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B.Sc. CHEMISTRY

THIRD YEAR

PAPER – IV : INORGANIC CHEMISTRY

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INORGANIC CHEMISTRY

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UNIT –I

CONCEPT OF ACIDS BASES AND NON-AQUEOUS SOLVENTS

1.1. Acids and Bases Arrhenius concept –Water Ion system

According to Arrhenius concept, an acid is a substance which contains hydrogen, and also it is a substance which gives H^+ions in aqueous solution. Similarly, a base is a substance which gives OH - ions in aqueous solution.

HCl contains hydrogen, gives H^+ ions in aqueous solution, and it is an acid. NaOH gives OH^- ions in aqueous solution and it is a base. The neutralization of Hcl and NaoH can be represented as follows:

$$HCl \rightarrow H^+ + Cl^-$$

$$NaOH \rightarrow Na^+ + OH^-$$

$$H^+ + OH \rightarrow H_2O$$

Uses:

1. Neutralization reaction involves the contribution of H^+ and OH^- ions. Hence, a constant value for molar heat of neutralization for a strong acid by a strong base in expected.
2. The variation of catalytic behaviour. with the concentration of the acid in understood.

Limitations

1) According to this concept, HCl is an acid only in aqueous solution and not in any other solvent.
2) It does not account for the fact that shows both acidic and basic character, eventhough it does not produce H^+ or OH^- ions.
3) The neutralization reaction is limited to reactions which take place in aqueous solution only.
4) It does not explain the acidic character of salts in $AlCl_3$ in aqueous solution.

Bronsted – Lowry theory – The proton – Donor –Acceptor system

According to this theory a molecule or a cation or an anion that can release a protion to any other substance is an acid, a molecule or a cation or an anion that can accept a proton from any other substance is a base. i.e., an acid is a proton donor and a base is a proton acceptor.

$$HCl \rightarrow H^+ + Cl^-$$

$$[Al(H_2O)_6]^{3+} \rightarrow H^+ + [Al(H_2O)_5(OH)]^{2+}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-}$$

In the above examples, $[Al(H_2O)_6]^{3+}$, HCO_3^{2-} donate a proton and hence they are Bronsted Acids.

$$Py + H^+ \rightarrow [PY\,H^+]$$

$$[Al(H_2O)_5OH]^{2+} + H^+ \rightarrow [Al(H_2O)_6]^{3+}$$

$$HCO_3^- + H^+ \rightarrow H_2CO_3.$$

Here, pyridine (Py), $[Al(H_2O)_5OH]^{2+}$ and HCO_3^- accept a proton and so they are Bronsted bases consider the following reaction,

$$HCl + H_2O \leftrightarrow H_3O^+ + Cl^-$$

Here, HCl donates a proton to H_2O), therefore HCl in a Bronsted acid. H_2O accepts a proton and hence it is a Bronsted base. In the reverse reaction, $H_3{}^+$ donates a proton to Cl^- and hence H_3O^+ is a Bronsted acid, Cl^- in a Bronsted base,

$$HCl \underset{H^+}{\overset{-H^+}{\Leftrightarrow}} Cl^-$$

HCl and Cl^- are called conjugate acid base pairs since they are formed from each other by gain or loss of electron.

Similarly, $$H_3O + \underset{+H^+}{\overset{-H^+}{\Leftrightarrow}} H_2O$$

H_3O^+ and H_2O are formed by gain or loss of electrons. Hence they are also called as conjugate acid base pairs.

Again, consider the reaction.

$$\underset{Acid_1}{HCl} + \underset{Base_2}{H_2O} \Leftrightarrow \underset{Acid_2}{H_3O^+} + \underset{Base_1}{Cl^-}$$

HCl and H_3O^+ are the acids competing to donate H^+ ions, but HCl donates H^+ ions faster hence HCl is a strong acid, H_3O^+ in a weak acid. The conjugate base of HCl, ie Cl^- accepts H^+ slowly compared to H_2O, hence Cl^- is a weak base H_2O in a strong base.

$$\underset{\substack{Strong\\acid}}{HCl} + \underset{\substack{Strong\\base}}{H_2O} \Leftrightarrow \underset{\substack{Strong\\acid}}{H_3O^+} + \underset{\substack{Strong\\base}}{Cl^-}$$

Stronger acid (HCl) and weaker base (Cl) are conjugate acid base pairs. Weaker acid (H_3O^+) and stronger base (H_2O) are conjugate acid base pairs.

Thus conjugate base of a strong acid is always a weak base and the conjugate acid of a strong base is always a weak acid.

Lux –Flood concept

This concept was proposed by Lux and extended by Flood. This theory considers reactions in terms of oxide ion. According to this theory, an acid is an oxide ion acceptor while a base is an oxide ion donor. Examples of acid are $SiO_2, CO_2, P_4O_{10}, SO_3$ etc and examples of base are CaO, BaO, Na_2O, PbO etc

$$CaO + SiO_2 \rightarrow CaSiO_3$$
$$BaO + CO_2 \rightarrow BaCO_3$$
$$PbO + SO_3 \rightarrow PbSO_4$$

In the first reaction CaO donates its oxide ion and it in a base SiO_2 accepts an oxide ion and it is a base SiO_2 accepts an oxide ion and it is an acid.

Lux-Flood concept is particularly useful in explaining reactions which takes place at high temperatures.

Solvent system (Cady-Esley concept)

Solvent system or cady-Esley concept gives definition of acids and bases applicable to protonic and non-protonic solvents. According to this concept an acid is a substance which gives the anion characteristic of the solvent and a base is a substance which gives cation chavacteristic of the solvent. The cation or anion of the solvent is given by the substances either by dissociation or by the reaction of the substance with the solvent.

For example H_3O^+ and anion of the solvent H_2O

$$2\,H_2O \xrightarrow{\quad} H_3O^+ + OH^-$$

All the compounds which can give H_3O^+ are acids and the compounds which can give OH^- are base when water is used as the solvent.

In the same way, NOCl dissociates to give NO^+ and Cl^- ion

$$NOCl \Leftrightarrow NO^+ + Cl^-$$

Hence NOCl is an acid since it gives NO^+ ions (cation of N_2O_4) in N_2O_4 as solvent.

Na NO_3 in N_2O_4 as solvent undergoes dissociation to give Na^+ and NO_3^- ions. $NaNO_3 \Leftrightarrow Na^+ + NO_3^-$

So, $NaNO_3$ is a base since it gives NO_3^- ions (anion of N_2O_4) in N_2O_4 as solvent

Neutralization reactions takes place in non-aqueous solvents just like Arrhenius concept.

$$NH_4Cl + NaNH_2 \Leftrightarrow NaCl + 2NH_3\ (in\ NH_3\ as\ solvent)$$
$$NOCl + NaNO_3 \Leftrightarrow NaCl + N_2O_4\ (in\ N_2O_4\ as\ solvent)$$

Solvent system concept is useful in explaining the reactions taking place in non-aqueous solvents.

Some of the limitations of the theory are:

1. Does not consider some acid base reactions
2. Considers acid base reactions only in the presence of solvents.
3. Cannot explain the neutralization rxns. occurring without the presence of ions.

Lewis concept

In this system an acid is one which accepts an electron pair to form coordinate covalent bond and base is one which donates an electron pair. In other words, an acid is an electron pair acceptor and a base in an electron pair donor.

For example,

$$NH_3 + H^+ \rightarrow NH_4^+$$

Here NH_3 molecule donates an e^- pair, is a base, H^+ accepts an electron pair from NH_3 is an acid. Moreover, according to Bronsted, NH_3 is a proton acceptor NH_4^+ is a Bronsted base. Hence both the Lewis concept and Lowry Bronsted are identical, but the definition for acids and bases are different. Few more example for Lewis bases are H_2O, OH^-, Cl^-, CN^-.

A Lewis acid is an e^- pair acceptor, i,e,. It should have at least one empty orbital to accept the e^- pair.

Lewis acids may be classified into the following types.

i) Molecules contaning a central atom with an incomplete octet, ex;

$BF_3 + C_2H_5OC_2H_5 \rightarrow (C_2H_5)_2O \rightarrow BF_3$.

ii) Molecules containing a central atom with vacant d orbitals $SiX_4, GeX_4, SnX_4\ (X = F, Cl, I)$

iii) Simple cation: All simple cations are e^- pair acceptors.

iv) Molecules having a multiple bond where there are atoms of dissimilar electronegativity. For ex : CO_2, SO_2 etc.

v) Elements with an electron sextet: For example oxygen and sulphur contain six electrons in their valence shell and hence can a concept an e^- pair.

$$SO_3^{2-} + O \rightarrow [O \leftarrow SO_3]^{2-}.$$

Limitations:

1. Generally, an acid base reaction is a fast reaction, but Lewis acid-base reactions are slow.
2. Strength of Lewis acids and base depends upon the type of reaction.

Relative strengths of Acids and Bases

Acids are substances which dissociate to give H^+ ions and bases are substances which dissociate to give OH^- ions. Strength of an acid or base is its capacity to give H^+ or OH^- ions in water.

An acid or a base is considered to be strong when it ionises completely in solution while those ionizing only to a certain extent are weak. HNO_3, H_2SO_4, $HClO_4$, HCl are strong acids, NaOH, KOH are strong bases.

An acid HA, when dissolved in water ionses as H_3O^+ and A^-

$$HA + H_2O \Leftrightarrow H_3O^+ + A^-$$

The equilibrium constant k for the above reaction is given as

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

In aqueous solution, water is used as the solvent which is in excess, hence $[H_2O]$ is constant

$$K \text{ X } H_2O = \frac{[H_3O^+][A^-]}{[HA]}$$

Dissociation constant of acid,

$$Ka = \frac{[H_3O^+][A^-]}{[HA]}$$

For a stronger acid, concentration of H^+ ions i,e., $[H_3O]$ is higher. Higher the concentration of H^+ ion, larger will be value of Ka.

Similarly for a base,

$$B + H_2O \Leftrightarrow BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

When the concentration of [OH^-] is higher, the value of Kb will be larger, which indicates the base will be stronger.

The dissociation constants of CH_3COOH and HCN are 1.8 X 10^{-5} and 7.1× 10^{10} respectively.

CH_3 COOH dissociates into CH_3COO^- ions H^+ ions,

i.e., H_2O + CH_3 COOH ⇔ H_3O^+ + CH_3 COO^-

$$K_{CH_3COOH} = \frac{[H_3O^+][A]}{[HA][H_2O]}$$

$$HCN + H_2O \Leftrightarrow H_3O + CN^-$$

$$K_{HCN} = \frac{[CN^-][H_3O^+]}{[HCN]} = 7.1 \times 10^{-10}$$

Since $K_{CH_3COOH} > K_{HCN,}$ acetic acid is stronger than HCN here considering the bases NH_4OH and $C_2H_5NH_2$. K_b for NH_4OH and $C_2H_5NH_2$ are 1.81 × 10^{-4} and 5.6 × 10^{-4}. Since $K_{C2H5NH2}$> K NH_4OH, $C_2H_5NH_2$ is a stronger base than NH_4OH.

There are many factors, which influence the acidity or basicity of a molecule. One such factor is electron delocalization. When the volume available to the electron increases, electron delocalization also increases. As the electron delocalization increases, electron density and attraction for a proton decreases, which means that basicity decreases.

Now, comparing the relative strength of some of the acids.

1) Relative strengths of CH_4, NH_3, H_2O and HF

The conjugate bases of CH_4, NH_3, H_2O and HF are CH_3^-, NH_2^-, OH^- and F^- ion respectively. In CH_3^- ion three fourth of the volume of carbon is occupied by 3 hydrogen atoms. Volume available for the electron is less i.e. electron delocalization increases. In NH_2^- (amide ion), two thirds of the volume of nitrogen is occupied by two hydrogen's, electron delocalization is more than

CH_3^- ion. Similarly in OH^- ion, the oxygen atom, and in F^- ion, the negative charge exists on the whole volume of F^- ion.

There is increase in ion electron delocalization from CH_3^- ion to F^- hence there is a decrease in electron density. As a result, the attraction for a proton decreases, i.e the basicity decreases from CH_3^- to F^-

$$CH_3^- (Strongest base), > NH_2^- > OH^- > F^- (Weakest base)$$

The conjugate acid of a stronger base is a weaker. CH_3^- ion being, a stronger base its conjugate acid CH_4 is a weaker acid. F^- ion a weaker base has its conjugate acid HF is stronger the acidity of the acids decreases in the order.

$CH_4 < NH_3 < H_3O < HF$

2) Relative strengths of HF, HCl, HCl, HI

The conjugate bases of HF, HCl, HBr, HI are F^-, Cl^-, Br^- and I^- The ionic size increases from F^- to I^-, i.e., there is increase in electron delocalization, which leads to decrease in electron density. Hence, there is decrease in attraction for a proton from F^- to I^-

To conclude, F^- is the stronger base, I^- in the weaker base. Hence,. HF, being the conjugate acid of F^-, is the weakest acid. HI, the conjugate acid of I^- is the strongest acid.

HF (weakest acid) < HCl< HBr < HI (strongest acid)

3) Relative strength of oxy acids

Consider the ox acids HClO, $HClO_2$, $HClO_3$, $HClO_4$. Here, the central atom is Cl. But the oxidation state or Cl is +1, +3, +5, and +7 respectively. As the oxidation state increases, acidic character also increase, i.e., in HClO, the oxidation number is +1, hence, it is the weakest acid. $HC10_4$ the oxidation number is +7, and it is the strongest acid.

Now comparing the basic character of the conjugate bases of the oxy acids, namely ClO^-, ClO_2^-, ClO_3^- ClO_4^-. As the number of oxygen atoms increases the delocalization of Π bond becomes more, which results in decrease in the electron density. As a result, attraction for the proton and hence basicity decreases.

ClO^- (Strongest base) > ClO_3^-

ClO^- being the strongest base, its conjugate acid HClO is the weakest acid. Similarly ClO_4^- is the weakest base, its conjugate acid $HClO_4$ is the strongest acid.

Effect of solvent, levelling solvent

The strength of a protonic acid varies from one solvent to another. HCl, HNO_3 when added to water, they donate protons. They show that they have equal strength i.e., the strength of these acids are levelled to the strength of H_3O^+. Strength of all the acids becomes equal to the strength of H_3O^+. This effect is called levelling effect Here, water is used as the solvent and it is a levelling solvent for all these acids.

Similarly, NaH, $NaNH_2$, $NaOC_2H_5$ when dissolved in water, liberate OH^- ions. The strength of these bases are leveled to the strength of OH^- ions.

Solvents in which there is 100% ionization are called levelling solvents. HF HCl are 100% ionized when dissolved in liquid NH_3, they have equal strength. Here NH_3 acts as levelling solvents. Whereas, the same acids (HF and HCl) when dissolved in water, ionization of these acids differ. HF is only partially ionized, HCl in 100% ionized.

Hence, H_2O is a differentiating solvent for HF and HCl. For bases, CH_3COOH acts as a levelling solvent.

1.2 Hard and soft Acids and Bases

Acids and Bases are classified as Hard and soft based on their electronegative character and Polarisability. The bases in which soft and hard bases atoms have low electronegativity and are easily polarized, those Lewis bases are classified as soft bases. Similarly, the bases in which the donor atoms have high electronegativity and low Polarisabilities are classified as hard bases. As we move down a group, softness increases from F^- to I^- F^- is the hardest Lewis base and I^- is the softest Lewis base.

Examples for hard bases are H_2O Cl^-, R_2O, NH_3, N_2H_4, OH^-, P^-, CO_3^{2-}, CO_3^{2-}, etc. R_2S, RSH, R_3P, C_2H_4, C_6, H_6, CN^- are soft bases

Softness and hardness.

A hard acid has a small size, high positive charge, noble gas configuration and difficult to polarize. A soft acid has a large size, low positive charge or zero charge and do not have a noble gas configuration.

There are many examples for hard acids H^+, Sr^{2+}, La^{3+}, Fe^{3+}, I^{7+},$M_oO_3^{3+}$ As^{3+}, Al^{3+}, Be^{2+} etc Cu^+, Pa^{2+},I^+, Ca^{2+}, Hg^{2+}, zero valent metal atoms are soft acids.

Pearson's HSAB concept

The reaction between a Lewis acid and a base can be written as:

$$A+ \quad :B \rightarrow A:B$$

Lewis acid   Lewis base   Adduct or complex

To predict the stability of adduct, a concept proposed by R.G. Pearson known as HSAB concept (Principle of Hard and Soft Acids and Bases) is useful. According to this concept, the adduct or complex formed between a Lewis acid and a base is more stable when both A and B are either soft or hard. When A is hard and B is soft and when A is soft and B is hard the adduct is least stable.

This principle also says that if there is a reaction between an acid and two bases or a base and two acids, a hard acid will prefer to react with a hard base and a soft acid will prefer to react with a soft base to obtain a more stable adduct.

Applications of the HSAB principle

1) Comparing the stability of AgI_2 with AgF_2. Ag^+ is a soft acid, F^- is a hard base, I^- is a soft base. Soft acid prefers to combine with a soft base to form stable adduct. So, Ag^+ prefers to combine with F^- than I^-. Hence, AgI_2 is a stable complex where AgF_2 does not exist. Similarly, CoF_6^{3-} is more stable than CoI_6^{3-} since Co^{3+} is a hard acid, F^- is a hard base, I^- is a soft base.

2) HgS is more stable than $Hg(OH)_2$

HgS an adduct formed by soft acid and soft base is more stable than $Hg(OH)_2$ formed by soft acid and hard base. Hence $Hg(OH)_2$ dissolves readily in acidic aqueous solution whereas HgS does not.

3) Certain metals exist as sulphides and certain metals exist as carbonates. The existence of metal ores can be explained by applying HSAB principle. Hard acids namely Mg^{2+}, Ca^{2+}, Al^{3+} exist as carbonates since CO_3^{2-} is a hard base and does not exist as sulphides since S^{2-} is a soft base. Soft acids as Cu^+, Ag^+,Hg^{2+} occur as sulphides. The borderline acids Ni^{2+}, Cu^{2+}, Pb^{2+} occur as carbonates and sulphides. Hard acids and hard bases combine through ionic bonding and that of soft acids and soft bases through covalent bonding.

Symbiosis

Soft ligands have a tendency to combine with a centre already associated with soft ligands and hard ligands have a tendency to combine with a centre already associated with hard ligands. This tendency has been termed as symbiosis. Thus, F^- ion, a hard ligand, readily combines with BF_3 to form a complex BF_4^-. Similarly, H^- ion, a soft ligand, readily combines with BH_3 to form a stable complex BH_4^-.

$$BF_3 + F^- \rightarrow BF_4^-$$

$$BH_3 + H^- \rightarrow BH_4^-$$

Mixed substituents are generally not preferred. Thus compounds such as BF_3H^- and BF_4^- i.e. compounds with the same substituents. Likewise, the following reaction occurs spontaneously.

$$CH_3F + CHF_3 \rightarrow CH_4 + CF_4$$

1.3 Non aqueous solvents

For a chemical reaction to take place, the reacting substances are dissolved in a particular solvent, so that interaction can take place. Some reactions take place in aqueous solution, some in non-aqueous solution. For example NH_4 Cl and $LiNO_3$ do not react in aqueous solution, whereas in NH_3 both react. Hence, non-aqueous solvents are chosen for some practical factors.

Physical properties of solvents

Some the physical properties of solvents to be discussed are: 1) Dipole moment 2) Dielectric constant 3) Electrical conductance 4) Viscosity 5) proton affinity.

1) Dipole moment

The product of charge and distance between two charges is called dipole moment. Polar substances dissolve readily in solvents having high value of dipole moment. When polar solutes are dissolved in solvents having higher dipole moment, solvation energy released is higher.

2) Dielectric constant

Columbic force of attraction, F between a cation and an anion is given by

$$F = \frac{q^+ q^-}{Dr^2.}$$

$q^+ \text{ and } q^-$ are the charge of the cation and anion D= Dielectric constant,

r = distance between the cation and anion.

When the columbic force of attraction is small D is large. When the dielectric constant of a solvent is higher, F will be lesser, when the force F in small, the force between the ions of ionic crystal will be weaker and hence ionic crystal will dissolve easily. Higher the value of dielectric constant, higher will be the solubility of the ionic crystal

3) Electrical conductance

The solvents undergo self ionization. Electrical conductance gives an idea of self ionization. When the ionization is higher, acid-base reactions occur easily.

4) Viscosity

Water, low molecular weight alcohols, liquid NH_3 is not viscous. Anhydrous H_2 SO_4, high molecular weight alcohols are viscous. Precipitation, crystallization, filtration are difficult in solvents of high viscosity.

5) Proton affinity

This property is applicable to solvents having hydrogen. NH_3 has greater affinity than water. Acetamide behaves like a weak base with water, shows acidic character in NH_3

$$CH_3CONH_2 + H_2O \Leftrightarrow CH_3CONH^- + NH_4^+$$

Classification of solvents

Solvents can be classified taking into account the physical and chemical properties.

I) Based on proton donor and proton-acceptor property of the solvents

i) Protic or protonic solvents

These solvents have hydrogen atom. It is divided into two types.

a) Acidic or protogenic solvents

Solvents which have strong tendency to donate protons.

E.g. $H_2SO_4, HF\ CH_3COOH, HCN$ etc.

b) Basic or protophobic solvents

Solvents which have strong tendency to accept protons.

E.g. NH_3, C_5H_5 amines.

ii) **Aprotic or non-protonic solvents**

These solvents neither donate nor accept protons and may or may not have hydrogen.

Ex: $C_6H_6, CHCl_3, SO_2, CCl_4$.

iii) **Amphiprotic or amphoteric solvents**

These have hydrogen and donate or accept protons. i.e., they can act as acids as well as bases.

Ex: CH_3COOH, H_2O

II) Based on solubility.

i) Ionizing solvents

These solvents are ionic is nature, undergo self ionization. They exist as ions in their pure state and ionic compounds dissolve readily. These are weak conductors of electricity and have high values of dielectric constants. Ex. NH_3, H_2O, HF etc

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

$$NH_3 \Leftrightarrow NH_4^+ + NH_2^-$$

$$2SO_2 \Leftrightarrow SO^{2+} + SO_3^{2-}$$

ii) Non-ionizing solvents.

These solvents are non ionic in nature. They do not exist as ions. They do not undergo self-ionization hence non-polar or neutral compounds dissolve in it. They have low dielectric constants. Examples C_6H_6, CCl_4

iii) Aqueous and non –aqueous solvents

Non-aqueous solvents are solvents other than water. H_2O, an aqueous solvent undergo self-ionization NH_3, a non-aqueous solvents also undergo self-ionization.

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

$$NH_3 \Leftrightarrow NH_4{}^+ + NH_2{}^-$$

This concept is called parent solvent concept.

Reactions is non aqueous solvents

a) Reaction occurring in liq NH_3 as a solvent

1) Auto ionization.

Liquid Ammonia undergoes auto ionization. But, the extent to which auto ionization occurs is less than that of water

$$2NH_3 \Leftrightarrow NH_4{}^+ + NH_2{}^-$$

2) Acid – base reactions

Ammonia ionizes to give ammonium ions which act as acids and amide ions which act as bases.

Neutralization reaction takes place when ammonium bromide results with potassium amide.

$$NH_4Br + KNH_2 \rightarrow KBr + 2NH_3$$

KNH_2 (a base) in neutralized by NH_4Br to give KBr (salt)

Just as metal hydroxides, metal oxides are precipitated in aqueous system; metal oxides, imides or nitrides are precipitated when liquor ammonia is used as a solvent.

$$AgNO_3 + KNH_2 \xrightarrow{liq\ NH_3} AgNH_2 + KNO_3.$$

$$PbI_2 + KNH_2 \xrightarrow{liq\ NH_3} PbNH + KI + HI$$

$$3HgI_2 + 2KNH_2 \xrightarrow{liq\ NH_3} Hg_3N_2 + 2KI + 4HI.$$

Metal amides, imides and nitrides get dissolved is potassium imide to form complexes.

$$AgNH_2 + KNH_2 \xrightarrow{liq\,NH_3} K[Ag(NH_2)_3]$$

$$NaNH_2 + 2KNH_2 \xrightarrow{liq\,NH_3} K_2[Na(NH_2)_3]$$

3) Precipitation reactions

Solubilities of various substances differ in different solvents. Reactions, which do not occur in water, occur in liquid NH_3.

When solutions of silver chloride and barium nitrate, in liquid ammonia are brought together, $BaCl_2$ gets precipitated.

$$Ag\,Cl + Ba(NO_3)_2 \xrightarrow{liq\,NH_3} BaCl_2 + 2Ag\,NO_3.$$

By mixing solution. KI and NH_4Cl liquor ammonia, a white precipitate of KCl is obtained.

$$KI + NH_4\,Cl \xrightarrow{liq\,NH_3} KCl + NH_4I$$

4. Complex formation reactions

AgCN formed but the addition of KCN with $AgNO_3$ forms the complex $K[Ag(CN)_2]$

$$AgNO_3 + KCN \rightarrow AgCN + KNO_3$$
$$AgCN + KCN \rightarrow K[Ag(CN)_2]$$

These complex formation reactions occur in aqueous solutions also.

5. Ammonolysis reactions

For many ammonolysis reactions, liquid ammonia is an ideal solvent.

i) Hydrides of alkali metal and alkaline earth metals are ammonolysed to the corresponding metal ammines with the liberation of hydrogen.

Metal hydrides + Ammonia → metal ammines + H_2

ii) Covalent hydrides also undergo ammonlysis reaction in liquid ammonia.

$$HgCl2 \xrightarrow{liqNH_3} HgNH_2Cl$$
$$Sicl4 \xrightarrow{Liq\,NH_3} Si(NH_2)_4$$
$$GeI_4 \xrightarrow{Liq\,NH_3} Si(NH_2)_4$$

6. Solvation reaction

Solvent molecule and solute are bonded together in this reaction.

$$BF_3 + NH_3 \rightarrow BF_3 . NH_3$$
$$SiH_4 + 2NH_3 \rightarrow SiNH_4 . 2NH_3$$
$$SO_3 + 2NH_3 \rightarrow SO_3 . 2NH_3$$

7. Metal – ammonia solutions

Metals, which have low ionization energies, low energies of sublimation, high solvation energy dissolves readily in ammonia yielding metal-ammonia solutions. In dilute solutions solution is blue in colour and in concentrated solutions, the solution is bronze coloured. The absorption spectra of the dilute solution of all metals are alike. Dilute metal- ammonia solutions are good electrolytes, and the electrolytic conductance is almost of that of the electrolytic solution (But the concentrated solution has high thermal coefficient similar to that of metal).

Alkaline earth metal-ammonia solutions are evaporation gives $M(NH_3)_6$, whereas alkali metal ammonia solution are evaporation gives the alkali metal, ie the metal can be recovered.

Dilute metal –ammonia solutions are paramagnetic, which indicates the presence of unpaired electrons. But as the concentration increases, magnetic susceptibility decreases. In dilute solutions the electrons and the metal ions are ammoniated.

$$M \Leftrightarrow M^{+} + e^{-}$$
$$M^{+} + xNH_3 \Leftrightarrow [M(NH_3)_x]^{+}$$
$$e^{-} + yNH_3 \Leftrightarrow [e(NH_3)_y]^{-}$$

The electrons are believed that they occupy the cavities in the NH_3 Molecules and the protons are oriented towards the free electrons. But in concentrated solutions, ammoniated metal ions and ammoniated electrons are bonded together.

Reactions of metal –ammonia solutions

Dilute metal –ammonia solutions contain moving, ammoniated electrons, hence this dilute solution can act as strong reducing agent. The blue coloured dilute metal ammonia solutions is a stronger reducing agent than hydrogen and so liberate hydrogen when it reacts with water. Some of the reaction where this solution is acting as a reducing agent.

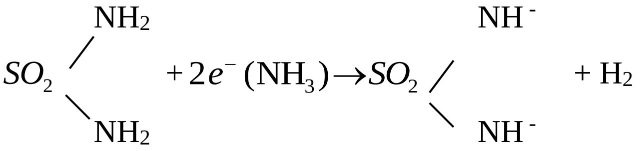
i) Reduction of non-metallic elements

When metal –ammonia solution is treated with non-metal reduction products are obtained.

ii) Metal –ammonia solutions undergo colourization immediately when they are treated with ammonium salts or by acids.

$$NH_4^+ + e^-\ (NH_3) \rightarrow NH_3 + \tfrac{1}{2}H_2$$

The blue colour of this solution is due to ammoniated electron.



$$SO_2\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} + 2e^-\,(\mathrm{NH_3}) \rightarrow SO_2\begin{matrix}\diagup NH^-\\ \diagdown NH^-\end{matrix} + \mathrm{H_2}$$

iii) Organic compounds are also reduced when they are treated with metal –ammonia solutions.

$$RC\equiv CH + e^-\,(NH_3) \underset{\text{metal dissolved is not excess}}{\xrightarrow{liqNH_3}} \underset{\text{Acetyeide ion}}{R-C\equiv C^-} + \tfrac{1}{2}H_2$$

$$RC\equiv CH + \tfrac{1}{2}H_2 \underset{\text{dissolved in excess liq } NH_3}{\xrightarrow{Metal}} RC\equiv CH_2$$

iv) A wide variety of organmetallic compounds of a various types are produced when they react with metal –ammonia solutions.

Reactions occurring in liq. SO_2

1) P**recipitation reactions**

Many precipitation reactions are carried out in liquid SO_2. Soluble compounds can be precipitated upon mixing with liquid SO_2

$$BaI_2 + Zn(CNS)_2 \Leftrightarrow Ba(CNS)_2 + ZnI_2$$
$$SbCl_3 + 3LiI \Leftrightarrow SbI_3 + 3LiCl$$

New thionyl derivatives are prepared from miscible solution of $SOCl_2$ in liquid SO_2.

$$2(CH_3COO)Ag + SOCl_2 \xrightarrow{SO_2(l)} 2AgCl + SO(CH_3COO)_2$$

Thionyl acetate

$$2KI + SOCl_2 \xrightarrow{SO_2(l)} 2KCll \downarrow + SOI_2$$

Thionyl iodide

$$2KBr + SOCl_2 \xrightarrow{SO_2(l)} 2KCl \downarrow + SOBr_2$$

Thionyl bromide

$$2NH_4SCN + SOCl_2 \xrightarrow{SO_2(l)} 2NH_4Cl + SO(SCN)_2$$

Thionyl thiocyanate

2) Auto ionization

Auto ionization takes place according to the following reaction.

$$SO_2 + SO_2 \Leftrightarrow SO^{2+} + SO_3^{\ 2-}$$

Compounds which give $SO_3^{\ 2-}$ in liq. SO_2 will act as bases. Alkali metal sulphides such as Na_2SO_3 behave as bases in liq SO_2.

Similarly compounds which give SO^{2+} will act as acids. The compounds such as $SOCl_2$ behave as acids in liq. SO_2.

Some neutralization reactions taking place in liq. SO_2 are.

$$SOCl_2 + Cs_2SO_3 \rightarrow 2CsCl + 2SO_2$$
$$SOBr_2 + [N(CH_3)_4]_2SO_3 \rightarrow [N(CH_3)_4]Br + 2SO_2$$
$$SO(SCN)_2 + K_2SO_3 \rightarrow 2K(SCN) + 2SO_2$$

3) Solvolysis

Many halides undergo sololysis in liq. SO_2.

$$PCl_5 + SO_2(l) \rightarrow POCl_3 + SOCl_2$$
$$NbCl_5 + SO_2(l) \rightarrow NbOCl_3 + SOCl_2$$

4) Solvation reaction

Most soluble salts form addition compounds with liq SO_2. The addition compounds formed are called solvates very similar to ammoniates.

Examples: $NaI.4SO_2, RbI.4SO_2, CS(SCN)5SO_2$

5) Complex formation reaction

$SbCl_3$ and $SbCl_5$ in liq. So2 from large number of complex compounds

$$SbCl_3 + 3KCl \xrightarrow{SO_2(l)} K_3[SbCl_6]$$
$$SbCl_5 + KCl \xrightarrow{SO_2(l)} K[SbCl_6].$$

$AlCl_3$ reacts with SO_3^{2-} in liq. SO_2 to from $Al_2(SO_4)_3$ which dissolves in excess of SO_3^{2-} to form the soluble complex.

$$AlCl_3 + 3SO_3^{2-}. \xrightarrow{SO_2(l)} Al_2(SO_3)_3 + 6Cl^-$$
$$Al_2(SO_3)_3 + 3SO_3^{2-}. \xrightarrow{SO_2(l)} 2[Al(SO_3)_3]^{3-}$$

6) Reaction with organic compounds

It is a useful solvent for organic synthetic reactions. It serves as a medium for sulphonation, Friedel crafts reaction, Bromination.

$$C_6H_6 + HSO_3Cl \xrightarrow{SO_2(l)} C_6H_5SO_3H + HCl$$
$$C_6H_6 + C_6H_5COCl \xrightarrow[in\,liq\,SO_2]{AlCl_3} C_6H_5COC_6H_5 + HCl$$
$$C_6H_5OH + C_6H_5COCl \xrightarrow[in\,liq\,SO_2]{AlCl_3} C_6H_5COC_6H_5 + HCl$$

Comparison of reactions taking place in liq. NH_3 and liq $S0_2$.

1) Both the solvents undergo auto ionization
2) Many precipitation reaction takes place is both the solvents.

Complex formation reactions, which do not take place in aqueous solution, take place in these solvents.

Chemistry of f-block elements

The elements in which the additional electron is added to the f orbital are called f block elements Electronic configuration of f block element is $(n-2)f^{0,2..........14}(n-1)d^{0,1,2}ns^2$.. . These f block elements have been classified as 4f and 5f block elements 4f block elements are the elements in which the additional electron goes to 4f orbital and are called as lanthanides or lanthanones, the elements in which the additional electron goes to 5f orbital are called 5f block elements or actinides or actinones.

Lanthanides are also called first inner Transition series while the actinides are also called second inner transition series.

Position of lanthanides in the periodic table

The fifteen elements having at no between 57 and 71 must be placed between Ba (at No.56) and Hf (at. No 72)

The electronic configuration of Ba is the same as that of Ca and Sr is placed just below Sr. Similarly, Hf is placed below Zr. There in only one space left between Ba and Hf. All the fifteen elements resemble one another; they must be placed in the same group. These elements resemble Y. One is due to lanthanide contraction, ionic radius of Y is same that of Er.

$$r_{Er^{3+}} = 0.93 A^{O}, \; r_{y^{3+}} = 0.96 A^{O}$$

The second is Y occurs in nature along with the ores of heavier lanthanides and has resemblance with Tb and Dy. So, it is necessary to place all the fifteen lanthanides at one place. The first element La_{57} is placed just below Y. The elements coming after La i.e from Ce_{58} to Lu_{71} are placed in the lower part of the periodic table.

Position of actinides in the periodic table

The naturally occurring heaviest elements Th_{90}, Pa_{91} and U_{92} were placed just below Hf_{72} to their resemblance with these elements. Trans uranium elements, i.e. the elements following uranium was expected to occupy the positions just below Re_{75}, OS_{76}, Ir_{77}, Pt_{78}, Au_{79}, Hg_{80}, Tl_{81} and Pb_{82}.

Chemical experiments with Np_{93} and Pu_{94} showed that they resemble U_{92} and not Re_{75}, and Os_{76}. The elements with atomic numbers 95 and 96 were expected to resemble U_{92}, Np_{93}, and Pu_{94}. This assumption was proved to be wrong. Later on, Seaborg said that the elements having atomic number greater than Ac_{89} would form another inner transition elements. The elements Ac_{89} was just below La and the elements following Ac is just below the lanthanide series in the periodic table.

General characteristics of lanthanides

1) Electronic configuration

In Ba (At No: 56), 6s orbital has 2 electrons, which is completely filled. In La_{57}, the 5d orbital has one electron. But after La, 4f orbital, which has more energy than 5d orbital, falls below 5d orbital. Hence, from Ce_{58}, 4f orbital starts filling up and is completely filled up to Lu_{71}

The general Electronic configuration of lanthanides can be represented as 2,8,18, $4s^2$. $4p^6$ $4d^{10}$ $4f^{0,2,------14}$ $5s^2$ $5p^6$ $5d^{0,1}$, $6s^2$.

