad + \quad I_2$

v. By the reaction of terminal alkyne with Na metal

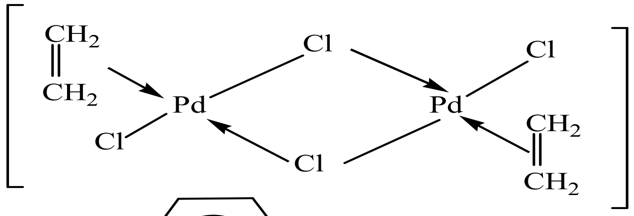
$CH_3—C{\equiv}C—H \quad + \quad 2Na \longrightarrow CH_3—C{\equiv}\overset{-}{C}\ Na^+ \ + \ H_2$

6.11 METAL-ETHYLENIC COMPLEXES

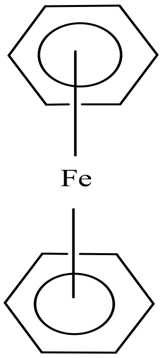
All the ligands having C-C multiple bond such as ethyine, propene, butene, benzene, cyclohepta triene are known as ethylnic ligands.

When the ethylenic ligand combined with the various metal ions such as Ni^{+2}, Pt^{2+} Pd^{+2} and Rh^{+2}, the complexes formed are called as organoethylenic complexes. Some of the most widely used organoethylenic complexes can be given as:

1. $K[Pt(Cl)_3(C_2H_4)]$
2. $[Mo(CO)_3(\ _6C_7H_8]$
3.



4.



6.11.1 Bonding in the organoethylenic complexes

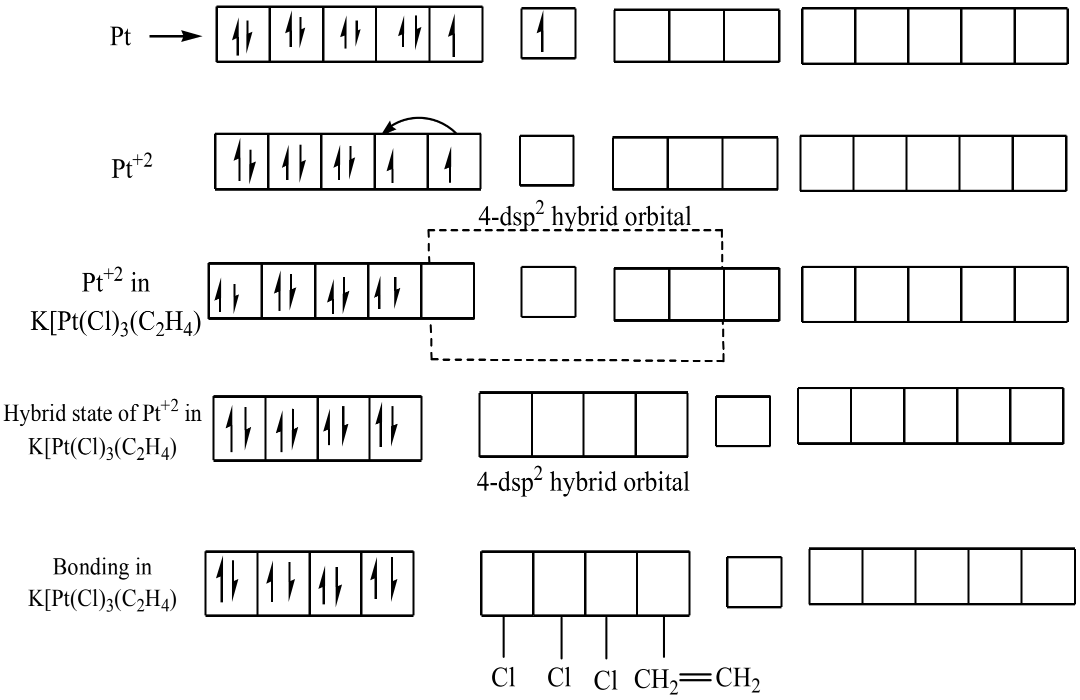
Organoethylenic complexes show two types of the bonding known as σ-bonding and π-bonding (back bonding) which can be defined as:

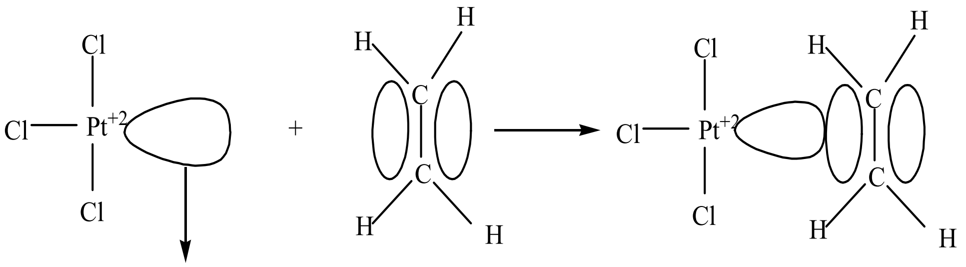
σ- Bonding in the organoethylinic complexes

We can explain bonding in organoethylenic complex using $K[Pt(Cl)_3(C_2H_4)]$ as an example.

In this complex, at first CMI (Pt^{+2}) undergoes dsp^2 hybridization to provide the 4 vacant dsp^2 hybrid orbitals and after that, out of these four vacant dsp^2 hybrid orbitals, the three dsp^2 hybrid orbitals undergo head-on overlapping with the σ orbital of three Cl^- ligands to form the three $Cl^- \longrightarrow Pt^{+2}$ σ bonds while the remaining fourth vacant dsp^2 hybrid orbital of Pt^{+2} undergoes overlapping with the filled π^b_{pz-pz} MO of C_2H_4 to from $C_2H_4 \rightarrow Pt$ σ bond which is known as organoethylenic bond that can be represented as:

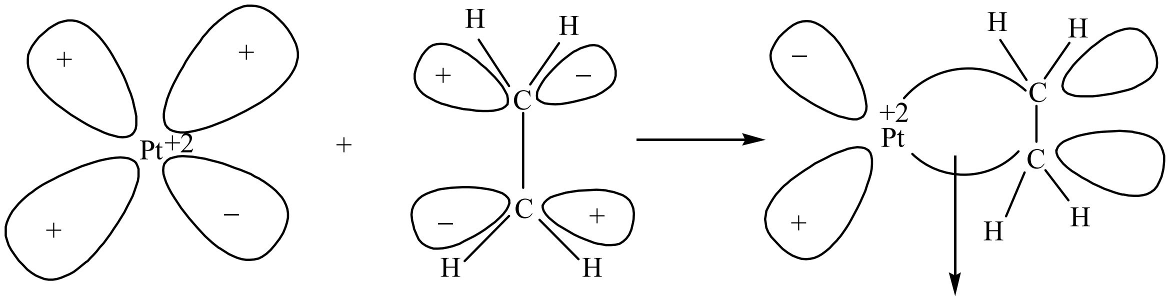
$_{78}Pt \longrightarrow 5d^9, 6s^1, 6d^o$





π- Bonding in the organoethylenic complexes

After the formation of normal $C_2H_4 \longrightarrow Pt^{+2}$ σ bond, there occur a side wise or lateral overlapping between the filled d- orbital of CMI (Pt^{+2}) and vacant $\pi^*_{pz\text{-}pz}$ molecular orbital of ethylene (C_2H_4) to form $C_2H_4 \longleftarrow Pt^{+2}$ π-bond or back bond that can be represented as:

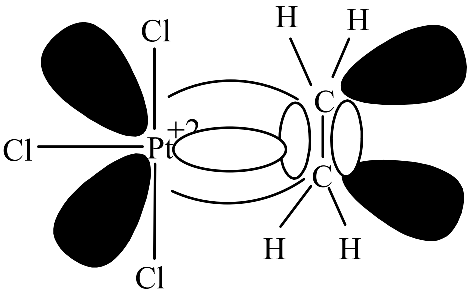


Filled d-orbitalof Pt^{+2}

vacant π* Pz-Pz MO of C_2H_4

$Pt^{+2} \longrightarrow C_2H_4$ π bond or back bond

Finally, the combined picture for both σ-bond and π-bond in the organoethylenic complexe can be represented as-



6.11.2 Methods of formation

Some of the main methods which can be used for the formation of organo ethylenic complexes can be given as:

1. **By the reaction of metal carbonyl with ethylenic ligand**

$Mo(CO)_6 + \eta_6\text{-}C_7H_8 \longrightarrow [Mo(CO)_3(\eta_6\text{-}C_7H_8)] + 3Co$

$Fe(CO)_5 + \eta_4\text{-}C_4H_6 \longrightarrow [Fe(CO)_3(\eta_4\text{-}C_4H_6)]$

2. **Through the reaction of halo complexes with the ethylenic ligand**

$K_2[Pt^{II}(Cl)_4] + C_2H_4 \longrightarrow K[Pt^{II}(Cl)_3] + (C_2H_4)] + KCl.$

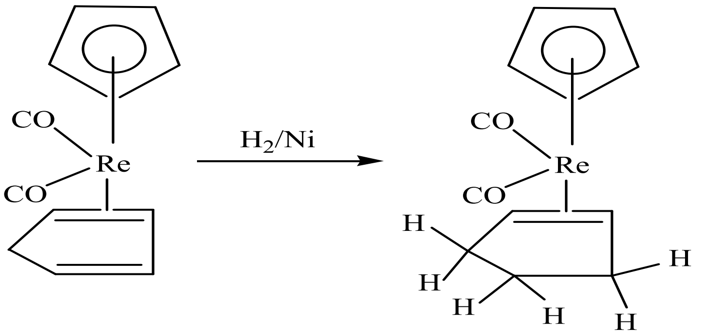
3. **By the reaction of metal halide with ethylenic ligand**

$$2RhCl_3 \quad + \quad 4\,C_2H_4 \xrightarrow{-\,4Cl} Rh_2Cl_2(C_2H_4)_4$$

6.11.3 Chemical properties of organoethylenic complexes

Some of the properties related with the organo ethylenic complexes can be given as:

1. **Reduction reduction:** When the organoethylic complexes react with the H_2 in the presence of Ni, than hydrogenation of π-bonds present in the ethylenic ligand occur and this reaction is called as reduction reaction of organoethylenic complexes.

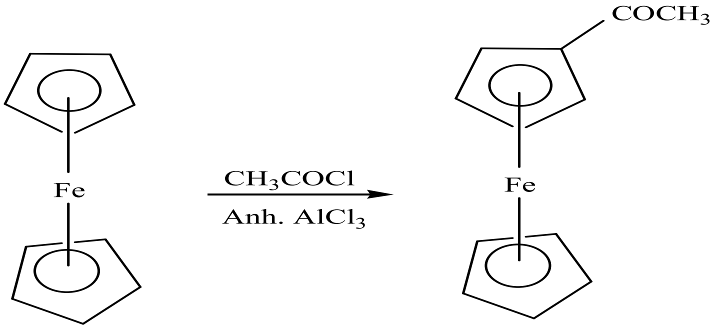


2. **Substitution reaction:** Organoethylenic complexes react with the phosphine ligands like PR_3 (R may be H, CH_3, C_2H_5) and substitute the ethylenic ligand.

$$K\,[Pt\,(Cl)_3\,(C_2H_4)] \quad + \quad PR_3 \longrightarrow K\,[Pt\,(Cl)_3\,(PR_3)\,] + C_2H_4$$

3. **Acetylation reaction**

   Acetylation reaction occurs in the presence of acetyl chloride and anhydrous aluminium chloride.



6.12 SUMMARY

Metal carbonyls are coordination complexes of transition metals with carbon monoxide ligands. Metal carbonyls are useful in organic synthesis and as catalysts or catalyst precursors in homogeneous catalysis, such as hydroformylation and Reppe chemistry. In the Mond process, nickel carbonyl is used to produce pure nickel. In organometallic chemistry, metal carbonyls serve as precursors for the preparation of other organometalic complexes. Metal carbonyls are toxic by skin contact, inhalation or ingestion, in part because of their ability to carbonylate hemoglobin to give carboxyhemoglobin, which prevents the binding of O_2.