4f orbitals are regularly filled up to Eu_{63}. But for Gd_{64}, 4f and 5d orbital have the same energy. Hence the additional electron in Gd goes to 5d levels to retain the half filled 4f orbital, which are morestable

Element	Electronic configuration
La$_{57}$	$[Xe]4f^{0}5d^{1}6s^{2}$
Ce$_{58}$	$[Xe]4f^{2}5d^{2}6s^{2}$
Pr$_{59}$	$[Xe]4f^{3}5d^{0}6s^{2}$
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Ea$_{63}$	$[Xe]4f^{7}5d^{0}6s^{2}$
Gd$_{64}$	$[Xe]4f^{1}5d^{1}6s^{2}$
Tb$_{65}$	$[Xe]4f^{9}5d^{0}6s^{2}$
Dy$_{66}$	$[Xe]4f^{10}5d^{0}6s^{2}$
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Lu$_{71}$	$[Xe]4f^{14}5d^{1}6s^{2}$

2) Oxidation states and oxidation potentials

The oxidation states of lanthanides in solution and in solid state are +3. The values of ionization energy i.e. the energy required for removing an electron from the gaseous corn ion and hydration energy, i.e. the energy released when 2 gaseous ion combine with water to form the aquated species, show that the tetra positive species and dipositive species revert back to the tri positive species. Hence tripositive states are more stable than and tetra positive states in aqueous solution.

In the solid state, the combination of ionization energy and the energy released when gaseous ions combine to produce crystalline solids is more negative hence tri positive species is more stable than dipositive and tetra positive species.

The ions Ce^{4+}, La^{3+} that has empty 4f orbital, Tb^{4+}, Eu^{2+}, Gd^{3+} which has half filled 4f orbital and the ion Yb^{2+}, Lu^{3+} which has fully filled 4f orbital are highly stable. The stability order of +2 state is Eu> Yb>> Sm>Tm~ Nd and the stability order of +4 state in Ce>> TB < Pr (Nd<Dy)

Standard electrode potentials E^{0} for couple of lanthanides as at 25^{0}C, for 1M perchloric acid are given in the table.

The high positive in E^0 for the $Ln^o + Ln^{3+} + 3e^-$, shows that lanthanide elements are powerful reducing agent which means that lanthanides undergo oxidation to tri positive state readiy; Moreover, there is a gradual decrease in E^0 values which shows a slight decrease in chemical activity from La_{59} to Lu_{71}.

Lanthanide Elements	E^0 Values in volls
La_{57}	2.52
Ce_{58}	2.48
Pr_{59}	2.46
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---------	---------------
Ea_{63}	2.40
Gd_{64}	2.39
----------	----------------
Tm_{69}	2.28
Yb_{70}	2.27
Lu_{71}	2.25

Further, in Eu^{2+} ion, which is a 4 f^7 species, Yb^{2+} which is a $4f^{14}$ species is more stable and hence they are the weakest reducing agents of the tripositive ions.

3. Atomic and Ionic Radii – Lanthanide contraction

Atomic and ionic radio of lanthanides are given in table

Elements	Atomic radius in A^o	Ionic radii of Ln^{3+} ion in A^o
La_{57}	1.88	1.06
Ce_{58}	1.82	1.03
Pr_{59}	1.83	1.01
Na_{60}	1.82	1.19
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Dy_{66}	1.77	0.91
Ho_{67}	1.77	0.89

Er_{68}	1.76	0.88
Tm_{69}	1.75	0.87
Yb_{70}	1.94	0.86
Lu_{71}	1.73	0.85

From the above table, we come to a conclusion that as the atomic number of the lanthanides increases, there is a decrease in atomic and ionic radii. The decrease in atomic and ionic radii is called lanthanide contraction.

Eu_{63} and Yb_{70} have high atomic radii values. This is due to the fact that all lanthanides elements contribute three electrons for metallic bond, whereas Eu and Yb contribute only 2 electrons. Each of the lanthanides contributes 3 electrons for metallic bonding.

In lanthanides the additional electron goes to 4f sub shell but not to the valence shell. The shielding effect of one electron in 4f sub shell by another electron is very little due to the diffused shape of f orbital. As atomic number increases, nuclear charge increases but there is no comparable increase in the shielding effect of 4f electron. But the outermost shell has more nuclear attraction as the atomic number increases. Hence the atomic and ionic radii goes on decreasing as the atomic number is increasing. This decrease in radii is called lanthanide contraction.

Consequence of lanthanide contraction

1) Anomalous behaviour of post lanthanide elements

The elements following lanthanides are called post lanthanide elements. Due to lanthanide contraction, properties of post lanthanides are affected.

i) Atomic and ionic radii of post lanthanide elements

As we more from 1st transition to 2nd transition series, there is increase in atomic radii. The same increase is expected when we move from 2nd transition series to 3rd one, but the increase disappears after lanthanides. The pairs of elements Zr-Hf, Nb-Ta, Mo-W have almost the same values since the atomic and ionic radii of second and third transition elements are almost the same, the properties of these pairs of elements are much close to one another due to lanthanide contraction, the atomic size of post lanthanide elements is small, but the atoms in the metallic crystals are closely packed. Hence, densities of 3rd transition series are almost double to those 2nd transition series

ii) Chemical properties of an element depend upon the size of the atom. Due to lanthanide contraction, the basicity of the ions decreases in the order $La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Pm^{3+} > Sm^{3+} > Eu^{3+}$>----------$Tm^{3+} > Yb^{3+} > Lu^{3+}$. As a result of this, from La^{3+} to Lu^{3+} covalent character increase, ionic character decreases between Ln^{3+} and OH$^-$ ion La (OH)$_3$ is the most basic and Lu (OH)$_3$ is least basic.

iii) Due to lanthanide Contraction, there is a small variation in properties of the lanthanides; hence the separation of lanthanides is very difficult.

iv) The crystal radii of and Y^{3+} are Er^{3+} equal ($r_Y{}^{3+}$ = 0.93 A^o, $r_{Er}{}^{3+}$ - 0.96A^o) which accounts for the occurrence of Y along with the lanthanides

4) Colour and absorption spectra

The colour of crystalline salts of Ln^{3+} ions remains unaffected by the change of anion. Ln^{3+} ions having x electrons and (14-x) electrons in 4f orbital have the same colour. For example, Nd^{3+} has 3 electrons and Er^{3+} which has (14-3) electrons have the same colour red. Similarly, Sm^{3+} which has 5 electrons and Dy $^{3+}$ which has (14-5) 9 electrons have the same colour pale yellow.

Colour depends upon the number of unpaired electrons in 4f orbital. But there are some exceptions to this. Eu^{3+} and Sm^{3+} have unpaired electrons in 4f orbital. It is expected to have the same colour. But Eu^{3+} is colourless and Sm^{2+} is red. Ions having 4f orbital, (4f^0- La^{3+}) and 14 electron in 4f orbital (4f^{14}- La^{3+}) is colourless.

The colours of Ln^{3+} salts is due to La Porte –forbidden f-f transitions. Hence, the absorption bands are very weak but sharp. When the temperature is lowered, bands become narrower. Since 4f electrons lie deep inside the atom, they are independent of the nature of the anion.

Another absorption band, which has been observed is Ce^{3+}, Tb^{3+}, Sm^{2+}, Ee^{2+}, Yb^{2+}. This band is due to La Porte-forbidden transitions which are strong and broader. A charge transfer band is observed where the electrical transfer is from ligand orbital to f orbital.

5. Magnetic properties

The paramagnetic property of an ion is due to the unpaired electrons present in it La^{3+} (4f^o) which has no electrons in 4f orbital and Lu $^{3+}$(4f ^{14}) which has 14 electrons are diamagnetic

The effective magnetic moment is given by

$$\mu eff = g\sqrt{J(J+1)}\ B.M$$

Where g = lande splitting factor

$$= 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

S = Resultant spin quantum number

L = Resultant orbital quantum number,

J = Resultant inner quantum number obtained by coupling L and S.

6. Complex formation

4f electrons of lanthanides are well shielded. Due to this availability of orbitals for bond formation between the ligands and Ln^{3+} ion, a few complexes are formed. The tendency of Ln^{3+} ion to from complexes increases from La^{3+} to $Lu^{3+.}$

Complexes are formed with ligands containing oxygen or oxygen and nitrogen.Lanthanides, are highly electro positive so they have no tendency to form complexes with Π-bonding ligands.

General characteristics of actinides

The elements in which the additional electron goes to 5f orbital are actinides or actinones.All the fifteen elements from Ac_{89} to Lw_{103} are actinides.

1) Electronic configuration

5f orbital start filling up from Pa_{91}. ($5f^2$ $6d^1$ $7S^2$). From the elements Ac_{89} to Np_{93}, 6d electrons are retained. From Pu_{94} the energy difference between 5f and 6d orbital in small.

In Cm_{96}. ($5f^2$ $6d^1$ $7S^2$) 6d orbital is filled up, due to enhanced stability of half filled 5f orbital.

2) Oxidation states

+3 is the most common oxidation state of actinides. The stability of this state increases as the atomic number increases. Actinides show variable oxidation states. For first half of the series, the energy required.for the conversion of 5f, 6d is less, and hence show oxidation states such as +4,+5, +6 and +7 for the second half of the series the energy required for the conversion of 5f $\rightarrow$ 6d is more. Hence show lower oxidation states as +2.

Considering the oxidation potential values An^o/An^{3+} becomes more positive from Ac to U becomes less positive till Am. Therefore Am^{4+} in a more powerful oxidizing agent. U^{3+} is a strong reducing agent.

3) Atomic and ionic radii – Actinide contraction

The atomic and ionic radii of actinides ions (An^{3+} and An^{4+}) decreases in size as the atomic number increases. This decrease in size is called actinide contraction similar to lanthanide contraction. Contraction is due to the lesser shielding of 5f electrons which are pulled strongly by the nucleus.

4) Color and absorption spectra

The absorption spectra of An and An^{3+} ions are observed in visible, near ultraviolet and near infrared regions. The bands observed are narrow which are due to the electronic transition between 5f orbitals.

The bands due to charge transfer phenomena are intense due to lower energy involved in transitions.

Extraction of lanthanides from monazite

Lanthanides are mainly extracted from monazite mineral by the following steps.

1) Concentration of the mineral

Monazite is concentrated by gravity separation followed by magnetic separation monazite sand is much more heavier than quartz sand hence monazite sand gets caught up on tables. The impurity quartz which is lighter in washed off. The heavier monazite sand is then passed through magnetic separator where monazite sand being less magnetic is separated from other gangue particles. The concentrated monazite has an average composition.

Tho_2 = 7.5%, Ce_2O_3 = 30%, other rare earth – 32%, P_2O_5 = 29%, SiO_2 =1.5%

2) Cracking of the mineral

The concentrated monazite sand is then treated with conc. H_2S0_4 or by NaOH. This chemical treatment is known as processing, (or) opening up (or) cracking.

a) Cracking by Conc. H_2S0_4

The finely powdered and concentrated monazite is heated with 9.3% cone H_2S0_4 at 210^0C for about 4 hours. The viscous part containing the sulphates of lanthanides and thorium is leached with water for 12 to 15 hours. The sulphates of Ln^{3+}, Th^{4+}, $Zr\ O_2^{3+}$ get dissolved, leaving behind unreacted monazite, insoluble siO_2, TiO_2, $ZiSiO_4$ which is crushed and returned for extraction.

The solution which contains sulphates of lanthanides is then treated with sodium pyrophosphates $Na_2P_2O_7$precipitate Ln as Th $(P_2O_7)_2$. The filtrate is then treated with oxalic acid and to precipitate lanthanide oxalates $Ln_2(C_2O_4)_3$ and traces of Th $(C_2O_4)_2$. This is then treated with $(NH_4)_2C_2O_4$ solution where $Ln_2(C_2O_4)_3$ are left behind as residue which is converted into sulphates by igniting with conc H_2SO_4, Na_2So_4 in then added to this clear solution, where the light lanthanides (La_{57} to Eu_{63}). Precipitate out as double sulphates and heavy lanthanides (Gd_{64} to Lu_{71}) remain in solution as simple sulphates.

Hot NaOH is then added to a mixture of double sulphates of light lanthanides to form a mixture of hydrated oxides. This mixture is dried in air at 100^0 C to get the mixture of oxides which is then treated with dil HNO_3; where the light lanthanide oxides get converted to nitrates which is then separated into individual elements. The sulphates of heavier lanthanides are separated into individual elements by the same method.

b) Cracking by NaOH

The concentrated monazite sand is treated with 74% NaOH at 140^0C. The mud so obtained is digested with water and then allowed to cool at 100^0C. The hydroxides of lanthanides get precipitated. This precipitate is treated with HCl and heated, chlorides of lanthanides go into solution and the individual lanthanides are separated.

3) Separation of individual lanthanides

Lanthanides are separated by classical methods and modern methods

Classical methods

1) Fractional crystallization
2) Fractional precipitation
3) Fractional Thermal Decomposition of oxy salts
4) Change of oxidation states by selective oxidation (or) reduction.

i) Fractional Crystallization

This method depends upon slight differences in solubility of salts.

The solution of mixture of lanthanides is evaporated when one half of the dissolved salts get crystallized. The liquor obtained is evaporated to get one half of the dissolved salts as crystals.

The crystals from the second evaporation is mixed with the mother liquor of the first crystallization and evaporated. This solution gets separated into three fractions. These three fractions are crystallised separated and dissolved in mother liquor of the adjacent solution.

This process is repeated when the more soluble components get collected in the mother liquor and the less soluble components accumulate in each crop of crystals. The intermediate components get distributed between the final crop of crystals and the end mother liquor, in the order of solubility.

ii) Fractional precipitation method

Due to lanthanide contraction, the basic character of lanthanides decreases from La_{57} to Lu_{71} i.e., the hydroxides of cerium group elements (La_{57} – Eu_{63}) are more basic than the hydroxides of Ytterbium group elements (Gd_{64} – Lu_{71}). When NH_3 is added to a solution containing the mixture of lanthanides, i.e., when the P^H of the solution is increased, the less basic ytterbium group elements gets precipitated first. The more basic cerium group elements are left behind in solution. From this individual lanthanides are separated by further fractional precipitation.

iii) Fractional thermal Decomposition of oxy salts

Rate of decomposition of oxy salts decreases form La_{57} to Lu_{71}, i.e., oxy salts of cerium group elements decompose more readily than oxy salts of ytterbium group elements. When the mixture of oxy salts of lanthanides is decomposed thermally and then leached with water, ytterbium group lanthanides get concentrated. The individual lanthanides are then separated by repeating this process several times.

iv) Change of oxidation states by selective oxidation or reduction.

The most stable oxidation state of lanthanides is +3. But some of the lanthanides show +2 and +4 oxidation states. By changing the oxidation state there is a remarkable change in properties which is explained by 2 examples

a) Ce can be separated from a mixture of lanthanides, when 99% pure Ce is obtained from a mixture which has 40% Ce.

This mixture is treated with strong oxidizing agents as alkaline $KMnO_4$.. Here, only Ce is oxidized where other lanthanides are not oxidized, Ce^{4+} is smaller in size than Ce^{3+} it is precipitated as Ce $(OH)_4$ by adding small amount of an alkali.

b) $Eu3^+$ separated from a mixture of Ln^{3+} ions. This mixture is treated with Zn amalgam where Eu^{3+} is reduced to Eu^{2+} leaving all other lanthanides. Eu^{3+} is then precipitated in $EuSO_4$ which is insoluble in water. The sulphates of all Lu^{3+} are soluble in water

By the above methods, reducing (or) oxidising selectively, some of the ions are separated.

Modern Methods

i) Ion exchange method
ii) Solvent extraction method
iii) Complex formation

i) Ion exchange method

This is an important and effective method. Lu^{3+} ions are exchanged with H^+ ions of the cation exchange resin which contains sulphonic acid ($-S0_3H$) or carboxylic acid groups (-COOH), Ln^{3+} ions get fixed on the resin.

$$Ln^{3+}(aq) + 3HR(solid) \Leftrightarrow LnR_3(solid) + 3H^+(aq)$$

Lu $^{3+}$ (aq) size and La^{3+} (aq) is smallest in size,La^{3+} attached to the resin with maximum firmness which is held at the top La^{3+} is attached with the resin with minimum firmness which is at the bottom of the column. To remove La^{3+} ions, the column is eluted with eluting agent namely ammonium citrate-citric acid buffer (P^{H}being 4 to 7) NH4 $^{+}$ ions of the eluting agent replace Ln $^{3+}$ ions from the resin.

$$LnR_3 + NH_4 \rightarrow NH_4R + Ln^{3+}$$

$$Ln^{3+} + citrate ion \rightarrow Ln - citrate complex$$

$Ln - citrate complex$ Which is at the bottom comes out of the column comes out first; La-citrate complex which is at the top comes out last.

ii) Solvent extraction method.

This method is based on the differences in the solubility of lanthanides salts. Lanthanide salts are dissolved in water. To this aqueous solution, an organic solvent which is called the extracting solvent is added. Tri –n – butyl phosphate (TBP) in medium like kerosene or xylene is used as the extracting solvent to extract lanthanides from nitric acid solutions.

$$Ln^{3+}(aq) + 3NO_3^{-}(org) \Leftrightarrow Ln(NO_3)_3(TBP)_3\, org$$

The distribution of lanthanide ions between the two solvents is given by

$$\lambda = \frac{Total\, cocentration\, of\, solute\, in\, one\, solvent}{Total\, concentration\, of\, solute\, in\, another\, solvent}$$

Where λ is the distribution ratio.

The values of λ is differenticult for different La^{3+} ions and hence lanthanides can be separated.

95% pure lanthanides have been separated by this method.

iii) Complex formation

Lanthanide oxalates are insoluble in water, so they are dissolved by treating them with EDTA.

Lanthanide EDTA complexes have different stabilities. The stability increases with increasing atomic number. These complexes are then treated with an acid, whereby the least stable complex is converted to oxalate, which remain unstable, can be separated from the rest of the lanthanides. By slightly increasing the concentration of acid step by step the individual lanthanide-EDTA complexes can be separated.

Preparation of metals

Lanthanides get easily oxidized to +3 states, it is very difficult to get the elements in the metallic state: By the following methods. Lanthanide metals are prepared.

i) Thermal decomposition of lanthanide – mercury amalgamd

By electrolyzing the aqueous solutions of lanthanides salts, and using mercury cathode, lanthanide- mercury amalgam is formed. By decomposing the thermally, metals are obtained. In this method, mercury is not completely eliminated.

ii) Electrolysis of fused chlorides

Anhydrous lanthanide chlorides are heated to a high temperature with sodium or potassium or calcium chloride. This molten mass is electrolyzed where graphite is used as the cathode, refractory lined pot act as anode. The molten metal gets collected at the bottom which is then removed.

iii) Metallothermic reduction of alloys

Anhydrous lanthanide chlorides and fluorides are heated with calcium, when lanthanide-calcium alloy is formed. At about 1000^0 C, calcium gets volatilized from the alloy, leaving behind lanthanide metals.

Pure lanthanide metals are obtained by vacuum distillation.

Actinides – occurrence

Th_{90}, Pa_{91} and U_{92} are extracted from their ores.

Thorium occurs in nature in small proportions. The important minerals of thorium are thorite, $SiO_2.ThO_2.nH_2O$ and thorianite which contain 55-80% $Th0_2$, 11-32% UO_2. Thorium is found in Ceylon and Travancore as monazite sands. 80% of the world's thorium is located in India as monazite sand.

Uranium is not found free in nature. It occurs in the combined state in a few scarce minerals. Its important minerals are i) pitchblende (U_3O_8). It is found in Australia, Bohemia, Hungary, Norway, India, East Africa etc, ii) Carnotite occurs in Jaduguda mines of Bihar iii) Autunite is found in Congo. In India the principal sources of uranium ore are the Jaduguda mines of Bihar. Rich deposits of high grade uranium ore have been found its Bhatin area of Bihar. Another important source in India is monazite sand of Travancore.

After the element U_{93}, the actinides with atomic number 94, 95,96 etc were synthesized Hence, the elements after uranium are called Tran uranium elements and are man –made elements

Actinides – preparation

Neptunium was synthesized from uranium

$${}_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239}.$$

$${}_{92}U^{239} \qquad \rightarrow {}_{93}Np^{239} + {}_{-1}e^{o}.$$

${}_{93}Np^{239}$ emits an electron giving ${}_{94}Pu^{239}$

$${}_{93}Np^{239} \rightarrow {}_{94}Pu^{239} + {}_{-1}e^{o}$$

Americium ${}_{95}Am$ was synthesized from ${}_{92}U^{238}$

$${}_{92}U^{238} + {}_{2}He^{4} \rightarrow {}_{94}Pu^{241} + {}_{O}n^{1}$$

$${}_{94}Pu^{241} \rightarrow {}_{95}Am^{241} + {}_{-1}e^{o}$$

Curium was synthesized from ${}_{94}Pu^{239}$

$${}_{94}Pu^{239} + {}_{2}He^{4} \rightarrow + {}_{96}Cm^{242} + {}_{O}n^{1}$$

Berkelium was synthesized from 241 Am_{95}

$${}_{95}Am^{241} + {}_{2}He^{4} \rightarrow {}_{97}Bk^{243} + {}_{O}n^{1}$$

Californium ${}_{98}Cf^{245}$ was synthesized from ${}_{96}Cm^{242}$

$${}_{96}Cm^{242} + {}_{2}He^{4} \rightarrow {}_{98}Cf^{245} + {}_{O}n^{1}$$

${}_{92}U^{255}$ With 7 electrons when einsteinium was sysnthesized.

$${}_{92}U^{238} + 17\ {}_{O}n^{1} \rightarrow {}_{92}U^{255}$$

$${}_{92}U^{255} \rightarrow {}_{99}Es^{255} + 7\ {}_{-1}e^{o}$$

From the same isotones of ${}_{92}U^{255}$, ${}_{100}Fm^{255}$ was synthesized.

$${}_{92}U^{255} \rightarrow {}_{100}Fm^{255} + 8\ {}_{-1}e^{o}.$$

Mendelevium ${}_{101}Md$, was synthesized from ${}_{99}Es$

$$_{99}Es^{253} \rightarrow \ _{2}He^{4} \rightarrow \ _{101}Md^{256} + \ _{O}n^{1}$$

Nobelium $_{102}No$, was synthesized from $_{98}Cm^{246}$

$$_{98}Cm^{246} + \ _{6}C^{12} \rightarrow \ _{102}No^{252} + 6\ _{O}n^{1}$$

Lawrencium, $_{103}Lw$ was synthesized from $_{98}Cf^{254}$

$$_{98}Cf^{254} + \ _{5}B^{10} \rightarrow \ _{103}Lw^{245} + \ _{O}n^{1}.$$

Comparison of Lanthanides and actinides

Lanthanides	Actinides
1) The additional electron goes to 4f orbital	The additional electron goes to 5f orbital
2) It is obtained in the form of ores.	Most of the elements are synthesized artificially
3) It has no radioactive property	It has radioactive properties
4) Most common and stable oxidation state is +3	It has oxidation states from +2 to +6
5) Ions are paramagnetic	Except Th^{4+}, U^{6+} all the ions are paramagnetic
6) Ions are coloured	Ions are coloured
7) Complexes formed are less	Complexes formed are more
8) It gives double salts	It gives double salts to a certain extent
9) It does not show isomorphism	It shows isomorphisom

Elements with atomic No 104 and 105 and their position in the periodic table and synthesis

The actinide series completes at 103 i.e. the element Lawrencium. The recently reported elements 104 and 105 are d block elements which should resemble Hf and Ta. The element 104 was first reported by Russian scientists Kurchatovium et al. their work was repeated by American scientists and they got different results, named as rutherfordium. The synthesis was achieved by Russians by bombardment of plutonium with a stream of neon 22 ions.

$$_{91}Pu^{242} + \ _{10}Ne^{22} \rightarrow \ _{104}X^{260} + 4\ _{0}n^{1}$$

They fission tracks of the reaction were examined under the microscope. They discovered the existence of an atomic species, which has a life period of 0.3 seconds.

Position in the periodic table

According to Seaborg theory, the element 104 must be one of the transition elements. It is because the 5f orbital is completely filled up and cannot have any more electrons. The additional electron cannot occupy 5f orbital, but occupies 6d orbital. Hence the element 104 is placed just below Hf. It is expected that the properties of the element with atomic number 104 is the same as Hf It has been found to be the same.

The element with atomic number 105 is named as Hahnium. It has a half life of about 1.6 seconds. It was synthesized by bombardment of ${}_{98}Cm^{246}$ with ${}_{7}N^{15}$

$$ {}_{98}Cm^{246} + {}_{7}N^{15} \rightarrow {}_{105}Ha^{260} + {}_{0}n^{1} $$

The electronic configuration of Kurchatovium is [Rn] $7s^2\ 6d^2$ and that of Hahnium is [Rn] $7s^2\ 6d^3$.

Question:

1) Explain Arrhenius theory of acids and bases
2) What is symbiosis?
3) What is HSAB concept?
4) Explain the reactions when liquid NH_3 in used as a solvent.
5) Discuss the positions of lanthanides in the periodic table.
6) What is lanthanide contraction? What are its consequences?
7) Compare lanthanides with actinides.
8) How lanthanides are are separated by ion exchange chromatography?

NOTES

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UNIT II

Co Ordination Chemistry

Definition of the term

1) Coordination compounds (or) complexes

When solutions of KCN and Fe $(CN)_2$ are mixed and evaporated, potassium Ferrocyanide Fe $(CN)_2$. 4 KCN is obtained. This compound when dissolved in water does not give tests for Fe^{2+} and CN^{-1} but gives the test for K^+ ions and

$[Fe(CN)_6]^{4-}$ ions.

$$Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2.4KCN \Leftrightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

$Fe(CN)_2.4KCN$, the individual compounds lose their identity. The molecular compounds where the individual compounds lose their identity is called coordination compound (or) complexes.

2) Complex ion

It is an electrically charged radical which is formed by the combination of a metal cation with one or more neutral molecules or anions.

3) Ligands

In the complex ion $[Fe(CN)_6]^{4-}$, CN^- ions are attached with Fe^{2+}, which is a ligand, i.e., ligands are either neutral molecules or ions which are attached with the cation.

Ligands donate one or more pair (or) pairs of electrons to the central metal cation.

4) Co ordination Number

The number of atoms of the ligand which can coordinate to the central metal ion. Coordination number is otherwise called as ligancy. In $[Fe(CN)_6]^{4-}$ ion, 6 bonds are formed between the six ligands and metal ion. hence coordination number of $[Fe(CN)_6]^{4-}$ is 6

5) Co ordination sphere

The central metal ion and the ligands that are directly attached to the metal ion are placed in a square bracket which is called as coordination sphere. This is also called as first sphere of attraction. The anions which are outside the first sphere form second sphere of attraction.

Classification of ligands

I. Based on donor and acceptor properties of the ligands

i) Some ligands contain Π type vacant orbital. These ligands donate electron pairs to the metal ion. The metal ions in turn donate Π electrons to the ligand. The ligands receive back donated an Π electron which gets fixed up in vacant Π orbital. Here, both the metal ion and ligands donate and accept electrons.

Ex: Co, No, CN^- RNC, R_3P, α, α' dipyridyl, unsaturated organic molecules.

ii) Some ligands donate electron pairs, but do not have vacant Π orbital, so they cannot receive back donated Π electrons from the metal ion

Ex: H_2O, NH_3, F^-.

iii) Ligands do not have electronpairs to donate but have Π bounding electrons to donate

Ex: C_2H_2, C_6H_6, cyclopentadienyl ion.

II. Based on the number of donor atoms

1) **Monodentate ligands:** ligands which have only one donor atom are called monodentate ligands. It coordinates to the metal ion at only one site

   Ex: H_2O, NH_3, F^-, Cl^- , CN^- , $NO_2{}^-$ etc.

2) **Bidentate ligands:** Ligands which has 2 coordinating atoms are called tridentate ligands ex: CO_3^{2-}, ethylene diamine (en) oxalate ion, 2, 2' dipyridyl etc.

3) **Tridentate ligands:** Ligands which have three coordinating atoms are called tridentate ligands.

   Ex: Diethylene triamine, $H_2N-(CH_2)_2-NH-(CH_2)_2-NH_2$

4) **Multidentate ligands:** Ligands which have more than three coordinating atoms are called multidentate ligands.

   Ex: ethylene diamine tetra acetic acid (EDTA)

Types of ligands

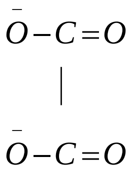
1) **Bridging ligands**: A monodentate ligand which has more than one free electron pair, may coordinate with 2 metal atoms at the same time is called a bridging ligand.

   Ex: OH^-, F^-, Cl^- NH_2^-.

2) Symmetrical and unsymmetrical bidentate ligands

When the two coordinating atoms are same in a bidentate ligand, it is called a symmetrical bidentate ligand.

Ex: oxalate ion

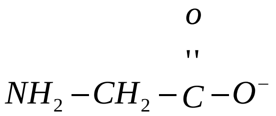


$$\begin{array}{l} \bar{O}-C=O \\ \quad | \\ \bar{O}-C=O \end{array}$$

Ethylene diamine $NH_2-CH_2-CH_2-NH_2$

When the two coordinating atoms are different in a bidentate ligand, it is called unsymmetrical bidentate ligand

Ex:



$$NH_2-CH_2-\overset{\overset{o}{\|}}{C}-O^-$$

3) Ambidentate ligands

Some ligands have two coordinating atoms among the two atoms, only one atom will coordinate with the metal ion. Such type of ligands are called as ambidentate ligands.

Ex: NO_2^- ion (M - NO_2, M - ONO)

CN$^-$ ion (M – CN, M - NC)

SCN$^-$ ion (M – SCN, M- NCS)

Nomenclature of mononuclear and polynuclear complexes

In naming the complexes, ligands are named first and the central atom is named last.

a) Naming of ligands

When naming the negative ligands, if the anion name ends in ide, ite, ate, the final letter ‘e’ is replaced by o.

Ex: SO_3^{2-} → Sulphito

SO_4^{2-} → Sulphato

NO_3^- → Nitrato

N_3^- → Azido

NH^{2-} → Imido

CH_3COO^- → Acetato

In some cases, the suffix ‘ide’ in replaced by ’o’

Ex: F^- → Fluoro

Cl^- → Chloro

CN^- → Cyano
O^{2-} → Oxo
OH^- → Hydroxo.

For less common neutral ligands, the names of molecules are written on such, for common neutral ligands, special names are used.

Ex: NH_3 → Ammine
H_2O → Aquo
CO → Carbonyl
NO → Nitrosyl
CS → Thiocarbonyl
NS → Thionitrosyl

Positively charged ligands have suffixium

$NH_2 NH_3^+$ → Hydrazinium
NO^+ → Nitrosylium

In the case of bridging ligand the letter 'μ' is written before the name of the ligand.

For ambidentate ligands, they are given special names.

--- NCS→ isothiocyanato
--- SCN→ thiocyanato
--- NO_2 → nitro
--- ONO→ nitrito

The number of ligands is denoted by the Greek prefixes di-tri-, tetra-, penta – etc. In the case of chelating ligands, the prefixes, bis tris, tetrakis etc is used.

The negative ligands are named first followed by neutral when and then positive ligands. When there are more than one type of ligand, the ligands are named in alphabetical order.

b) Naming of anionic complexes.

For naming complexes, the ligands are named first followed buy the central metal ion and the oxidation state of the metal ion is written in Roman numerals within brackets. When oxidation state in negative, the negative sign is written before the Roman numeral. The central metal ion is named by writing the suffix 'ate' to its name.

Ex: $[Cr (en) I_4]^-$ → Tetra iodo ethylene diammine chromate (III) ion
$[PE (NH_3) Cl_5]^-$ → Pentachloro monoamine platinate (IV) ion

$[Ag\,Cl_2]^-$ → Dichloro argenate (I) ion

$[Fe\,(CN)_6]^{4-}$ → Hexacyano ferrate (II) ion

$[Fe\,(CN)_6]^{3-}$ → Hexacyano ferrate (III) ion

C) Naming of cationic and neutral complexes

In naming cationic and neutral complexes the ligands are named first and then the central ion. The oxidation state of the metal ion is written is Roman numerals. The suffix ate is not writen to the name of the metal.

Ex: $[Cr\,(H_2O)_4\,Cl_2]^+$ → Dichloro tetraaquo chromium (III)ion

$[Ag\,(NH_3)_2]^+$ → Diammine silver (I) ion

$[Ni\,(en)_2Cl_2]^{2+}$ → Dichlobis (ethylenediammine nickel (IV) ion

$[Ni\,(CO)_4]^o$ → Tetra carbonyl nickel (o)

$[Co\,(NH_3)_3\,(NO_2)_3]^o$ → Trinitro triammine cobalt (III)

d) Naming of ionic complexes

In naming of ionic complexes, the cation is named first and then the anion.

Ex: $K_2\,[Pt\,Cl_6]$ - This complex has a simple cation and a complex anion. It is named as, potassium hexachloro palatinate (IV)

Similarly $NH_4\,[Cr(SCN)_4(NH_3)_2]$ - Ammonium tetra thiocyanato diammine chromate (III)

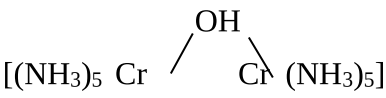
$[Pt\,(NH_3)_4\,Br_2]\,Br_2$ has complex cation and simple anion, which is named as Dibromo tetra am mine platinum (III) bromide.

When the both ions are complex ions, for example. $[Pt\,(Py)_4]\,[PtCl_4]$ is named as Tetra pyridine platinum (II) tetrachloride platinate (II)

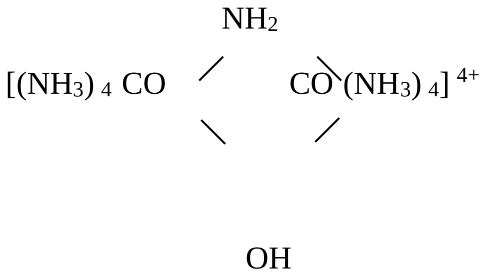
e) Naming of bridged polynuclear complexes

Complexes having more than one metal atom or ion is a poly nuclear complex. Bridging ligands are named first. The letter μ is written in front of the bridging ligands. The rest of the ligands are named after the bridging ligands, followed by the metal atom (or) ion with the oxidation number within brackets.

Ex:



$[(NH_3)_5\,Cr\diagup\overset{OH}{\;}\diagdown Cr\,(NH_3)_5]\,Cl_5$ - μ- hydroxo – tris [Pentraammine chromium (III)] chloride.

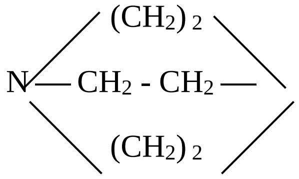


- μ - amido μ- hydroxo octaammine diwnalt (III) ion.

Chelating ligands and chelates

Poly dentate ligands which has 2 or more donor atoms attachet to the same metal ion simultaneously forming rings. Such type of ligands which produce rings when it gets attached to the metal ion (or) atom is called a chelating ligand (or) chelates (or) chelating groups. Some poly dentate ligand may get coordinated to the same metal ion at more than one site and some may not.

For ex: $NH_2 - CH_2 - CH_2 - NH_2$ is a chelating ligand. And



is not a chelating ligand.

The formation of rings is called chelating. The complexes formed are called chelating complexes. The word 'chelate' in Greek work meaning 'claw like'

Chelate effect

Chelated complexes are more stable than non chelated complexes, due to the smaller dissociation of the chelated complex. The increase in stability on a chelate is called chelate effect.

The stability of the chelated complex increases with the increase in the number of donor atoms. As the size of the chelated ring increases, stability also increases, 4-membered chelate are not stable 5-membered and 6-membered chelates are more stable.

Werner's theory.

Tassaert, a scientist prepared a compound $CoCl_3.6NH_3$ by mixing $CoCl_3$ with NH_3.$CoCl_3$ are stable compounds. When these two are mixed he was able to get another stable compound. Later on precipitation studies and conductivity measurements were done.

$CoCl_3.6NH_3$ precipitates 3AgCl when it is treated with $AgNO_3$, $CoCl_3$ $5NH_3$ precipitates 2 AgCl $CoCl_3$ 4 NH_3 precipitated. When they are treated with $AgNO_3$.

Another property studied was molar conductivities of their solutions. The molar conductivity of $CoCl_3.6NH_3$ is 430 ohm $^{-1}$, $CoCl_3.5NH_3$ is 250 ohm $^{-1}$, and CoCl3.4NH3 is 100 ohm 1 respectively, while $CoCl_3.3NH_3$ is Ohm^{-1}.

Greater the molar conductivity of the solution greater will be the total no.of ions.