6.13 TERMINAL QUESTIONS

A. Short Answer type Question:

1. What are the π-bonded organometallic compounds?

2. Give the methods for the preparation of $Fe_2(CO)_9$.

3. Write down the classification of organometallic compounds? Discuss with one example each.

4. Calculate the EAN value for each of the following species.

(a) $Cr(C_2H_5)(CO)_3$ (b) $Fe(\pi\text{-}C_5H_5)(CO)_3$ (c) $Co(\pi\text{-}C_2H_5)(CH_3)_2$

5. Draw the structure of the following compounds.

(a) $Ni(CO)_4$ (b) $Fe_2(CO)_9$ (c) $Co_2(CO)_8$ (d) $Fe(CO)_5$

6. What are metal carbonyls? Give structures of two dinuclear metal carbonyls having different structure.

7. Discuss the nature of bonding in metal olefin complexes.

8. Give two methods of preparation of transition metal carbonyl.

9. What are metal olefin complexes?

10. Write short notes on the following.

(a) The effecting atomic number

(b) Back bonding of metal carbonyls

(c) β-elimination of metal alkyls.

11. Give the mode of bonding in metal conjugated diene complexes.

12. Write a short note on EAN rule as applied to organometallic compounds.

13. Discuss the metal carbon sigma bonding.

14. Give three important methods of prepration of metal carbonyls.

15. Discuss the structure of $Fe_2(CO)_9$.

UNIT -7 BIO-INORGANIC CHEMISTRY

CONTENTS:

7.1. OBJECTIVES

By going through this unit, you will be able to understand the following terms and definitions:

- Introduction to bioinorganic chemistry
- Biometals and their common oxidation states
- Biological ligands
- Metal binding sites in biological systems
- Hemoglobin
- Myoglobin

7.2 INTRODUCTION

Bioinorganic chemistry is a branch of chemistry that deals with the study of the role of metals in biology or biological system. Bioinorganic chemistry includes the study of both natural phenomena (behaviour of metalloproteins) as well as artificially introduced metals (essential or non-essential metals in medicine and toxicology). Many biological processes like respiration depend upon the molecules which fall within the boundries of inorganic chemistry. This particular discipline also includes the study of inorganic models that mimics the behaviour of metalloproteins. As a mixture of biochemistry and inorganic chemistry, bioinorganic chemistry is very important in elucidating the involvement of electron-transfer proteins, substrate bindings and activation, atom and group transfer chemistry and metal properties in biological chemistry. It also involves the study of role of metal species in biological systems. In this unit, we will discuss about the essential chemical elements, the occurrences and purposes of metal centres in biological molecules, the geometries of ligand fields surrounding these metal centers, and ionic states preferred by the metals.

7.3. ESSENTIAL AND TRACE ELEMENTS IN BIOLOGICAL PROCESSES

An essential element is required for the maintenance of life and its absence results in several malfunctions of the organs or death. A total of 112 elements are known, of which 30 elements are essential for life processes in plants and animals. Chemical elements essential to life forms can be categories into four major groups:

1. **Bulk elements-** H/H^+, C, N, O^{-2} O_2^- /O_2^{-2}/P, S/S^{-2})
2. **Macro minerals and ions-** Na/Na^+ , K/K^+ , Mg/Mg^{2+}, Ca/Ca^{2+}, Cl^- , PO_4^{3-}, SO_4^{2-}
3. **Trace elements-** Fe/Fe^{II} /Fe^{III} /Fe^{IV}, Zn/Zn^{II} , Cu/Cu^{I} /Cu^{II} /Cu^{III}
4. **Ultratrace elements-** non-metals (F/F^-, I/I^-, Se/Se^{2-} , Si/Si^{IV}, As, B) and metals (Mn/Mn^{II} /Mn^{III}/Mn^{IV}, Mo/Mo^{IV} /Mo^{V} /Mo^{VI}, Co/Co^{II} /Co^{III}, Cr/Cr^{III} /Cr^{VI}, V/V^{III} /V^{IV}/V^{V}, Ni^{I} /Ni^{II} /Ni^{III} , Cd/Cd^{2+}, Sn/Sn^{II} /Sn^{IV}, Pb/Pb^{2+}, Li/Li^+).

Criteria for essential elements

(1) Removal of the element from the diet causes a physiological deficiency.

(2) The deficiency is relieved by the addition of that element in the diet.

(3) A specific biological function is associated with a particular element. Table 7.1 is indicating the approximate percentages of some selected essential elements by weight for adult human.

Table 7.1 Percentage cmpositions of selected essential elements in the human body

Elements	**Percentage (by weight)**
Oxygen	53.6
Carbon	16.0
Hydrogen	13.4
Nitrogen	2.4
Sodium, potassium, sulfur	0.10
Chlorine	0.09
Silicon, magnesium	0.04
Iron, fluorine	0.005
Zinc	0.003
Copper, bromine	$2. \times 10^{-4}$
Selenium, manganese, arsenic, nickel	$2. \times 10^{-5}$
Lead, cobalt	$9. \times 10^{-6}$

7.3.1 Essential bulk elements

Sodium (Na)

Sodium is the major component of extracellular fluid. It mainly exists as chloride and bicarbonate. It is the primary cation (positive ion) in extracellular fluids such as blood plasma of animals and humans. These fluidstransport nutrients and wastes. Sodium regulates acid base equilibrium in biological systems. It also helps in maintaining osmotic pressure of the body fluid and thus, protects the body against fluid loss. Sodium regulates osmotic pressure of the body. Many enzyme reactions are controlled by Na^+ ion.

Potassium (K)

Potassium is a very important element required for the proper function of all cells, tissues, and organs in the human body. It is an electrolyte that conducts electricity in the body, along with sodium, chloride, calcium, and magnesium. Various functions of potassium in biological systems are as follows:

(1) Potassium plays a key role in skeletal and cardiac systems and smooth muscle contraction.
(2) It also regulates acid base equilibrium like sodium in extracellular fluid.
(3) Potassium controls osmotic pressure and water reaction.
(4) It is important for metabolic function such as protein biosynthesis by ribosome.

7.3.2 Trace elements

Trace elements are necessary for human body to maintain normal but complex physiological functions related to body's growth and development. They are called trace elements because of their body concentration, which are few milligrams per kg or less. They are also known as micronutrients. The trace elements are categorized into three categories which are; essential, probably essential or non-essential. This is based upon their biological effect, diseases that may occur due to their deficiency and toxicity due to overdose.

Trace elements are defined by their extremely low concentrations in the body, such as less than 50 mg of iron per kg of tissue. Daily animal requirements of trace elements are in the milligram range. Needs for trace elements in human body are determined by nutrient requirement models and nutrient response models.

Biological functions of trace elements

Iron (Fe)

Iron is a part of haemoglobin which is the pigment of red blood cells and myoglobin, the muscle pigment. In addition, iron is responsible for oxygen storage and oxygen transport in the body. As an enzyme component, iron plays an important role in energy metabolism as well as in the anti-oxidative system (immune system). In fact that iron is much more common than any other trace elements. In excess amount, iron can lead to poor absorption for copper and manganese.

Copper (Cu)

Copper is mainly stored in the liver and is an enzyme component that is part of many essential metabolic processes. As an enzyme activator, Cu provides strong bones and joints and is involved in the utilization of iron and thus, the synthesis of hemoglobin. In addition, the pigmentation of the hair coat is fundamentally influenced by copper levels. Copper is involved in cell protection and thereby provides a healthy immune system.

Zinc (Zn)

Znc is also the most common trace element. It is a component of more than 300 enzymes and hormones as an activator. Zinc plays an important role in metabolism. In particular, protein biosynthesis and the regulation of gene activity can be affected by zinc. Zinc is mainly stored in the liver, pancreas, bone, skin and hair. Its deficiency causes poor growth, loss of appetite, and a bad feed conversion rate.

Manganese (Mn)

Manganese is mainly stored in the bone, liver, kidney and pancreas. It works as an enzyme activator and is crucial for energy, protein- and fat metabolism. Furthermore, it has important enzymatic functions in cell protection. Deficiencies of manganese causes reduced growth, skeletal deformities, poor fertility and birth defects in newborn calves.

Iodine (I)

Iodine is present in the thyroid glands and is responsible for the formation of thyroid hormones (T_3 and T_4 hormone). These hormones control energy metabolism processes and are thus, particularly important for growth, fertility and milk yield. Iodine deficiency causes an enlarged thyroid gland and poor milk production.

Cobalt (Co)

Cobalt is present as a central atom of Vitamin B_{12} (Cobalamin). Ruminants can synthesize Vitamin B_{12} in their rumen. Vitamin B_{12} is necessary for a functioning energy- (utilization of propionic acid, gluco neogenesis) and protein metabolism (methionine formation) in the liver. A prolonged deficiency of cobalt leads to a decrease in feed intake, limited growth and reduced milk yield.

Selenium (Se)

Selenium is an essential component of the glutathion peroxidase enzyme,that deactivates harmful hydrogen peroxide radicals and is thus, important in cell protection. It also supports the effects of Vitamin E and vice versa. Selenium also regulates the metabolism of thyroid hormone and thus, indirectly affects fertility in dairy cows.

7.4 METALLOPORPHYRINS WITH SPECIAL REFERENCES TO HAEMOGLOBIN AND MYOGLOBIN

Metalloporphyrin along with protein globule performs several important biochemical functions in biological systems. Hemoglobin, cytochromes catalase, myoglobin, chlorophyll, and paroxidases are well known examples of metalloporphyrins. Porphyrin is a universal molecule present in almost all living organisms in one form or other. The basic unit of porphyrin consists of four pyrrol units linked together by four methine bridges. It is an 18-electron system and hence, exhibits stability and aromaticity.

The porphyrin ring provides a vacant site at the centre which is suited for metal incorporation (Figure 7.1). With very few exceptions, the porphyrinato dianion acts as a tetradentate ligand with metal ions. Thus, the minimum coordination number of the metal ion possible in a metalloporphyrin is four (Figure 7.2). The extensive electronic delocalisation in the porphyrinato ligand leads to a considerable planarity of the macrocycle and an essentially square planar environment for the metal ion in four-coordinate complexes. Coordination number greater than four is also possible through ligation of suitable moieties either neutral or anionic. The five coordination complexes have generally a square-pyramidal geometry with the single axial ligand occupying the apical position of the square pyramid. The two ligands of the six-coordinated metalloporphyrins are present on the opposite sides of the porphynato plane forming complexes with tetragonal/octahedral geometries.

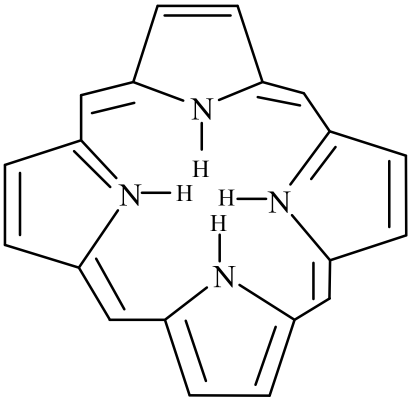


Fig. 7.1 Porphyrin

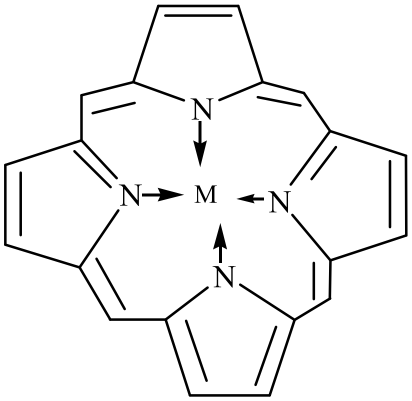


Fig. 7.2 Metal complex with porphyrin ring

Figure 7.1*: Structure of porphyrin ring,* ***Figure 7.2****: Structure of porphyrin ring*

Two types of the most widely used metallopophyrin ring systems can be defined as:

(1) **Heme**: WhenFe in the +2 oxidation state is placed in the cavity of porphyrin ring then the metalloporphyrin obtained is known as Heme. The structure of two important metalloporphyrin heme and chlorophyll are being considered here: Heme Figure 7.3 contains iron (II) which is present in haemoglobin and myoglobin.

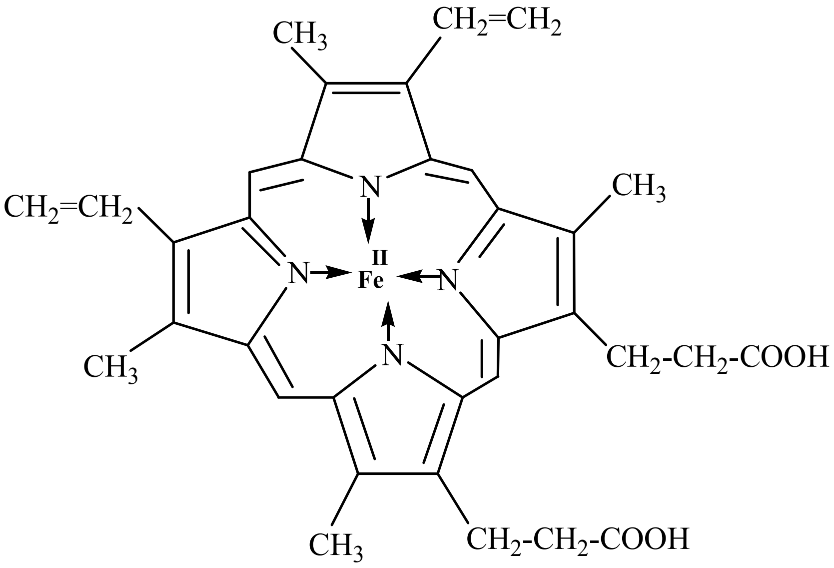


Fig. 7.3 Heme skeleton

When the heme skeleton combine with the globular protein than the macromolecule (pigment) which is obtained is known as haemoglobin which acts as an oxygen carer within the human body.

Chlorophyll: when the metal in the +2 oxidation state is occupied in the cavity of porphyrin ring system then the metalloporphyrin which is obtained is knows as Chlorophyll (Figure 7.4). A simple diagrammatic representation for the chlorophyll metolloporphyrin can be given a-

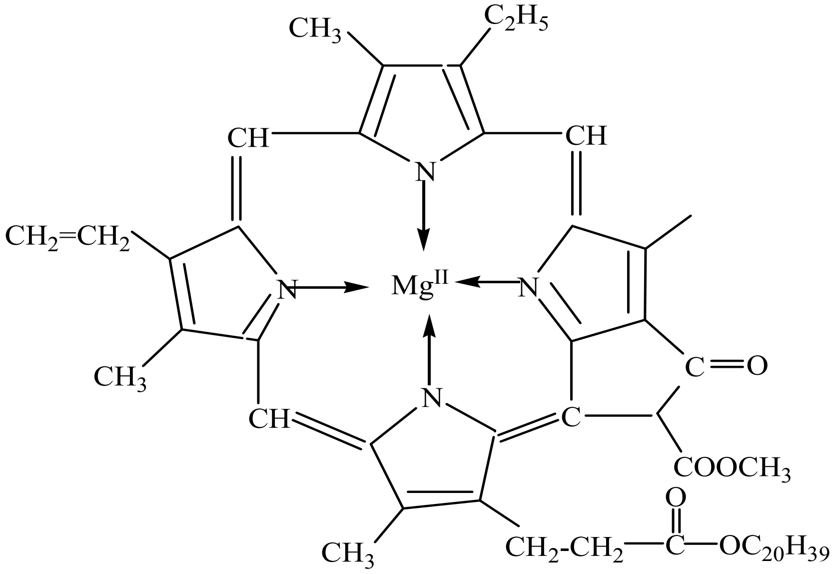


Fig. 7.4 Chlorophyll

Chlorophyll is present in the green plants and participates in the photosynthesis reaction in which CO_2 and moisture of atmosphere combined together in the presence of sunlight produce the glucose and O_2 gas. Glucose obtained from this process is further converts into polysaccharide like starch, cellulose.

$$6\,CO_2 + 6H_2O + \text{Solar energy} \xrightarrow{\text{Chlorophyll}} \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$

7.5 BIOLOGICAL ROLE OF ALKALI AND ALKALINE EARTH METAL ION WITH SPECIAL REFERENCES TO Ca^{+2}

It has been found that an average human body contains 0.07 kg of sodium, 0.25 kg of potassium, 0.042 kg of potassium, 1.7 kg of calcium and rests other elements. Na^+ and K^+ ion play different role in metabolism Na^+ being an extra cellular ion and K^+, an intracellular ion. The size of ions and their types of bonding characteristics of a given ionare the two factors that determine which ion can be substituted by others in metabolic processes. The K^+ ion may be substituted in living tissuesby large single charged Rb^+, Cs^+, $NH4^+$ and Ti^+ ion while the small Na^+ ions can be substituted by Li^+ ions. The mammalian tissues incorporate a sodium or potassium ions transport system is called as sodium/potassium pump.

Biological role of Calcium ions:

Ca^{+2} ions play an important role in biological processes and in skeletal formation. With phosphorous in the mineral hydroxyalatite $Ca_5(PO_4)OH$, it is the major constituent of bones, teeth and shells. Ca^{+2} play many biochemical roles such as:

(i) It acts as a messenger for hormonal action
(ii) It acts as a trigger for muscular contraction
(iii)It acts as initiation of blood clotting
(iv)It also play an important role in the stabilization of protein structure

Role of Ca^{+2} in transport:

Ca^{+2} ions play an important role in muscels. The triggers a signal that stimulates muscles to contract. In the normal state, the concentration in the intracellular fluids is very low because nearly all the Ca^{+2} ions in muscle is pumped into a complex network of vehicle known as sarcoplasmic reticulum (SR). Their concentration in intracellular fluid is about 10,000 times less than thei concentration in the extra cellular fluids.

The maintenance of low calcium in concentration in the intra cellular fluids are done by biochemical process is known as calcium pump.

The mechanism of Ca^{+2} pumps is as under.

$$E + ATP \xrightleftharpoons{Ca^{+2},\ Mg^{+2}} \underset{\text{Intermediate}}{ADP + E\text{-}P}$$

$$E\text{-}P + H_2O \xrightleftharpoons{Mg^{+2}} E + HPO_4^{2-}$$

During the cycle, two Ca^{+2} are transported for each ATP hydrolysed.

7.6 NITROGEN FIXATION

The process of conversion of atmospheric nitrogen into useful nitrogenous compounds by natural or artificial methods is called nitrogen fixation. Nitrogen present in these nitrogenous compounds is called fixed or combined nitrogen. Nitrogen can be fixed either by natural methods or artificially.

7.6.1 Natural methods of the fixation of nitrogen

1. **By lightening discharges:** The nitrogen and oxygen present in air combine together to form nitric oxide under the influence of lightning discharges. Nitric oxide gets oxidised by excess of oxygen present in the atmosphere to form nitrogen peroxide which dissolves in water to form nitric acid. This acid is washed down by rain into the soil, where it reacts with limestone and alkalis of the soil to form nitrates and is stored thee as plant food.

$$N_2 + O_2 \longrightarrow \underset{\text{Nitric oxide}}{2NO}$$

$$4NO + 3O2 \longrightarrow \underset{\text{Nitrogen pentoxide}}{2N_2O_5}$$

$$N_2O_5 + H_2O \longrightarrow \underset{\text{Nitric acid}}{2HNO_3}$$

$$2HNO_3 + CaCO_3 \longrightarrow Ca(NO_3)2 + CO_2 + H_2O$$

2. **By symbiotic bacteria:** The atmospheric nitrogen is being constantly transferred to the soil through certain bacteria called symbiotic bacteria (*Rhizobium*). They grow in small nodules present in the roots of leguminous plants (pea, gram etc.) and directly assimilate atmospheric nitrogen and convert it into products useful for plant growth.

Nitrogen and ammonium salts present in the soil are converted by nitrosifying bacteria into nitrites and by nitrifying bacteria into nitrates. The final products nitrate serve as a plant food. In this process nitrates serve as a plant food. This process of oxidation is known as nitrification which causes the combined nitrogen to be available to the plants (Figure 7.5).

The species of *Rhizobium* is specific for each species of plant. Cyanobacteria (blue-green algac) perform nitrogen fixation in the ocean, and to some extent, in fresh water. All these microorganisms produce ammonia through the activity of nitrogenase. Most free nitrogen bacteria perform nitrogen fixation an aerobically whereas cyannobacteria do it aerobically.

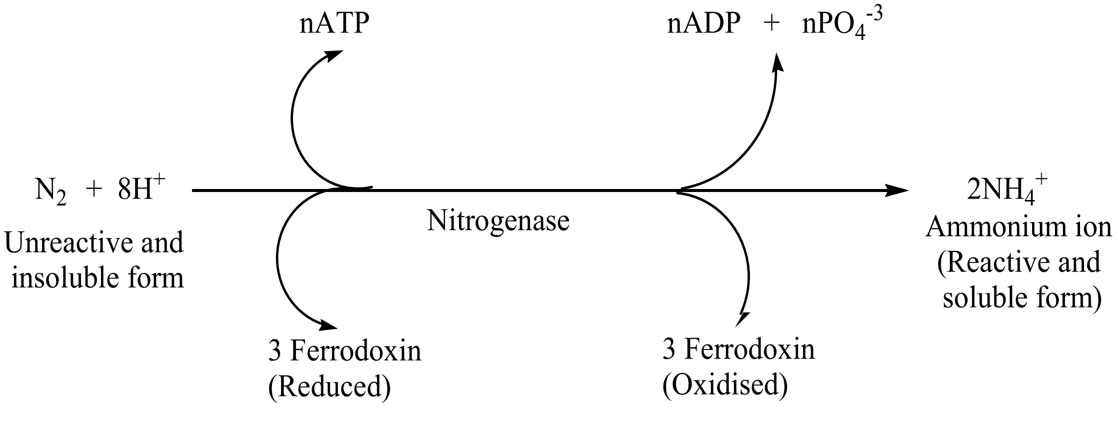


***Figure 7.5**: Process of nitrogen fixation*

The reaction involves three reduced molecules of ferredoxin which donate six electrons. Te source of this reducing power is NADPH. Twelve to eighteen molecules of ATP supply the necessary energy of the production of ammonia at a rate which is regulated by the inhibitory effect of the product on the association of the two components of the nitrogenase.

Denitrification: The biological reduction of nitrate (NO_3^-) to nitrogen gas (N_2) by facultative heterotrophic bacteria is called denitrification. “Heterotrophic” bacteria need a carbon source as food to live. “Facultative” bacteria can get their oxygen by taking dissolved oxygen out of the water or by taking it off of nitrate molecule.

Denitrification occurs when oxygen levels are depleted and nitrate becomes the primary oxygen source for microorganisms. The process is performed under anoxic conditions, when the dissolved oxygen concentration is less than 0.5 mg/L, ideally less than 0.2. When bacteria break apart nitrate (NO_3^-) to gain the oxygen (O_2), the nitrate is reduced to nitrous oxide (N_2O), and, in turn, nitrogen gas (N_2). Since, nitrogen gas has low water solubility; it escapes into the atmosphere as gas bubbles. Free nitrogen is the major component of air, thus its release does not cause any environmental concern. The ammonia may be further converted into nitrate or nitrite or directly used in the synthesis of amino acids or other essential compounds. This reaction occurs at atmospheric condition of temperature and pressure in Rhizobia, bacteria in nodules on the roots of leguminous plants such as peas and beans. In contrast, industrial synthesis of ammonia requires high temperatures and pressures and catalysts. All nitrogen fixation processes have the following fundamental features:

(i) The bacterial enzyme called nitrogenase catalyses the process.
(ii) Strong reductant such as ferredoxin which behaves as an electron carrier with a very low redox potential.
(iii)The energy rich molecule ATP in biological systems
(iv)Oxygen free conditions (anaerobic).

The enzyme nitrogenase is the heart of biological nitrogen fixation. It is an important enzyme which catalyses the conversion of molecular nitrogen to ammonia. The nitrogenase enzyme responsible for nitrogen fixation consist of two metalloproteins:

(i) Fe-protein als known as Fe-S protein or nitrogenase reductase
(ii) Mo-Fe-protein also known as Mo-Fe-S Protein.

Thus, nitrogenase is a complex of two proteins in a dynamic equilibrium with its components:

$$\text{Mo-Fe protein} + \text{2Fe-protein} \rightleftharpoons \text{Nitrogenase complex}$$

Thus, nitrogenise is complexe of iron-sulphur protein (Fe-S-Protein) and molybdenum-iron-sulphur protein whose activity couples ATP hydrolysis to electron transfer from ferredoxisn for carrying out reduction of nitrogen to ammonia.