The molar conductivity in the range 430 ohm $^{-1}$ shows that the ion is of the type (3+,1-) 350 ohm-1 is of the type)(2+,1-1) and 100 ohm^{-1} of the type (1+,1$^-$)

The results of there studies are given in the table.

Complexes	No.of Cl ions precipitated	Molar conductivity ohm^{-1}	Total no. of ions	Charge type	Ionic formulate
$CoCl_3.6NH_3$	3	430	4	(3+, 1-)	$[Co\ (NH_3)_6]^{3+}\ (Cl^-)_3$
$CoCl_3.5NH_3$	2	250	3	(2+, 1-)	$[Co\ (NH_3)_5\ Cl]^{2+}\ (Cl^-)_2$
$CoCl_3.4NH_3$	1	100	2	(1+, 1-)	$[Co\ (NH_3)_4Cl_2]^+\ Cl^-$
$CoCl_3.3NH_3$	0	0	0	-	$[Co(NH_3)_3Cl_3]$ (Non electrolyte).

These observations were explained by Werner. He proposed a theory known as Werner's theory.

Postulates of this theory are:

i) Elements possess 2 types of valencies primary valency and secondary valency.

a) Primary valency: It corresponds to the oxidation state of the metal ion; it is also known as principal, ionisable or ionic valency. This is satisfied by anions and the attachment of these anions with the metal ion is shown by dotted lines.

b) Secondary valency: This valency corresponds to coordination number of the metal ion. It is also known as auxiliary valency, non-ionisable and non-ionic valency, which is satisfied by negative ions or neutral molecules. These are attached to the metal ion by thick lines.

Each element satisfies both primary and secondary valencies. Negative ion satisfies both primary and secondary valencies.

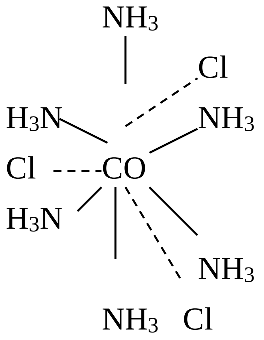
Based on these postulates and also on the precipitation and conductivity studies. The cobalt ammines are represented as below.

$CoCl_3.6NH_3$ → $[Co\ (NH_3)_6]^{3+}\ (Cl^-)_3$

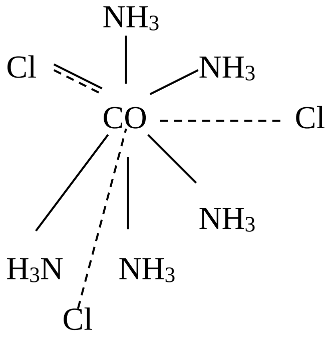
$CoCl_3.5NH_3$ → $[Co\ (NH_3)_5\ Cl]^{2+}\ (Cl^-)_2$

$CoCl_3.4NH_3$ → $[Co\ (NH_3)_4\ Cl_2]^+\ Cl^-$

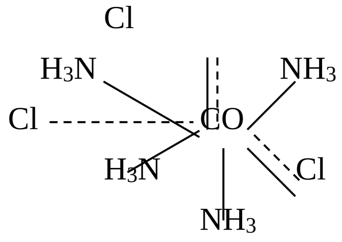
$CoCl_3.3NH_3$ → $[Co\ (NH_3)_3\ Cl_3]$ (Non electrolyte).



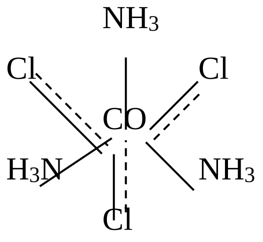
$CO\ Cl_3.\ 6\ NH_3$



$CO\ Cl_3.\ 5\ NH_3$



$CO\ Cl_3.\ 4\ NH_3$



$CO\ Cl_3.\ 3\ NH_3$

In the first example $CoCl_3$ $6NH_3$, $3Cl^-$ ions are precipitated, i.e. they are attached by primary valency and hence shown by dotted lines. Similarly, in the other examples also, the ions which are loosely bound are attached by dotted lines. The solution of this compound gives altogether four ions ie $[Co\ (NH_3)_6]^{3+}$ and 3Cl in the same way, in $CoCl_3$, NH_3, 2 chloride ions are loosely held and are precipitated as AgCl by the addition of $AgNO_3$, Hence, the attachment is shown by dotted lines. Among 3 Cl^- ions, 2 Cl^- ions are precipitated, the other Cl^- ion which is not precipitated satisfies both primary and secondary valency. It‘s solution gives 3 ions namely $[Co\ (NH_3)_6]^{2+}$ and $2Cl^-$.

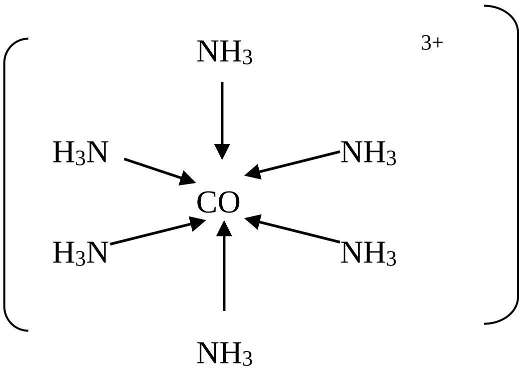
$CoCl_3$ $4NH_3$ shows that it has only one Cl^- to get precipitated, the other two cl^- ions are attached by both primary and secondary valencies. Finally. The last compound $CoCl_3$ 6 NH_3 has no Cl^- ions to get precipitated. All the three cl^- ions are attached by both primary and secondary valencies.

Sidgwick’s Theory EAN concept

Sidgwick followed Lewis concept of two electron bond. He introduced a new concept of bond which is called coordinate bond or dative bond. According to him, ligands which are attached with the central metal ion have at least one unshared electron pair. The atoms which donate electron pairs are called donors and the metal ion accepts these electronpairs and hence is called acceptor. The bond formed between the ligands and the central metal ion is a dative bond or semi polar bond. The bond formed between the ligand and the metal ion is usually written as M ← L, where M is the metal ion and L is the ligand.

Based on sidgwick’s concept, the structure of $[CoCl_3.6\ NH_3]^{3+}$in written as

$[CO\ (NH_3)_6]^{3+}$ in written as



Here, the ligand NH_3 donates an electron pair to the metal ion, Co^{3+}. Since there are 6 NH_3 molecules, six electron pairs, i.e. 12 electrons are donated to Co^{3+} ion. The donation of electron pair from NH_3 to Co^{3+} ion is shown by an arrow pointing towards the Co^{3+} ion.

EAN concept – Effective Atomic Number concept.

This is also known as Noble Gas Rule. Ligands are donating electron pairs to the metal ion. The total no. of electrons on the metal ion including the electrons gained from ligand is equal to the atomic number of the nearest noble gas.

Example:

EAN of $[CO\ (NH_3)_6]^{3+}$ is calculated as follows,

No of electons in Co atom = 27

No.of electrons in Co^{3+} ion = 27-3

= 24

Electron donated by 6 NH_3 molecules = 6X 2 =12

= 24 +12 = 36

EAN of CO^{3+} ion in $[Co (NH_3)_6]^{3+}$ is 36 which is equal to the atomic number of Kr. Hence, it obeys

EAN rule.

To calculate EAN of $Ni (Co)_4$

No. of electrons in Ni atom = 28

No.of electrons donated by = 4X2 =8

EAN of Ni in $[Ni (Co)_4]$ = 28+8 =36

36 is the atomic number of Kr It obeys EAN Rule

To calculate $Fe (NO)_2 (CO)_2$

No. of electrons in Ni atom = 26

No.of electrons donated by = 2X2 =4

NO. of electrons donated by = 2X3 =6 (NO molecules donates 3 electrons) EAN of Ni in $[Fe (Co)_2 (No)_2]$ = 26+4+4 =36(Kr) So, $Fe (Co)_2 (No)_2$ obeys EAN Rule.

Exceptions to EAN Rule

There are some complexes which do not obey EAN Rule. Metal ions which have more than one coordination number do not obey EAN Rule depending upon the nature of the ligand. For example, EAN of $[Fe Cl_4]^-$ is 31, and that of $[Fe(CN)_6]^{4-}$is 35. Both do not obey EAN Rule.

Isomerism in complexes

Compounds which have some chemical composition but have different structural arrangement of their atom are called isomers and the phenomena are called isomerism. Isomerismis of 2 types, structural isomerism and stereoisomerism,

Structural isomerism

Isomerism due to the difference in structures of complexes is called structural isomerism. It is of 5 types They are i) Ionization isomerism ii) Hydrate isomerism iii) Ligand isomerism iv) Linkage isomerism v) coordination position isomerism.

Ionization isomerism

Complexes with have same empirical formula but gives different ions in solution are said to exhibit ionization isomerism

Ex: $[CO\,(NH_3)_5\,Br]\,SO_4$ and $[CO\,(NH_3)_5\,SO_4]\,Br$.

$[CO\,(NH_3)_5\,Br]\,SO_4$ gives a white precipitate with $Bacl_2$ and does not give yellow precipitate while $[Co\,(NH_3)_5\,SO_4]Br$ gives a yellow precipitate with $AgNO_3$, but does not give a white precipitate with $BaCl_2$, even though the empirical formula is the same.

$[Co\,(NH_3)_5\,Br]\,SO_4$ ionizes to give $[Co(NH_3)_5\,Br]^{2+}$ and So_4^{2-}. SO_4^{2-} ions are free in solution and hence react with $BaCl_2$ to give a white precipitate. Br^- is involved in coordination with Co^{3+} ion, and does not react with $AgNO_3$.

$[Co\,(NH_3)_5\,SO_4]Br$ ionizes to give $[Co\,(NH_3)_5\,SO_4]^+$ and Br^-. Br^- ions are free in solution and reacts with $AgNo_3$ to give a yellow precipitate So_4^{2-} ion is involved in coordination and does not react with $Bacl_2$.

Both these complexes give different ions in solution and are said to exhibit ionization isomerism.

Another example is

$[Co\,(NH_3)_4\,Cl_2)]\,NO_2$ and $[Co\,(NH_3)_4\,Cl\,NO_2]\,Cl$.

ii) Hydrate isomerism

Complexes having the same empirical formula but differ in the no. of water molecules which can be removed are said to exhibit hydrate isomerism.

Ex: $[Cr\,(H_2O)_6]\,Cl_3$ is violet and does not lose any water molecule.

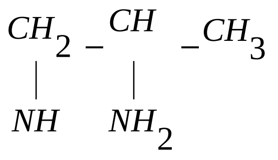
$[Cr\,(H_2O)_5]\,Cl_2.\,H_2O$ is green loses are water molecule over H_2SO_4.

$[Cr\,(H_2O)_5]\,Cl_2.\,2H_2O$ is green and loses 2 water molecule over H_2SO_4.

iii) Ligand isomerism

Some ligands exhibit isomerism. When such ligands are involved in complex formation, those complexes are isomers of each other.

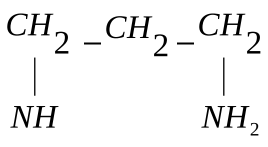
Ex:



$$\underset{NH}{\underset{|}{CH_2}} - \underset{NH_2}{\underset{|}{CH}} - CH_3$$

1,2 *diamino propane*(*Pn*)

and



$$\underset{NH}{\underset{|}{CH_2}} - CH_2 - \underset{NH_2}{\underset{|}{CH_2}}$$

1,3 *dianimo propane*(*tn*)

When these ligands are involved in complexes, the complexes are isomers of each other.

Ex: $[CO\,(Pn)_2\,Cl_2]^+$ and $[CO\,(tn)_2\,Cl_2]^+$ ions.

iv) Linkage isomerism

When ambidentate ligands are involved in complexes, such complexes are said to exhibit linkage isomerism. Most common ligands are NO_2^-, SCN^- and $S_2O_3^{2-}$ ions.

In complexes containing NO_2^- ion as the ligand, coordination may be through o atom or through N-atom.

Ex: $[Co(NH_3)_5ONO]^{2+}$ and $[Co(NH_3)_5NO_2]^{+}$.

$[Pd(diph)(SCN)_2]$ and $[Pd(diph)(NCS)_2]$.

v) Coordination isomerism

When cation and anion of a complex are complex, there way be exchange of ligands between the two co-ordinations spheres.

Ex: $[Cr(NH_3)_6]^{3+}[Cr(SCN)_6]^{3-}$

And $[Cr(NH_3)_4(SCN)_2]^{+}\ [Cr(NH_3)_2(SCN)_4]^{-}$

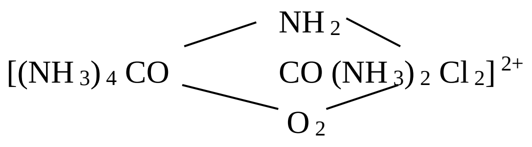
$[Cu(NH_3)_4]^{2+}[PtCl_4]^{+}$

$[Pt(NH_3)_4]^{2+}\ [CuCl_4]^{2-}$

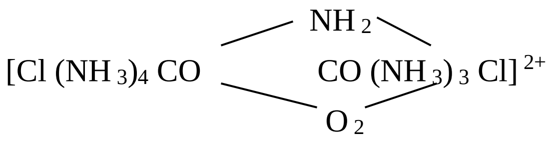
vi) Coordination position isomerism

In poly nuclear complexes, there is interchange of ligands between the two metal nuclei. This type of interchange gives rise to coordination position isomerism.

Ex:



$$[(NH_3)_4CO \begin{matrix} NH_2 \\ \\ O_2 \end{matrix} CO(NH_3)_2Cl_2]^{2+}$$



$$[Cl(NH_3)_4CO \begin{matrix} NH_2 \\ \\ O_2 \end{matrix} CO(NH_3)_3Cl]^{2+}$$

Stereoisomerism (or) space isomerism

Complexes having the same empirical formula, but differ with the arrangement of ligands in space is said to exhibit stereoisomerism. It is of 2 types i) Geometrical or cis-trans isomerism ii) optical isomerism or mirror – image isomerism.

Geometrical isomerism (or) cis Trans isomerism

Complexes having the same empirical formula but differ in physical and chemical properties due to the difference in the arrangement of ligands. In a complex when the identical ligands are adjacent to each other they are said to be in is position and the isomer is a cis isomer. When the identical ligands are diagonal to each other, they are said to be intrans position.

Tetrahedral complex cannot exhibit geometrical isomerism because all the four ligands are of the same distance with respect to one another.

Geometrical isomerism in square planer complexes

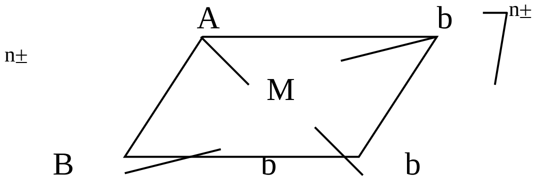
Square planar complexes of the type $[Ma_4]^{n\pm}$ $[Ma_3]^{n\pm}$ do not show geometrical isomerism.

Square planar complexes of the following types show geometrical isomerism.

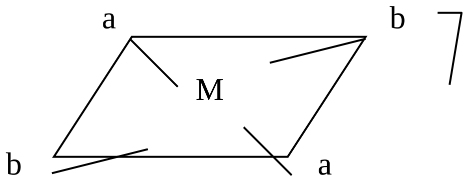
i) $[Ma_2b_2]^{n\pm}$, $[Ma_2bc]^{n\pm}$, $[M_{abcd}]^{n\pm}$, $[M(AB)_2]^{n\pm}$, $[M(AA)_2]^{n\pm}$, $[M_2a_2b_4]^{n\pm}]$

$[Ma_2b_2]^{n\pm}$ type complexes

Here M = metal ion, a and b are unidentate ligands

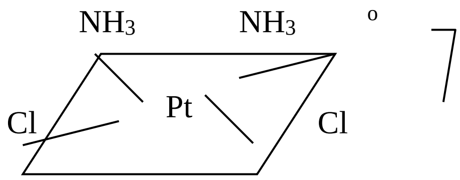


cis isomer

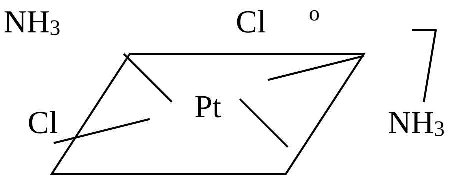


trans isomer

Ex: $[Pt(NH_3)_2Cl_2]^o$



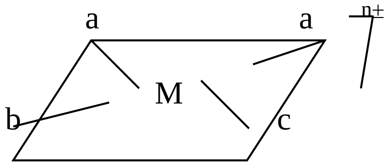
Cis isomer



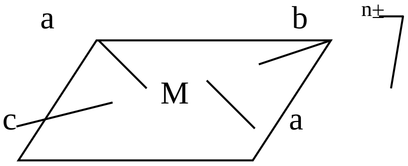
trans isomer

$[Ma_2bc]^{n\pm}$ type complexes

M – Metal ion, a = neutral ligand (NH_3, H_2O) b and c = anionic ligands (Cl^-, Br^-, NO_2^- etc)

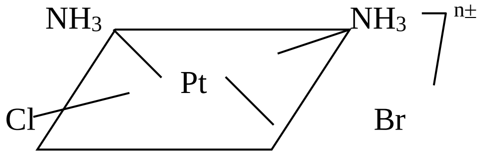


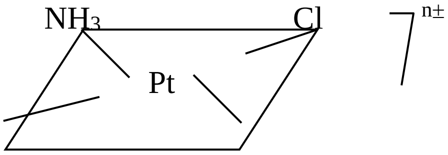
Cis isomer



trans isomer

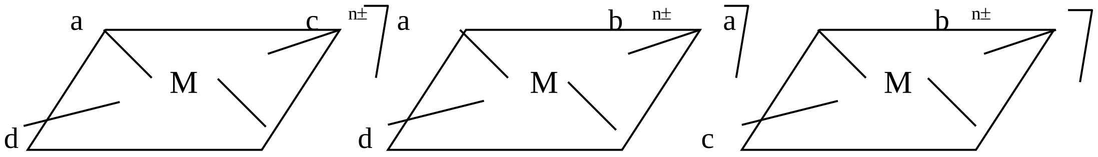
Ex: $[Pt(NH_3)_2ClBr]^{2+}$



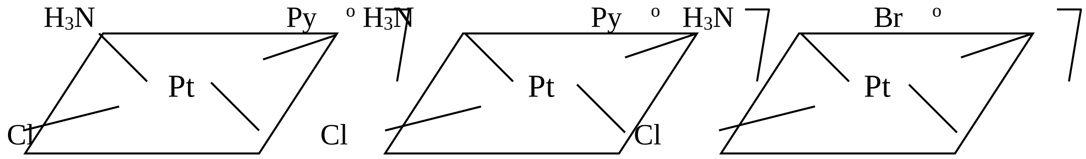


$[Mabcd]^{n\pm}$ type complexes

M= Metal ion a,b,c,d = 4 different ligands. This type of complex exists in 3 geometrical isomers. Among the four ligands, ang 2 ligands in fixed in trans position

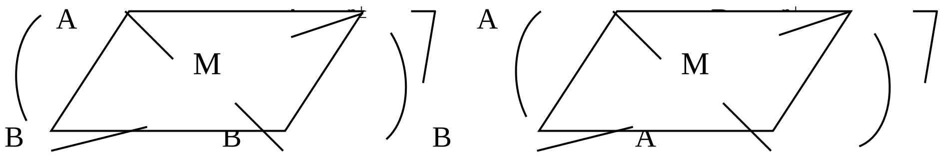


Ex: [Pt (NO_2) Py NH_3 NH_2OH] + exists in 3 isomeric form another example in [Pt (NH_3) (Py) (Cl) (Br)]^o



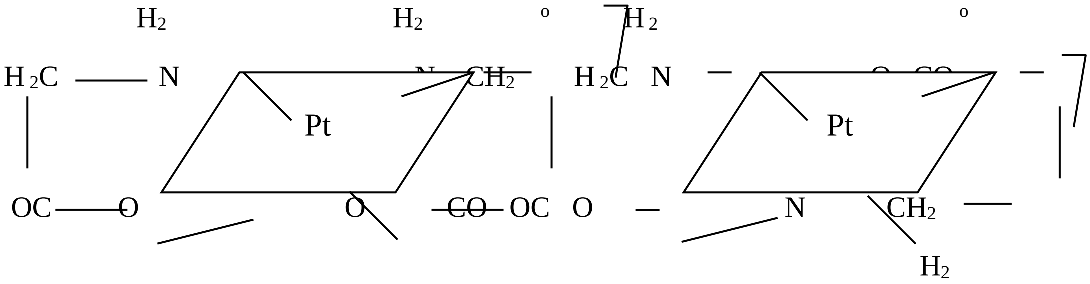
[M (AB)$_2$]$^{n\pm}$ type complexes

M - Metal ion, AB = unsymmetrical tridentate ligand A and B are the two coordinating atoms of the ligand



cis form trans isomer

Ex: [Pt (gly)$_2$]^o ; gly = NH_2 CH_2 COO^-

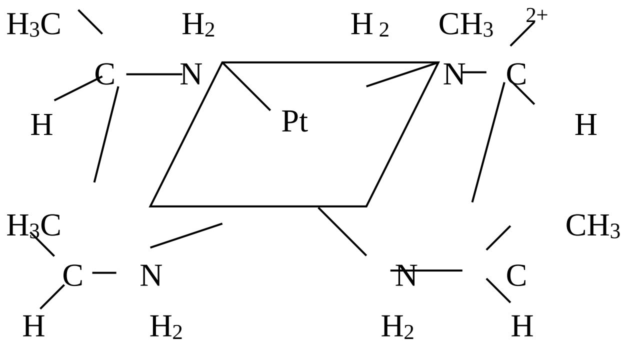


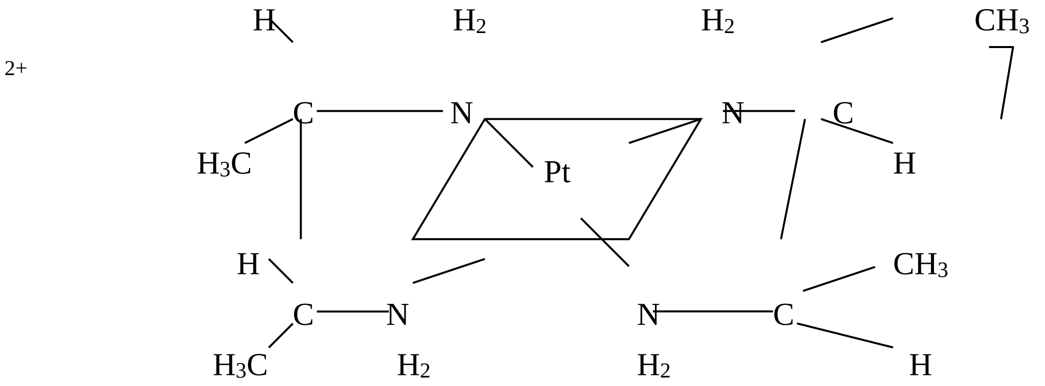
Cis isomer trans isomer

M (AA)$_2$ type complexes

M-Metal ion, AA→ symmetrical tridentate ligand

Ex: $[Pt(NH_2CH(CH_3).CH(CH_3)(NH_3)_2)]^{2+}$

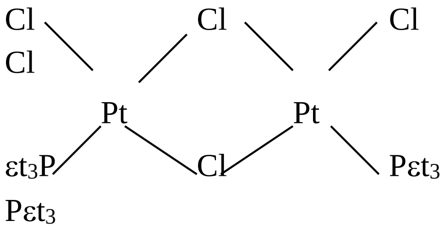




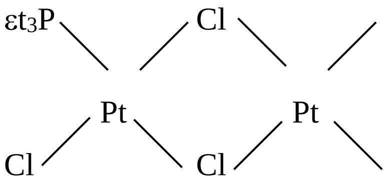
$[M_2a_2b_4]^{n\pm}$ type complex

In such type of complexes, cis isomer, trans isomer and unsymmetrical isomers are possible.

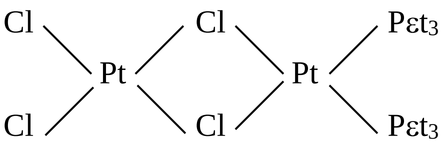
Ex: $[Pt(PEt_3)_2Cl_2]_2$



Cis form



trans isomer

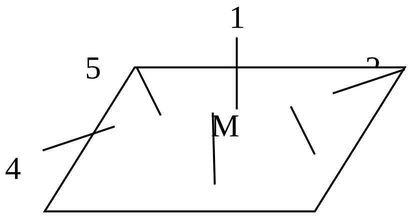


Un symmetrical isomer

Geometrical isomerism in octahedral complexes

Octahedral complexes only mono dentate ligands

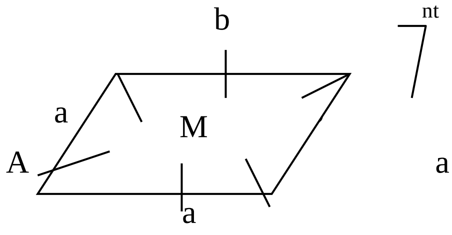
The positions in octahedral complex is



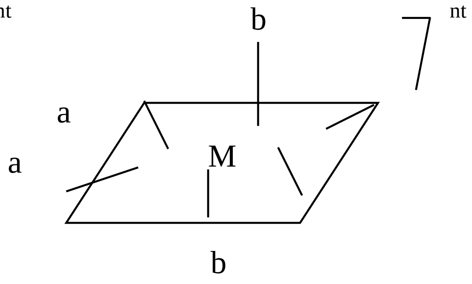
When identical ligands are in adjustment position i.e. (1,2) (1,3) (1,4), (!,5), (2,3), (2,5), (2,6), (3,4) , (3,6), (4,5), (4,6), (5,6) they are called cis isomer when identical ligands are diagonal to each other ie when they are in (1,6), (3,5), (2,4) positions, they are called trans isomers.

Complexes of the type $[Ma_4b_2]^{n\pm}$

M=Metal ion; a and b = memo dentate ligands.

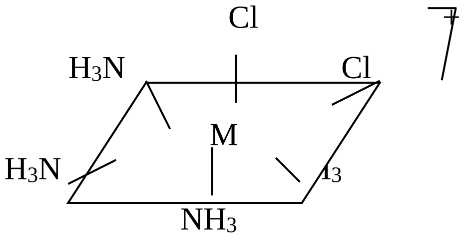


Cis isomer

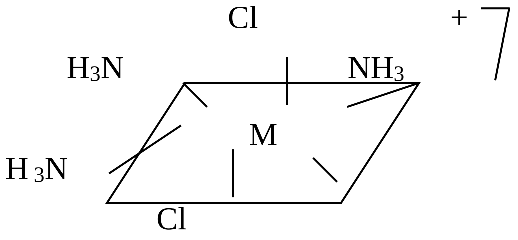


Trans isomer

Ex: $[CO (NH_3)_4 Cl_2]^+$



Cis isomer

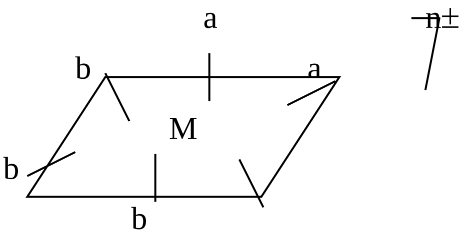


Trans isomer

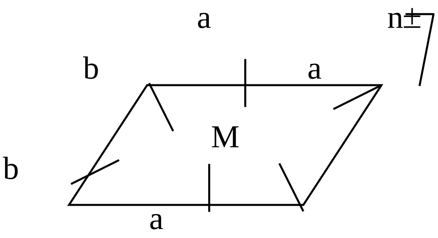
<u>Complexes of the type $[Ma_3b_3]^{n+}$</u>

In air isomer, three ‘a’ ligands occupy 1, 2, 3 positions and in trans isomer,

these are 1, 2 and 6 position.

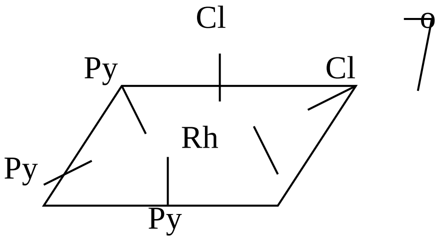


Cis isomer

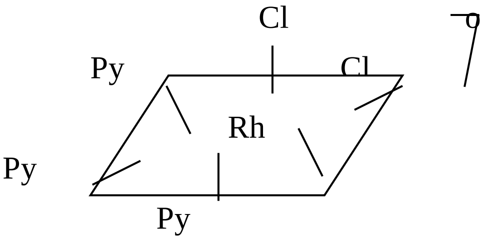


Trans isomer

Ex: **[Rh (Py)$_3$ Cl$_3$]** ^{o}



Cis isomer



Trans isomer

Complex of the type $[M_{abcdef}]^{n\pm}$

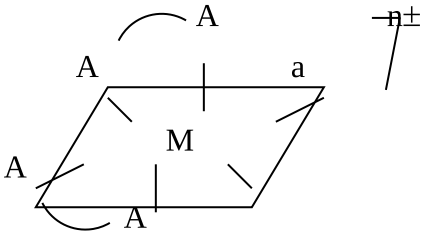
Namely 15 isomers are possible for such a type of complex.

Ex: [Pt (py) (PH$_3$) (NO$_2$) (Cl) (Br) (I)]

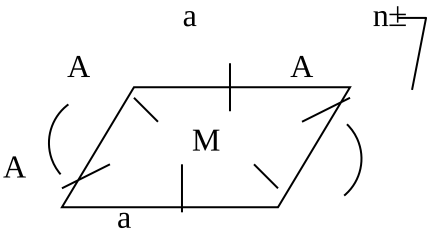
Octahedral complexes containing monodentate and symmetrical tridentate chelating ligands

Complex of the type is $[(AAl_2\ a_2)]^{n\pm}$

Here M= Metal ion, (AA) is a symmetrical bidentate ligand, a = mono dentate ligand.

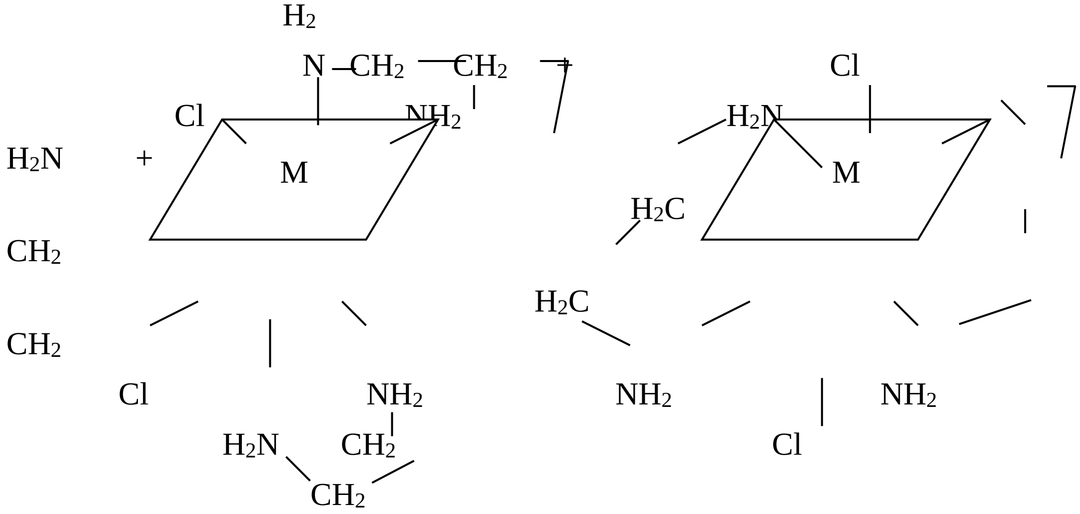


Cis isomer



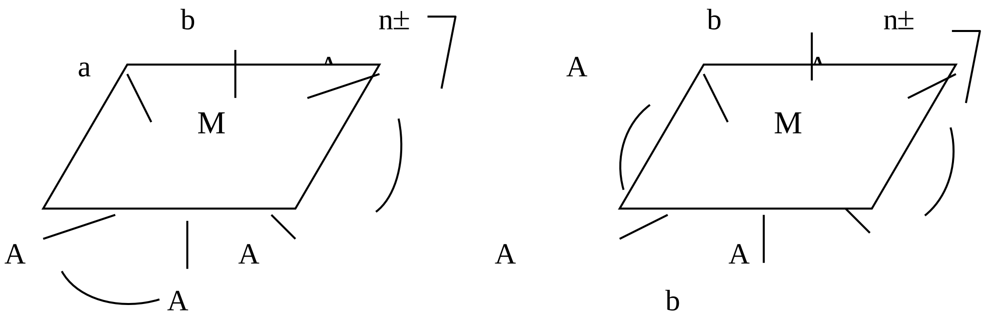
Trans isomer

Ex: **$[Co(en)_2Cl_2]^+$, $[CO(en)_2(NO_3)_2]^+$, $[Ir(C_2O_4)_2Cl_2]^{3-}$**



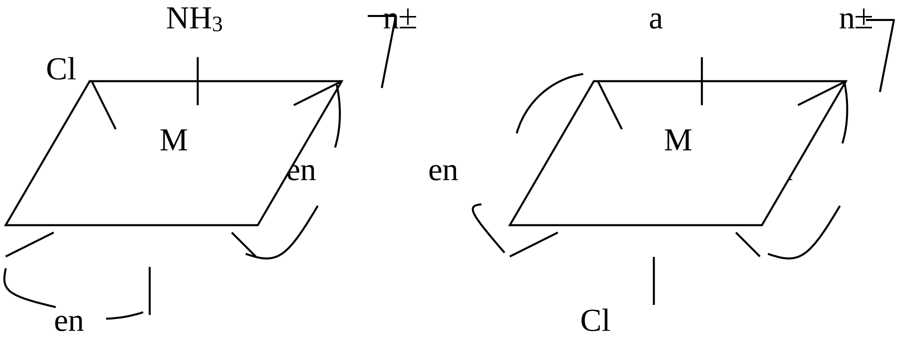
Cis form Trans form

Complexes of the type [M (AA) $_2$ ab] $^{n\pm}$



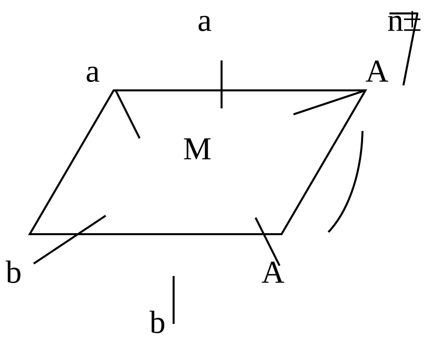
Cis isomer Trans isomer

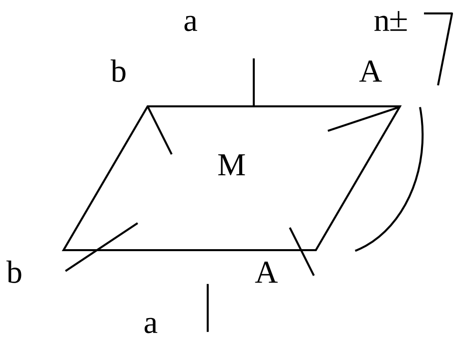
Ex: **$[Co(en)_2NH_3Cl]^{2+}$**



Cis isomer **Trans isomer.**

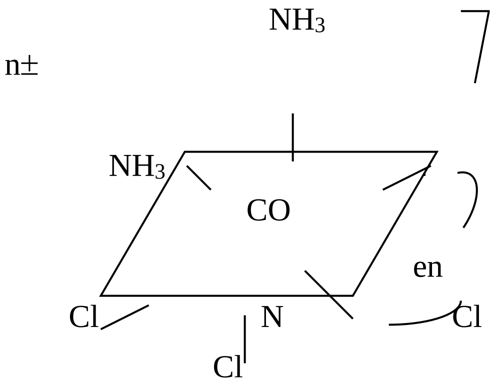
Complexes of the type $[M(AA)_2a_2b_2]^{n\pm}$

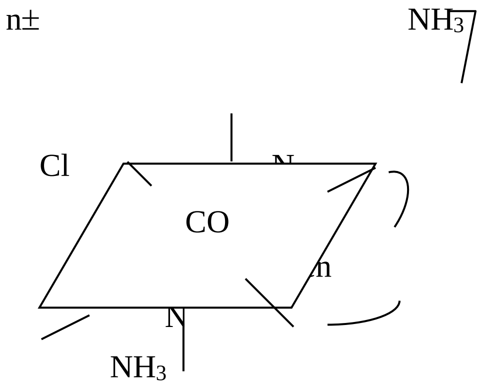




Cis isomer **Trans isomer**

Ex: $[CO(en)(NH_3)_2Cl_2]^+$

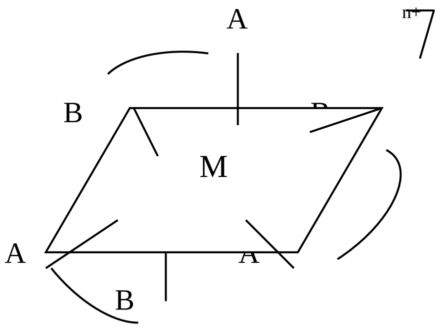


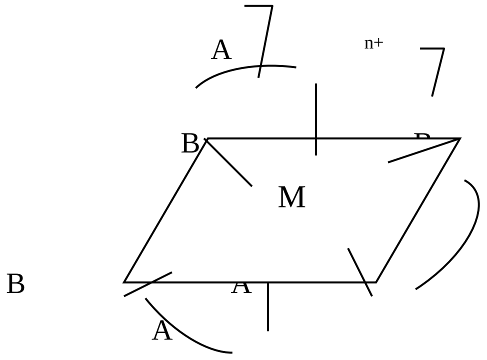


Cis isomer **Trans isomer**

Complexes of type $[M(AB)_3]^{n\pm}$

AB= unsymmetrical tridentate ligand



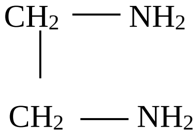


Cis isomer **Trans isomer**

Complexes containing optically activity and

Ex: **[CO (en) (Pn) $(NO_2)_2]^+$**

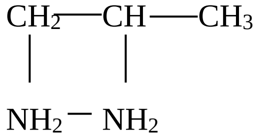
en is



$\begin{array}{l} CH_2 - NH_2 \\ | \\ CH_2 - NH_2 \end{array}$

is optically inactive.