7.6.2 Artifical methods used for the fixation of nitrogen

1. **Fixation of nitrogen as HNO_3**: Under the influence of high tension electric arc where the temperature is very high, nitrogen of the air combines with oxygen to form nitric oxide. It combines with more of oxygen to form nitrogen peroxide. This may be absorbed in water in presence of excess of air to give nitric acid which may be used for the manufacture of nitrogenous fertilisers.

$$N_2 + O_2 \rightleftharpoons \underset{\text{Nitric oxide}}{2NO}$$

$$2NO + O_2 \longrightarrow \underset{\text{Nitrogen peroxide}}{2NO_2}$$

$$\underset{\text{Nitrogen peroxide}}{4\,NO_2} + 2H_2O + O_2 \longrightarrow \underset{\text{Nitric acid}}{4HNO_3}$$

2. **Fixation of nitrogen as NH_3 and ammonium salts:** A mixture of nitrogen and hydrogen in the ratio 1:3 is compressed to a pressure of 200-500 atmospheres and is passed over a catalyst (finely divided Fe + Mo) heated to about 550°C. This forms the Haber's process for the manufacture of ammonia which then can be converted into ammonium salts by treatment, with suitable acids.

$$N_2 + 3H_2 \xrightleftharpoons[\text{200-500 atm/5500}^{C}]{\text{Fe-Mo}} 2NH_3$$

3. Fixation of nitrogen as nitrides. Nitrogen combines with magnesium and aluminium at high temperature to give nitrides which are employed as a source of ammonia. These nitrides are decomposed by H_2O and NH_3 is evolved.

$$3Mg + N_2 \longrightarrow \underset{\text{Magnesium nitride}}{Mg_3N_2}$$

$$2Al + N_2 \longrightarrow \underset{\text{Aluminium nitride}}{2AlN}$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

Nitrogen Cycle

The nitrogen cycle is the biogeochemical cycle by which nitrogen is converted into different chemical forms as it circulates among the atmosphere and terrestrial and marine ecosystems. The conversion of nitrogen can be carried out through both biological and physical processes. Important processes in the nitrogen cycle include fixation, ammonification, nitrification, and denitrification (Figure 7.6). The majority of Earth's atmosphere (78%) is nitrogen, making it the largest pool of nitrogen. However, atmospheric nitrogen has limited availability for biological use, leading to a scarcity of usable nitrogen in many types of ecosystems.

The nitrogen cycle is of particular interest to ecologists because nitrogen availability can affect the rate of key ecosystem processes, including primary production and decomposition. Human activities such as fossil fuel combustion, use of artificial nitrogen fertilizers, and release of nitrogen in wastewater have dramatically altered the global nitrogen cycle.

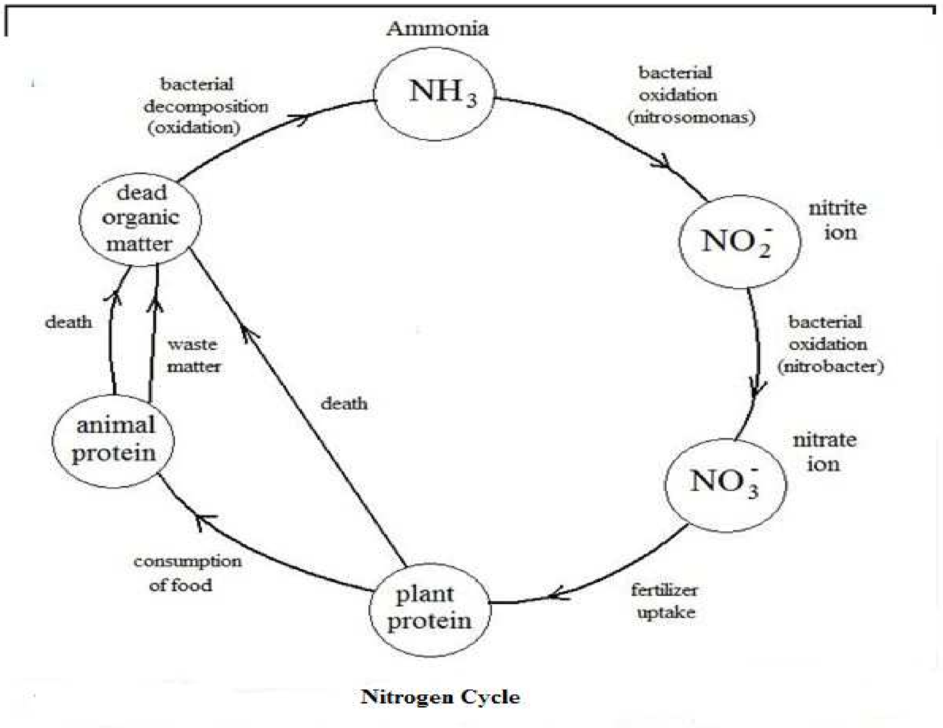


Figure 7.6: *Nitrogen cycle*

7.7 SUMMARY

This unit deals with the Bio-inorganic Chemistry which is the intermediate of inorganic chemistry and biochemistry, it explain the mutual relationship between the function of inorganic substances in living systems and including the use of inorganics in medicinal therapy and diagnosis.

7.8 TERMINAL QUESTIONS

1. What is the oxidation state of iron in haemoglobin and myoglobin?
2. What are porphines?
3. What does ATP stand for?
4. Name two widely distributed oxygen carrier proteins.
5. Define nitrogen fixation.
6. Name the two metallorpoteins which comprise nitrogenise.

7. What abnormality is caused due to iodine deficiency?
8. Name three essential trace elements.
9. What is the name of enzyme that hydrolyses ATP in Na^+ and K^+ pump?
10. Discuss the structures of myoglobin and haemoglobin. Discuss in detail the roles played by these bioinorganic compounds in biological systems.
11. Name the essential non-metals which constitute the living systems. Discuss the role of any three of these.
12. Name the essential non-metals which constitute the living systems. Discuss the role of any three of these.
13. Describe the possible mechanism of conversion of N_2 into NH_3 using a Mo or W dinitrogen complex.
14. Write a short note on nitrogen fixation.
15. What is porphyrin? Draw the structure of heme.
16. How are met-myoglobin and methemoglobin formed?
17. What is nitrogenase? What role does it play innitrogen fixation?
18. What is porpyrin? Draw the structure of heme.
19. Discuss biological role on Na and K ions.
20. Fe(II) salts undergo easy oxidation in air but it is not so in Mb or Hb. Explain why?
21. Oxygen acts as π acceptor ligand in its interaction with heme. What happens when CO interact with heme in place of oxygen?
22. What is porpyrin? Draw the structures of heme.
23. Discuss the important features of Na^+-K^+pump.
24. What are metalloporphyrins? Discuss the structure and role placed by haemoglobin and myoglobin as O_2 carriers.
25. Discuss the biological importance of Ca^{2+}. How is it different from that of Mg^{2+}?
26. What do you mean by nitrogen fication? Discuss the role of nitrogenise reductase in biological N_2 fixation.
27. What is the function of haemoglobin and myoglobin? What ae similarities and differences in their structures.
28. What are the functions of haemoglobin and myoglobin? What are similarities and differences in their structures?

29. Write a short note on nitrogen fixation.
30. Explain biological role of alkali and alkaline earth metal ions.
31. What are the functions of myoglobin?
32. Name one metalloprotin which comprises nitrogenase.
33. Draw a cyclic process showing role of Hb and Mb as oxygen and CO_2 tranporters.
34. What do you understand by cooperativity in Hb?
35. What is the biological role of Zn^{2+}.
36. Discuss reasons why Fe(II) in Mb does not oxidise.
37. Name at least two oxygen carriers and give their importance in biological systems.
38. What happens when Fe-porphyrin complex, without polypeptide chain, comes in contact with O_2?
39. Explain biological role of alkali and alkaline earth metal ions.
40. What are the functions of myoglobin?

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UNIT-8 SILICONES AND PHOSPHAZENES

CONTENTS:

8.1. OBJECTIVES

The aims and objectives of this unit are to learn and discuss the structural features of different types of inorganic polymers.

8.2. INTRODUCTION

All the covalent macromolecules, which do not have carbon in their compounds, are considered to be inorganic polymers. Covalently-bonded crystals (like oxides and halides), condensed phosphate etc., are the examples of inorganic polymers. These polymers possess distinctive physicchemical characteristics and unique physical, mechanical and electrical properties. These polymers are of extensive utility in everyday life, particularly in the area of engineering and technology.

The main point of similarity between inorganic and organic polymers is, that both can be prepared by the addition and condensation methods. The former method is used when polymers of higher molecular weight and greater mechanical strength are needed. Silicones and phosphazenes are examples of inorganic polymers. Inorganic elements can have different valences than carbon and therefore, different numbers of side groups may be attached to a skeletal atom. This will affect the flexibility of polymers, their ability to react with chemical reagents and interactions with other polymers. Among inorganic polymers, silicones and phosphazenes are two important classes of polymers with high commercial potential.

All the macromolecules which are formed by the combination of a large number of the small units are known as polymer and the process of their formation is called as polymerisation process.

$$n\,M \longrightarrow \left(M \right)_n$$

Where n= Degree of polymerisation

$(M)_n$ = Polymer

M = Monomer

8.3 CLASSIFICATION OF POLYMERS

Depending on the catinating nature of elements, polymers can be divided into two different types which are given below:

(a) **Organic polymer:** All the macro molecules which are formed by the catenation of the carbon atom are known as organic polymers.

Example:

$$n\ CH_2{=}CH_2 \longrightarrow \left(CH_2 - CH_2 \right)_n$$

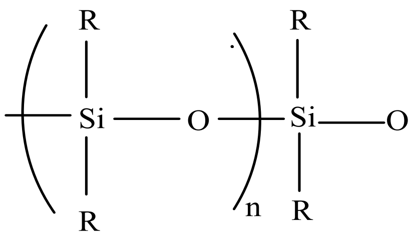
Organic polymers are further divided into types, which can be given as:-

i. Synthetic polymer.
ii. Natural polymer.

(b) **Inorganic polymers:** All the macromolecules which are formed by the catenation of elements other then carbon are known as inorganic polymer.

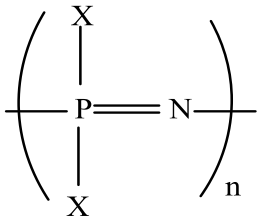
Example:

1.



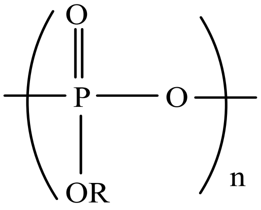
Silicon polymer

2.



Phosphorzener

3.



Polyphosphate

4.

$$-\left(SN \right)_n-$$

Poly sulphur nitride

8.3.1 Classification of inorganic polymers

There are different ways of classifying inorganic polymers.

Classification I: Depending on whether the polymer contains the atoms of only one element or of different elements in its back bone, the polymers are classified into the following two groups.

1. **Homo-atomic polymers:** These polymers contain the atoms of only one element in their back bones. Silicon, phosphorus, sulphur, germanium and tin form homo-atomic inorganic polymers. For example, sulphur has a tendency to form chain or rings in its elemental form (S_8) and in several compounds, like persulphides (H-S-S-H, H-S-S-S-H, H-S-S-S-S-H etc.), polythionic acids etc.

2. **Hetero-atomic polymers:** These contain the atoms of different elements in their backbones.

Classification II: Inorganic polymers can also be classified in another way, which is based on the type of reaction by which the polymes are formed. On this basis, inorganic polymers may be of the following ways:

1. **Condensation polymers:** Condensation polymers are those, which are formed by condensation process. In this process, two or more simple molecules of the same substance polymerize together and form the condensation polymer. One or more H_2O, NH_3, H_2, HCl etc. molecules are also eliminated.

   Examples

   (a) Cross-linked silicone is obtained by the polymerisation of many $RSi(OH)_3$ units.

   (b) When PCl_5 is partially hydrolysed by water, dichloro phosphoric acid, $PO(OH)Cl_2$ is obtained. When $PO(OH)Cl_2$ is heated, many molecules of this substance get polymerized and give rise to the formation of a condensation polymer. In this process HCl is eliminated.