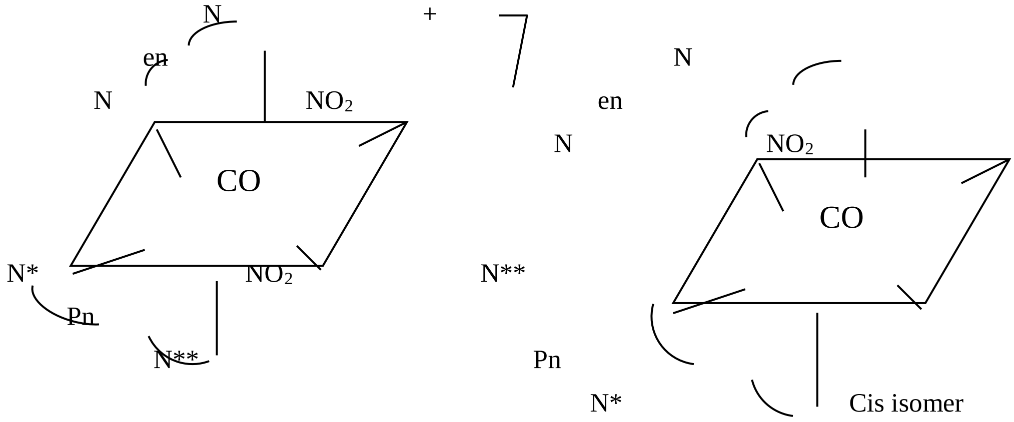
pn —



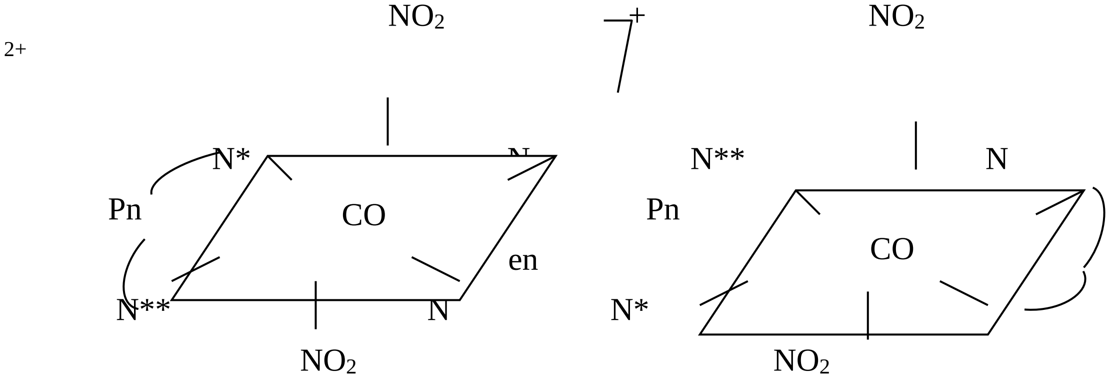
$\begin{array}{lll} CH_2 - & CH - & CH_3 \\ | & | & \\ NH_2 - & NH_2 & \end{array}$

is optically active.

The two nitrogen atom of pn which is optically active is shown by 2 asterisks, by attaching $\overset{*}{NH_2}$ and $\overset{**}{NH_2}$ at 4 and 6 positions, 2 is isomers are obtained.



Cis isomer



Trans isomer

Optical isomerism (or) mirror image isomerism

When solutions of certain complex compounds are placed in the path of plane-polarized light they rotate the plane through a certain angle. This property is called optical activity and the complex having this property is said to be optically active. The compound which rotates the place of polarized light towards the right is said to be dextro rotatory (or) d – form. The compound, which rotates the plane of polarized light towards the left, is said to be laevorotatory (or) l-form. For a complex to be optically active it should have no plane of symmetry and it should not be super imposable on its mirror image.

Optical isomerism in 4-coordination compounds

In complexes of the type [Ma_4], [Ma_3b] and [Mab_3] no optical isomerism is not possible for both square planar and tetrahedral complexes.

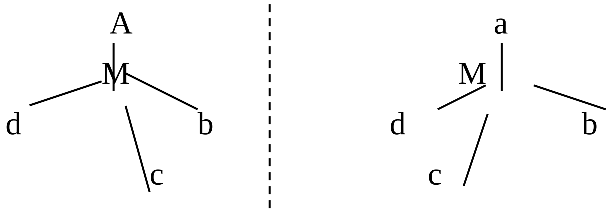
Optical isomerism in square planar complexes.

Optical isomerism rarely occurs in square planar complexes. Since square planar complex has plane or axis of symmetry one square planar complex has been resolved into d and l form. Iso-buytlenediamine- meso stilbenediamine platinum (11). Cation

$\left[Pt(NH_2\,CH(C_6\,H_5)CH(C_6\,H_5)\,NH_2)\;(NH_2\,CH_2\;C(CH_3)_2\,NH_2)\right]^{2+}$ Has been synthesized and the complex has been resolved into d and l form.

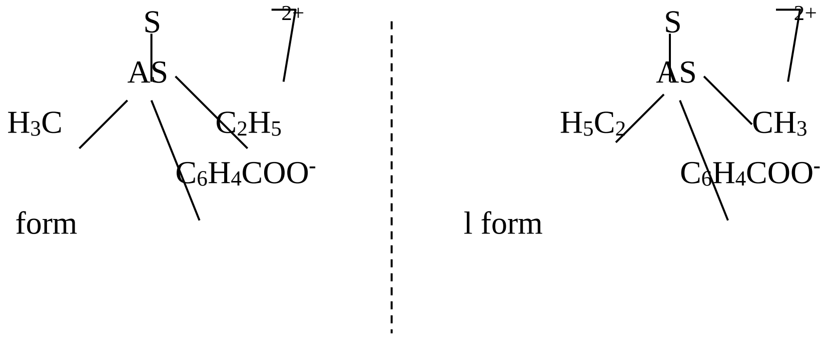
Optical isomerism of tetrahedral complexes

A tetrahedral complex of type [Mabcd] exists in two optical isomers.



d form e form

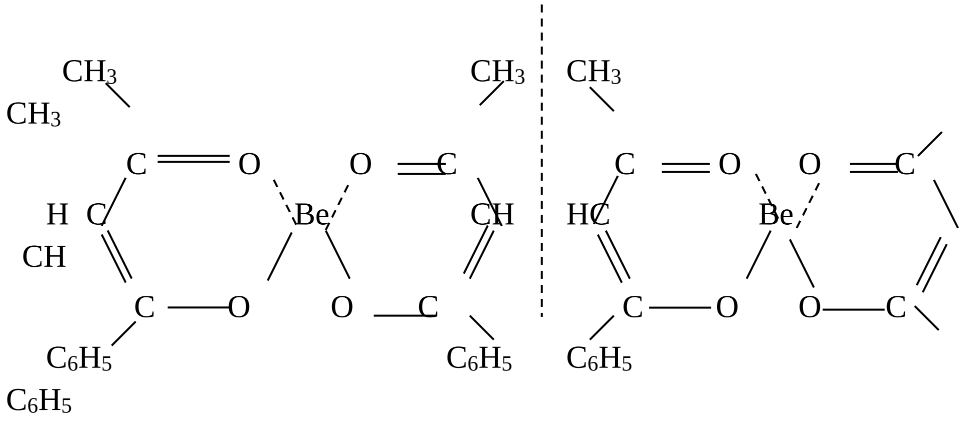
Ex: [As (CH_3) (C_2 H_5) (S) (C_6 H_4 COO^-)]$^{2+}$



d form l form

Tetrahedral complex of Be^{2+}, Zn^{2+} with ligands which is optically active have been synthesized and resolved.

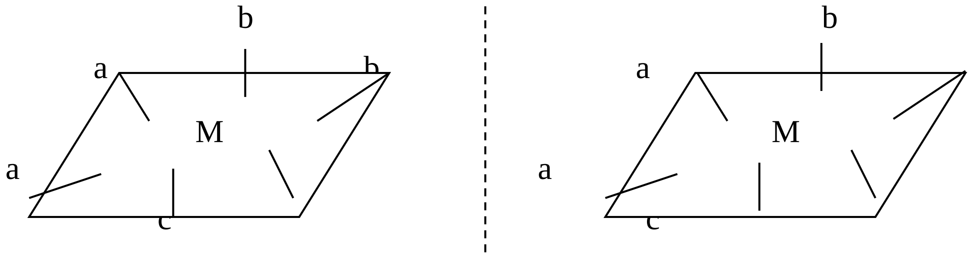
Ex: **$[C_2H_5COCHCO(CH_3)_2Be]^{o}$**



d form

Optical isomerism of octahedral complexes

1) Complex of type $(Ma_2b_2c_2)^{n+}$



Complexes of type $[M_{abcdef}]^{n\pm}$

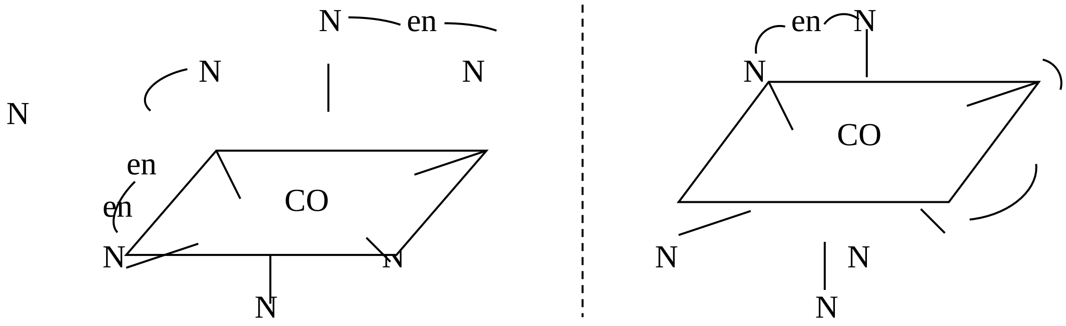
Complexes of this type have been prepared for Pt (IV). There are 15 geometrical isomers for this Type and each geometrical isomer will exist is d and l form 30 optical isomers are possible for this type of complex

Ex: **$[Pt(Py)(NH_3)(NO_2)(Cl)(Br)(I)]$.**

Complexes of type $[M(AA)_3]^{n\pm}$

AA is a symmetrical tridentates chelating ligand.

Ex: **$[CO(en)_3]^{3+}$, $[Pt(Pn)_3]^{3+}$**

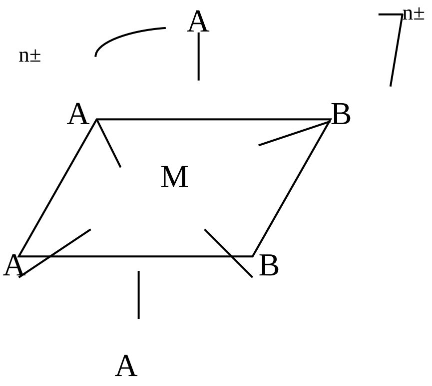


d form   l form

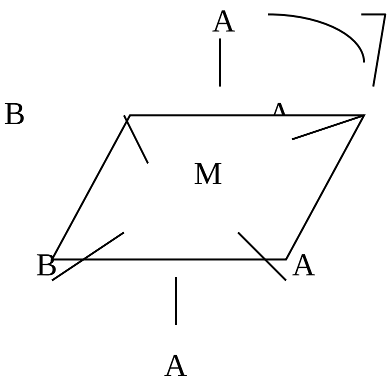
Complexes of type [M $(AA)_2$ BB] $^{n\pm}$

AA and BB are two different symmetrical bideutate chelating ligands.

Ex: **[CO $(en)_2$ CO_3]$^+$, [CO $(en)_2$ C_2 O_4]$^+$**



d form



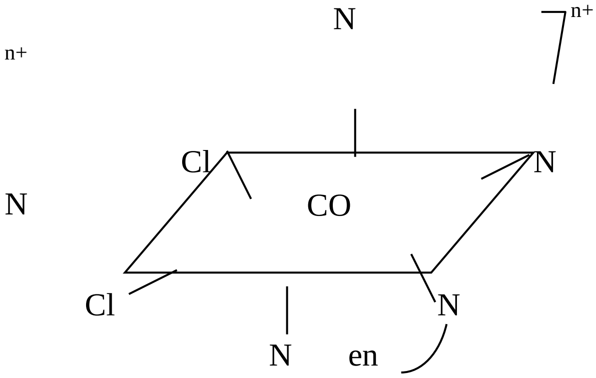
l form

Complexes of Type [M $(AA_2$ $a_2]$ $^{n\pm}$

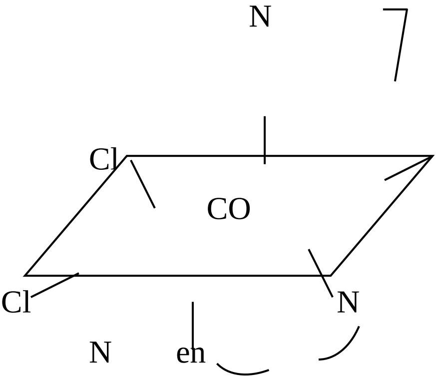
AA is a chelating ligand and a is a monodoutate ligand.

Ex: **[CO $(en)_2$ Cl_2]$^+$, [Rn $(C_2 O_4)_2$ Cl_2]$^{2-}$**

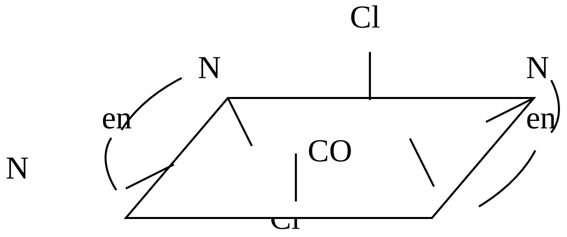
This type of complex has is and trans isomers in isomer is optically active and exists in a d and l form. Trans isomer has plane of symmetry and hence is optically in active.



d cis form



l cis form

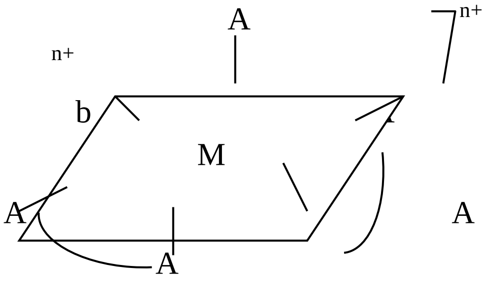


meso trans form

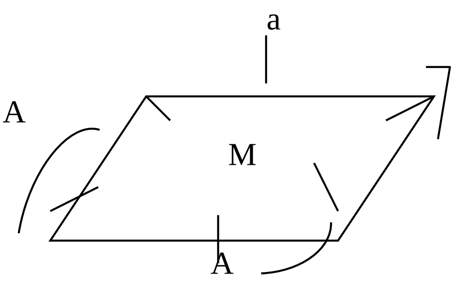
Complexes of type [M $(AA)_2$ ab] $^{n\pm}$

These complexes exist in 3 form 2 optically active forms and 1 optically inactive form.

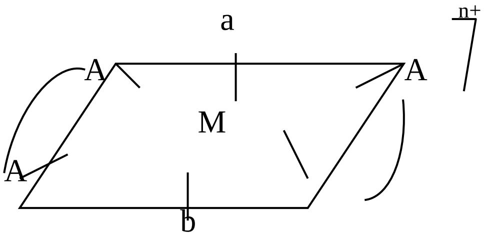
Ex: **$[CO (en)_2 NH_3 Cl]^{2+}$, $[Ru (Py) (C_2 O_4)_2 (NO)]^-$**



d cis form



l cis form

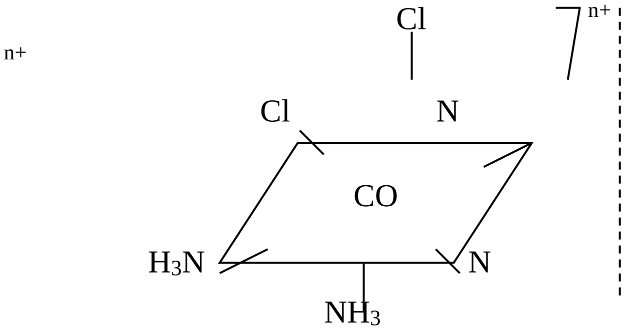


meso trans form

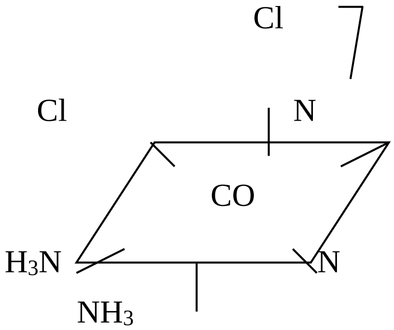
Complexes of Type $[M (AA)a_2b_2]^{n\pm}$

These also exist is 3 form. 2 optically active forms and 1 optically inactive form.

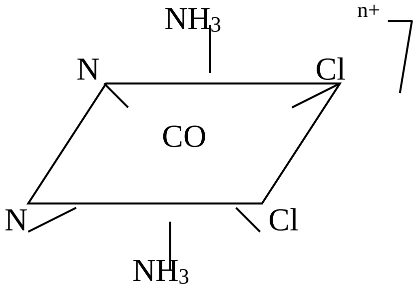
Ex: **$[CO (en) (NH_3)_2 Cl_2]^+$**



d cis isomer



l cis form



Meso trans form

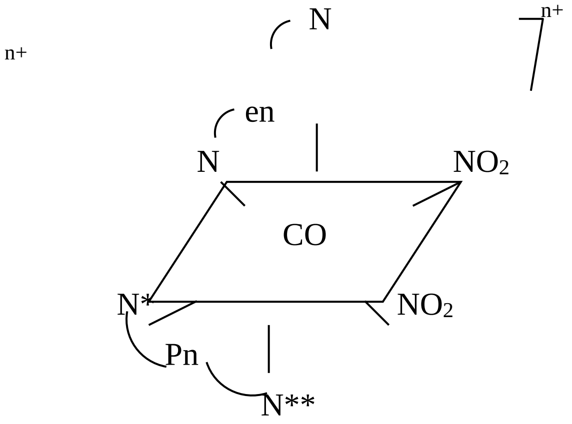
Complexes containing optically active ligands

Ex: **$[CO (en) (Pn) (NO_2)_2]^+$**

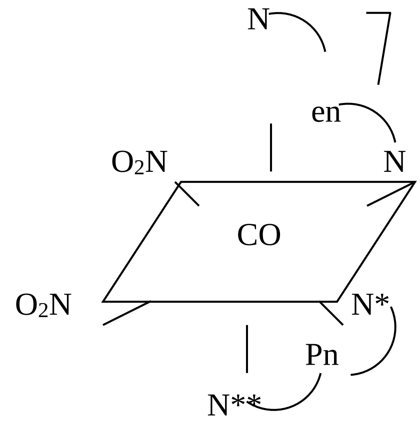
En→ ethylene diamine which is optically inactive

Pn→ 1,2 diamino propare which is optically active

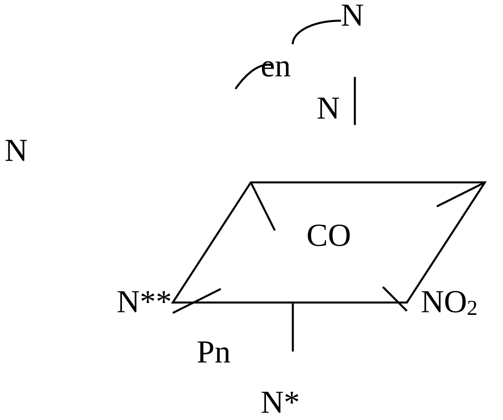
This complex exits in 2 cis and 2 Trans isomers. For 2 in isomers, 4 optically active isomers are possible.



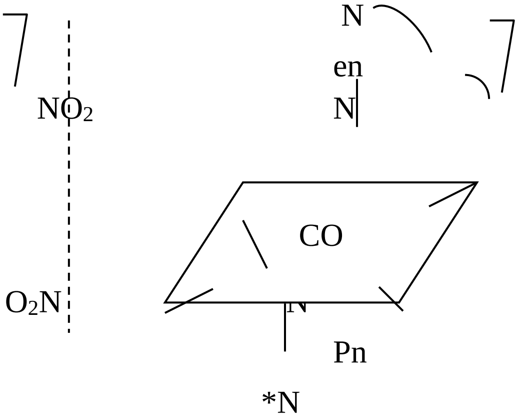
Cis d form



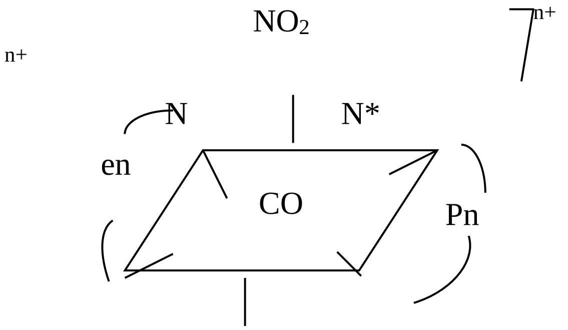
cis l form

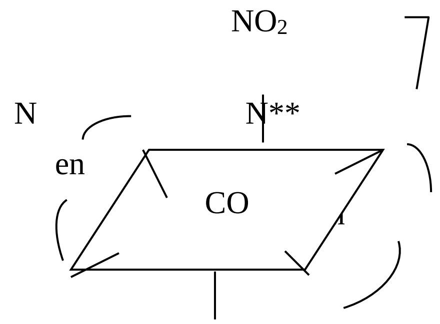


Cis d form



cis l form



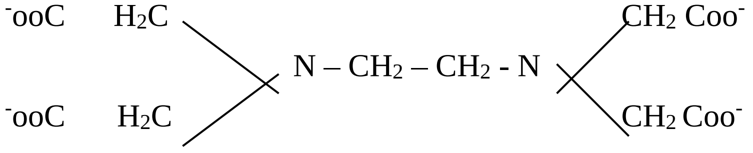


N N** N N*

NO_2 NO_2

Meso trans form meso trans form

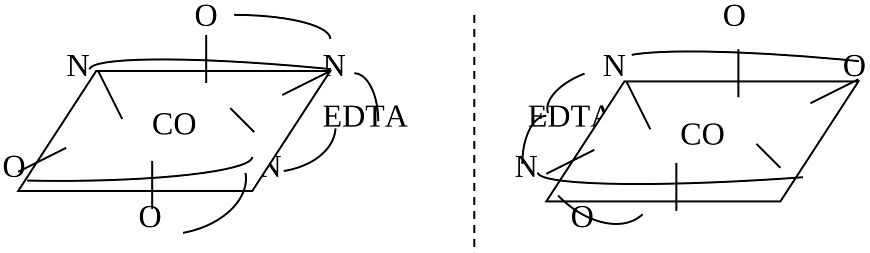
Complexes containing poly dentate ligands



EDTA

EDTA has four donor oxygen atoms and 2 nitrogen atom

Ex: **$[CO (EDTA)]^-$**



d form l form

2.4 factors affecting the stability of complexes

When we say that a complex is stable it means that it exists under suitable conditions, but a complex is stable to one reagent and unstable to another reagent. There are two kinds of stabilities to be studied.

i) Thermodynamic stability and kinetic stability

Thermodynamic stability is a measure of the extent to which the complex will be formed or will be converted into another complex. This stability deals with metal-ligand bond energies, stability constants etc.

Kinetic stability is a measure of the rate to which the transformation of one complex to another occurs. This stability deals with the rates and mechanisms of chemical reactions such as substitution, isomerization, racemisation etc.

There are many factors which affect the stability of complex. These depend upon nature of the metal ion and also on the nature of the ligand.

Nature of the metal ion

a) Charge and size

The metal ion with larger charge and smaller size form more stable complexes. A smaller size and larger charge is attached more closely towards the metal ion and hence a more stable complex is formed.

For example, the stability constant of hydroxide complexes of Be^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+} are 10^7, 120, 30 and 4 respectively. Here there ions have the same charge +2, but size of these ions increases in the order $Ba^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}$. At the size increases, the stability decreases, comparing the stability of the complexes having the same central meta ion, i.e of almost the same size, but with different charge, the stability increases with increase in charge, when the charger is greater, electrostatic force of attraction between the metal ion and the ligands is more, hence the ligands approved the metal ion more closely, leading to a more stable complex.

Ex: $[Fe(CN)_6]^{3-}$, charge in +3, stability constant = $10^{31.0}$

$[Fe(CN)_6]^{4-}$, charge in +2, stability constant = $10^{8.3}$

Based on size of the metal ion. The stabilities of the complexes on the same group is in the following order.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Ra^{2+}$

$Al^{3+} > Sc^{3+} > Y^{3+} > La^{3+}$

b) Irving- William order of stability – crystal field effects

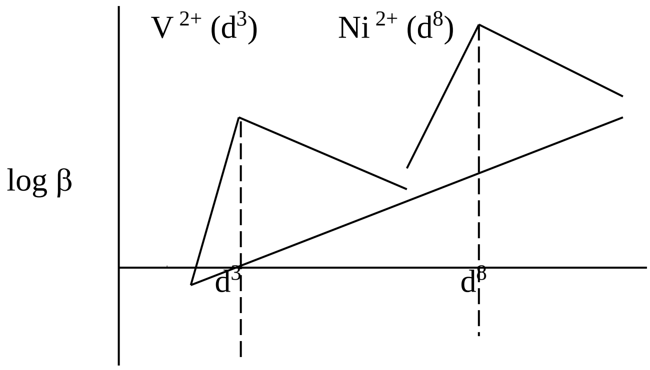
Comparing the stabilities of high spin octahedral complexes of ions between Mn^{2+} and Zn^{2+}. The stability is in the following order.

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

This order is called natural order of stability. The size of these ions is in the following order.

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

Cu^{2+} forms tetragon ally distorted octahedral complexes.



From the above graph, we can observe that High spin octahedral complexes of V^{2+} (d^3 ion) and Ni^{2+} (d^3 ion) are the most stable. Since these ions have highest Crystal. Field stabilization energy values, The CFSE values for V^{2+} and Ni^{2+} are 1.2 Δ_0. In the above graph, the experimental values are shown by dots and the corrected values by crosses. The corrected values give a straight line for the ions Ca^{2+} (d^o), Mn^{2+} (d^5), Zn^{2+} (d^{10}) which do not have CFSE, the experimental values is the same as corrected values.

c) Classification of metals

Based on the electron acceptor properties of the metal, they are classified into a,b, and borderline metals, class a metals has H, alkali and alkali earth metals, the metals from Sc to Cr, from Al to Cl, from Zn to Br, In , Sn, Sb, I, the lanthanides and actinides. These metals from more stable complexes with ligands where the coordinating atoms are from second period elements than from third or later period.

Class b metals include Rh, Pd, Ag, Ir, Pt, Au, and Hg. These metals from more stable complexes with ligands, where the coordinating atoms are from ligher period elements and from less stable complexes with elements from second period. This class of metals has d –electrons beyond inert an gas core. These d electrons forms Π bond with the ligand atoms. There is covalent contribution of the ligand to the metal ion and transfer of Π electrons from the ligand to the metal ion. Due to this, class b metals form more stable complexes.

Borderline metals include the elements from Mn→Cu, Tl→ Po, Mo, Te, Ru, W, Re, Os, Ed.

iv) Electronegativity of the central metal ion.

The bonding between the ligand and the metal ion is due to the donation of electron pairs from ligand to the metal ion and the metal ion should be in a position to accept electrons. Hence the metal ion with greater electro negativity will give the most stable complexes.

Nature of the ligand

The properties of the ligand also play an important role in the stability of the complexes.

a) Size and charge of ligand

When the ligand is of smaller size and greater charge, it forms more stable complexes. Among the halides, the size of F^- ion is smaller; hence it forms more stable complexes. This is shown by stability constant values of $[FeF]^{2+}$ and $[FeCl]^{2+}$ which are 10^6 and 20 respectively.

When the ligand is a neutral molecule, the dipole moment in taken into consideration. Higher dipole moment and smaller size neutral molecules forms more stable complexes.

b) Basic character of ligands

The tendency of a ligand is to donate electron pairs, ie the when the ligand donate electrons easily, it will form stable complexes. In other words when the basic character of the ligands is higher, more stable complexes will be formed. F^- forms more stable complexes than Cl^-, Br^-, I^- and H_20 is a better ligand than NH_3

C) Chelate effect

Complexes which have chelate rings are more stable than complexes which have mono dentate ligands. This effect is called chelate effect.

Consider the 2 complexes of Ni^{2+} with unidentate and chelating ligands.

$$Ni^{2+}(aq) + 6\,NH_{3\,(aq)} \Leftrightarrow [Ni(NH_3)_6]^{2+}_{aq} \;\log\beta = 7.99$$

$$Ni^{2+}(aq) + 3en_{(aq)} \Leftrightarrow [Ni(en)_3]^{2+}_{aq} \;\log\beta = 18.1$$

NH_3 is a mono dentate and en is a bidentate ligand. Here $[Ni\ (en)_3]^{3+}$ is more stable than $[Ni(NH_3)_6]^{2+}$

Considering the Cd^{2+} complexes with $CH_3\ NH_2$ which is a mono dentate ligand, en a bidentate ligand.

$$Cd^{2+} + 2en \Leftrightarrow [Cd(en)_2]^{2+},\ \log\ \beta = 10.6,$$

$$\Delta H^o = -56.3 KJ/m,\ \Delta G^o = -60.7 KJ/m,\ \Delta S = +14.1 KJ/m$$

$$Cd^{2+} + aCH_3\,NH_2 \Leftrightarrow [Cd(CH_3\,NH_2)_4]^{2+}, \log\beta = 6.52$$

$$\Delta H^o = -57.3 KJ/m, \Delta S^o = +14.1 KJ/m, \Delta G^o = -60.7 KJ/m$$

As the stability constant increases, ΔG^o becomes more negative and ΔS^o more positive. As ΔG becomes more negative, the complex will be more stable. Hence, chelated complexes are more stable.

$$[Co(H_2O)_6]^{2+} + 6\,NH_3 \Leftrightarrow [Co(NH_3)_6]^{2+} + 6\ H_2O.$$

$$[Co(H_2O)_6]^{2+} + 3en \Leftrightarrow [Co(en)_3]^{2+} + 6H_2O.$$

When a chelate is formed, the number of particles increases. When a non-chelated complex is formed the number of particles remains unaltered. Hence, the chelated complex $[Co\ (en)_3]^{2+}$ is more stable than the non - chelated complex $[Co(NH_3)_6]^{2+}$

The stability of chelated complexes also depends on the size of the ring formed in the complexes. The chelated complexes containing 4-membered rings are not stable while those containing 5 and 6 membered rings are quite stable. If the number of rings present in a chelated complex increases, its stability also increases.

2.5 THEORIES OF BONDING IN COMPLEXES VALENCE BOND THEORY

Postulates

i) The central metal atom or ion makes available a number of empty s, p and d atomic orbital equals to its coordination number.

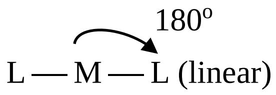
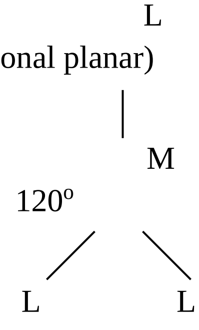
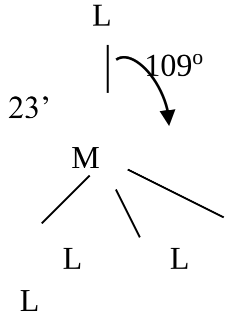
These vacant orbitals hybridize together to form hybrid orbitals which are the same in number as the atomic orbitals. These are vacant, equivalent in energy and have definite geometry.

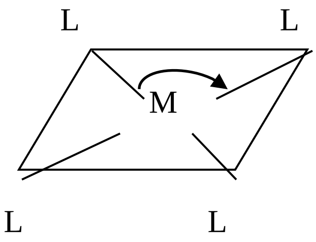
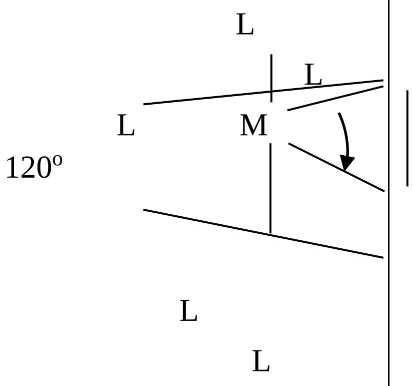
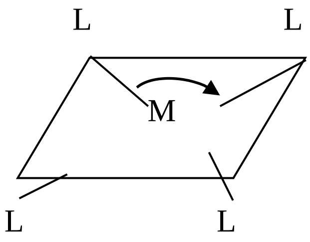
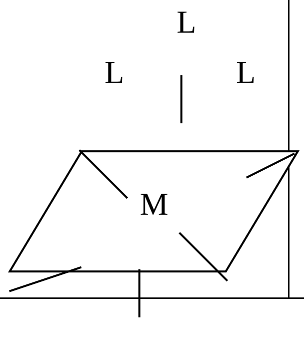
ii) The ligands have at least one σ orbital containing a lone pair of electrons.

iii) Vacant hybrid orbital of the metal atom or ion overlap with the filled σ orbital of the ligands to form ligand→ metal σ bond.

Hybridization and geometries of complexes

Depending upon the hybridization complexes possess different geometries. The following table gives the hybridization along with the geometries.

Coordination Number	Hybridization	Geometry	Examples
1.	Sp	 (linear)	$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$
2.	Sp^2	(Trigonal planar) 	$[HgI_3]^-$
3.	Sp^3		$Ni(CO)_4$, $[Zn(NH_3)_4]^{2+}$

		(Tetrahedral)	
4.	d Sp^2	 (Squ	$[Ni (CN)_4]^{2-}$ $[Zn (NH_3)_4]^{2+}$
5.	d Sp^3		$[Cu Cl_5]^{3-}$, $[Fe (CO)_5]$
6.	Sp^3 d	 (Square Py ramidal)	$[SbF_5]^{2-}$
7.	Sp^3d^2 (or) d^2 Sp^3		$[Co F_6]^{3-}$, $[Co (NH_3)_6]^{3+}$

		L L L (Octahedral complexes)	

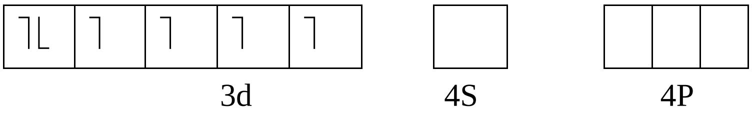
Outer orbital and inner orbital octabedral complexes

Octahedral complexes result from the hybridization of d^2sp^3 or sp^3 d^2 when the hybridization is d^2sp^3, it is an inner orbital complex, when the hybridization is sp^3 d^2,it is an outer orbital complex.