2. **Addition polymers:** These polymers are obtained, when many simple molecules (monomers) combine together.

   Examples:

   (a) Many molecules of sulphur trioxide may be polymerized by the addition of a small amount of water. This gives addition polymer.

   (b) When SO_2 reacts with propylene, $CH_3\text{-}CH{=}CH_2$ in presence of benzoyl peroxide, an addition polymer is obtained.

3. **Coordination polymers**: These are formed by the addition of saturated molecules to each other or by combining a ligand with a metal atom. These polymers contain chelated metal atoms or ions.

Classification-III: According to this classification, the inorganic polymers can be classified into the following categories:

- **i.** Polymes containing two bridgint bonds per units, e.g, homo-atomic sulphur, selenium and teturium polymers.
- **ii.** The alternating silicone-oxygen polymers. Examples are silicones and related compounds.
- **iii.** The alternating phosphorus-nitrgoen polymers. Examples are phosphonitrilic halides, $(NPX_2)N$.
- **iv.** The alternating phosphorus-oxygen polymers. Examples are metaphosphates, polyphosphates and cross-linked phosphates.

Classification-IV: The classification is based on the element which forms inorganic polymers. Thus we have:

- **i.** Polymers containing boron. Examples are: (a) Borazine, $(BH)_3$ $(NH)_3$ or $B_3N_3H_6$. (b) Substituted borzines like (i) B-trimethyl borzine, $[B(CH_3)_3$ $(NH)_3]$ (ii) Borozine $(BH)_3O_3$ (iii) N-timethyl borzine, $[B(CH_3)_3(NH)_3]$ (c) Boron nitride (BN)n.
- **ii.** Polymers containing phosphours. Examples are: (a) Metaphosphates, (b) Polyphosphates, (c) Cros-linked phosphates, (d) Phosphonitricli halides, $[PNX_2]n$
- **iii.** Polymers containg phosphorus. Examples are: (a) Metaphosphates, (b) Polyphosphates, (c) Cross linked phosphates, (d) Phosphonitrilic hladies, $[PNX_2]n$.
- **iv.** Polymeic compounds of sulphur. Examples are nitrides of sulphur, thiazyl halides and imides of sulphur.
- **v.**

8.3.2 General properties of inorganic polymers

Some properties of inorganic polymers are given below:

(1) With a few exceptions, inorganic polymers do not burn. They soften or melt at high temperatures.

(2) Most of the inorganic polymers are built up of highly polar substances. Most of these polymers, however, react with the solvents. There are thus only a few inorganic polymers which actually dissolve in solvents properly.

(3) Inorganic polymers having cross-linked structures with a high density of covalent bonds are generally stiffer and harder than the organic polymers.

(4) The chain segments between cross links in polymers having cross-linked structures are usually short. Consequently, these structures are not flexible enough to permit interaction of solvent molecules.

(5) Inorganic polymers are generally much less ductile than the organic polymers. Thus, while organic polymers such as polyethylene can extend by about 20 percent or more before breaking, inorganic polymers break even when stretched by about 10 percent.

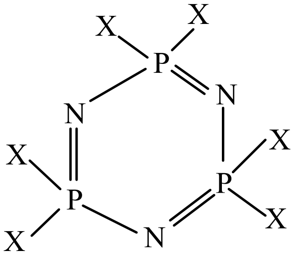
(6) Inorganic polymers, in general, are stronger, harder and more brittle than the organic polymers.

(7) Inorganic polymers can usually be obtained in pure crystalline as well as in pure amorphous forms. Organic polymers, on the other hand, have partial crystalline and partial amorphous structure.

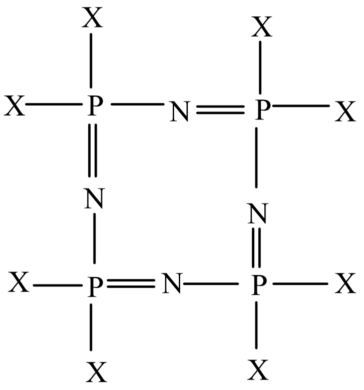
8.4 PHOSPHO NITRILIC HALIDE

Those macro molecules which are having the general formula $-\!\left(PNX_2\right)_n\!-$ are called as phosphor nitrite halides where X = F, Cl, Br and n = 3 to 7

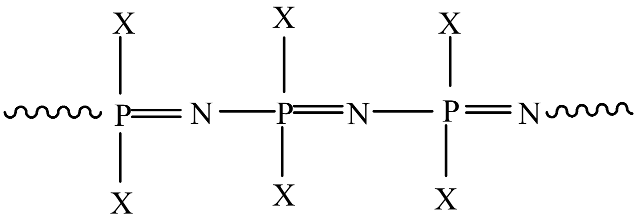
(1) Cyclic trimer



(2) Cyclic tetramer



(3) Linear polymer

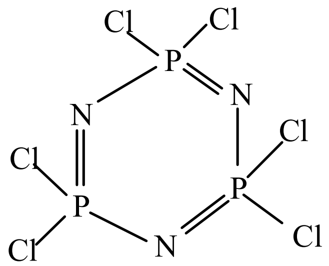


8.4.1 Phospho nitrilic chloride or phosphazenes

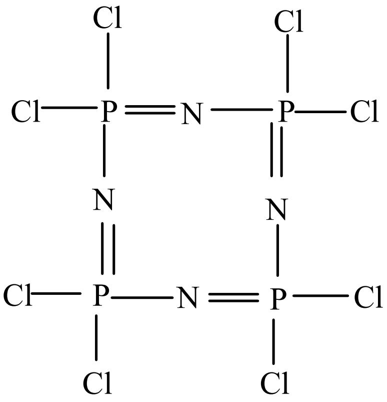
Phosphazenes were initially termed as phosphonitrilic polymers. Later on, the new term was used to represent phosphorus, nitrogen (azo) and P = N double bonds (ene) which are always present in these polymers. They are thus 'unsaturated PN compounds' containing phosphorus, mostly in +V state. As is usual with polymers, they may have cyclic or chain structure. The nitrogen in groups is in 2-coordination and phosphorus in 4-coordination. They contain the group which is isoelectronic with the groups of silicones. Their polymers differ in substitution on phosphorus and on the nature of those substitutents besides the way and the extent, to which polymerization have taken place. They are usually classified on the basis of number of phosphazene units that are incorporated in the structure:

All the compounds which having the general formula $(\text{-PNCl}_2\text{-})_n$ are known as phosphor nitrialic chloride or those compound which having the $(\text{-PNCl}_2\text{-})_n$ repeating unit are known as a phosphonitrilec chloride or phosphazene. In the phosphor nitrilic chloride n= 3 to7. Phosphonitrilic chloride can exist in the three different forms which are given below:

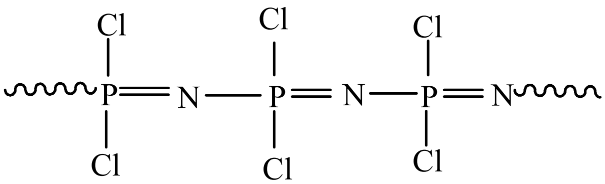
1. **Cyclic trimer**



2. **Cyclic tetramer**



3. **Linear polymer**



8.4.2 Nomenclature

Phosphor nitrilic chlorides are nomenclatured according to the number of repeating unites.

$(PNCl_2)_3$: Triphospho nitrilic chloride.

$(PNCl_2)_4$: Tetra phospho nitrilic chloride.

$(PNCl_2)_5$: Penta phospho nitrilic chloride.

$(PNCl_2)_6$: Hexo phospho nitrilic chloride.

$(PNCl_2)_7$: Hipta phospho nitrilic chloride.

8.4.3 Method of formation

Some of the methods by which phosphornitrilic chloride can be obtained are given below

1. **By the reaction of PCl_5 with ammonia:** Phosphorus penta chloride (PCl_5)when react with ammonia gives corresponding phospho nitrilic chloride.

$$nPCl_5 + nNH_3 \longrightarrow (PNCl_2)_n + 3\,nHCl$$

Where n = 3 to 7

Example:

$$3PCl_5 + 3NH_3 \longrightarrow (PNCl_2)_3 + 9HCl$$

$$4PCl_5 + 4NH_3 \longrightarrow (PNCl_2)_4 + 12HCl$$

$$5PCl_5 + 5NH_3 \longrightarrow (PNCl_2)_5 + 15HCl$$

2. **By the reaction of PCl_5 with NH_4Cl:** Phosphorus pentachloride (PCl_5) when react with ammonium chloride gives corresponding phospho nitrilic chloride.

$$nPCl_5 + n\,NH_4Cl \longrightarrow (PNCl_2)_n + 4\,nHCl$$

Where n = 3 to 7

$$3PCl_5 + 3NH_4Cl \longrightarrow (PNCl_2)_3 + 9\,HCl$$

$$4PCl_5 + 4NH_4Cl \longrightarrow (PNCl2)_4 + 16HCl$$

$$5PCl_5 + 5NH_4Cl \longrightarrow (PNCl_2)_5 + 20HCl$$

8.4.4 Properties of the phosphor nitilic chloride

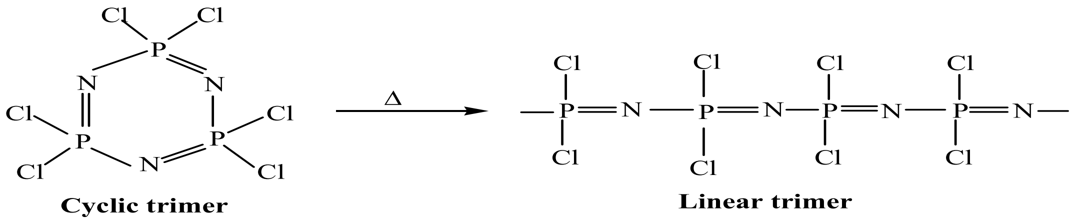
A. Physical properties

(1) $(NPCl_2)_3$ have melting point 114°C and boiling 256°C at 1 atm. pressure. It is readily soluble in ether, benzene and carbon tetrachloride.

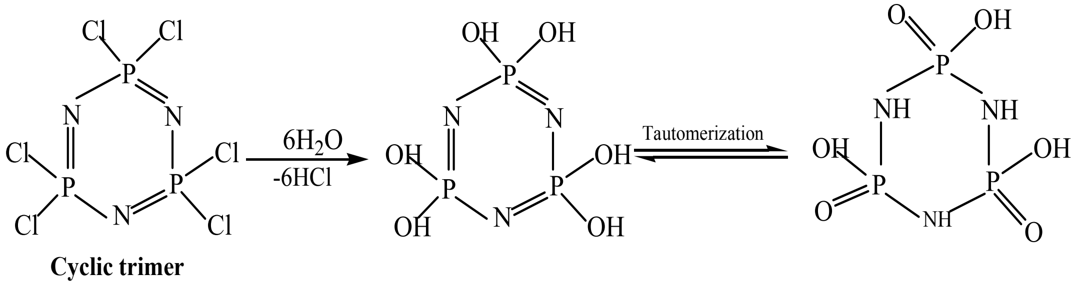
(2) $(NPCl_2)_4$ have melting point 123ºC and boiling point 328.5ºC. It has lower solubility in ether, benzene and carbon tetrachloride than $(NPCl_2)$.

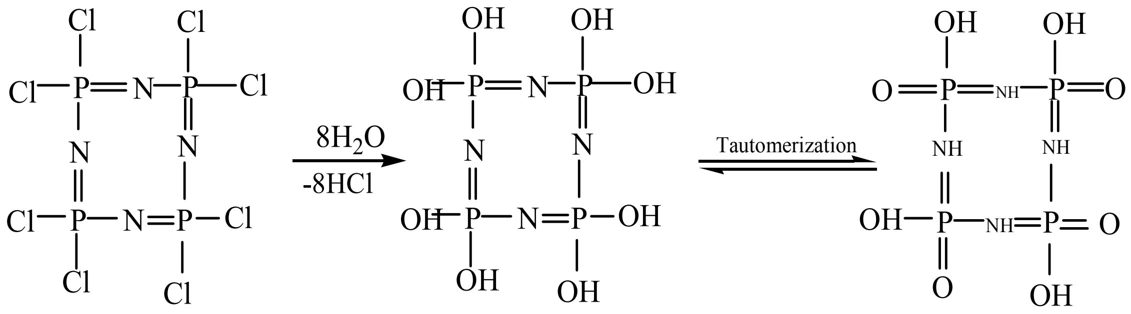
B. Chemical properties

(1) Effect of heat: When the cyclic trimeric phosphor nitrilic chloride are heated than they are converted into their corresponding liner trimer and tetramer respectively, but the liner phosphor nitrilic choride are not effected on heating.



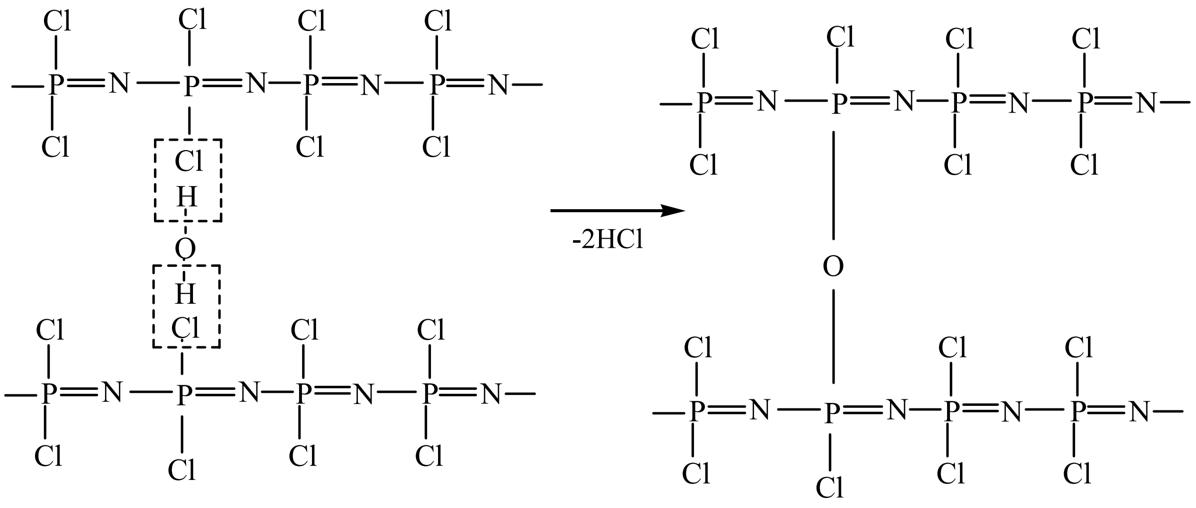
(2) Hydrolysis: When the cyclic trimeric or tetrameric phosphonitric chlorides undergo hydrolysis than there can occur the formation of their hexa-hydroxy and octa-hydroxy derivative which can further undergo telomerisation.





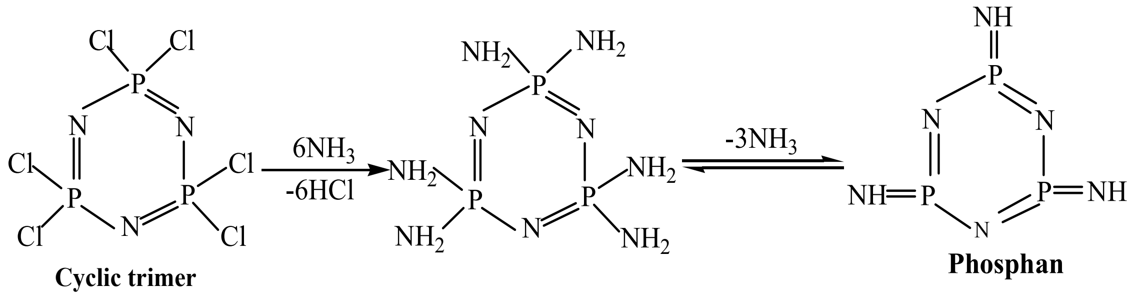
Cyclic tetramer

While, when the liner phosphor nitrilic chlorides react with the H_2O than there occur the formation of cross link polymer through the oxygen bridge.

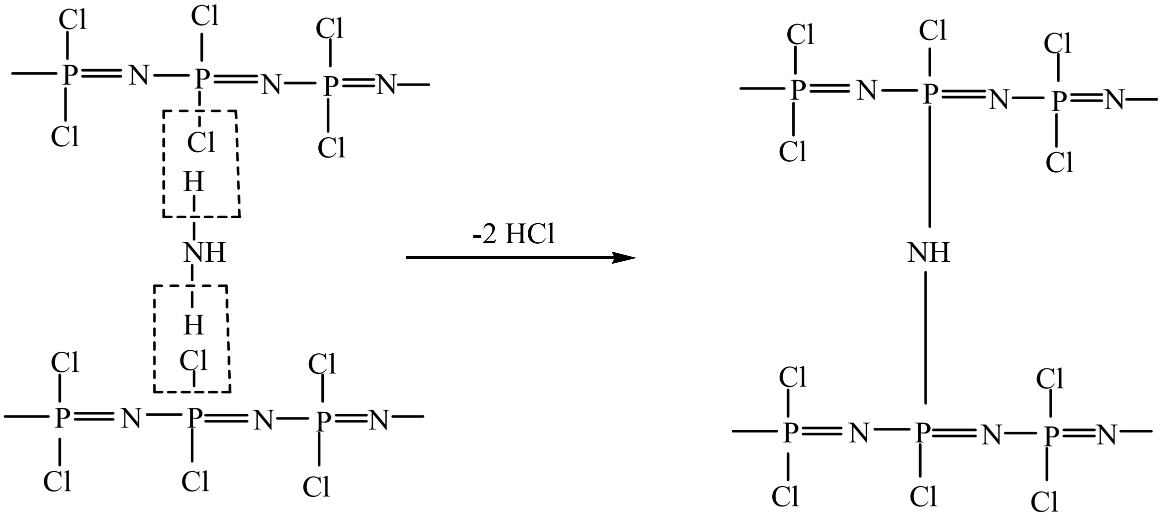


Linear trimer **Cross link polymer**

3. Reaction with the NH_3: When the cyclic trimeric or tetrameric phosphonitrilic chloride reacts with the NH_3 than there occur the formation of hexa- amino derivative and octa-amino derivative respectively, which can further eliminate the NH_3 to form the imino derivative.



While when the liner phosphor nitrilic chloride reacts with the NH_3 then there occurs the formation of cross liked polymer with the -NH-bridge.



4. **Nucleophylic substitution reaction:** When the phospho nitrilic chlorides react with the nucleophilic reagents than there can occur the various nucleophilic substitution reaction, some of them can be given as:

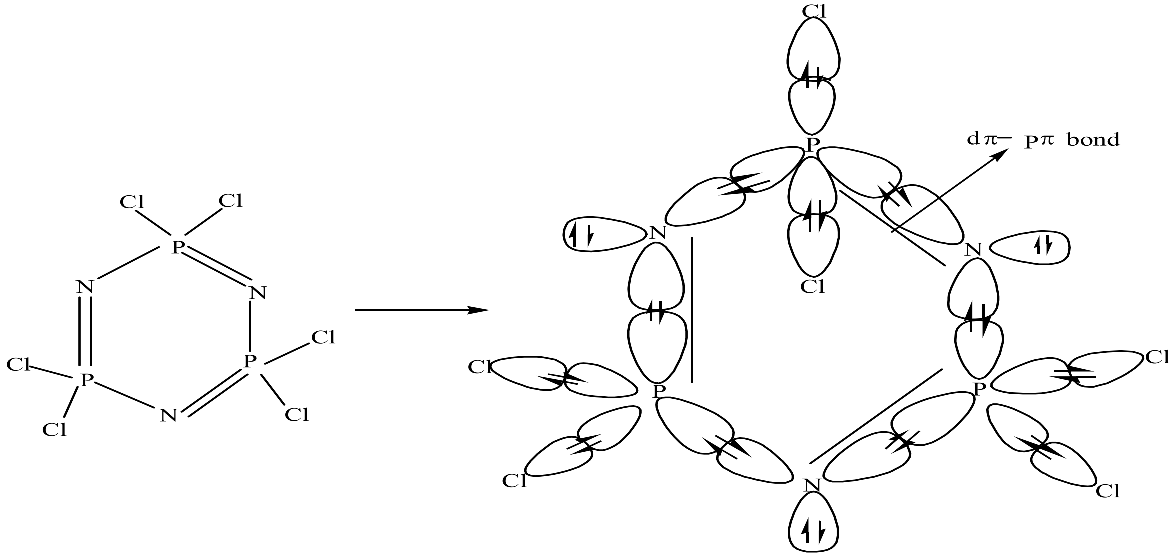
$$(PNCl_2)_3 \;+\; 6\,CH_3^-\,Li^+ \xrightarrow{-6LiCl} [PN(CH_3)_2]_3$$

$$(PNCl_2)_3 \;+\; 6\,L^+\,F^- \xrightarrow{-6LiCl} (PNF_2)_3$$

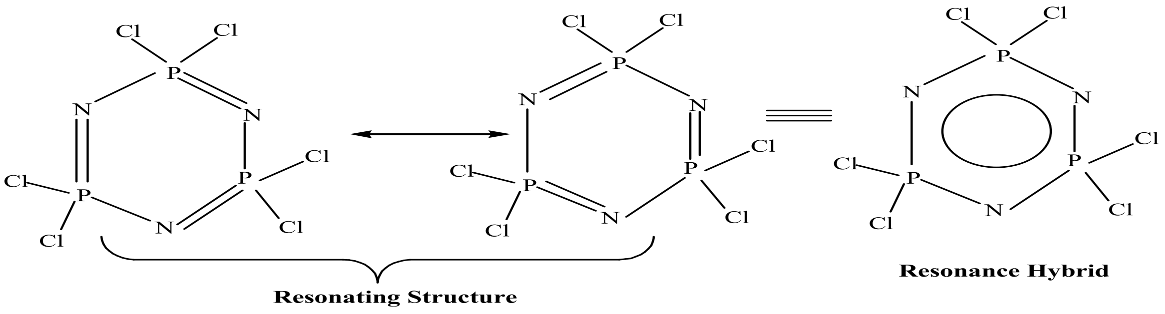
$$(PNCl_2)_3 \;+\; 6Na^+\,NH2^- \xrightarrow{-6NaCl} [(PN\,(NH_2))_2]_3$$

8.4.5 Structure of cyclic tri phospho nitrilic chloride

From X-ray diffraction method it was observed that each P atom and N atom in the cyclic tri phosphor nitrilic chloride having sp^3 and sp^2 hybridization receptively, according the Molecular orbital picture for this molecule can be represented as:



Due to the presence of an electron pair at one of the sp^2 hybrid orbital of each N atom, the cyclic tri phosphornitrilic chloride exhibit basic character. According to the above stricture cyclic tri-phosphonitrilic chloride should exhibit two types of the P-N bond length but experimentally it was observed that all the P-N bond length in the cyclic tri phosphor nitrilic chloride bring identical and intermediate to P=N and P-N, this indicate that this molecule will exist in the two different resonating structure as like to C_6H_6 and its actual structure will be somewhere intermediate to these two resonating structures known as resonance hybrid structure.

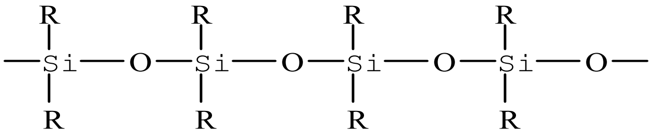


8.5 SILICON POLYMER

These compounds are polymeric organosilicone derivatives containing Si-O-Si linkages. These are also called polysiloxanes. We can represent them by the general formula $(R_2SiO)_n$. These may be linear, cyclic or cross linked polymers and have very high thermal stability and are therefore, also called high temperature polymers. Because of the high thermal stability of Si-O-Si chains, chemists have prepared a large variety of silicone polymers, which are very useful in high temperature processes. Therefore, these find uses in high temperature applications such as heat transfer agents and high performance elastomers. Such qualities are not expected of organic polymers, which cannot withstand high temperatures.