Ex: **$[Co\ (NH_3)_6]^{3+}$**

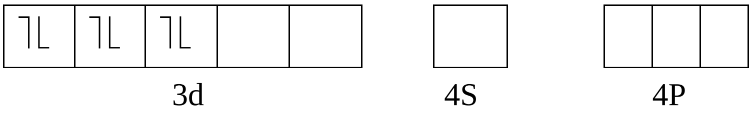
In this complex cobalt is present as Co^{3+} ion.

Electronic Configuration of $C0^{3+}$



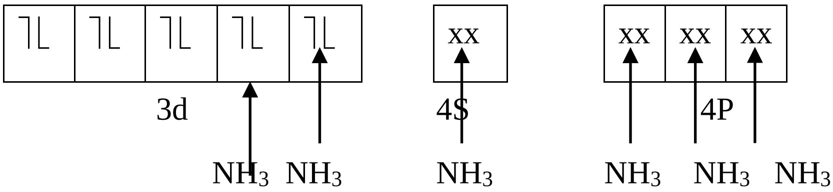
$NH_3$is a strong ligand, electrons have sufficient energy for pairing and hence get paired. So, two orbitals are vacant. The two 3d orbitals, one 4s orbital, three 4p orbitals hybridise together to form 6 d^2sp^3 hybrid orbitals.

Electronic Configuration of $C0^{3+}$ ion in $[Co\ (NH_3)_6]^{3+}$



The six d^2Sp^3 hybrids orbitals are equivalent in energy. These orbitals accept 6 electron pairs from 6 NH_3 molecules.

Electronic configuration of $[Co\ (NH_3)_6]^{3+}$

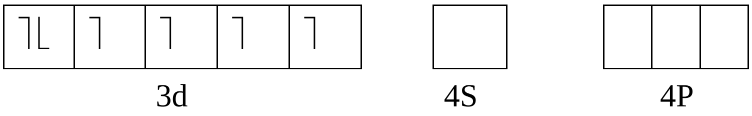


$[Co\ (NH_3)_6]^{3+}$ is an inner orbital complex. Since the d orbital involved in hybridization are from a lower shell than s and p orbital. Complexes using the inner d orbital are called inner orbital complexes. They are also known as covalent complexes or spin paired or low spin complex.

Ex: $[Co\,F_6]^{3-}$

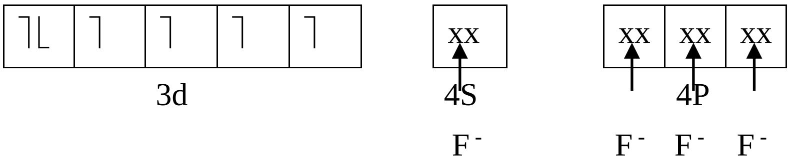
Here Co is present as Co^{3+} ion.

Electronic configuration of Co^{3+} ion



F^- is a weaker ligand and hence electrons do not have sufficient energy needed for pairing one 4s, three 4p, two 3d orbital undergo $sp^3\,d^2$ hybridization. These six $sp^3\,d^2$ hybrid orbitals are of the same energy. The six electron pairs from six F^- ions occupy these six hybrids orbital.

Electronic configuration of $[Co\,F_6]^{3-}$



$[CoF_6]^{3-}$ is an outer orbital complex since the d orbital involved in hybridization are from the same shell as s and p orbital. They are also known as ionic complexes or spin free or high spin complex. In this complex, there are 4 unpaired electrons. Hence, it is paramagnetic. Moreover, the number of unpaired electrons in the free metal ion is the same as that in the complex. The magnetic moment of the complex and the metal ion are equal.

Square planar and tetrahedral complexes

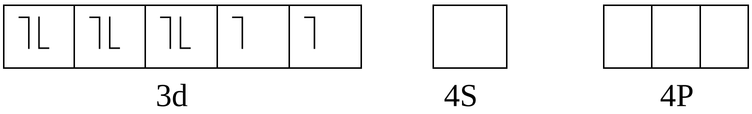
Square planar complexes

The hybridization involved is dsp^2. d orbital involved is of a lower shell than s and p orbital.

Ex: $[Ni\,(CN)_4]^{2-}$

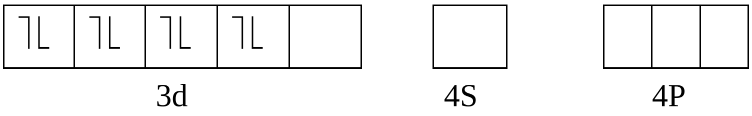
Here Ni is present as Ni^{2+} ion

Electronic configuration of Ni^{2+} ion



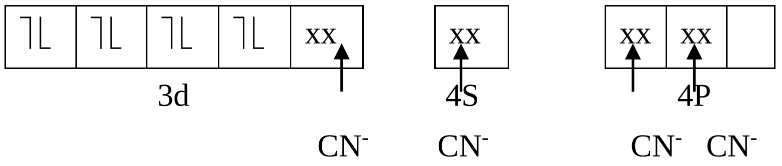
Since CN^- is a stronger ligand, the 2 unpaired the electrons in 3d orbital get paired. One 3d orbital, one 4s orbital and two 4p orbital get hybridized together to form 4 dsp^2 hybrid orbital which are of equivalent energy.

Electronic configuration of Ni^{2+} ion in $[Ni\,(CN)_4]^{2-}$



4 Pairs of electrons from 4CN^- occupy the hybrid orbital.

Electronic configuration of Ni^{2+} ion in $[Ni(CN)_4]^{2-}$



In this complex all the electrons get paired. Hence, it is diamagnetic, moreover, the magnetic moment of the free metal ion is more than the complex.

Tetrahedral complexes

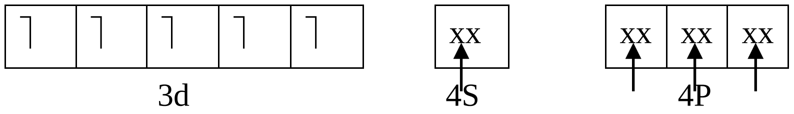
The hybridization involved in sp^3. All the 4 orbitals are of the same energy level.

Ex: **$[Mn Cl_4]^{2-}$**

Here Mn is present as Mn^{2+} ion.

Since Cl^- is a weaker ligand, the electrons do not get paired. One 4s, three 4p orbitals hybridize together to form 4 sp^3 together to from 4 sp^3 Hybridize together to form 4 sp^3 hybrid orbitals or equivalent energy. 4 pairs of electrons from 4 Cl^- ions occupy these hybrid orbitals.

Electronic configuration of $[Mn Cl_4]^{2-}$



Number of unpaired electrons in the complex is the same as that of the metal ion. Hence the magnetic moment of the metal and the at of the complex of equal.

V.B. Theory and magnetic properties of complexes.

Complexes which have no unpaired electrons do not have magnetic property; they are diamagnetic complexes which have one or more unpaired electrons, have definite magnetic moment and are paramagnetic. The magnetic moment of a complex is a calculated by using the formula.

$$\mu_{eff} = \sqrt{n(n+2)} \ B.M$$

Where n = number of unpaired electrons. Using this formula, number of unpaired electrons in an ion can be calculated.

Limitations of V.B. theory

1) Octahedral, tetrahedral and square planar complexes of d^1 d^2 d^3 and d^{10} ions have the same number of unpaired electrons. Hence, from the magnetic moment values, the geometry cannot be predicted.

2) Due to the presence of unpaired electrons, both colour and magnetic behavior are exhibited by the complexes. But, the colour of the complexes is not explained by VBT

3) VBT does not provide any satisfactory explanation for the existence of inner orbital and outer orbital complexes.

4) Too much stress has been laid on the metal ion while the importance of ligand is not properly stressed.

5) VBT cannot explain the reaction rates and mechanism of reactions.

2.6 CRYSTAL FIELD THEORY

Postulates

1) CFT regards the ligands as point charges or as point dipoles

2) Bonding between the metal cation and the ligands is due toe the electrostatic attraction between the nucleus of the metal cation and the partial negative charge present on the ligands. The interaction between the electrons of cation and those of ligands is entirely repulsive. Due to these repulsive forces, splitting of d orbitals of the metal cation occurs.

3) There is no overlap of metal ion orbitals with the orbitals of the ligand.

4) Bond formed between the metal ion and the ligand is purely ionic.

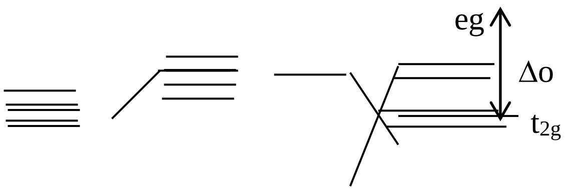
d - Orbital splitting in octahedral tetrahedral and square planar complexes.

There are 5 d orbitals. The orbitals d_{xy} d_{yz} d_{xz} have their lobes in between the axes. These three d orbitals are called non axial or t_{2g} orbital the d orbital

$d_x{}^2$-y^2 and d_{z2} have their lobes along the axes. These are called axial or eg orbitals.

d - Orbital splitting in octahedral complex.

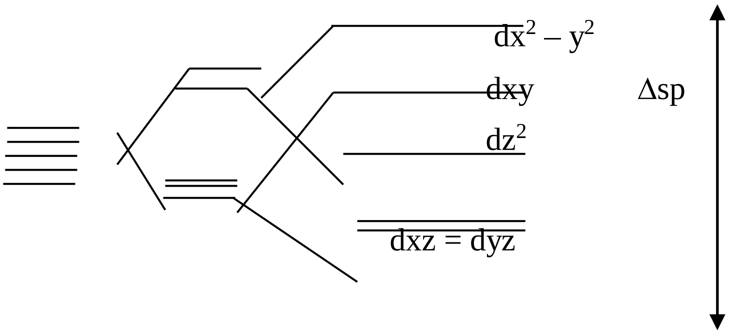
In an octahedral complex, all the six ligands lie along the axes. When the ligands approach the metal cation, the d orbital of the metal cation are repelled by the negative point charge of the ligands. Due to this repulsion, the energy of all the d orbitals will raise. Since the lobes of the eg orbitals lie directly in the path of the approaching ligands, the energy of eg orbitals in increased while that of t_{2g} orbitals is decreased. The separation of five d orbitals into two sets having different energies is called crystal field splitting or energy level splitting.



The energy gap between t_{2g} and eg sets is denoted by Δo or 10 Dq, which is called crystal field splitting energy. The energy of the t_{2g} orbitals is 0.4 Δo or 4Dq and that the energy of eg orbitals is 0.6 Δo or 6 Dq more than that of degenerate d orbitals.

d - Orbital splitting in square planar complex

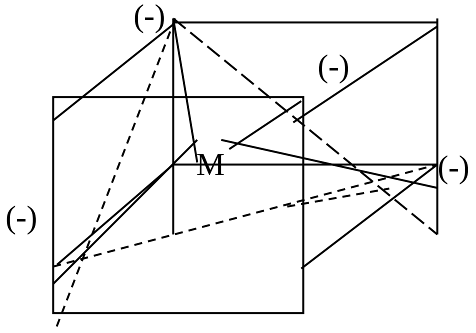
If the two ligands along the z axis in an octahedral complex is removed, square planar complex is obtained this is accompanied by a further rise in the energies of dx^2-y^2 and d xy orbitals and a further fall in the energies of dz^2, dzx and dyz orbitals.



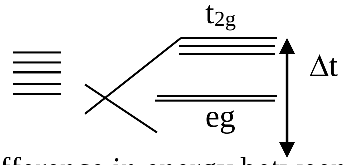
It has been found that Δsp is greater than Δo, because of the reason that dxz and dyz orbitals interact with only two ligands in the square planar complexes, while in octahedral complexes, interaction takes places with four ligands.

Δsp = 1.3 Δo

d - Orbital splitting in tetrahedral complex.



In a tetrahedral complex, all the four ligands lie in between the axes. Hence t_{2g} orbitals experience more repulsion than eg orbitals.



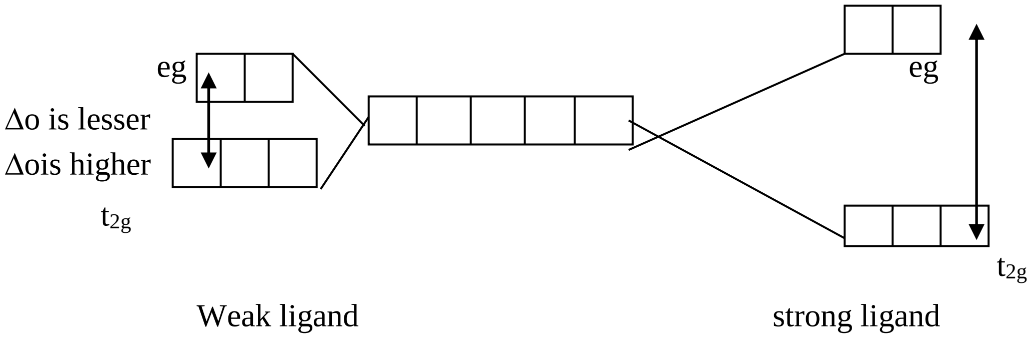
The difference in energy between t_{2g} and eg orbitals is Δt.

$\Delta t < \Delta o; \Delta t = 0.45\ \Delta o$

Energy level of t2g set in raised by 0.4 Δt (or) 0.18 Δo while that of eg set is lowered by 0.6 Δt (or) 0.27 Δo. Since $\Delta t < \Delta o$, crystal field splitting favours the formations of octahedral complexes.

Strong and weak ligands (Spectrochemical series).

The magnitude of Δo varies from stronger to weaker ligands. Stronger ligands are those which exert a strong field on the central metal ion and hence have higher splitting power, while the weaker ligands are those which have a weak field on the central metal cation and consequently relatively lower splitting power.



The common ligands can be arranged in the order of their increasing splitting power to cause d orbitals splitting. This series is called spectrochemical series which is given below.

$I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^- < H_2O^- < NH_3^- < SO_3^{2-} < NO^{2-} < CN^-$,CO.

High spin and Low spin complexes

Under the influence of weaker ligands, the energy difference Δo is relatively small, i.e. all the d orbitals have the same energy. Distribution of d electrons in t_{2g} and eg sets takes place according to Hund's Rule which states that electrons will pair up only when each of the five d orbitals is singly filled. Distribution of electrons is as follows:

$$t_{2g}^{1,2,3} \rightarrow eg^{4,5} \rightarrow t_{2g}^{6,7,8} \rightarrow eg^{9,10}$$

The first 3 electrons goes to t_{2g} level 4th and 5th electrons to eg level, 6th 7th and 8th electrons to the t2g level. The last two electrons to eg level. The complexes which contain weaker ligands are called weak field (or) low field (or) high spin complexes. Here, $\Delta o < p$, where p = average pairing energy which is the energy required to pair two electrons in the same orbital and Δo = crystal field splitting energy for octahedral complex which tends to force as many electrons to t_{2g} set while p tends to prevent the electrons to get paired pair in the t_{2g} level.

In the case of complexes containing stronger ligands distribution of d electrons does not obey Hund's Rule. The first 6 electrons go to t_{2g} level while last 4 electrons goes to eg level.

$$t_{2g}^{1,\ 2,3,4,5,6} \rightarrow eg^{7,8,9,10.}$$

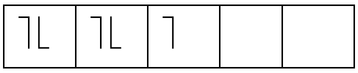
Complexes which contain stronger ligands are called strong field (or) high field (or) low spin complexes. Here $\Delta o > p$.

C.F. Theory and magnetic property of complexes.

The magnetic properties of complexes can be interpreted by CFT. Transition metals consist of one or more partially filled d orbitals. The filling up of these d orbitals depends upon the strength of the ligands.

Ex: The magnetic moment of $[FeF_6]^{3-}$ is 5.9 B.M while that of $[Fe(CN)_6]^{3-}$ 1.8 B.M. In both the cases Fe^{3+} is the central metal ion which is d^5 ion. Since F^- is a weaker ligand, the electrons are filled up in d orbitals following Hund's Rule. In $[FeF_6]^{3-}$ complex, there are 5 unpaired electrons, which is a high spin complex, due to the presence of 5 unpaired electrons, the magnetic moment value is 5.9 B.M. In $[Fe\ (CN)_6]^{3-}$ complex CN^- ion is stronger ligand, the d orbitals are filled up following Hund's Rule, so there is only one unpaired electron, hence the magnetic moment value is 1.8 B.M.

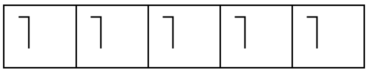
Fe^{3+} in$[Fe\ (CN)_6]^{3-}$



3d

μ = 1.8 B.M Low spin complex

$[FeF_6]^{3-}$



3d μ = 5.9 B.M, High spin complex

Crystal field stabilization Energy and its uses

Consider a d^{p+q} ion with p electrons in t 2g level and q electrons in eg level.

Change in energy

for d^{p+q} ion = $[-0.4p + 0.6\ q]\ \Delta o + mp$.

Where p = pairing energy and

m = Number of paired electrons.

This change in energy is called crystal field stabilization energy, since it stabilizes d orbitals by lowering their energy which results from their splitting into t_{2g} and eg orbitals.

Uses of CFSE values

1) CFT helps in predicting the structure of spinels. With the help of CFT, it can be shown whey the oxide Mn_30_4 or Mn^{2+} $Mn_2{}^{3+}0_4$ is a normal spinel while the oxide Fe_3o_4 or Fe^{2+} $Fe_2^{3+}O_4$

	Mn^{3+} (d^4)	Mn^{2+} (d^5)	Fe^{3+} (d^5)	Fe^{2+} (d^6)
CFSE (octahedral complex)	0.60 Δo	0	0	0.40 Δo
CFSE (tetrahedral complex)	0.18 Δo	0	0	0.27 Δo

For Mn^{3+} and Fe^{3+} ions, CFSE values are greater for octahedral than for tetrahedral sites. Thus, they preferentially occupy the octahedral sites. Hence, in Mn_3O_4, all the Mn^{3+} ions occupy octahedral sites Mn^{2+} ions occupy tetrahedral sites, ie it is a normal spinel. In Fe_3O_4 Fe^{2+}ions occupy octahedral sites, half of Fe^{3+} ions are in the octahedral sites, while the remaining half of Fe^{3+} ions occupy tetrahedral sites. Hence Fe_3O_4 in an inverse spinel.

2) CFSE values also explain why certain oxidation states are preferentially stabilized by coordinating with certain ligands. H_2O in a weak ligand, is expected to coordinate with Co^{2+} and Co^{3+} ions, Experiments show that H_2O stabilizes Co^{2+} ion and not Co^{3+} ie $[Co\ (H_20)_6]$ is more stable than $[Co\ (H_20)_6]^{3+}$. This is because of the fact that Co^{2+} has a much higher value of CFSE than Co^{3+}.

3) CFSE values also predict why Cu^{2+} ions form square planar complexes rather than octahedral or tetrahedral complexes.

Calculation of CFSE values of d^1 to d^{10}

Octahedral and tetrahedral complexes.

CFSE value is calculated by taking into account the number of electrons in t_{2g} and eg levels.

$$CFSE = [-4p+6q]\ Dq + mp\ \text{(or)}$$

$$= [-0.4\ p + 0.6q]\ \Delta o + mp$$

CFSE values for d^1 to d^{10} ions in high spin and low spin octahedral complexes.

d^{p+q}	$t_{2g}^{p}\ {}_{2g}^{q}$ (High spin)	CFSE	$t_{2g}^{p}\ {}_{2g}^{q}$ (Low spin)	CFSE
d^1	$t_{2g}^1\ eg^o$	- 4 D q	$t_{2g}^1\ eg^o$	- 4 D q
d^2	$t_{2g}^2\ eg^o$	- 8 D q	$t_{2g}^2\ eg^o$	- 8 D q
d^3	$t_{2g}^3\ eg^o$	- 12 D q	$t_{2g}^3\ eg^o$	- 12 D q

d^4	$t_{2g}^3 \, eg^1$	- 6 D q	$t_{2g}^4 \, eg^o$	- 16 D q + 1p
d^5	$t_{2g}^3 \, eg^2$	0	$t_{2g}^5 \, eg^o$	- 20 D q + 2p
d^6	$t_{2g}^4 \, eg^2$	- 4D q + p	$t_{2g}^6 \, eg^o$	- 24D q + 3p
d^7	$t_{2g}^5 \, eg^2$	- 8 D q + 2p	$t_{2g}^6 \, eg^1$	- 18 D q + 3p
d^8	$t_{2g}^6 \, eg^2$	- 12 D q + 3p	$t_{2g}^6 \, eg^2$	- 12 D q + 3p
d^9	$t_{2g}^6 \, eg^3$	- 6 D q + 4p	$t_{2g}^6 \, eg^3$	- 6 D q + 4p
d^{10}	$t_{2g}^6 \, eg^4$	0 + 5p	$t_{2g}^6 \, eg^4$	0 + 5p

CFSE values for d^1 to d^{10} ions (both high spin and low spin) in tetrahedral complexes.

d^{p+q}	$eg^{p} + {}_{2g}{}^{q}$ (High spin)	CFSE	$eg^{p} + {}_{2g}{}^{q}$ (Low spin)	CFSE
d^1	$eg^1 \, t_{2g}^{o}$	2.67 Dq	$eg^1 \, t_{2g}^{o}$	2.67 Dq
d^2	$eg^1 \, t_{2g}^{o}$	5.34 Dq	$eg^2 \, t_{2g}^{o}$	5.34 Dq
d^3	$eg^2 \, t_{2g}^{1}$	3.56 Dq	$eg^3 \, t_{2g}^{o}$	8.1 Dq + 1p
d^4	$eg^2 \, t_{2g}^{2}$	1.78 Dq	$eg^4 \, t_{2g}^{o}$	10.8 Dq + 2p
d^5	$eg^2 \, t_{2g}^{3}$	0	$eg^4 \, t_{2g}^{1}$	9.0 Dq + 2p
d^6	$eg^3 \, t_{2g}^{3}$	2.67Dq + p	$eg^4 \, t_{2g}^{2}$	7.2 Dq + 2p
d^7	$eg^4 \, t_{2g}^{3}$	5.34 Dq + 2p	$eg^4 \, t_{2g}^{3}$	5.34 Dq + 2p
d^8	$eg^4 \, t_{2g}^{4}$	3.56 D q + 3p	$eg^4 \, t_{2g}^{4}$	3.56 Dq + 3p
d^9	$eg^4 \, t_{2g}^{5}$	1.78 D q + 4p	$eg^4 \, t_{2g}^{5}$	1.78 Dq + 4p
d^{10}	$eg^4 \, t_{2g}^{6}$	0 + 5p	$eg^4 \, t_{2g}^{6}$	0 + 5p

CF Theory and colour of complexes

Solutions of transition metal complexes formed by metal cations having no unpaired electrons in their d orbitals are colourless while the solution of transition metal complexes having one or more unpaired electrons are coloured.

Ex: **$[Ti\ (H_2O)_6]^{3+}$**

This complex is purple coloured. It absorbs green light of wavelength $5000A^0$ and acquires energy equal to 57 kcal / mole. Ti^{3+} is d^1 ion. There is one electron in t_2g level, when green light in absorbed, the electron in t2g level in excited to eg level and Δ0 for t_2g and eg in 57 kcal /mole.

Since $[Ti (H_2O)_6]^{3+}$ absorbs green colour, it exhibits the complimentary colour purple.

Hydrated $CuSO_4$ is coloured while anhydrous $CuSO_4$ is white. This is because hydrated $CuSO_4$ is in aqua complex of Cu^{2+}ion where d-d transitions are possible. It absorbs near the red region of the spectrum. So, it appears blue. A solution containing $[Ni (H_2O)_6]^{2+}$ is green. On adding cyanide $[Ni (CN)_4]^{2-}$ is formed. The colour disappears. This is because H_2O is a weak ligand, CN^- in a strong ligand. In cyanide complex, there is no unpaired electron, d-d transition is not possible and is colourless. In aqua complex d-d transition is possible and is coloured.

Limitations of CF theory

1) CFT consider only metal ion d orbitals and gives no consideration at all to other metal orbitals such as s, px, py and p_2 orbitals and ligand Π orbitals.
2) CFT does not consider the formation of Π - bonding in complexes.
3) CFT is unable to account satisfactorily for the relative strengths of ligands
4) The bond between the metal and the ligands are purely ionic. It gives no account of the partly covalent nature of the metal-ligand bonds.

Comparison between VBT and CFT

Similarity

The inner orbital octahedral complexes of VBT are the same as the spin paired or low spin octahedral complexes of CFT. Similarly, outer orbital complexes of VBT are same as the spin free or high spin octahedral complexes of CFT.

Differences

1. In the formation of some inner orbital octahedral complexes of VBT, the promotion of an electron from d-orbitals to s-orbital in required, while in the formation of spin paired octahedral complexes of CFT no such promotion is required.
2. According to VBT, metal ligand bonding in complexes is only covalent whereas in CFT, the bonding in purely ionic.
3. In VBT, the ligand orbitals mix with metal ion orbitals. Whereas in CFT ligand electrons are not allowed to enter the metal ion d orbitals.

Questions

1) What are chelates?
2) Give the names of the following complexes.
   a) $[Co(NH_3)_5Cl]S0_4$ b) $K_4[Fe(CN)_6]$ c) $[Ni(CO)_4]$
3) Explain Werner's theory
4) Discuss structural isomerism
5) What are the factors affecting the stability of complexes.
6) What are the postulates of VBT, CFT?
7) What are the limitation of VBT and CFT?
8) Discuss the splitting of d orbitals in octahedral, tetrahedral and square planar complexes.
9) Calculate CFSE values for d^5 and d^6 ions is octahedral field (both high spin and high spin)
10) $[Co(NH_3)_6]^{3+}$ is diamagnetic, while $[CoF_6]^{3-}$ is paramagnetic, why?

NOTES

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UNIT III

APPLICATIONS OF COMPLEXES AND ENVIRONMENTAL CHEMISTRY

3.1 Complexometric titrations.

These titrations depend upon reactions between, ions, usually a metal ion and a ligand ion to form a soluble, slightly dissociated complex. For example, a solution of cyanide can be titrated with silver nitrate.

$$2CN^- + Ag^+ \rightarrow [Ag(CN)_2]^-$$

Principles and types of titrations using EDTA

Certain metal ions react quantitatively with ligand solutions forming stable metal complexes. Ag^+ reacts with CN^- forming a soluble colourless complex.

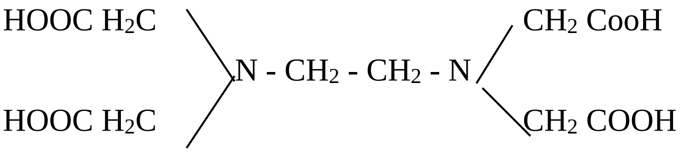
$$Ag^+ + 2CN^- \rightarrow [Ag(CN)_2]^-$$

Therefore, Ag(I) solution can be titrated with a cyamide solution, when $AgNO_3$ solution is added to a cyanide solution, $[Ag(CN)_2]^-$ is formed when all the CN^- has been removed, the first excess of $AgNO_3$ reacts with $[Ag(CN)_2]^-$ to form insoluble $Ag[Ag(CN)_2]$.

$$Ag^+ + [Ag(CN)_2]^- \rightarrow Ag[Ag(CN)_2]$$

The end point is the appearance of turbidity in the reaction medium. Such a titration is called complexometric titration. The formation of a chelate by a metal ion is an advantage because chelation is a single step process. Chelates are much more stable and location of end points is precise.

Ethylenediamine tetracetic acid [EDTA] is an amino polycarboxylic acid. It is a tetraprotic acid and is represented as H_4Y



$$\begin{array}{l} HOOC\,H_2C \\ HOOC\,H_2C \end{array} \Big\rangle N - CH_2 - CH_2 - N \Big\langle \begin{array}{l} CH_2\,CooH \\ CH_2\,COOH \end{array}$$

It is a weak acid. The four - Carboxyl groups and the two nitrogens act as ligand sites and thus it is a hexadentate ligand. The ion Y^{4-} forms very stable complexes with all metal ions. The general reaction between a metal ion and EDTA may be written as

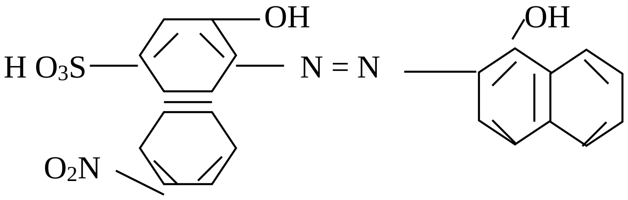
$$M^{n+} + Y^{4-} \rightarrow MY^{n-4}$$

M^{n+} = hydrated metal cation of charge n+. These titrations are performed in neutral or alkaline solution. In presence of an acid, the complexes decompose.

$MY^{n-4}+2H^{+} \rightarrow Mn^{+}+H_2Y^{2-}$

The formation of H^+ during the titration would decrease the p^H and the reaction will be stopped. To avoid this, buffer solution such as acetic acid-sodium acetate or ammonia-ammonium nitrate is added.

In these titrations, metallo chromic indicators are used. They form stable, brightly coloured complexes with most metal ions A common metallo chromic indicator is Erichrome black T.



When the indicator Eriochrome Black – T is added to a solution of metal ion M^{n+} to be estimated, a little of metal ions will be used to form brightly coloured M-In complex. The metal –indicator complex has one colour and the indicator alone has another colour. Initially the solution being titrated contains M-In and the free metal ion to be estimated. When EDTA is added, the free metal ions will react. When all these free metal ions have been reacted by EDTA, EDTA added will abstract M^{n+} ion of M-In forming M-EDTA complex. This will release the free indicator and hence the colour of the solution will change to the colour of the indicator.

M-In + EDTA $\rightarrow$ M-EDTA+In

The end point in an EDTA titration is the disappearance of the colour M-In and the appearance of the colour of the free indicator.

3.2 EDTA and its applications.

Complexometic titrations are commonly known as EDTA titrations since EDTA acts as a most versatile complexation agent. A wide range of metal ions could be removed as complexes with least difficulty

EDTA has greater advantages due to

i. Its ability to form 1:1 M-EDTA complex
ii. Its availability in pure form
iii. Its disodium salt’s solubility in water
iv. The solution is stable for over a period.

Estimation of metals:

The formation and stability of metal – EDTA complex is governed by many factors which include

1) The metal ion concentration of the solution
2) P^H of the medium
3) The concentration of the metal ion indicator solution
4) The selection of the metal ion indicator for the particular estimation

Estimation of zinc

Zinc ions form a complex with EDTA.

$Zn^{2+} + H_2Y^{2-} \rightarrow ZnY^{2-} + 2H^+$

Initially when the P^H of the medium maintained at p^H, 7 to11, the zinc ion combine with indicator molecule to form Zn – indicator complex which appears as a wine red colour. Near the end point, EDTA breaks Zn- indicator complexation resulting in the formation of Zn- EDTA complex. Hence at the end point, the liberated free indicator yields a blue colour to the solution. Thus, the end point is the sharp charge from wine red to blue.

Estimation of hardness of water

The hard water contains metals such as calcium and magnesium. As these ions can readily complex with EDTA, they are estimated as a whole by titrating against as a whole by titrating against standard EDTA solution using Erichrome black T as indicator. The total hardness of water in expressed in terms of parts per million of $CaCo_3$.

$$Thus, total Hardness = \frac{Volume of\ 0.01 m\ EDTA}{Volume of\ EDTA} \times 10$$

Sequesterisation

The introduction of a reagent to eliminate the interference by a substance in estimation is called masking or sequesterisation. The reagent added is called masking or sequestering agent. Generally, the masking agent forms highly stable, soluble complexes with the interfering, species. In the EDTA titrations, cyanide ion is employed as a masking agent for estimating Mg and Ca in the presence of ions of Cd, Cu, Co, Ni and Pd. All of the latter ions form stable, soluble Cyanide complexes and these complexes do not react with EDTA. In the estimation of copper, iron will interfere. Iron is rendered inactive by the addition of masking agent F^-, which forms stable complex with Fe^{3+}. This complex of Fe(111) , will not oxidize I^- ions.

3.3 Environmental chemistry

3.3.1 Bhopal gas tragedy

The Bhopal gas tragedy which took place in India on December 3rd 1984, is a case of serious air pollution in which MIC (Methyl Isocyante) gas released from a fertilizer manufacturing plant of union carbide caused death of approximately 3200 persons. This gas causes irritation which may be followed by blindness and various lung diseases causing death.

On December 3rd 1984, at 11 pM MIC tank pressure gauge was pegged. The pressure indicator had gone above 55 psi, the safety valve had opened and the MIC Vapour escaped from an atmospheric vent line 120 feet in the air. The safety valve remained open for about two hours releasing over 50000 1bs of gaseous and liquid MIC associated with $CoCl_2$ and HCN.

The deadly poisonous gas spread over 40sq.km seriously affecting the people at a distance of 5 to 8 km. An estimated 5,00,000 people fled that night, most on foot. Out of 2,50,000 people exposed, 65000 were severely hit from eye, respiratory, neuromuscular, gastro intestinal, lung fibrosis, pulmonary oedema and gynecological disorders.

The hospitals were crowded by 25,000 patients. In Bhopal's Jai Prakash Nagar, everything was so quiet goats, cows, whole families all lying silent still. About 1000 people became blind, while more than 1 lakh will continue to suffer. The death drama continued for four days.

Chernobyl disaster

Chernobyl city in Russia is the site for V.I Lenin nuclear power plant. The reactors installed at Chernobyl nuclear power plant were designated RBMK 1000. These reactors employed graphite as a moderator, water as a coolant and uranium (IV) oxide that is 2% enriched in uranium -235 as a fuel.

On April 26,1986, a major accident occurred at reactor 4 of the Chernobyl power plant. It was scheduled to be shut down for maintenance at 1.00 am on April 25, 1986. The shut down operation began with a reduction in the power supply produced by the reactor. This is done by inserting control rods at regular intervals. Some power is needed to run the coolant pumps because the reactor remain hot for a long time after the shut down and has to be fed with the coolant.

But, the power dipped to an extremely low level. Since the power level was low, it was essential to inject only a small amount of water into the reactor since all the pumps were functional, the reactor received excessive water, steam production declined and power level dipped further. Hence speed of the pumps was reduced and nearly all the control rods were withdrawn. When the accident took place there were neither control rods nor liquid water. Since both the control rods and liquid water were absent reactivity developed. The number of projective neutrons increased and the power level increased many times. Hence, the core temperature shot up, pressure became very high. At 1.23 hours on April 26 1986, an explosion occurred in the reactor. Due to this, the power level raised 120 times the normal level. About 3 seconds later, the power level had risen 440 times the normal value and a second explosion occurred.

Consequences:

On the first day of the accident 31 people died and 200 were injured. Since the plume was rich in iodine-131, cesium -134, cesium -137 it was feared that the accident would cause long term health effects. Thyroid cancer is one of tragic consequences. This type of cancer is caused by iodine-131, which is ingested mainly through milk and milk products. Since children consume more milk, infants are more prone to thyroid cancer. After the chernobyl accident, the surrounding areas of Belarus, Ukraine and Russia registered a 200 fold increase in the incidence of thyriod cancer among children.

Minamata disease

One of the most visible tragedies caused by water pollution is minamata disease originating about five decades ago in the Japanese fishing port of Mina mata, the disease remains the most disastrous case of mercury poisoning.

The cause of the disease was contamination of water with mercury- rich efficient discharged into the Bay by Chisso chemical company. By 1963, when it was determined, the illness in due to methyl mercury poisoning caused by eating contaminated fish from the Bay, the disease had claimed about 50 lives and permanently paralyzed over 700 people.

3.3.2 Air pollution

Contamination of air with harmful gases, dust, smoke et is called air pollution.

Sources

1) Carbon monoxide: produced by the incomplete combustion of all carbon-containing fuels used in automobile engines. Cigarette smoke contains Co. When coal, wood and oil are burnt, black smoke is produced. This smoke contains Co. Co is also generated by natural sources like forest fires, volcanic eruptions.
2) Carbon dioxide: when fossil fuels like coal, natural gas are burnt carbon dioxide is produced. Cultivation of soil also releases large amount of CO_2. $CO0_2$. is also given to the atmosphere through the eruption of volcanoes. Decay of dead organisms also evolves CO_2.