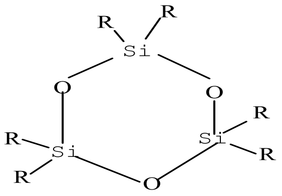
Types of silicone polymers

1. **Linear silicon polymer**

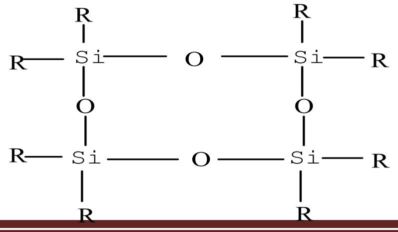


$$-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-$$

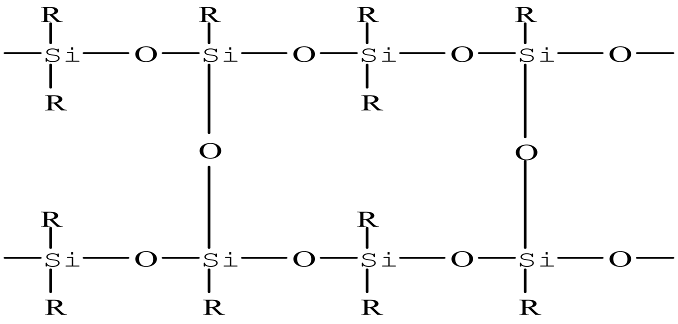
2. **Cyclic silicon polymer**
   a. **Cyclic trimer silicon polymer**



b. **Cyclic tetra meric silicon polymer**



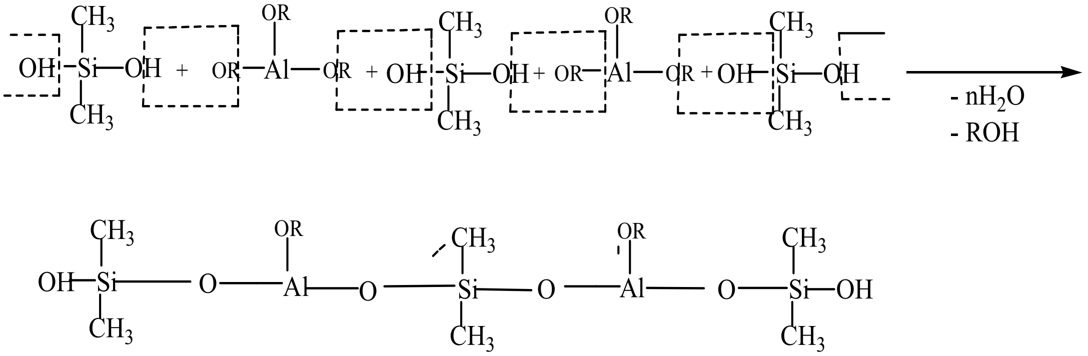
c. Cross linked silicon polymer



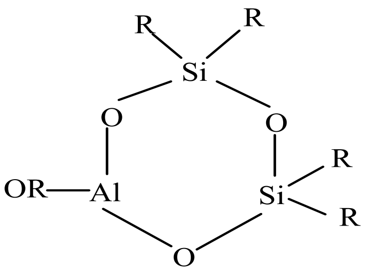
8.5.1 Types of the silicon polymer on the industrial bases

On the basis of industrial use silicon polymer can be divided into four different types, which are given below:-

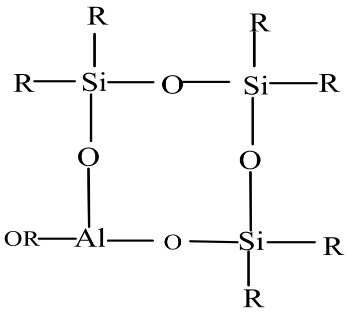
(i) High thermal silicon polymer: When hydrolysis of an organo silicon halde is carried out in presence of the halides or alkoxides of Al, or Ti, two-dimensional linear or cyclic silicone polymer is obtained. In this polymer, some Si-atoms are replaced by Al or Ti atoms. High thermal silicones have exceptionally high thermal stability and remain unchanged, even in contact with a white-hot electrically-heated wire. The presence of Al and Ti atoms in the structure of the polymer increase the thermal stability.



Linear polymer



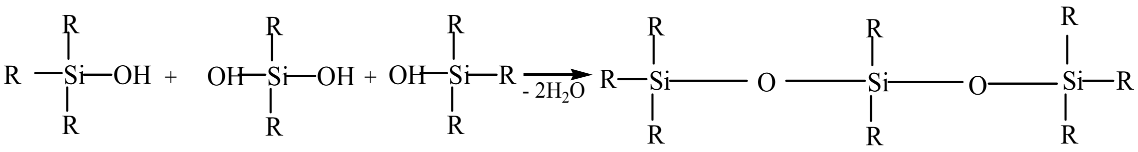
Cyclic trimer



Cyclic tetramer

Uses: Due to the high thermal resistive this type of the silicon polymer can be use in the formation of extern cover of the elective wires.

(ii) Silicon fluid/oil: When the alkyl di-hydroxyl saline undergoes condensation with the tri alkyl monohydroxy silane, than there occur the formation short chain silicone polymer known as silicon fluid or oil.

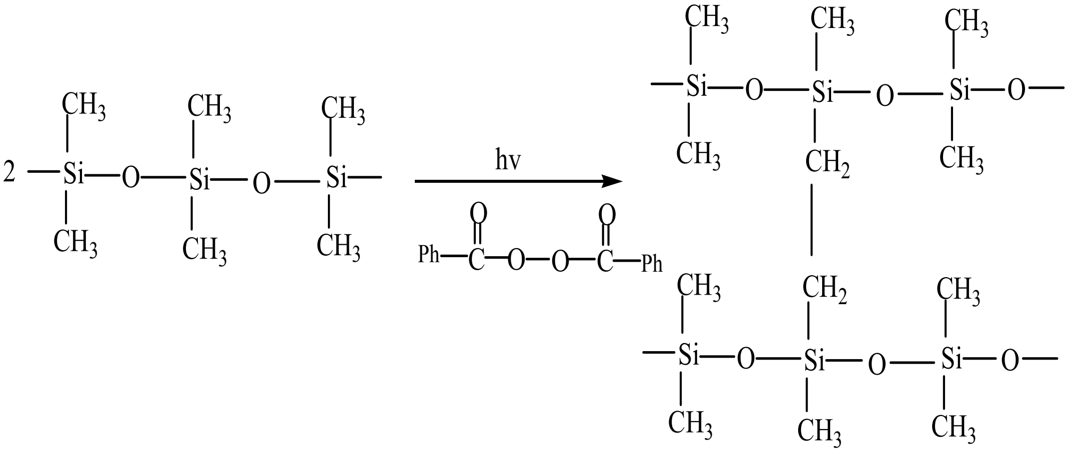


Silicon fluid/oil

Uses: Due to water repellent tendency of silicon fluid, it can be used as a water repentant material in the bather industry or paper industry.

(iii) Silicon rubber: These are long china polymers, with some cross-linking between the chains. They are made by the hydrolysis of $(CH_3)_2$ Si-O-Si$(CH_3)_3$ may be added to the reaction mixture to control the chain length of the polymer. Silicone rubbers consist of cros-linked type silicones with SiO_2 or ZnO as filler and vulcanizer, such as benzoyl peroxide. Silicone rubbers are especially valuable, since they retain their elasticity over a range of temperatures and are resistant to oils.

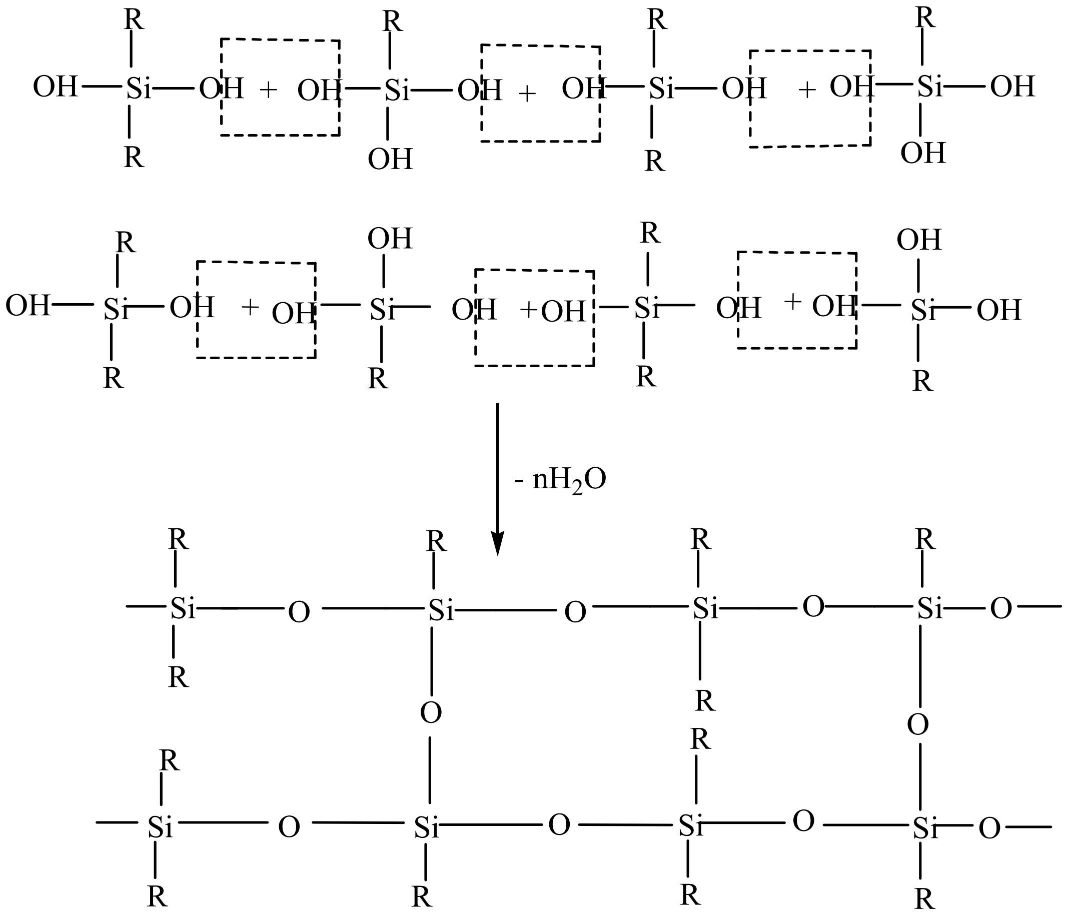
Silicone rubbers, which can withstand temperature upto 400°C for 200 hours and upto 540°C for 90 hours, have also been prepared. Their resistance to 400°C for 200 hours and upto 5400ºC for 90 hours have also been prepared. Their resistance to heat is much higher than that of many organic rubbers. It is due to their property to withstand high temperatures, that they are used in sealing joints and steams of jet aircraft and insulating electrical parts like transistors, which cannot be heated.



Uses: Silicon rubber can be used in the formation of the parts of air craft.

(iv) Silicon resin: Silicone resin is obtained by blending silicone with organic resin, such as acrylic ester. If the hydrolysis of $(CH_3)_2SiCl_2$ is carried out in presence of (CH_3) $SiCl_3$ and then polymerisation is allowed, a rigid silicone is obtained. This silicone is called silicone resin. These are of many types, like coating resins, laminating resins, release resins, water-repellent resins, mokding resins and electrical resins. These are stable to heat, water-repellent and have good electrical conductivetiy, chemical inertness and weather resistance. To develop best properties in them, baking or heat treatment in given to them. These can withstand temperature as high as 250ºC and coating made up treatment is given to them. These can withstand temperature as high as 250°C and coating made up of silicone resin plus organic resins and Al can withstand temperature upto 500°C.

Silicone rubber retains its shape and elasticity permantely, even after vulcanisation and has, therefore been used in a number of ways. High molecular weight silicones, containing long chain or ring structure, are generally waxy or rubber-like solids.