3) Oxides of nitrogen: The smoke released by the automobile engines contain NO and NO_2. Many chemical plants also produce NO_2. large amounts of SO_2 and nitrogen oxide also emitted from power plants and many industrial processes.
4) Oxides of sulphur: when coal is burnt, sulphur present in coal is converted into SO_2 oils have some sulphur compounds, which give SO_2 on burning when sulphide ores are roasted in air, SO_2 is produced. A part of SO_2 present in the atmosphere is oxidized to $S0_3$ by photolytic and catalytic oxidation processes. Thus, So_2 present in the atmosphere also contains SO_3.
5) Ozone: Ozone is produced during various combustion processes taking place in the air around us.

Green- house effect

There is a protective layer of O_3 gas in the atmosphere at a height between 15 km and 60km and then a blanket of $C0_2$ gas exists in the lower part of the atmosphere. Now when sunlight, consisting of ultraviolet rays, visible light and infra –red rays on the top of the atmosphere, the harmful ultra-violet rays are absorbed by the O_3 layer and hence do not reach the earth's surface. On the other hand, visible light and infrared rays pass through the Co_2 layer and fall on the earth. Since the infrared radiations have heating effect, they heat the earth and its various objects.

Since the earth and its various objects become hot, they start emitting infrared rays, which are of longer wavelength. These infrared radiations are absorbed by $C0_2$ layer in the atmosphere. These rays heat the earth's atmosphere. The heating up of earth due to trapping of infra –red radiations by Co_2 layer in the atmosphere is called green house effect.

Green House Gases:

Burning of the fossil fuels emit $C0_2$, growing paddy or live-stock releases methane, the use of aerosols as coolants in refrigerators and the air conditioning devices or sprays release chlorofluoro carbons into the atmosphere. These gases trap the solar radiation reflected back from the earth's surface, leading to atmospheric and elimatic changes.

Impact of green house effect- effects on ecosystem

Some scientist fear that if proper precautions are not taken the concentration of the green house gases in the atmosphere may double within the next 50-100 years.

1) If this happens, the overall global temperature may increase by 4 to 5^0 C. This will increase the evaporation of surface water, which may

influence climate change depending upon the pattern of cloud formation.

2) Even 1.5^{0}C raise in temperature can adversely affect the food production in the world.
3) The biological productivity of the ocean would also decrease.
4) Melting of the polar ice caps, could happen resulting in lifting up of the sea.
5) Sea level would increase the flooding possibility of low-lying areas, so important cities and ports may face the threat of floods.
6) Global warming may cause organisms to migrate or face extinction.
7) It is reported to alter the habitats, migration and breeding habits of animals
8) Out of the total 1191 Maldivian islands, most of them are expected to sub merge in the sea in the next 100 years.
9) It will cause desertification, drought and soil erosion.

Measures to reduce green house effect

The best way of preventing the atmosphere from the pollution caused by excess quantity of $C0_2$ is that a balanced quantity of CO_2 should be maintained in the atmosphere. Green plants absorb $C0_2$ gas from the atmosphere to manufacture their food and also at the same time release O_2 gas into the atmosphere. Thus if we grow more trees, our atmosphere will get rid of its excess $C0_2$ gas we should not cut down trees.

3.3.3 Depletion of ozone layer

Ozone in present in the lower region of stratosphere that is between 25 km and 30km from the earth's surface. The ultra violet rays emitted by the sun are very harmful to man and animal. The ozone layer present in the upper atmosphere absorbs these UV radiations and there by prevents them from reaching the earth's surface. Thus, the ozone layer has reduced the effect of ultraviolet radiation, thereby making the life possible on the earth.

Ozone is formed from oxygen by the action f UV radiation in the stratosphere.

$O_2 \rightarrow [O]+[O]$

$[O] + O_2 \rightarrow O_3$

$O_3 \xrightarrow{M} [O] + O_2$ M = pollutants

The concentration of both O_2 and O_3 are constantly maintained in the stratosphere by the above reaction and the UV radiation are absorbed.

Preventing them from reaching the earth. When this mechanism is disrupted, ozonal hole is formed.

Effect of oxides of nitrogen on ozone layer.

The jet airplanes that fly at the heights of O_3 layer omit NO into the atmosphere. This NO reacts with the ozone and breaks it into diatomic oxygen and the NO becomes NO_2. This NO_2 in turn react with another ozone molecule and break it into diatomic oxygen and NO_3 will be formed. This NO_3 will combine with another NO to form two molecules of NO_2. As a result both NO and NO_2 will be available for continuous destruction of O_3. Thus, the O_3 is not permitted to absorb incoming UV radiation consequently, the concentration of O_3 also gets depleted.

Fluorocarbons and their effect on ozone layer.

The chlorofluorocarbons, so called CFC's widely used in refrigeration and other cooling systems, aerosols, foams and solvents reach the stratosphere and causes O_3 depletion. The UV rays hit the CFC molecules and free radical combines with O_3 to form diatomic oxygen and a chlorine oxide radical. This radical combines with atomic oxygen to form diatomic oxygen and again the chlorine free radical is regenerated. Now, the regenerated radical is ready to attack another molecule of ozone. However, a single radical can break down 100000 ozone molecules. This cycle continues several times to destroy about a million molecule of ozone consequently the O_3 concentration gets depleted.

Harmful effects of ozone depletion.

1. With the depletion in atmospheric ozone there is danger of the increase in the flux of ultra violet radiation over earth's biosphere. These radiations are harmful for man's life.
2. The skin cancer namely basal cell carcinoma, squamous cell carcinoma and melanoma are rapidly climbing the list of human diseases cause by UV rays.
3. UV radiations cause blood vessels near the skins surface to carry more blood, making the skin hot, swollen or red causing sunburns.
4. UV radiations are also absorbed by cornea and lens in the eye leading to photokeratitis and cataracts.
5. The increased UV radiation will increase the mortality rate of larval of Zooplanktons. Enhanced radiation also impairs fish productivity.

Methods to control ozone depletion.

Scientists are worried over the gradual destruction of ozone layer by the oxides of nitrogen and fluorocarbons.

Nitrogen oxides can be removed by scrubbing process. These oxides are allowed to react with H_2SO_4 so that the following reaction takes place.

$SO_2 + NO_2 + H_2O \rightarrow H_2SO_4 + NO$.

SO_2 and NO_2 present react in presence of water and produce H_2SO_4 and NO. NO. Thus produced, reacts with NO_2 to form N_2O_3 which reacts with H_2SO_4 to form $H(NO)SO_4$.

$NO + NO_2 \rightarrow N_2O_3$

$N_2O_3 + H_2SO_4 \rightarrow 2H (NO) SO_4 + H_2O$

Since the oxides of nitrogen are acidic in nature, they are removed by scrubbing them with alkaline solution of $Ca(OH)_2$ and $Mg (OH)_2$.

In order to save the destruction of O_3 layer by fluoro chlorocarbons, their usage should be banned or some new types of substances should be discovered which may be used as aerosol spray propellants and should not react with O_3 layer, so that it may be saved.

3.3.4 Smog

The word ‘smog’ was coined to describe the ‘smog-fog’ which is prevalent in London. The combination of carbon soot particles and gaseous oxides of sulphur present in the atmosphere, is known as classical smog. This smog is also called London type smog. It is produced by the combustion of industrial and household fuel carbon particles and SO_2 present in classical smog make it show-reducing character. This smog is formed in the early morning hours in winter months. It causes severe, lung and throat irritation.

Photochemical smog.

The main constituents of this type of smog are O_3 and oxides of nitrogen. Due to the presence of O_3, NO_2 and some other photochemical oxidants, this smog is oxidizing in character.

Mechanism of formation

Photochemical smog is formed only when the atmosphere contains soot particles, hydrocarbons and oxides of nitrogen. When the atmosphere containing the above constituents is exposed to sunlight, NO_2 present in the atmosphere absorbs ultraviolet radiations of the sunlight and undergoes.

Photolysis, giving NO and atomic oxygen

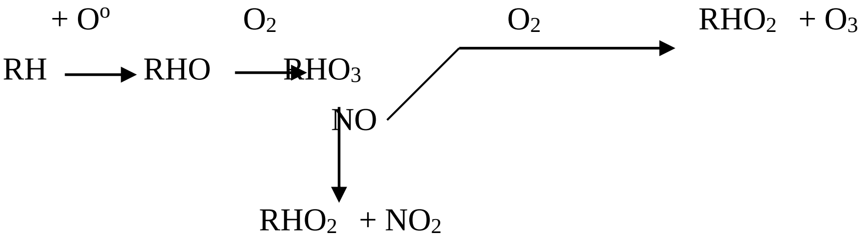
$NO_2 + \text{UV light} \rightarrow NO+[O]$

Atomic oxygen reacts with O_2 (molecular oxygen) in presence of collisional molecule (M) which conserves energy and O_3 is formed. O_3, thus produced, reacts with NO to regenerate NO_2 and O_2.

$O+O_2+M \rightarrow O_3 +M$

$O_3 + M \rightarrow NO_2 + O_2$

If the atmosphere contains hydrocarbons (RH), the atomic oxygen produced reacts with RH to give a variety of free hydrocarbon radicals. (RHO, RHO_2, RHO_3.etc) which produce O_3 and other secondary pollutauts like aldehydes, ketones, peroxyacetyl nitrate (PAN) etc, all the pollutauts are called photochemical pollutants.



Peroxy acetyl nitrate

PAN.

O_3 aldehydes, ketones etc present in the photochemical smog induce eye irritation. O_3 adversely affects vegetation and cracks the stretched rubber.

3.3.5 Water pollution.

When insoluble solid particles, soluble salts, sewage, garbage, radioactive substances, industrial wastes, algae, bacteria etc go into water, water gets polluted. This type of pollution is called water pollution.

Sources

i) Inorganic pollution

Inorganic pollution may be due to the presence of acids, alkalies, soluble salts or other inorganic substances. The most common acid present is sulphuric acid discharged by many industries. Textile and tanning industries are known to discharge alkalies. In steel industries, steel is treated with HCl to remove iron oxide coated on it. This process is called pickling. The pickling solution is strongly acidic. When such solution is allowed to mix with water in ponds, lakes or rivers, the water will be contaminated with a high concentration of iron (III) chloride. The use of phosphates in detergents causes water pollution.

ii) Organic pollution

The common organic pollutants are carbohydrates, proteins, fats, acids, oils, organic fertilizers etc. Water from distillery, running, and food processing laughter houses, dairy antibiotics and sugar industries are a few examples of biodegradable effluents.

iii) Domestic sewage:

Domestic sewage consists of human faeces, urine and the dirty used up water from the houses.

iv) Sewage wastes

Sanitary sewage is the spent water supply of the community. Domestic sewage in the wastewater from kitchens, bathrooms, Laundries etc.

v) Industrial effluent

The effluents from industries such as paper and pulp, distillery, fertilizer, electroplating pollute the water when their effluents are discharged into river.

vi) Fertilizers and Agricultural waste

Fertilizers, plant nutrients, pesticides, insecticides, herbicides, manure, slurry and soil erosion results in heavy pollution of the water sources.

vii) Insecticides.

The chemicals that are used to kill insects on plants and animals are called insecticides. When agrochemicals such as fertilizers, perticides are used and when water flows on the surface of crop fields, they are polluted by these chemicals.

viii) Oil

Oil refineries and petrochemical industries discharge the mixture of wastes containing hydrocarbons, phenolic compounds and a large number of organic and inorganic sulphur compounds.

BOD and COD and its importance:

Biological oxygen Demand (BOD)

BOD is the amount of oxygen required for biological oxidation by microbes in any unit volume of water. The test is done at 20^0 C for atleast five days. BOD value generally approximates the amount of oxidized bioorganic matter and is, therefore, used as a measure of degree of water pollution and waste level. Thus, due to the addition of sewage and waste oxygen level are depleted which are reflected in terms of BOD values of water. The number of bacteria as Escherchia coli in unit volume of water is also taken as a parameter of water pollution.

The quantity of oxygen in water called dissolved oxygen or DO along with BOD is indicated by the kind of organism present in water. For example, fish becomes rare at DO value of 4 to 5 ppm of water. Further decreases in DO value may lead to increase in anaerobic bacteria. Typical BOD values for raw sewage run from 200 to 499 mg of oxygen per liter of water. Water for drinking should have a BOD less than.

Chemical oxygen Demand (COD)

COD is the quantity of oxygen required for complete oxidation of all reducing substances of organic as well as inorganic origin present in water. COD of a given sample of water in determined by combination of impurities with strong oxidants such as $k_2Cr_2O_7$ in an acidic solution. Under these conditions all elements are oxidized, carbon is oxidized to CO_2 sulphur to SO_2, phosphorus to P_2O_5 and hydrogen to H_2O.

If only organic matter is present in sewage and the amounts of the pollutants and their composition are known, COD can be determined by stoichiometric equation. COD is always higher than total BOD, because not all pollutants are universalized in biochemical processes and the metabolites of cell microorganisms which are not mineralized by incubation are returned into the medium.

COD of industrial effluents can be calculated if the composition of the organic pollutants in known.

3.3.6 Soil pollution

The contamination of soil with acid rain, excess of fertilizer, insecticides and herbicides is called soil pollution.

Sources

i) Indiscriminate use of fertilizers and pesiticides

Repeated use or excess use of the same fertilizer pollutes the soil. When $(NH_4)_2 SO_4$ is used as a fertilizer into the soil again and again, $NH_4{}^+$ ions are used up by the successive crops but SO_4^{2-} ions get accumulated into the soil. Being acidic SO_4^{2-} ions make the soil highly acidic and hence unfit for plant growth.

It $NaNO_3$ or KNO_3 is used again and again, NO_3^-ions are used up by the successive crops, but Na^+ or K^+ ions get accumulated into the soil. These cations make the soil alkaline and hence the soil cannot be used for the crop growth.

When the standing vegetables and fruit plants are sprayed with insecticides, and herbicides, to save them from harmful insects and herbs etc., the insecticides or herbicides enter the living tissues of the growing plants and accumulate in them. When we eat these grains, fruits or vegetables, the insecticides in them may damage our heart. The chemicals like $CaCl_2$ are used for ripening fruits like banana and mangoes, these fruits should be washed with water before they are eaten up.

ii) Industries waste and & Radioactive waste.

Solid, liquid and gaseous chemical from various industries such as paper and pulp, iron and steel, fertilizers, dyes, automobiles, pesticides, tanneries, coal based thermal power plant etc contain a variety of thermal power plant etc contain a variety of pollutants such as toxic heavy metals, solvents, detergents, plastic suspended particulates and refractory, non biodegradable chemicals, radioactive water. There wastes should be treated at source. Indiscriminate dumping of untreated or inadequately treated domestic, mining and industrial wastes on land is an important source of soil pollution.

iii) Urban wastes

Tonnes of urban waste are produced every year from polluted cites. The inadequately treated or untreated sewage sludge not only pose serious health hazards but also pollute soil and decrease its fertility and productivity. Other waste materials such as rubbish, used plastic bags, garbage, sludge, hospital wastes lead to soil pollution. Suspended matter present in sewage can act as a blanket on the soil and interfere with its productivity.

Methods of disposal of wastes.

The most commonly used solid waste disposal methods are i) Composting ii) sanitary landfill iii) thermal processes iv) Recycling and reuse

Microorganisms play a vital role in compositing and sanitary land filling.

i) Compositing

Composting is the aerobic and thermophilic decomposition of organic matter present in the refuse by microorganisms. The organic matter is transformed into a stable humus like substance during this process. The reactions taking place during composting generate heat and hence the compost temperature raises during the process. Depending upon the composition of waste, the waste volume is reduced by about 30% to 60%

Composting may be carried out naturally under controlled conditions (or) in mechanized composting plants. In natural systems, the garbage is mixed with nutrient source and a filler (wood chips) which permits the air to enter into the pile. The mixture, which is maintained at about 50% moisture content, is kept in windows having a width of about 2.5 m. the mixture is turned over twice a week within about 4 to 6 weeks, the temperature falls, the colour darkens and a musty odour develops. This indicates completion of the process.

ii) Sanitary land filling

Land filling is the most common and economic method of solid waste disposal in many countries. In this type of disposal, complex organic wastes are slowly degraded or decomposed bacteria or fungi. Since air cannot enter through a compacted land fill, the aerobic bacteria decompose oxygen is present inside the landfill. Then decomposition begin. The water soluble organic acids generated in this process enter the water media and diffuse through the landfill soils. The bacteria and fungi present in the soil metabolize these organic acids into CO_2 and water.

iii) Thermal processes

The important thermal processes used in solid waste treatment are incineration and pyrolysis. In incineration, solid organic wastes are subjected to controlled combustion, so as to convert them into incombustible residue and gaseous products.

iv) Recycling and reuse.

Recycling and reuse of the waste helps to reduce the problem of waste disposal. Recycling of the plastics may be carried out in any of the following ways:

A) Primary recycling where the same plastic product is manufactured again.

B) Secondary recycling where the material is reprocessed to a new product with different composition.

C) Tertiary recycling where the plastic material is completely processed to a new form.

3.3.8 Noise pollution and Radio active pollution – health hazards.

Noise pollution

The unwanted sound is called noise. The sounds of high decibels like 95,100,110. 150,170 etc create harmful effect on human health. This is called noise pollution.

Sources:

i) The increasing speed and length of railway train increase the volume of noise produced by them during their journey.

ii) In factories, the high-speed machines create more and more noise. Loud speakers, aero planes, motor horn, rocket, siren etc create harmful effects.

Effects of noise pollution

i) Excessive noise disturbs the blood pressure, modifies rhythm and affects the digestive systems.

ii) Prolonged exposure to noise is harmful to nervous system and also affects memory adversely.

iii) Noise leads to gradual loss of learning capacity of human beings.

iv) The sound pollution causes confusion in colour perception and thus may reduce the field of vision.

v) Excessive sound disturbs sound sleep and proper rest.

vi) A sound of high decibels (160 dB) creates headache.

Radioactive pollution

Radioactive substances and nuclear radiations produced during nuclear reactions affect our environment adversely and thus radioactive pollution is created.

Sources and its effects

1. Low-level radioactive liquid wastes, radioactive gaseous wastes and dusts are released during nuclear explosions. The radioactive gaseous wastes are injected into the upper layer of atmosphere, where due to cooling they condense to fine dust particles and thus radioactive cloud is formed. This cloud moves in the direction of the wind settles down slowly to the surface of the earth and thus pollutes air, water and soil.
2. The radioactive substances produce energy which is so strong that living cells are damaged or destroyed.
3. Nuclear explosions which are operated in sea make sea water polluted. This affects the aquatic life.
4. Among the radioactive radiations, rays are the most dangerous. They have high penetrating power. They pass freely in the human body, resulting in leukaemia and cancer.

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UNIT IV

4.1 Bio inorganic Chemistry.

Essential and trace elements in Biological processes.

There are elements that are essential for biological functions in the body. Depending upon their abundance, they are classified as essential elements and trace elements.

Essential elements

There are about 7 elements such as Ca, P, K,S, Cl,. Na and Mg, which constitute about 0.7% of the atoms in the human body. They perform variety of biological functions with body. Absence of these elements in the body results in disease and sometimes may result in death. These elements are present in greater concentration in the body. They perform variety biological functions in the body.

Trace elements

There are 14 elements, which are present in the body in small concentrations. Which are called trace elements. The trace elements are Fe, I, F, Mg, Zn, Mo, Cu,Co, Cr,Se, As, Ni,Si and B. These elements in the body produce toxic effect.

Biological importance of iron

In the body, iron is absorbed in the small intestine in the form of Fe^{2+} ion. Which is the central metal ion is red blood corpuscles.

A healthy adults needs between 10 to 18mg of iron each day in his food. Ferrous ions are found in many important enzymes and electron carrier molecules. A small reduction in the level of iron in the blood will result in a conditions known as anemia, which causes body weariness, fatigue and apathy.

Children with iron deficiencies show a decreased growth rate, mental slowness and abnormal red blood cell growth. Abnormally high levels will cause cirrhosis of the liver, fibrosis of the pancreas resulting in diabetes and congestive heart failure. It has significant role in respiration and photosynthesis.

Biological aspects of Zinc:

It is an important micronutrient, which is a co-factor in a number of enzyme systems especially carbonic anhydrase which is concerned in the excretion and transport of carbon dioxide. An average mixed diet contains 10-15 mgZn. It is an element essential for normal growth, reproduction and longevity of animals. Zinc is necessary for maintaining the plasma concentration of vitamin A, essential for many enzymes, normal liver function, and DNA synthesis, Zinc deficiency lead to delayed wound healing and impairment of waste participates in protein synthesis.

Biological aspects of magnesium:

The magnesium ion forms the central metal ion of the chlorophyll molecule, which traps energy from sunlight in the process of photosynthesis and which gives green colour to the plants. These ions activate many of the enzymes that control the addition and removal of phosphate groups from compounds in the cell. They are crucial in regulating nerve functions and muscle contraction.

When the magnesium level in the body is lowered, a person may suffer emotional irritability and aggressiveness muscle spasms.

Deficiency in magnesium also effect heart rhythm and general cardiovascular function. Too much magnesium produce paralysis.

Biological aspects of cobalt:

Cobalt is a part of vitamin B_{12}. which is required for the formation of erthyocytes or red blood cells. Cobalt that we need are obtained from dairy products and meat. A lack of cobalt in the diet results in disease called pernicious anemia, which produces symptoms of fatigue and general weakness. Too much vitamin B_{12} in the diet will stimulate the production of too many erythrocytes, producing a condition called polycythemia.

Biological aspects of molybdenum.

Dietary sources of molybdenum include plants in the pea family, cereals, yeast. Molybdenum participates in the energy transfer reactions in the cell. It is necessary for the function of certain intestinal enzymes. The chief role of molybdenum is to activate nitrate reductase enzyme during nitrogen metabolism.

Biological aspects of sodium

Forms the alkali reserve of the body and acts as a buffer of blood and tissue. It is the main base of the body. It is one of the most important cation responsible for maintaining the internal environment by maintaining the osmotic pressure, volume and composition of the extra cellular fluid. It maintains neuromuscular conductivity and irritability. Human requirement of salt 1-2 grams per day.

Biological aspects of potassium

Potassium is present in the intracellular fluid of the body. Average daily requirement of potassium in an adult is 4g. It is responsible for maintaining cardiac – rhythmicity. Excess or lack of potassium depresses neuro-muscular conduction. It serves as an activator for about 40 different enzymes. Potassium deficiency is known as hypokalemia.

Biological aspects of calcium:

Calcium is the fifth most common element in the body. Calcium is Important for the formation of strong bones and teeth. It is especially important in maintaining the rhythmic contraction of the heart muscle. A specific level of calcium ions in the fluid of the brain is critical in maintaining body temperature. Calcium ions play a vital role in the clotting of blood. Calcium aminosalicylates are used as antitubercular drug.

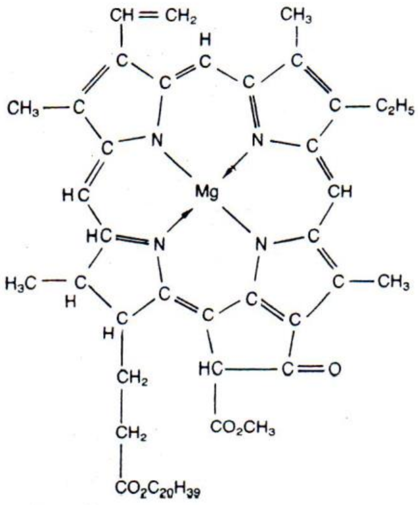
Biological aspects of Phosphorus:

Phosphorus is an important element in the formation of bones and teeth. The dihydrogen and monohydrogen phosphate ion act as buffers, which help to maintain the proper P^H of body fluids. It is essential for fat and albumin formation. It plays important role in energy transfer reaction and in oxidation – reduction reaction.

Biological aspects of chlorophyll:

Chlorphyl is a magnesium porphyrin complex. It is present in the green plants. It consists of two distinct but chemically related substances. They are i) Chlorophyll – a of blue colour and

iii) Chlorophyll of yellow colour. The most common chlorophyll is chlorophyll a



Biological importance

Its presence in essential for photosynthesis in plants. Chlorophyll causes the combination of CO_2, H_2O in presence of sunlight to form starch.

$nCO_2 + n_{H2}O \rightarrow (CH_2O)n + no_2$

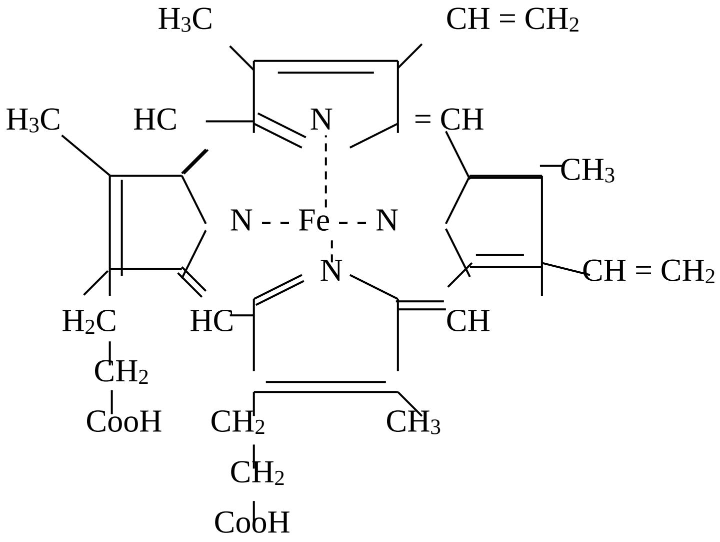
CO_2 and H_2O being colourless do not absorb any portion of visible light. But chlorophyll, the green colouring matter of the plants can capture and transmit the light energy for the chemical reaction taking place in photosynthesis.

Mg^{2+} ions act as a source of phosphorescence, which in turn is responsible for making the light energy available for photosynthesis. Free porphyrins show only florescent emission. So, if free porphyrins alone are present, then the absorbed light energy will be lost through fluorescence and thus will not be available for photosynthesis.

Biological role of haemoglobin

Hemoglobin is the red pigment of the blood and comprises a chromo protein. It consists of a non-specific simple protein and a specific prosthetic group haem, which is an iron containing pigment. The empirical formula of hemoglobin is $C_{738} H_{1166} FCN_{203} O_{208} S_2$ and its molecular weight is 64500. One molecule of hemoglobin contains 4 atoms of iron and 8 atoms of sulphur.

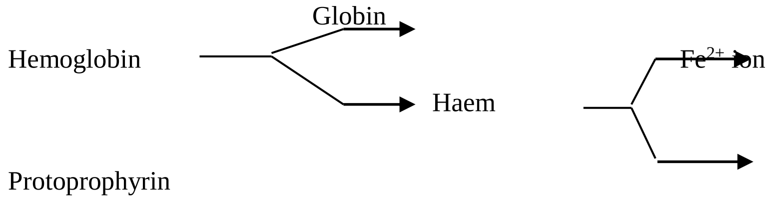
Structure



Protoporphyrin

Haem is a compound of protoporphyrin and a metallic iron, hence it is a metallo porphyrin in which the metal is the iron. Porphyrin unit consists of heterocyclic compounds containing a ring structure which is formed by linking four pyrrole rings by methylidene bridges to form a porphyrin. The two hydrogens atoms in the –NH groups of 2 pyrrole rings are replaced by Fe^{2+} ion. The porphyrin ring can be readily synthesized from simple substance like glycine.

The globin of hemoglobin molecule, Consists of four polypeptide chains on either side. In each side, the polypeptide chain is divided into two chains: one α-chain containing 141 amino acids and a βchain containing 146 amino acids. Each chain is attached with the iron of the harm. A bond of iron remains free which combines with oxygen.



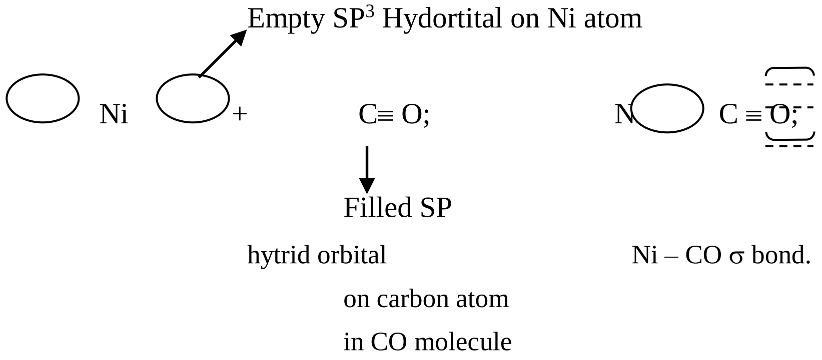
The iron content of haemoglobin is about 0.34% and the iron content of the total amount of blood in an adult is about 3g. In haemoglobin iron remains in ferrous form and when it combines with oxygen it is not converted intoferric form, in other words, oxyhaemoglobin is oxygeneated haemoglobin and not oxidized haemoglobin. The combination of harm with globin helps in keeping the iron in ferrous state and at the same time it also helps to combine molecular oxygen loosely.

4.2 Metal carbonyls

Bonding in Carbonyls

The electronic configuration of CO molecule shows that it has a lone pair of electrons on carbon and oxygen atom each. Carbon atom can donate its electron pair to a transition metal atom (M) forming OC → M coordinate bond. The compounds formed by the combination of CO molecules with transition metals are known as metallic earbonyls

Empty orbitals on the metal atom hybridise to form empty hybrid orbitals, which overlaps with the filled sp hybrid orbital on C atom of CO molecule. For example, in the formation of Ni← CO σ bond in Ni $(CO)_4$ molecule takes place by the overlap between empty Sp^3 hybrid orbital on Ni atom and filled sp hybrid orbital on C atom of CO molecule.



Since the metal atom in metal carbonyls is in Zero oxidation state, the formation of M← CO σ bond accumulates a negative charge on the metal atom. This accumulation of negative charge is counterbalanced by the transfer of some negative charge from the metal to CO molecule through Π bond, hence, in carbonyls, we have a double bond between the metal atom and CO molecule. One of these bonds is a $M \leftarrow CO$ σ bond and the other is a $M \rightarrow Co$ Π bond. The presence of both the bonds in Carbonyls strengthens M-CO bonds and hence the stability of carbonyls is increased.

$Ni(CO)_4$- Nickel tetra carbonyl

Preparation

i) It is prepared by passing CO over finely divided nickel at 60^0C

$Ni + 4CO \xrightarrow{60^0C} Ni(CO)_4$

ii) It is prepared by the action of CO on nickel (Π) phenyl dithiocarbamte, $Ni(S.S.C\ NH.\ C_6H_5)_2 + 4CO \rightarrow Ni(CO)_4 + Ni(S.S.C\ NHC_6H_5)_2$

iii) By passing CO through an alkaline suspension of $Ni(CN)_2$ or Nic.

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

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

Properties

i) It is a colourless liquid, boiling at 43° C and solidifying at -25°C. It is miscible with benzene and is almost insoluble in water.

ii) It reacts with $H_2 SO_4$ forming $NiSo_4$

$Ni + (CO)_4 + H_4SO_4 \rightarrow NiSO_4 + H_2 + 4CO$

iii) Moist NO gives a blue coloured compound, Ni (NO) (OH) with $Ni(CO)_4$ while dry No gives a blue solution of the composition, $Ni(NO)(NO_2)$.

$2Ni(CO)_4 + 2NO + 2H_2O \rightarrow 2Ni(NO)(OH) + 8CO + H_2$

$Ni(CO)_4 + 4NO \rightarrow Ni(NO)(NO_2) + 4CO + N_2O$

iv) Some or all CO molecules are replaced by monodentate ligands.

$Ni(CO)_4 + 4CNR \rightarrow Ni(CNR)_4 + 4CO$

$Ni(CO)_4 + 4Pcl_3 \rightarrow Ni(PCl_3)_4 + 4CO$

$Ni(CO)_4 + O\text{-}phen \rightarrow Ni(CO)_2(o\text{-}phen) + 2CO$

v) Upon heating to 180^0 C, 4 CO molecules are lost leading to metallic Ni.

$Ni(CO)_4 \xrightarrow{180^0C} Ni + 4CO$

vi) It reacts with halogens to form nickel halides.

$Ni(CO)_4 + 2HCl \rightarrow NiCl_2 + H_2 + 4CO$

vii) Gaseous Hcl decomposes the solution of $Ni(Co)_4$, evolving H_2 and Co.

$Ni(CO)_4 + 2HCl \rightarrow NiCl_2 + H_2 + 4CO$

Uses:

i) Since Ni $(CO)_4$ non heating is decomposed to metallic nickel, it is used in the production of nickel by mond's process.

ii) It is used a catalyst.

Structure:

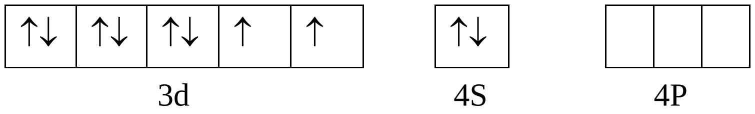
i) The vapour density of $Ni(CO)_4$ and the freezing point of its solution in benzene has shown that the molecular formular is Ni $(CO)_4$

ii) Electron diffraction studies made on this compound in the vapour state and x-ray diffraction studies made on this compound shows that the molecule has tetrahedral shape with Ni-C-O linear units.

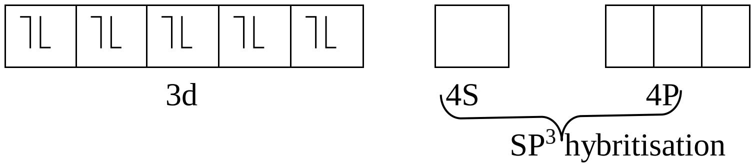
iii) Ni-C bond length is $1.50A^0$ which is shorter by 0.32 A^0in comparison to Ni-C single bond length ($1-82A^0$). The C-O bond length is this carbonyl has been found to be equal to $1.15A^0$ which is larger than C-O band length is CO molecule.

Tetrahedral shape of $Ni(CO)_4$ results from Sp^3 hybridisation of Ni atom. Since $Ni(CO)_4$ molecule is diamagnetic, all the ten electrons present in the valence shell of Ni atom get paired in 3d orbitals. OC→ Ni bond results by the overlap between the empty sp^3 hybrid orbital on Ni atom and doubly filled sp hybrid orbital on C atom in CO molecule:

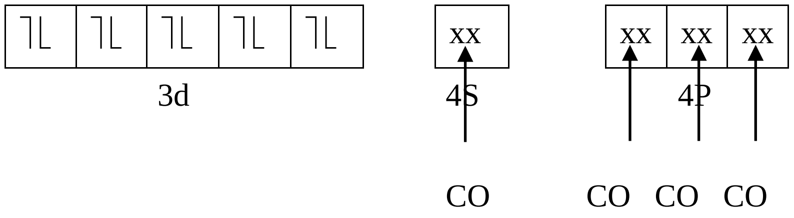
Electronic configuration of Ni atom

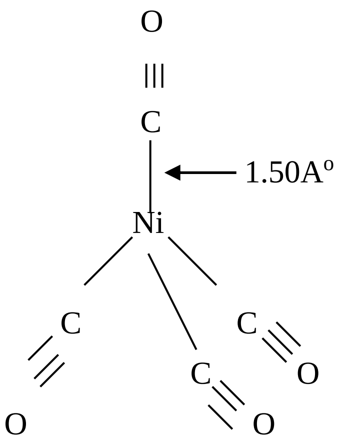


Ni atom in Ni $(CO)_4$



Ni $(CO)_4$ molecule





$Fe(CO)_5$ - Iron pentacarbonyl.

Preparaion:

i) By the direct combination of CO and iron metal.

$$Fe + 5\,CO \xrightarrow[\text{100 atm. pressure}]{200^{o}\,C} Fe\ (CO)5$$

ii) By corbonylating FeI_2 or FeS in presence of Cu metal

$$Fe\,I_2 + 5\,CO + 2\,Cu \xrightarrow[\text{Pressure}]{200^{o}\,C,\ 200\ \text{atm}} Fe\ (CO)5 + Cu\,I.$$

$$2\,Fe\,S + 10\,CO + 2\,Cu \xrightarrow[\text{200 atm. Pressure}]{200^{o}\,C} 2Fe\,(CO)_5 + Cu_2\,S.$$

Properties:

i) $Fe(CO)_5$ is yellow liquid which is soluble in methyl alcohol, ether, acetone and C_6H_6.

ii) On thermal decomposition at 250^0 C, it gives pure Fe

$$2\,Fe(CO)_5 \xrightarrow{250^0C} Fe + 5CO$$

iii) When cooled solution of $Fe(CO)_5$ in glacial CH_3COOH is irradiated with ultraviolet light, $Fe_2(CO)_9$ is formed

$$2\,Fe(CO)_5 \xrightarrow[\text{light}]{\text{ultra violet}} Fe_2(CO)_9 + CO$$

iv) $Fe(CO)_5$ is hydrolysed by H_2O and acids.

$$Fe(CO)_5 + H_2SO_4 \rightarrow FeSO_4 + 5CO + H_2$$

v) When heated with aqueous or alcoholic solution of NaOH, carbonylate anion $[Fe(CO)_4 H^+]^-$ is formed. Fe is in -2 oidation state.

$Fe(CO)_5 + 3 NaOH \rightarrow Na[Fe(CO)_4] + Na_2 CO_3 + H_2O$

vi) With NH_3 it gives $Fe(CO)_4 H_2$ and carbonic acid, NH_2COOH.

$Fe(CO)_5 + H_2O + NH_3 \rightarrow Fe(CO)_4 H_2$ and carbamic acid, NH_2COOH

vii) It reacts with halogens in non aqueous solvents to form stable tetracarbonyl halides, $Fe(CO)_4X_2$.

$Fe(CO)_5 + X_2 \rightarrow Fe(CO)_4X_2 + CO$

viii) When $Fe(CO)_5$ reacts with ethylene diamine, an addition product $Fe(CO)_5$ is formed. Pyridine reacts with it to give $(Fe(py)_6)[Fe_4 (CO)_5]$

$Fe(CO)_5 + en \rightarrow Fe(CO)_5\, en$

$5Fe(CO)_5 + 6\, py \rightarrow [Fe(py)_6]\, [Fe_4 (CO)_{12}] + 12\, CO$.

ix) When $Fe(CO)_5$ reacts with No at 95^0C,

$Fe(CO)_5 + 2No\ 95^0C \longrightarrow Fe(Co)_2\, (NO)_2 + 3CO$

x) When $Fe(Co)_5$ reacts with halides, $FeCl_2$ or carbonyl halides of Fe(Π) are formed.

$Fe(CO)_5 + SO_2Cl_2 \rightarrow FeCl_2 + SO_2 + 5CO$

$Fe(CO)_5 + SnCl_4 \rightarrow Fe(CO)_4 + Sncl_2 + CO$

xi) When $Fe(CO)_5$ is burnt in air, $Fe_2\, O_3$ is obtained

$4\, Fe(CO)_5 + 3O_2 \rightarrow 2Fe_2O_3 + 2OCO$

Uses:

i) Sometimes it is used as a antiknocking agent

ii) It is useful for the preparation of metal powders containing spherical particles.

Structure:

i) The Vapour density and freezing point depression of iron pentacarbonyl in C_6H_6 solution has shown that the molecular formula of this compound in $Fe(CO)_5$.

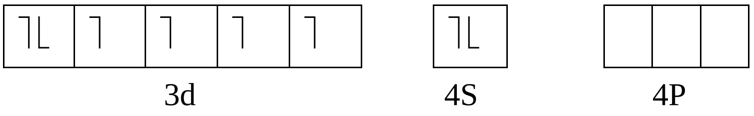
ii) Electron diffraction, Raman and infra red studies of this compound have shown that $Fe(CO)_5$ molecule has trigonal bipyramidal shape.

iii) Electron diffraction study of $Fe(Co)_5$ in the vapour state has shown that Fe-C axial bond and Fe-C basal bond lengths are equal to $1.797A^0$ and $1.842\ A^0$.

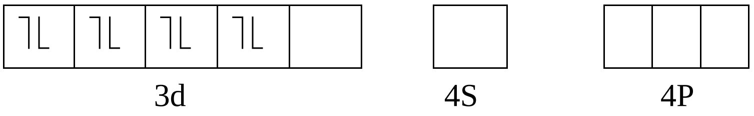
iv) Trigonal bipyramidal shape results from dsp^3 hybridisation of Fe atom.

In this molecule, Fe is in Zero oxidation state and since Fe(CO)$_5$ is diamagnetic, all the eight electrons in the valence shell of Fe atom get paired in 3d orbital. OC → Fe σ bond results by the overlap between empty dsp^3 hybrid orbital on Fe atom and doubly filled sp hybrid orbital. On C atom in co molecule.

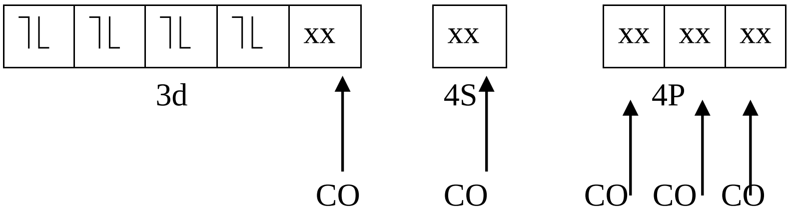
Electronic configuration of Fe atom

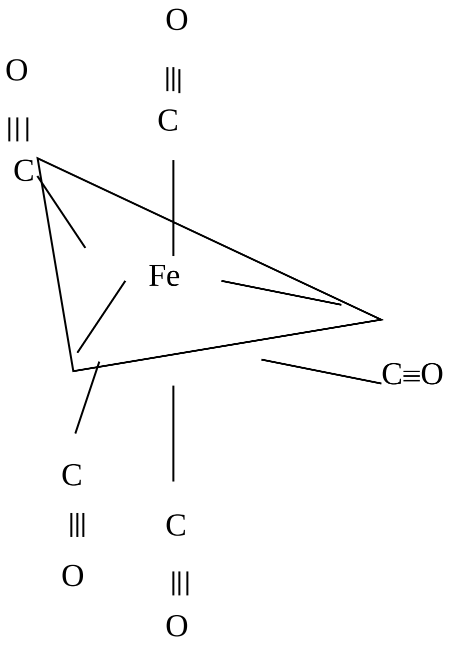


Fe atom in Fe (CO)$_5$



Fe(CO)$_5$molecule





Fe$_2$ (Co)$_9$ Diiron ennea carbonyl

Preparation:

When cooled solution of $Fe(CO)_5$ in glacial CH_3COOH is irradiated with ultraviolet light for six hours.

$2\ Fe(CO)_5 \xrightarrow{\text{UV light}} Fe_2(CO)_9 + CO$

Properties:

i) $Fe_2(CO)_9$ forms triclinic crystals, which are diamagnetic. It is slightly soluble in alcohol, acetone and more so in toluene and pyridine and insoluble in water.

ii) When warmed to 50^0 it gives $Fe_3(CO)_{12}$.

$3Fe_2(CO)_9 \xrightarrow{50^0C} 2Fe_3(CO)_{12} + 3CO$

iii) When its solution in toluene is heated to 70^0C, and then cooled, green crystal of $Fe_3(CO)_{12}$ are obtained.

$3Fe_2(CO)_9 \xrightarrow[\text{Cool}]{70^0C} 3Fe_3(CO)_{12} + Fe_3(CO)_5 + Fe_3(CO)_{12} + 6CO$

iv) With NO, it gives $Fe(CO)_2(NO)_2$ along with $Fe(CO)_5$ and $Fe_3(CO)_{12}$

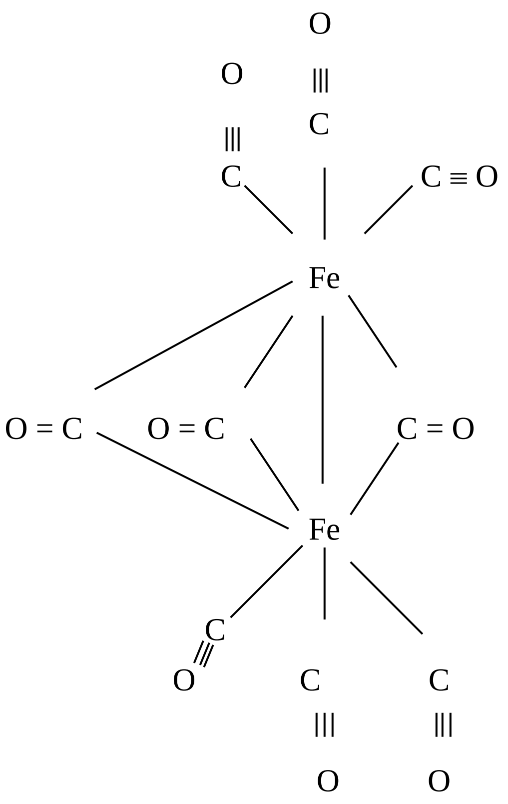
$3\ Fe_2(CO)_9 + 4NO \rightarrow 2Fe(CO)_2(NO)_2 + Fe(CO)_5 + Fe_3(CO)_{12} + 6CO$.

v) Carbonylate anion is formed when it is treated with Na in liq NH_3 Solution.

$Fe_2(CO)_9 + 4Na \rightarrow 2Na_2[Fe(CO)_4] + CO$

Structure:

I) Infra red and X-ray crystal studies made on $Fe_2(CO)_9$ molecule have shown that in this molecule each Fe atom in directly linked with the other Fe atom by a 8 bond, to three bridging carbonyl groups by σ bond, and to three terminal carbonyl groups by a coordinate bond. Fe-Fe bond distance is found to be equal to $2.46A^0$. The terminal C-O bond distances are smaller than the bridging C-O bond distances.



Fe_3 $(Co)_{12}$ Tri-iron dodeca carbonyl

Preparation:

i) By heating toluene solution of $Fe_2(CO)_9$ to 70^0 C and then cooling the solution.

$$3Fe_2(CO)_9 \xrightarrow{700C} 3Fe_3(CO)_5 + Fe_3(CO)_{12}$$

ii) By the oxidation of Fe $(CO)_4H_2$ with H_2O_2 or Mno_2.

$$3Fe_2(CO)_4 + 3H_2O_2 \rightarrow Fe_3(CO)_{12} + 6H_2O$$

$$3Fe_2(CO)_4 H_2 + 3MnO_2 + 3 H_2 SO_4 \rightarrow Fe_3(CO)_{12} + 3MnSO_4 + 6H_2O$$

Properties

i) $Fe_3(CO)_{12}$ forms deep green crystals, which are soluble in organic solvents like toluene, alcohol, ether and pyridine.

ii) When heated to 140°C, $Fe_3(CO)_{12}$ decomposes to give metallic iron and CO

$$Fe_3(CO)_{12} \xrightarrow{140^0C} 3Fe + 12CO$$

iii) Carbonylate anion is obtained when $Fe_3(Co)_{12}$ reacts with Na metal in liq NH_3

$$6Na + Fe_3(CO)_{12} \xrightarrow{liq.\ NH3} 3Na_2[Fe(CO)_4]$$

iv) Substitution reactions occur with methyl alcohol and pyridine.

$2Fe_3(CO)_{12} + 3py \rightarrow Fe_3(CO)_9(py)_3 + 3Fe(CO)_5$

$2Fe_3(CO)_{12} + 3CH_3OH \rightarrow Fe_3(CO)_9(CH_3OH)_3 + 3Fe(CO)_5$

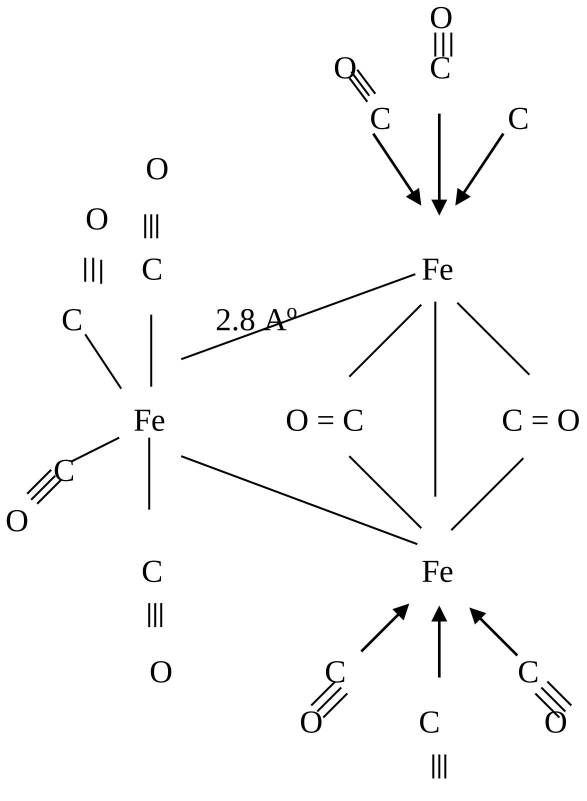
v) At 85^0 C, it reacts with No to form iron. Dicarbonyl dinitrosyl, $Fe(CO)_2(NO)_2$.

$Fe_3(CO)_{12} + 6NO \rightarrow 3Fe(CO)_2(NO)_2 + 6CO$

Structure:

Molecular weight determination of this compound corresponds to the molecular formula $Fe_3CO)_{12}$ X-ray study has shown that in this molecule a) Each of the two Fe atoms is inked with three terminal carbonyl groups, two bridging carbonyl groups and to the third. Fe atom, b) the remaining thire Fe atom is linked with four terminal carbonyl groups and to each of the two Fe atoms, c) Three

Fe-Fe bonds are also present. Fe-Fe bond distance is $2.8A^0$.



Cr (Co)$_6$ - Chromium hexacarbonyl.

Preparation:

i) By treating $COCl_3$ with CO in presence of a reducing agent like lithium aluminum hydride, Li Al+

$CrCl_3 + CO + LiAl\,H_4 \xrightarrow[\text{Pr.}]{175^0C,\ \text{To atm}} Cr\,(CO)_6 + Li\,Cl + Al\,Cl_3$

ii) By treating $CrCl_3$ with CO in presence of $C_6\,H_5\,Mg\,Br$ under appropriate conditions.

Properties:

i) It is a white solid, soluble in ether, chloroform, CCl_4 and $C_6\,H_6$

ii) It does not react with air, cold aqueous alkalies and acids.

iii) It is decomposed by F_2 at - 75^0C to form CrF_6

iv) When $Cr\,(CO)_6$ is treated with Na metal or $NaBH_4$ in liq. NH_3, carbonylate anion is formed.

$Cr\,(CO)_6 + 2Na \xrightarrow{\text{liq } NH_3} Na_2\,[Cr\,(CO)_5] + CO$

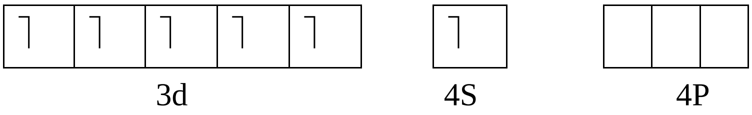
v) Some Co groups present in $Cr\,(CO)_6$ can be replaced by pyridine to get a number of products.

$Cr\,(CO)_6 \xrightarrow{py} Cr\,(CO)_4(py)_2 \xrightarrow{py} Cr_2\,(CO)_7\,(py)_5$

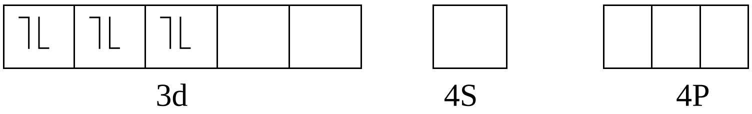
Structure:

The electron diffraction study of $Cr(Co)_6$ molecule in vapour state has shown that the molecule has octahedral shape. Cr-C and C-O bond lengths are 1.92^0. Cr atom is in zero oxidation state and $Cr(CO)_6$ is diamagnetic, all the six electrons get paired in 3d orbitals. OC → C_r σ bond results from the overlap between an empty d^2Sp^3 hybrid orbital on Cr atom and doubly filled sp hybrid orbital on C atom in CO molecule.

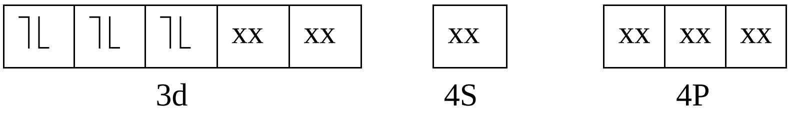
Electronic configuration of Cr atom



Cr atom in $Cr\,(CO)_6$



$Cr\,(CO)_6$ molecule



$CO_2\,(CO)_8$ – Dicobalt octacarbonyl

Preparation:

i) By direct combination of CO with cobalt metal.

$2\,Co + 8CO\ 200^0C,\quad Co_2\,(CO)_8$

$\xrightarrow[\text{100 atm.pr}]{}$

ii) By treating COS with CO in presence Cu metal

$2\ Co + 8CO + 4Cu\ 2000C, \xrightarrow[\text{100 atm.pr}]{} Co_2\ (CO)_8 + 2Cu_2S$

Properties:

i) It is thermally decomposed at 50^0 C to give tetracobalt dodeca carbonyl, $2Co_2\ (CO)_8 + 50^oC, \longrightarrow Co_4\ (CO)_{12} + 4CO$

ii) When $Co_2\ (CO)_8$ reacts with H_2 at 165^0C and 200 atmospheric pressure, it gets reduced to cobalt carbonyl hydride. $[Co\ (CO)_{4H}{}^{+}]$.

iii) $Co_2\ (CO)_8 + H_2\ 165^0C$, 200 atm

$$\xrightarrow[\text{Pressure}]{} 2[Co(CO)_4\ H^+]$$

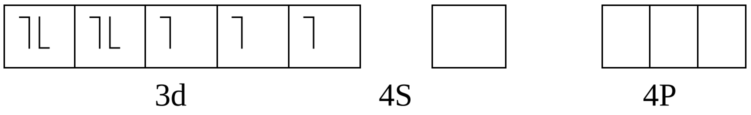
iv) When $Co_2\ (CO)_8$ reacts with Na metal in liquid NH_3, below -75^0C, it gets reduced to carbonylate anion, $[Co\ (CO)_4]^-$

$Co_2(CO)_8 + 2Na \xrightarrow{liqNH_3} 2Na[Co(CO)_4]$

Structure

Infra –red study has shown that in solution, this compound exists in two isomeric forms. One of these forms has a bridged structure and the other has a non –bridged structure. The bridged structure has two bridging carbonyl groups, six terminal carbonyl groups and one Co - Co bond. Each of the two Co atoms is directly linked with other Co atom by a Co-Co bond. Co-Co bond distance is equal to $2.52A^0$.

Electronic configaration of CO atom

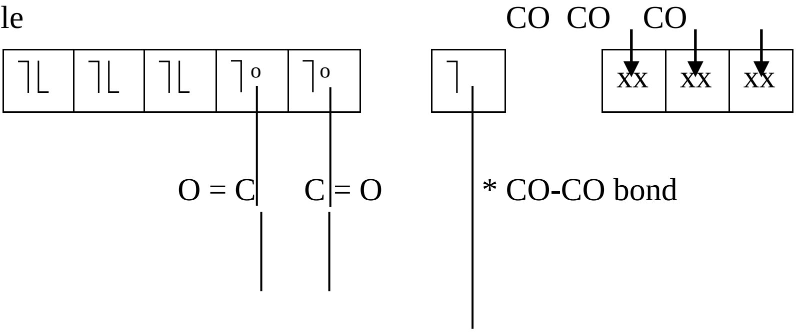


One CO atom in

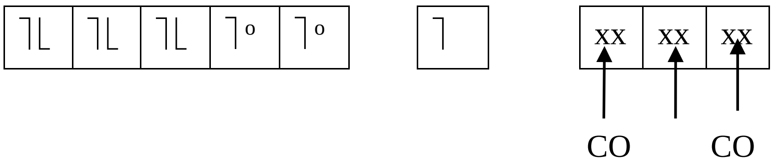
$CO_2\ (CO)_8$ molecule

Other CO atom in

$CO_2\ (CO)_8$

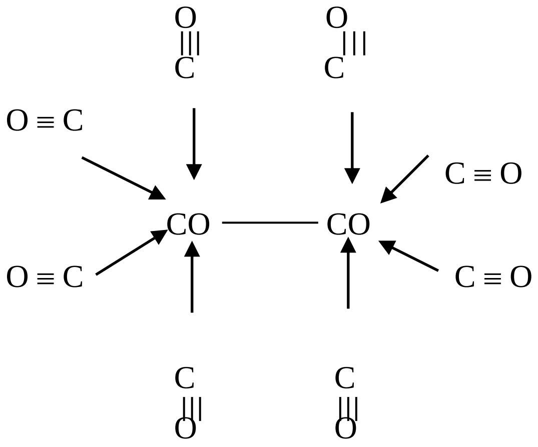


Molecule



CO

The non –bridged structure has one C0-Co bond and eight terminal carbonyl groups. Each of the two Co atoms is directly linked with the other by a Co-Co bond and with four terminal groups.



At very low temperature, the bridged structure predominates and as the temperature is raised, non - bridged structure appears.

$Mn_2(CO)_{10}$ – Dimanganese decacarbonyl

Preparation

i) By treating MnI_2 with CO in presence of Mg which acts as a reducing agent.

$$2MnI_2+10CO+2Mg \xrightarrow[\text{Pressure}]{25^0C,\ 210atm.} Mn_2(CO)_{10}+2MgI_2$$

ii) By treating $MnCl_2$ with co in presence of $(C_6H_5)_2$ CoNa.

$$2MnCl_2+10CO+4(C_6H_5)_{2CoNa} \xrightarrow[\text{Pressure}]{165^0C,\ 140atm.} Mn_2(CO)_{10}+4(C_6H_5)_2Co+4Nacl.$$

Properties:

i) It reacts with halogens to form carbonyl halides, Mn (CO) $(CO)_5$ X.

$Mn_2(CO)_{10} + X_2 \rightarrow 2Mn\,Co_5\,X$.

ii) Na metal in liquid NH_3 converts $Mn_2(CO)_{10}$ into carbonylate anion.

$Mn_2(CO)_{10}$ + 2Na liq NH_3 Na [Mn (CO)]$_5$

iii) $Mn_2(CO)_{10}$ gives carbonyl hydride, Mn $(CO)_5$ H.

$Mn_2 (CO)_{10}$ (Mn = 0) +H_2 $\xrightarrow{200^0C,\ 200\ atm.\ Pressure}$ 2 $[Mn^-(CO_5H+]^0$

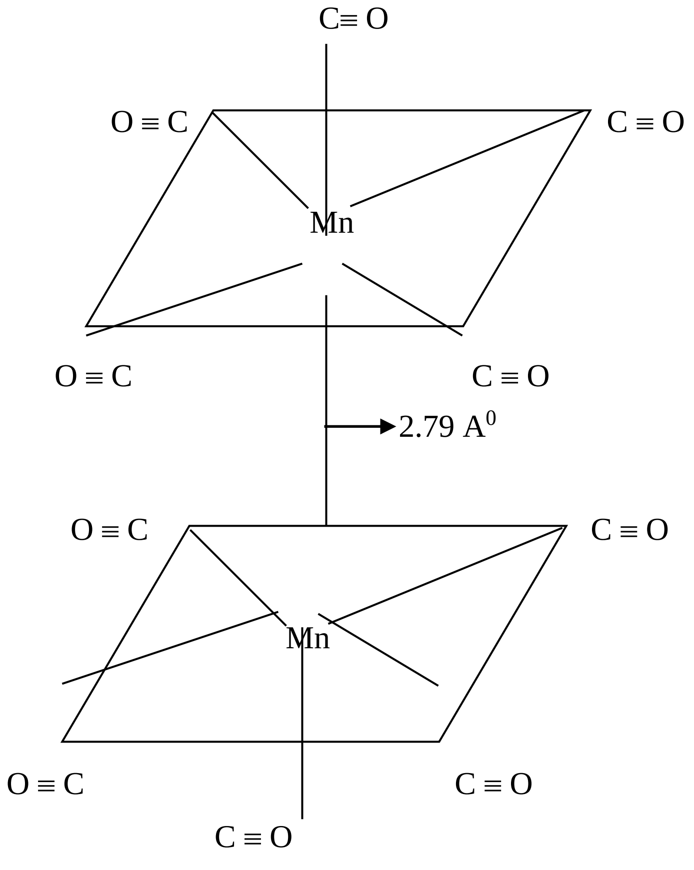
iv) Mn_2 (Co) $_{10}$ react with PR3 to form Mn (CO) 4 (PR3)

$Mn_2 (CO)_{10} + PR_3 \rightarrow 2Mn(CO)_4 (PR_3) + 2CO$.

Structure:

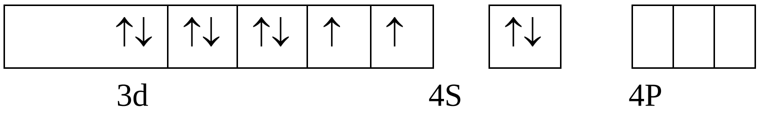
The molecular weight of this compound indicates that this compound has dimeric formula, Mn_2 $(Co)_{10}$.The infrared absorption spectral and x-ray diffraction studies made on Mn_2 $(Co)_{10}$ molecule have shown that in this molecule each Mn-atom is directly linked with the other Mn-atom by a σ- bond (Mn – Mn σ - bond) and to five terminal carbonyl groups (- C ≡ 0). By a co-ordinate bond (Mn ← Co- coordinate bond). The presence of Mn – Mn σ - bond is also supported by the diamagnetic character of Mn_2 $(Co)_{10}$ molecule. Mn – Mn bond distance has been found to be equal to 2.79A°. It may be seen that co-ordination number of each

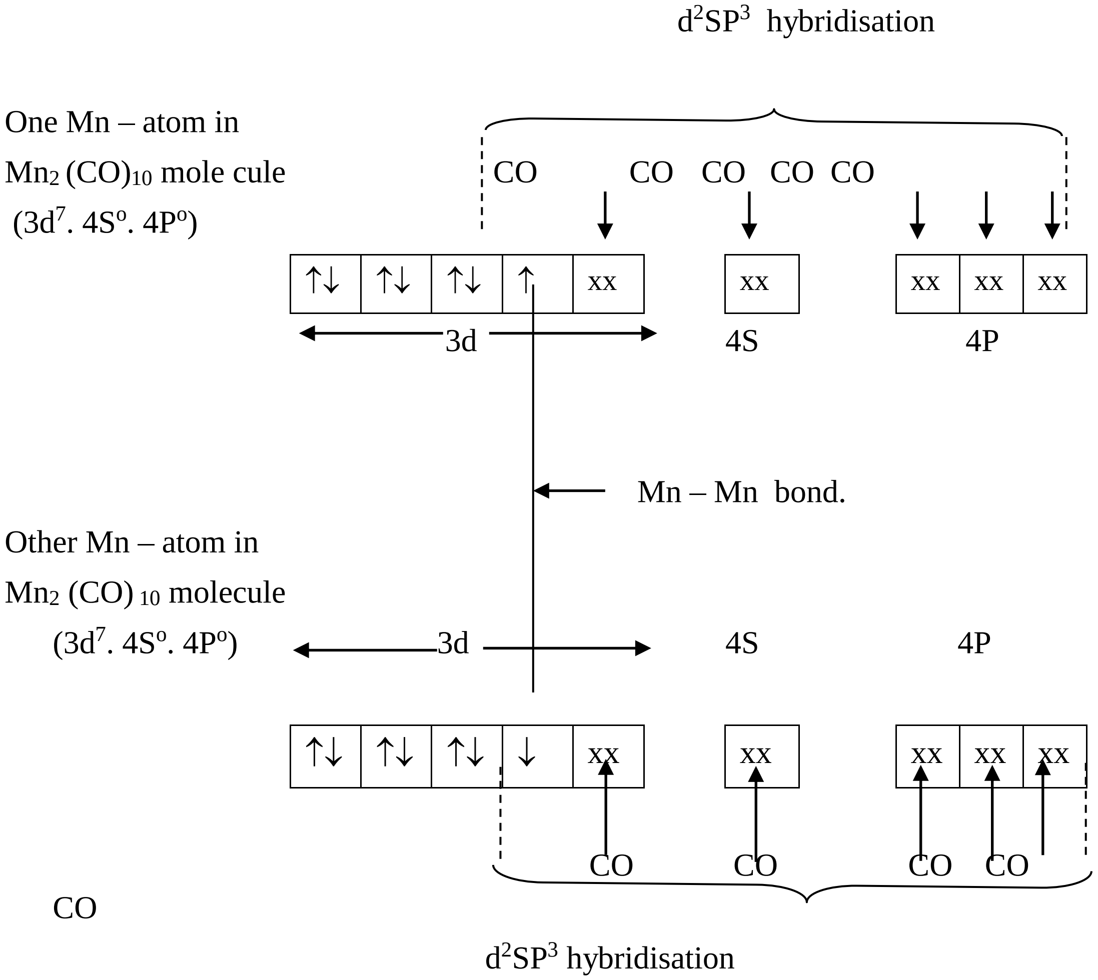
Mn – atom in this molecule is six and the molecule has no bridging carbonyl groups (> C = 0) in between two Mn – atoms.



Free – Mn - atom

($3d^5$. $4S^2$. $4P^o$)





4.3. Silicates:

Silicates may be regarded as the metal derivatives of the silicic acid, H_4SiO_4. Silicates can be prepared by fusing metal oxides or metal carbonates with sand (SiO_2). For example.

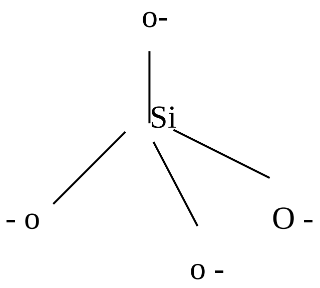
$Na_2Co_3 \xrightarrow{\text{fuse with sand } (SiO_2)} Na_2SiO_4,(Na_2SiO3)_n$ etc.

Only some silicates of alkali metals are soluble in water while others are insoluble. The insolubility is due to the great strength of Si-O bond. When silicates are treated with HF, Si-O bond is broken.

Classification and structure of silicates:

X-ray diffraction studies of various types of silicates have shown that all the silicates have SiO_4^{-4} anions, which are formed by Sp^3 hybridization of Si atom. Si atom in its excited state contains 4 unpaired electrons and hence forms

4 covalent bonds with four negatively - charged O-atoms, resulting in the formation of SiO_4^{4-} anion. Each O – atom becomes negatively charged by picking up an electron from some metal. Since Si atom under goes Sp^3 hybridization, SiO_4^{4-} anion has tetrahedral shape.



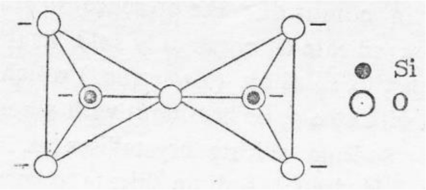
Silicates are classified according to the nature of linking between the tetrahedral SiO_4^{4-} anions.

i) **Orthosilicates:**

These silicates contain discrete SiO_4^{4-} tetra hedral anions. The O – atom of each SiO_4^{4-} is coordinated to the metal ion. Examples are phenacite, Be_2SiO_4, will mite, Zn_2SiO_4, zircon $ZrSiO_4$.

ii) **Pyrosilicates:**

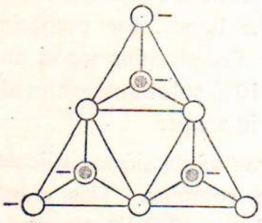
These silicates contain the discrete $Si_2O_7^{6-}$ anion which is formed by joining two SiO_4 tetrahedral units through one oxygen atom. Examples are thortereitite, $Sc_2(Si_2O_7)$ and hemimorphite, $Zn_3Si_2O_7 . Zn(OH)_2 . H_2O$.



iii) **Cyclic or ring silicates:**

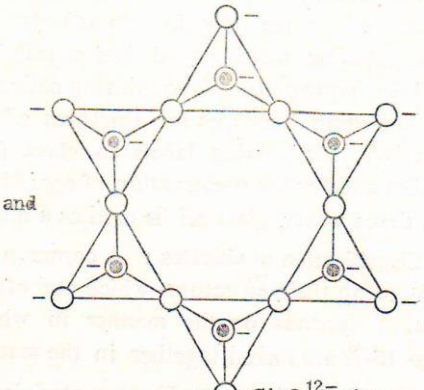
These contain cyclic or ring anions like $Si_3O_9^{6-}$ or $Si_6O_{18}^{2-}$.

Examples are benitoite, $BaTiSi_3O_9$, and wollastonite, $Ca_3Si_3O_9$.



$Si_3O_9^{6-}$ ion

and



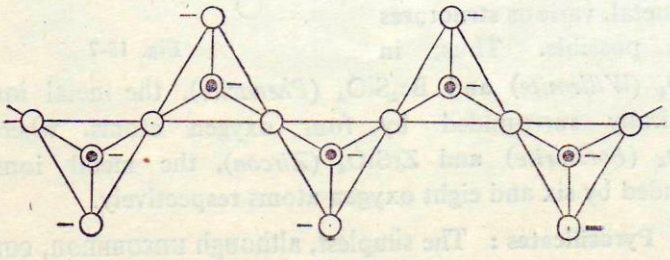
$Si_6O_{18}^{12-}$ ion

iv) Chain silicates:

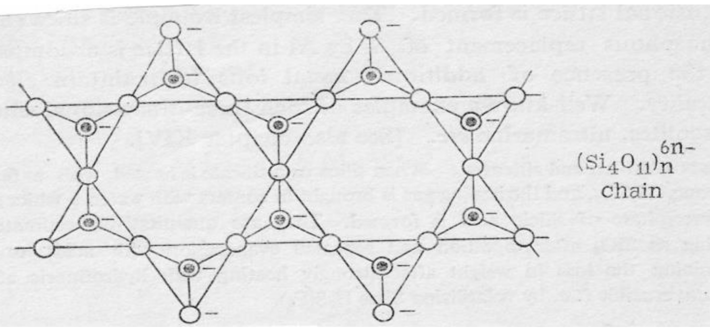
Such silicates contain the anion, which are formed by sharing of two oxygen atoms by each tetrahedron. The anions may be one of the types.

a) $(SiO_3)^{2n-}$ b) $(Si_4O_{11})^{6n-}$

Examples are synthetic silicates, Li_2SiO_3. And pyroxene minerals spodurene, $LiAl(SiO_3)_2$



$(SiO_3)_n^{2n-}$ chain

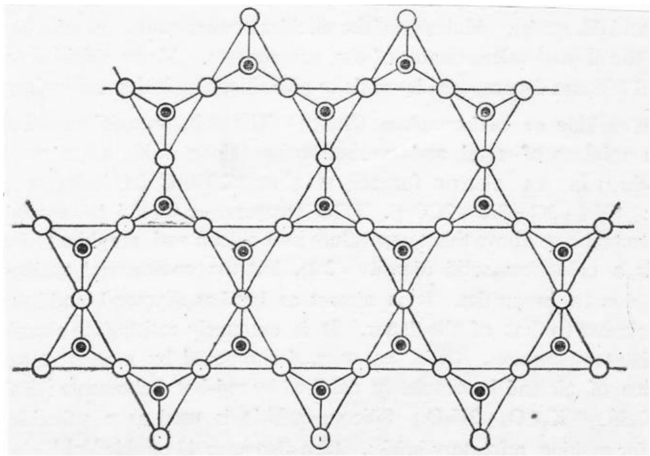


$(Si_4O_{11})_n^{6n-}$ chain

v) Two dimensional sheet silicates:

When 3 O-atoms of each SiO_4 tetrahedron are shared with adjacent SiO_4 tetrahedra, an infinite two dimensional sheet structure of the composition. $(Si_2O_5)_n^{2n-}$ results. Talc, $Mg_2(Si_2O_5)_2.Mg(OH)_2$ and kaolin, $Al_2(OH)_4((Si_2O_5)$ are the common examples.

FIGURES



vi) Three dimensional sililcates:

When all the four oxygens of a SiO_4 tetrahedron are shared with adjacent tetrahedral and the process is repeated, leads to three-dimensional silicate. Examples, quartz, tridymite.

4.4 Organometallic compounds.

4.4.1 Definition.

Organometallic generally denotes compounds in which organic groups are linked directly to the metal through at least are carbon atom.

Classification:

Ionic compounds:

The organo metallic compounds of highly electropositive metals are ionic with the exception of Li, Be and Mg. Three are generally colorless, extremely reactive, nonvolatile solids, insoluble in hydrocarbon solvents. On heating they generally decompose without melting. The stability and reactivity of ionic compounds are affected by the stability of their carbanions. With stable carbanions, the metal derivatives are comparatively more stable and less reactive.

σ- Bonded compounds:

Organometallic compounds, in which a carbon atom of the organic moiety is bonded to the metal by 2- electron, two centered covalent bond, are generally formed by most elements with values of electro negativity higher than 1. The chemistry of these compounds is in general similar to that of organic compounds. The σ – bonded organo metallics of transition metals are generally less stable than those of the main group elements.