Silicon resin

8.5.2 Preparation of silicones

Silicones are prepared from pure silicon which has been obtained by the reduction of silicon dioxide (silica) in the form of sand with carbon at high temperatures.

$$SiO_2(s) + 2C(s) \longrightarrow Si(s) + 2CO(g)$$

The production of silicones from silicon takes place in three stages:

a) Synthesis of chlorosilanes

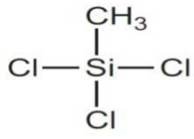
b) Hydrolysis of chlorosilanes

c) Condensation polymerization

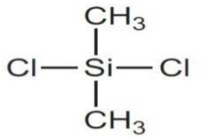
a. Synthesis of chlorosilanes: Silicon is first converted into chlorosilanes, e.g. $RSiCl_3$, R_2SiCl_2 and R_3SiCl, where R is an organic group. When chloromethane is passed through heated silicon at about 550 K under slight pressure and in the presence of a copper catalyst (often copper itself but other copper-containing materials can be used, for example, brass or copper (II) chloride), a volatile mixture of chlorosilanes distils over.

$$Si_{(s)} + 2CH_3Cl_{(g)} \longrightarrow (CH_3)_2SiCl_{2(g)}$$

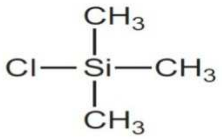
The mixture of liquids contains these three compounds:



CH_3SiCl_3

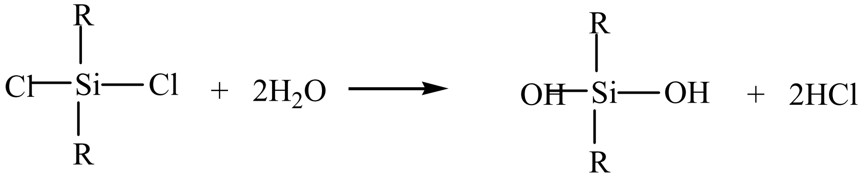


$(CH_3)_2SiCl_2$



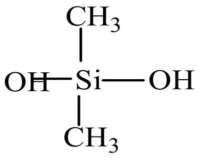
$(CH_3)_3SiCl$

b. Hydrolysis of chlorosilanes: A dichlorosilane is hydrolyzed to a molecule with two hydroxyl groups:



$$Cl-\overset{R}{\underset{R}{Si}}-Cl + 2H_2O \longrightarrow OH-\overset{R}{\underset{R}{Si}}-OH + 2HCl$$

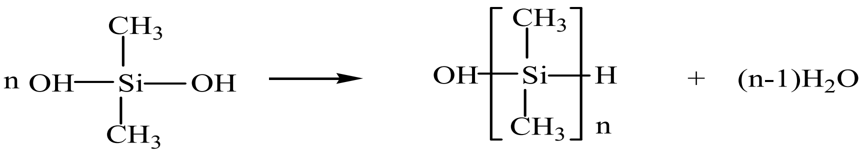
The product is a disilanol. The suffix -ol in a silanol is to show that the molecule contains at least one hydroxyl group attached to a silicon atom and the simplest example is dimethyldisilanol:



$$OH-\overset{CH_3}{\underset{CH_3}{Si}}-OH$$

Diethyldisilanol

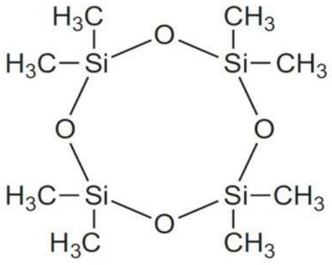
The hydroxyl groups of silanols react spontaneously to form a siloxane:



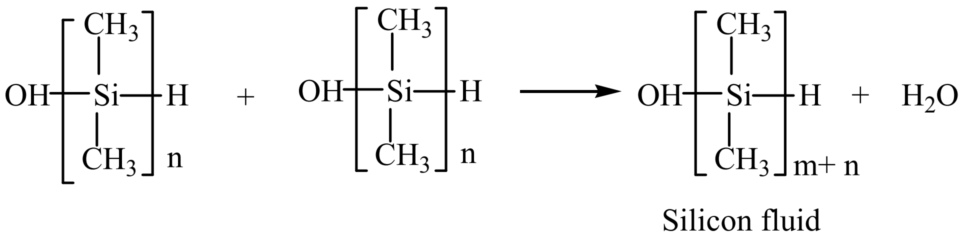
$$n\ OH-\underset{CH_3}{\overset{CH_3}{Si}}-OH \longrightarrow OH\left[\underset{CH_3}{\overset{CH_3}{Si}}\right]_n H + (n-1)H_2O$$

If R is a methyl group, the polymer is a poly(dimethylsiloxane).

Cyclic polymers, for example $\{(CH_3)_2SiO\}_4$, are also produced and than separated out.



c. Condensation polymerization: The oligomers condense rapidly in the presence of an acid catalyst to form long chain polymers:



$$OH\left[\underset{CH_3}{\overset{CH_3}{Si}}\right]_n H + OH\left[\underset{CH_3}{\overset{CH_3}{Si}}\right]_n H \longrightarrow OH\left[\underset{CH_3}{\overset{CH_3}{Si}}\right]_{m+n} H + H_2O$$

The value of (m+n) is usually between 2000 and 4000.

8.5.3 Properties and uses of silicones

Physical properties: The following physical properties are common to all type of silicones:

(i) They have high thermal stability in the absence of air and withstand temperature upto 250-300^0C.

(ii) They remain unaffected by most of the chemical reagents, such as weak acids, alkalies and salt solutions. Thus, silicones are chemically inert.

(iii) Many of low molecular weight silicones dissolve in solvents like C_6H_6, ether and CCl_4.

(iv) They do not become too viscous on cooling and are, therefore used for low-temperature, lubrication.

(v) They are water repellent, i.e, they are not wetted by water and are, therefore used in making waterproof cloth and paper by exposing cloth or paper to the silicone vapours.

(vi) All silicones have good insulating properties and can withstand high temperature without charring. It is due to these properties that silicones are used as insulating materials for electricotors and other electric appliances.

(vii) They are non-toxic.

(viii) Properties and uses of high-thermal silicones, silicones resins, silicones oils, silicone rubbers and silicone greases have been give on the subsequent pages.

Uses:

a. Silicones have been used for making water-proof papers, wools, textiles, wood etc., after coating these articles with silicones.
b. The viscosities of silicones do not change with changes in temperature; therefore, these are used as all weather lubricants.
c. As antifoaming agent in industrial processes.
d. As a mould releasing agent in rubber industry and foundry. It avoids the sticking of the castings to the mould.
e. For making body implants in cosmetic surgery due to its inert nature.
f. Silicones are now incorporated in paints for resisting dampness and for water proofing.
g. Due to their water repellent nature and high dielectric constant, silicones are used in electrical condensers.

8.6 SUMMARY

Silicones and phosphazenes are examples of inorganic polymers. Inorganic elements can have different valences than carbon and therefore, different numbers of side groups may be attached to a skeletal atom. This will affect the flexibility of polymers, their ability to react with chemical reagents and interactions with other polymers. Silicones are polymeric organo silicone derivative containing Si-O-Si linkages. These contain alternate silicon and oxygen atoms in which the silicone atoms are joined to organic groups. These are also called Polysiloxanes. These have the general formula $(R_2SiO)_n$.

The silicones polymers are highly stable towards heat. They exhibit thermal stability up to 200 to 300°C and have low glass transition temperature.

The silicon fluids are usually linear polysiloxanes of 50 to 200 units having low molecular weight. They make up about 60% the silicones used. If they are prepared by the hydrolysis of a mixture of $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$, then the chain lengths may vary considerably. Silicon oils/fluids are used as water repellents for treating building and fabrics.

Silicone resins are solvent solutions of branched chain siloxanes containing residual hydroxyl groups. Silicone resins are made by dissolving a mixture of phenyl substituted trichlorosilane, $PhSiCl_3$ and dichlorosilane n toluene and hydrolysis with water.

8.7 TERMINAL QUESTIONS

8.7.1 Short answer questions

1. What is meant by glass transition temperature?
2. Draw the general repeating unit in silicones.
3. What is the structure of cyclic $(NPF_2)_3$?
4. Which groups of elements in the periodic table have been explored for the formation of inorganic polymers?
5. Draw the general repeating unit in phosphazenes.
6. Draw resonance hybrid structures of cyclic $(NPCl_2)_3$.
7. Give one important use of silicone rubbers.
8. Give one important use of silicone oils.
9. What is meant by ring opening polymerisations?
10. Give the IUPAC names of $Cl_2siH_2HSi(OH)_3$ and $H_3Si\text{-}O\text{-}SiH_3$

11. General questions.How is cyclic $(NPCl_3)_2$ prepared? Give an account of it nucleophilic substitution reactions.
12. Name four main structural units of silicones and designate them.
13. Why do polyphosphazene chains prefer cis-trans conformations to a trans-trans conformation? Give thre important uses of polyphosphazenes.
14. Give equations to indicate the following reactions:
15. Draw polymeric backbones of silicones and phosphazenes.
16. Draw resonance hybrids of $(HPCl_2)_3$.
17. Explain important consequences of cross-linking in macromolecules.
18. Draw polymeric backbone of silicones.
19. What are silicones? How are cross linked silicones prepared?
20. Give islands model of bonding in cyclic $(NPCl_2)_3$.
21. Give a brief account of inorganic polymers with special reference to polyphosphazenes.
22. Silicones and phosphazenes are isoelectronic. What are its consequences?
23. Name three major classes of silicones elastomers.
24. What are silicones? Discus their polymerisation.
25. Draw polymeric backbones of silicones and phosphazenes.
26. Why does the π-system in cyclic $(NPCl_2)_3$ differ from p-system in C_6H_6?
27. What are silicones oils, silicones rubbers and silicones resins?
28. What is IUPAC name of $[-Si\ (CH_3)_2O-]$?
29. What are silicones? How will you prepare them?
30. What are phosphazenes? How will you prepare them? Discuss the structure of $(PNCl_2)$.
31. Write a short note on Silicones?
32. Discuss general properties of inorganic polymers.
33. What are different types of Silicones?
34. What are inorganic polymers? Classify them?
35. Discuss the preparation, properties and important reactions of phosphonitrilic halide.

8.7.2 Objective type questions

1. Hydrolysis of borazine gives:

(a) B_2O_3 (b) B $(OH)_3$

(b) B_2H_6 (d) H_3N- BH_3

2. Which of the following bonds is present in silicones?

(a) Si-Si-Si-Si (b) Si-C-Si-O-Si

(b) Si-C-Si-C-Si (d) –Si-O-Si-O-Si-

3. Hydrolysis of trialkyl chloro sialne gives:

(a) R_3 Si-O-SiR_3 dimer

(b) Cyclic (ring) silicone

(c) Cross-linked silicone

(d) None of these.

4. The strength and inetness of silicones are related to:

(a) Stability of silica-like skeleton of -Si-O-Si-O-Si-

(b) Very high bond energy of Si-O bond

(c) High strength of Si-C bond

(d) All of the above.

5. Hydrolysis of dialkyl dichloro silane gives:

(a) Linear silicone

(b) SiO_2

(c) Cross-linked silicone

(d) None of these

6. The number of P-O-P bonds in cyclic metaphoshoric acid is:

(a) Zero (b) 2

(c) 3 (d) 4

7. Which of the following is a cyclic oxo acid?

(a) $H_5P_3O_{10}$ (b) $H_6P_4O_{13}$

(c) $H_5P_5O_{15}$ (d) $H_7P_5O_{16}$

8. Sodium hexametaphosphate is used:

   (a) As fertilizser

   (b) For softening water

   (c) In fruit ripening

   (d) None of the above.

9. Which of the following is obtained when P_4O_{10} is is heated with Na_2O at $1000^{\circ}C$.

   (a) Sodium tripolyphoshate ($Na_5P_3O_{10}$)

   (b) Sodium tripolyphosphate hexahydrate (NaH_2PO_4)

   (c) Sodium dihydrogen phosphate (NaH_2PO_4)

   (d) Sodium hydrogen phosphate (Na_2HPO_4)

10. Sodium hexametaphosphate is known as:

    (a Calgo (b) Permutit

    (c) Nataliet (d) Nitrolim

11. Using Chlorobenzene (C_6H_5Cl) as solvent, the reagents needed for the synthesis fo borazine are:

    (a) NH_4Cl, BCl_3

    (b) NH_4Cl, BCl_3, $NaBH_4$

    (c) NH_4Cl, $NaBH_4$

    (d) NH_3, BCl_3

8.8 ANSWERS

1.(b) 2.(d) 3.(a) 4.(d) 5.(a) 6.(c) 7.(c) 8.(b) 9.(a) 10.(a) 11.(b)