Non - classically bonded organometallics:

An electron deficient compound $[Be(CH_3)_2]_n$ which uses one s & p^3 hybrid orbital of each methyl group and all of the Sp^3 hybrid orbitals of Be in bridge bonds.

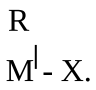
4.4.2 General methods reactions:

Formation by addition reactions:

These reactions constitute one of the principal routes for the formation of metal-carbon bonds and occur with metals of high electro positivity.

$2M+RX \rightarrow MR+MX$

$M+ RX \rightarrow$



$\overset{R}{\overset{|}{M}}-X.$

These reactions involve changes in oxidation states. With more electropositive metals e.g. Sodium or caesium, the initially formed metal alkyl has a strong tendency to undergo Wurtz – fitting reaction, which is avoided by using finely divided metals and efficient stirring. The alkyls of less electro positive metals have generally been prepared, by using the metal in the form of an alloy.

$2EtI + 2Hg/Na \longrightarrow HgEt_2 + 2NaI$

$4RX + 4Sn/Na \longrightarrow SnR_4 + 3Sn + 4Nax$

$4EtX + rpB/Na \longrightarrow PbEt_4 + NaX + Pb$

Substitution reactions:

$M + M'R \rightarrow MR + M'$

More electro positive metals take part in these reactions and the reaction of any metal whole M-C bond energy in higher than M' – C bond energy will occur as:

$2Li + MgR_2 \rightarrow 2LiR + Mg$

$2Na + HgR_2 \rightarrow 2NaR + Hg.$

Benzene and toluene are easily mercurated in ethanol to afford mono-substituted products.

$C_6H_6 + Hg(O_2CCH_3)_2 \longrightarrow Hg(O_2CCH_3)C_6H_5 + CH_3COOH$

General properties of organo metallic compounds.

i) Reaction with oxygen and halogen

Most organo metallic compounds of the first three groups react exothermally with oxygen. The lower alkyls of alkali and earth metals are spontaneously inflammable in air. Tetra alkyls of main group IV elements, on the other hand, show stability towards molecular oxygen.

$MR_n + \text{excess } O_2 \rightarrow M_2O_n + CO_2 + H_2O$

$Al\,Et_3$ + limited $O_2 \rightarrow Al\,(OEt)_3$

$Mg\,(R)_X$ + limited $O_2 \rightarrow Mg\,X\,(O_2R)$

Halogens generally cleave the metal- carbon bonds:

$LiR + X_2 \rightarrow LiX + RX$

$BR_3 + I_2 \rightarrow BIR_2 + RI$

$AlR_3 + 3X_2 \rightarrow AlX_3 + 3Rx$

ii) Reactions with protic reagents

Alteyls of the first three main group elements are highly reactive towards water and in most cases lead to violent reactions.

$MR_n + nH_2O \rightarrow M(OH)n + nRH$

The reactivity of metal alkyls towards alcohols, amine having acidic hydrogen atoms is generally milder.

$BeMe_2 + MeOH \rightarrow Be\,(OMe)\,Me + MeH$

$AlMe_3 + MeOH \rightarrow al\,(Ome)\,Me_2 + MeH$

iii) Reactions with hydridic hydrogen

A few organometallic regents such as organolithium or organomagnesium compound can substitute an organic group for hydrogen.

$LiMe + Si\,(H)\,Ph_3 \rightarrow Si\,(Me)\,Ph_3 + LiH$

iv) Pyrolysis

The thermally unstable alkyls of some metals like lead on heating lead to generation of radicals, which play a key role in the antiknock properties.

4.4.3. Organo metallic compounds of Li and B.

Organo lithium compounds.

Preparation:

i) By direct reaction of Li with alkyl or aryl chloride in benzene or petroleum.

$2Li + RCl \longrightarrow LiR + LiCl$

ii) Lithium aryls are best prepared by this method using n- butyl lithium and an aryl iodine.

$n\text{-}C_4H_9Li + ArI \longrightarrow LiAr + nC_4H_9I.$

$n\text{-}C_4H_9Li + C_5H_4NBr \longrightarrow C_5H_4Ni + nC_4H_9Br.$

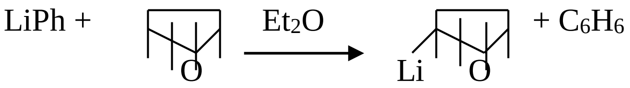
iii) Vinyl, allyl and other unsaturated derivatives can be obtained by transmetallation.

$4\,Liph + Sn\,(CH = CH_2)_4 \longrightarrow 4\,Li\,CH = CH_2 + Sn\,Ph_4.$

iv) Methyl lithium is also prepared by exchange through interaction of n- C_4H_9Li and CH_3 I in hexane at low temperature where it precipitates as insoluble white crystals.

$$n\text{-}\ C_4H_9Li + CH_3I \rightarrow CH_3Li + nC_4H_9I$$

v) By metal – hydrogen exchange.



vi) By deprotonation of alkynes in liquid ammonia solution. Lithium acetyl,

ides and dicarbides are obtained by this method using Li metal and acetylene.

$$Li + Hc \equiv CH \longrightarrow LiC \equiv CH + \frac{1}{2} H_2$$

vii) Excess of Li reacts with an organomerarry compound forming litrium organo metallic compound.

$$2Li + Hg\,R_2 \rightarrow 2LiR + Hg.$$

Properties:

i) Organolithium compounds are thermally unstable and most of them decompose to Li H and an alkene on standing at room temperature.

ii) They are covalent substances, soluble in hydrocarbons or other non-polar liquids.

iii) They react rapidly with oxygen and are usually spontaneously flammable in air, with liquid water and with water vapour.

iv) Li Me and Li Bu are usually synthetic reagents and are used in organic synthesis.

1. Reactions with alkyl iodides give compounds having C-C bonds.

   $$LiR + R'I \longrightarrow LiI + R\text{-}R'$$

2. Reactions with proton donor give the corresponding hydrocarbons

   $$LiR + H^+ \longrightarrow Li^+ + RH$$

3. Reactions with halogens give parent alkyl halide.

   $$LiR + X_2 \longrightarrow LiX + RX$$

4. Reaction with CO gives symmetrical ketones.

   $$2LiR + 3CO \longrightarrow 2LiCO + R\text{-}CO\text{-}R$$

5. Metal – halogen exchange reactions give other organometallic compounds.

   $$3LiR + BCl_3 \longrightarrow 3\,LiCl + BR_3$$

$4LiR + SnCl_4 \longrightarrow 4LiCl + SnR_4$

6. Reaction of lithium aryls in non- polar solvents with CO_2 gives carboxylic acid and with aryl ketones gives tertiary carbinols.

   $LiAr + CO_2 \longrightarrow ArCOO\,Li \xrightarrow{H_2O} LiOH + ArCOOH$

7. Alkyl lithium reacts with chloramines to form a primary amine.

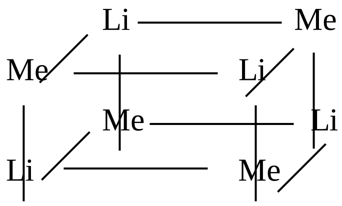
   $RLi + ClNH_2 \longrightarrow RNH2 + Licl$

Uses:

Organolithium compounds are as reactive as grignard reagents. Hence, many organic compounds are prepared using organo lithium compounds.

Structure:

Lithium alkyls are polymeric and generally exist as tetra meric units such as $(Li\,CH_3)_4$. In lithium methyl, there is a tetrahedral set of four lithium atoms with a methyl group placed symmetrically above each Li_3 face. The carbon atoms have coordination number 7 being bonded directly to three H and four Li atoms. The Li – C distance is 231 pm. The Li – Li distance is the structure is 268 pm.



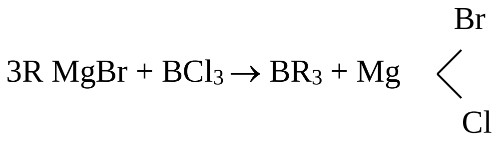
Organoboron compounds

Preparation:

i) Alkyl borons can be easily prepared by hydroboration.

   $6C_2H_4 + B_2H_6 \rightarrow 2B\,(C_2H_5)_3$

ii) The alkyl and aryl borons can be prepared from boron halides by lithium or grignard reagents.



$$3R\,MgBr + BCl_3 \rightarrow BR_3 + Mg\langle{}^{Br}_{Cl}$$

iii) Sodium tetraphenyl borate, $Na\,[B\,(C_6H_5)_4]$ is obtained when boron halides are treated with sodium and four equivalent of alkylation agents such as grignard reagents.

   $BCl_3 + 4C_6\,H_5\,Mg\,Br + Na \rightarrow Na\,[B(C_6\,H_5)\,4] +$

Properties:

i) Lower boron alkyls are reactive but boron aryls are stable.

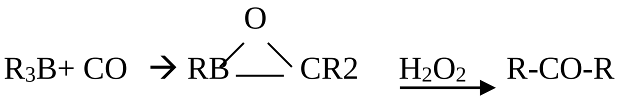
ii) The compound Li (B Me_4) is readily soluble in benzene and can be sublimed.

iii) Hydrolysis of alkyl boron forms many organic compounds. The nature of products depends on the reagent used for hydrolysis.

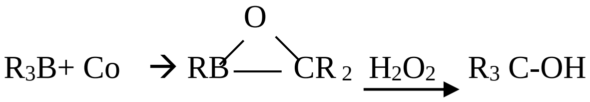
$R_3B + 3HOH \xrightarrow{H^+} 3RH + B(OH)_3$

$R3B + 3H_2O_2 \xrightarrow{OH^-} 3ROH + B(OH)_3$

iv) It reacts with CO to form aldehydes and ketones.



$R_3B + CO \rightarrow RB\overset{O}{\text{——}}CR2 \xrightarrow{H_2O_2} R\text{-}CO\text{-}R$



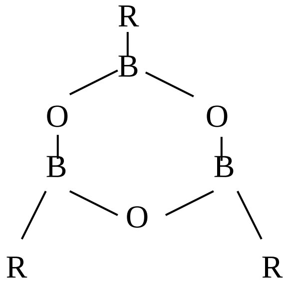
$R_3B + Co \rightarrow RB\overset{O}{\text{——}}CR_2 \xrightarrow{H_2O_2} R_3\,C\text{-}OH$

v) Alkyl boranes in presence of alkaline silver nitrate forms alkanes.

$$RBH_2 + R'BH_2 \xrightarrow[NaOH]{Ag\,NO_3} R\text{-}R'$$

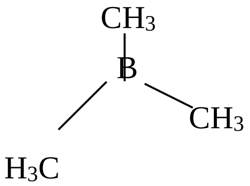
Structure of trialkeylboroxines:

Trialkeyl or aryl boroxines have trimeric, cyclic structures with planar rings of alternating boron and oxygen atoms. The alkyl groups are also in the plane of the ring.



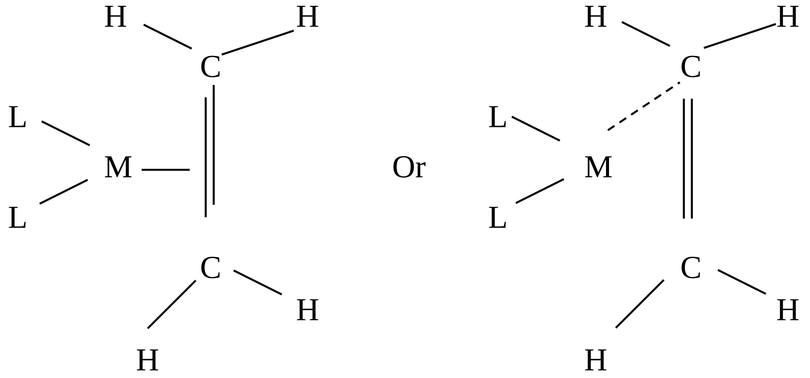
Structure of BMe_3

It is monomeric in solid phase and has trigonal planar shape.



4.4.4. Olefin complexes:

Π - Bonded organometallics of transition metals are much more common. The interactions of the orbital of unsaturated hydrocarbons with these metals bring about novel and non- classical type of bonding. These complexes play an important role in the catalytic reactions of alkenes, alkynes and their derivatives. The alkene – metal bond involves both σ donor and Π -acceptor linkages of these ligands, which plays an important role on the strength of these bonds. The bonding of alkenes to metals is similar to that in metal carbonyls. Derivatives of alkenes are also generally more stable with the metal in low oxidation state and are governed by EAN Rule. The transition metal alkene complexes may be of two general types.



Mono alkenes behave as mono dentate ligands, by occupying one coordination site where as polyalkenes with non- conjugated C=C double bonds may exhibit either chelating or bridging bonding modes.

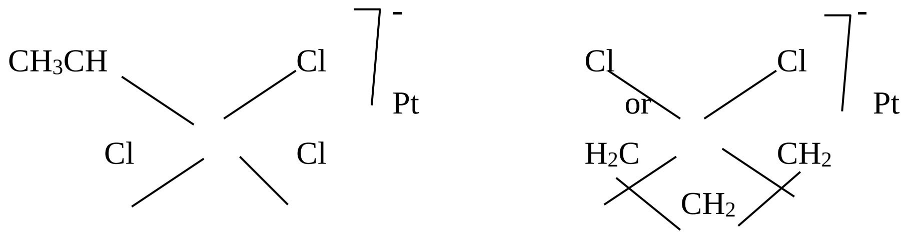
Zeise salt: K [$PtCl_3$ (C_2H_4)].

Preparation:

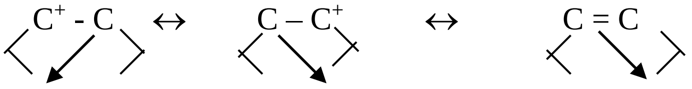
It is prepared by the action of platinum (V) complex on ethylene.

$$K_2[PtCl_4] + C_2H_4 \rightarrow K[PtCl_3.(C_2H_4)] + KCl.$$

Structure:



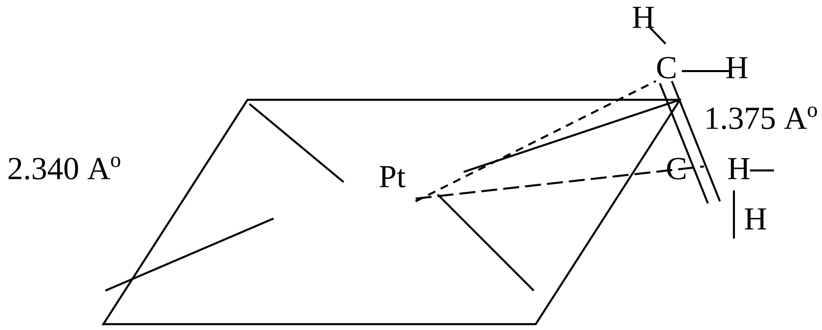
These are the structures suggested for zeise's salt. The bonding is described in terms of a resonating hybrid of the contributing structure.



$PtCl_3$ $PtCl_3$ $PtCl_3$

1. A vacant 5d 6P orbital of the platinum overlaps with bonding molecular orbital of ethylene to give σ- type bond.
2. A π - type bond is formed by overlapping a filled 5d 6P hybrid orbital of

   the platinum atom with ant bonding π_Z 2P molecular orbital of the alkenes. Both donation of π - electron density from the alkene to metal and accumulation of electronic charge in the olefin would be expected to lower the π - bond order of the coordinated alkene.



The C-C bond distance (1.37A°) in the complex is slightly longer than in free ethane which is explained to arise from the population of electrons in the Π^*orbital of ethane, which brings about a change in the bature of the hybrid orbital at carbon atoms.

4.4.5. Cyclopentadienyl complexes- ferrocene.

Preparation:

i) The most general method is the reaction of sodium cyclopentadienide with metal derivative (usually halide or carbonyl) in a solvent like THF, DMF etc.

$FeCl_2 + 2\,Na\,C_5H_5 \rightarrow Fe\,(C_5H_5)_2 + 2NaCl.$

$FeCl_2 + 2\,C_5H_5\,Mg\,Br \rightarrow Fe\,(C_5H_5)_2 + 2\,Mg\,BrCl.$

It is also prepared by the action of $FeCl_2$ with C_5H_5 Mg Br.

ii) The reaction of Ferrous halides with cyclopendtadiene in the presence of a base (in excess) like diethyl amine, piperidine.

$FeCl_2 + 2\,C_5H_6 + 2\,Et_2\,NH \rightarrow Fe\,(C_5H_5)_2 + 2Et_2\,NH_2\,Cl.$

$FeCl_2\,.4H_2O + 2\,C_5H_5 + 3\,KOH \rightarrow Fe\,(C_5H_5)_2$

iii) By the reaction of cyclopentadiene with activated free metal.

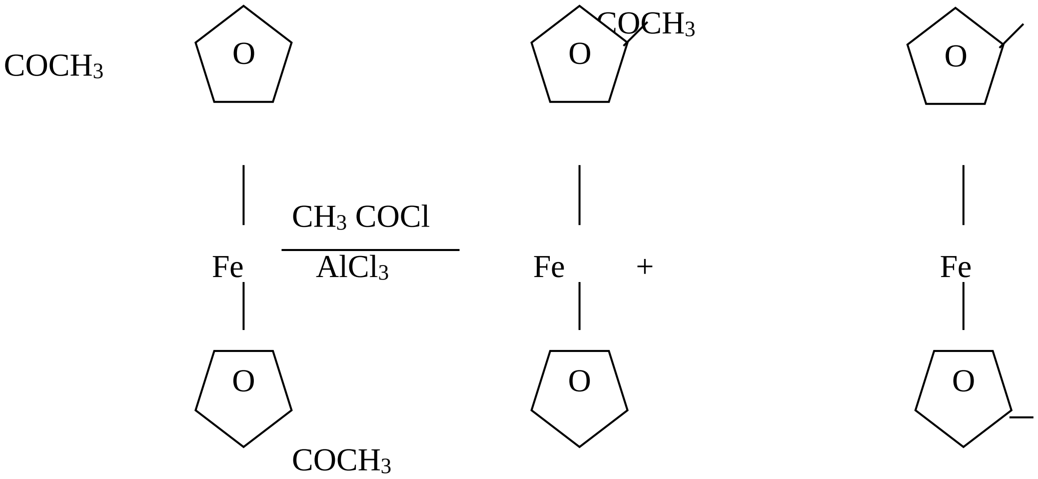
$2C_5\,H_6 + Fe \rightarrow Fe\,(C_5H_5)_2 + H_2$

Properties:

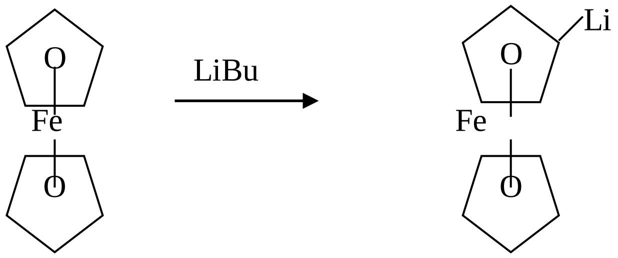
Ferrocene is paramagnetic, have constant melting points near 173^o C ferrocene is air- stable. It oxidizes to $Fe(C_5H_5)_2^+$ which is diamagnetic.

Some reactions of ferrocene depict its aromatic behavior.

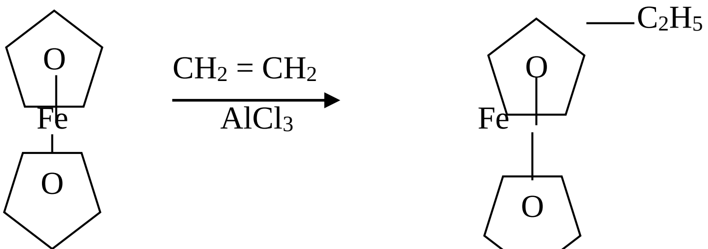
i) Ferrocene reacts with acetyl chloride in presence of $AlCl_3$ (Friedel crafts reaction) to form acetyl ferrocene.



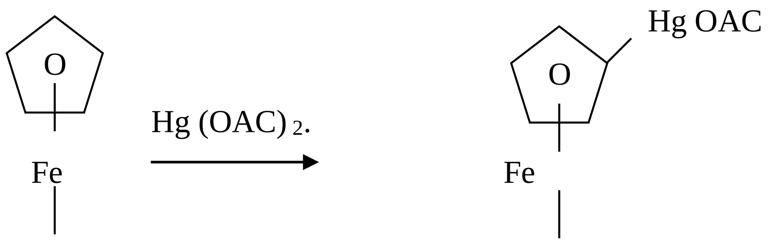
ii) Ferrocene reacts with Li Bu to form Ferrocene lithium compound.

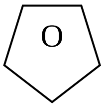


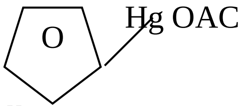
iii) With ethylene, ethyl ferrocene is obtained



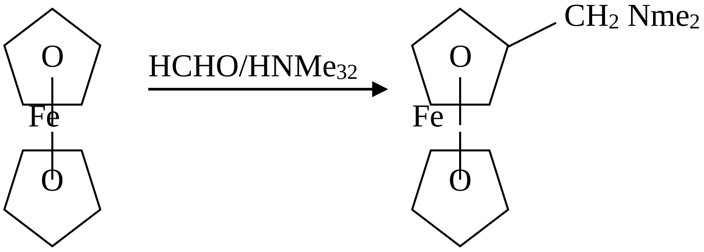
iv) With mercuric acetate, it forms, dimercurated compound is formed.





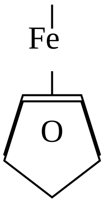


v) With N, N dimethylamine, the reaction in as follows.

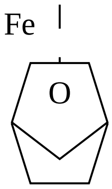


Structure:

Two alternative formulations of the bonding in ferrocene were suggested. From crystallographic studies, ferrocene is found to possess staggered conformation of two planar cyclopentadienyl rings. Gas phase electron diffraction data suggests eclipsed conformation.



Eclipsed form



Staggered form

4.6. Uses of organometallic compounds.

a) In medicine:

A silver compound being currently used in medicine is silver Sulphadiazine. Gold organic compounds containing Au- S bonds were earlier investigated for treatment of tubercloss. Mercurochrome and merthiolate are used as antiseptics. Numerous organoboron compounds have been investigated for cancer therapy. Cis platin (cis dichlorodiammine platinum II), a diorganotin dihalide exhibit antitumour activity. Two organogermanium compounds, a derivative of 1,1-diethyl -|- germacyclohexane has anti- cancer activity.

b) In agriculture:

A large number of organo mercury and this compound have been used as fungicides, algaecides, herbicides and pesticides. The compound ethephon (2- chloroethyl phosphoric acid) is used in inducing the fruits and vegetables to grow sooner and ripen earlier. Some organometalic compounds have been able to activate molecular nitrogen and form complexes.

Questions:

1) What are essential elements?
2) Explain the biological role of hemoglobin.
3) Explain the preparation, properties and structure of iron corbonyls.
4) What are silicates? How are they classified?
5) How are organ boron and organo lithium compounds prepared?
6) How is ferrocene prepared?
7) What are the uses of organo metallic compounds?
8) What is sequesterisation?
9) Give a brief note on Bhopal gas tragedy.
10) What is green house effect?
11) What are the differences between BOD and COD.
12) Explain soil pollution
13) What are the adverse effects of noise pollution and radioactive pollution?

NOTES

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UNIT-V

5.1 Solids – band theory of conductors, semiconductor and insulators.

Band theory:

This is the quantum mechanical treatment of the metallic crystal and is similar to molecular orbital theory of covalent molecules. According to this theory, metallic bonding is formed due to the delocalisation of free electron orbital. When atomic orbitals of equal energy combine, 2 molecular orbitals are formed. In a metal, 10^{23} atomic orbitals combine to form 10^{23} molecular orbitals, which are of the same energy. Hence these molecular orbitals are so closely spaced that they appear to be like a band. Hence, this theory is called as band theory.

Taking for examples, the formation of Li crystal. The electronic configuration of Li is $1s^2$ $2s^1$ 2p. If atoms of Li combine to form Li crystal, there bonds are formed.

i) 1s – Band:

It is by the combination of n 1S atomic orbital of n lithium atoms and hence contains n energy levels all of which are completely filled. 2n electrons can be accommodated in this band. Since there are 2n electrons in 1S orbital in Li crystal, this band is completely filled. Hence, it is called non- conducting or non- conduction band.

ii) 2s – Band:

This is called the valence band. Each Li atom contains only one electron in 2s level is 2s band contain n electrons from n lithium atoms. But, 2S band can accommodate 2n electrons. Hence, this band is half filled. Upper half of this band is empty, while lower half is completely filled. Even at ordinary temperature, the electrons from the lower half can go over to the upper half, of the band.

2p band:

n atoms of Li crystal will give 3n levels in 2p band. This band can accommodate 6n electrons. Since 2s levels and 2p levels are near in energy, both the bands overlap. The portion where 2s and 2p bands over lap is called over lap zone. This zone contains n electrons, i.e, it is 1/8th filled, since the maximum capacity in 8n electrons.

The electronic energy bands where the electrons can move are called the permitted bands. These are also called brilliouin zones, two brillouin zones are separated from each other by empty bands which are called forbidden zones or forbidden energy gap. The energy gap between 1s and 2s bands is quite high and hence the promotion of electrons from the lower conducting 2s band is prevented. The level below which all energy levels are filled is termed fermi level.

With the help of band theory, we can explain the properties of metals, non- metals and semiconductors.

i) Metals (conductors):

The conduction band of a conductor is partly filled and contains a very large number of electrons. These electrons can be promoted to the nearby vacant levels in the same band by electric or thermal energy. This explain high electrical and thermal conductivity of the metals.

ii) Non- conductors or insulators (non- metals)

Insulators are those materials in which valence electrons are bound tightly to their parent atom. An insulator has empty conduction band. The energy gap between the valence shell band, which is completely filled, and the conduction band is very large. Thus energy required for shifting an electron from the completely filled valence shell band to the empty conduction band is very high, hence non- metals are insulators.

iii) Semiconductors:

Semi conductors are those materials whose electrical properties lie between those of insulators and good conductors. Where these semi conductors are in their extremely pure form, these are called intrinsic semi conductors. Germanium and silicon are the common examples of semiconductors or intrinsic semiconductors. These have filled valence band and empty conduction band. The forbidden energy gap between them is so small that even at room temperature many electrons from the filled valence band jump to the vacant conduction band. As the temperature is increased, the width of the forbidden energy gap is decreased and hence some more electrons jump to the conduction band. i.e as the temperature is increased, thermal conductivity also increases. Substances, which are normally insulators, can be made semiconductors when small amounts of impurities are added to them such substances are called extrinsic or impurity semiconductor. Depending on the nature of impurity added, extrinsic semiconductor is of two types.

a) n- type semiconductors:

These are obtained when impurity atom added l as more valence electrons than the parent insulator atoms. When phosphorus, arsenic are added to pure silicon or germanium we get n- type extrinsic semiconductors. Each antimony atom forms four covalent bonds with four germanium atoms and the fifth electron are unused. Hence, there is an extra electron at the lattice points occupied by antimony atoms compared to the lattice points occupied by germanium atoms.

There are as many extra electrons in the lattice points of antimony. There extra electrons occupy delocalized level which is called donor impurity level which is just below the empty conduction band of germanium crystal. These extra electrons can be easily excited to the empty conduction band by increasing the temperature or by applying electric field. Due to the presence of extra electrons, germanium crystal is a semiconductor. Hence, the name n-type semiconductors.

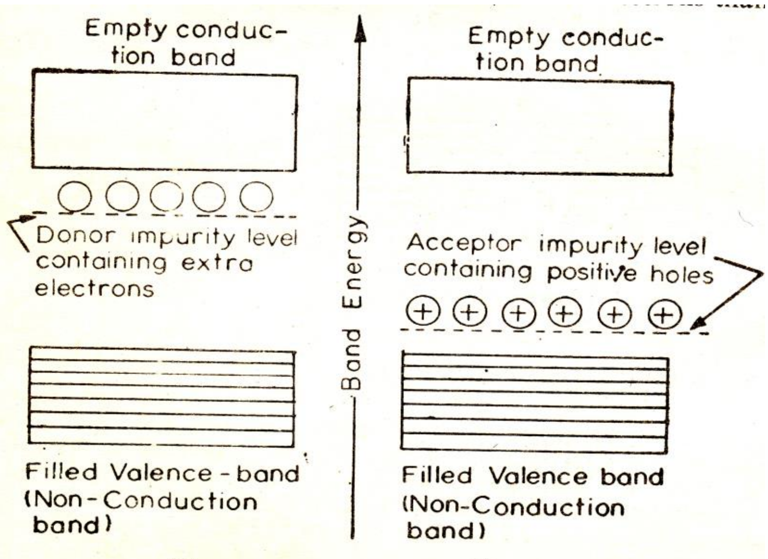


Fig. 4·18. Energy bands for (*a*) *n*-type and (*b*) *p*-type extrinsic semi-conductors

P-type semiconductor:

These are obtained when an impurity atom to be added has four valence electrons than the parent atom. When boron or aluminium atoms are added to pure silicon or germanium, we get P-type extrinsic semiconductor. Valence electron of each boron atom forms three bonds with three germanium atoms. The fourth germanium atom in linked with the boron atom by incomplete bond. Thus, in this bond in the lattice, there is an electron in the valence band of germanium. Positive hole are the places where the electrons are missing, which occupy acceptor impurity level close to the filled valence band of germanium. Electrons from the filled valence band can thermally be promoted to this empty acceptor impurity level of positive holes. Under the influence of an applied potential, an electron from an adjacent atom moves into a hole which is replaced by an electron from other atom. The conduction is due to the migration of positive holes, hence the name P-type semiconductor.

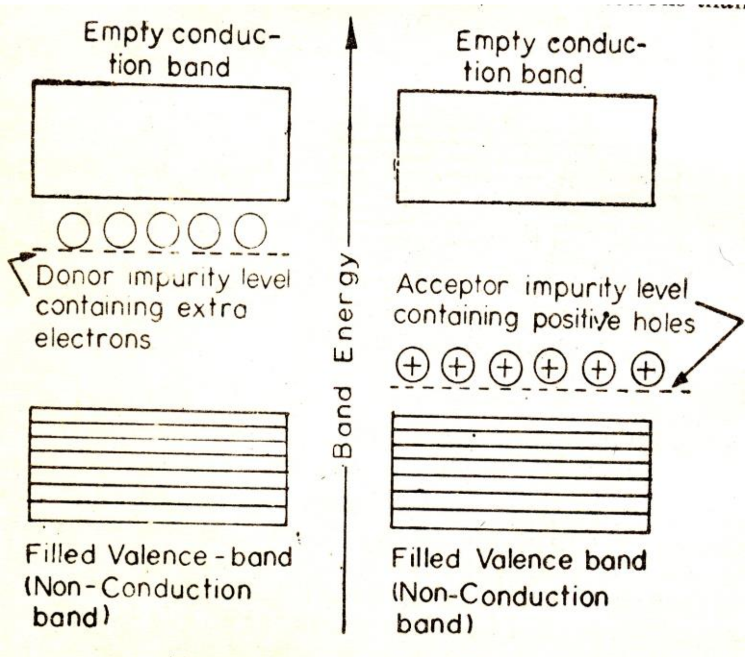
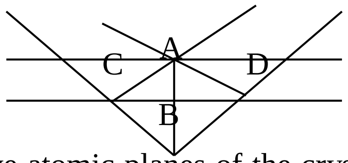


Fig. 4·18. Energy bands for (*a*) *n*-type and (*b*) *p*-type extrinsic semi-conductors

5.2. Bragg's law and application of X-ray diffraction to crystal studies.

Bragg's law:

X – rays are electro magnetic radiations of the order of 10^{-8} cm. Laue suggested that the distance between the lattice planes in the crystals are in the order of A°. Hence, crystal should act as a diffraction grating for x-rays. Bragg suggested that the crystal can act as reflection grating also. He developed a simple equation to determine the structure of a crystal using x-rays. Which is Bragg's equation.



Two successive atomic planes of the crystal is represented by d. let the x-rays of wavelength λ strike the first plane at an angleθ. Some of the rays will be reflected at the same angle. Some of the rays will penetrate and get reflected at the same angle. Some of the rays will penetrate and get reflected from the second plane. These rays will reinforce those reflected from the first plane of the extra distance traveled by them is equal to the integral multiple of wavelengths.

Reflection of x-rays from two different planes of a crystal.

$$n\lambda = CB+ CD$$

$$CB = BD = AB \sin\theta.$$

$$\therefore \quad n\lambda = 2AB \sin\theta.$$

$$\therefore \quad n\lambda = 2d \sin\theta.$$

This is Bragg's equation

This equation is used chiefly for determination of the spacing between the crystal planes 'd'. for x-rays of specific wavelength λ, the angle θ can be measured with the help of Bragg x-ray spectrometer. The interplayed distance 'd' is calculated with the help of Bragg's equation.

Uses:

i) By knowing λ and θ, and n, d can be calculated knowing θ.

ii) From Bragg's law, can be determine the structure of NaCl, Kcl and CsCl.

iii) Avagadro's number can be determined using Bragg's law.

Bragg's method of determining the crystal structure.

In the Bragg's method, λ the wavelength of the x-ray is fixed and θ is varied by rotating the crystal about its axis. This angles for which reflections are maximum give 'θ' values which are substituted in the equation.

$$n\lambda = 2d \sin \theta.$$

The lowest angle at which maximum reflection occurs corresponds to n=1. This is called first order reflection. The next higher angle at which the maximum reflection occurs corresponds to n=2.

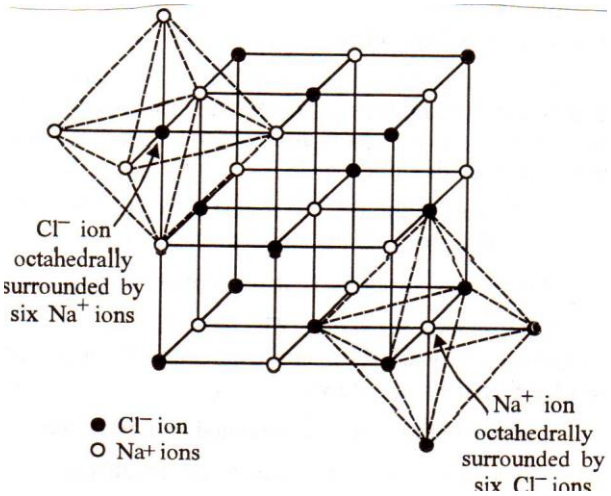
x - Rays are generated in the x-rays tube 'A'. They are passed through a focusing slit 'S'. A narrow beam is got. It is allowed to strike a single crystal 'c' which mounted on a rotating table. A particular face is exposed to the x – ray. The crystal is rotated gradually and the glancing angle θ at which the reflections are maximum is determined using a recording device 'R'. The experiment is repeated for different values of 'n'. 'θ' are determined from which the'd' values are calculated and crystal structure is determined.

Structure of NaCl:

For NaCl, the θ values for first order reflection for the three planes (100), (110) and (111) planes are found to be 5.9°, 8.4° and 5.2°. The ratio d_{100}: d_{110}: d_{111} is calculated. It is found to be 1: 0.704: 1.136. Which is close to the spacing among the three planes of a face centered cube, it is concluded that sodium chloride has a face centered cubic structure.

The first order reflection patterns of (111) planes has weak and strong peaks, which is due to the alternate layers or planes of chlorine atoms and sodium atoms. The radius ratio of NaCl Li 0.59/1.81 = 0.24. This value lies in between 0.414 and 0.732. so, coordination number is 6. X-ray structure of NaCl shows that it has octahedral shape. Each Na$^+$ ion is surrounded by 6 Cl$^-$ and each Cl$^-$ ion is surrounded by 6 nations, i.e the coordination number is 6:6.

Every chloride ion at the corner of the unit cube is shared by light adjacent unit cubes. Each cube has 1 Cl$^-$ ion. Besides, there are six chloride ions at the centre of each face. Therefore, each cube has ½ 6 is 3Cl$^-$ ion. Total no. of Cl$^-$ ions per cube is 1 + 3 = 4. In this unit cell, there is one central sodium ion, and 12 others at the centers of edges each of which is shared by four adjacent cubes. So, there are 1+12/4 = 4. Sodium ions. Therefore, every unit cell contains 4 Na$^+$ and 4Cl$^-$ ions. i.e 4 NaCl molecules.



Structure of LiCl:

The radius ratio value of NaCl is 0.53 and the radius ratio of LiCl is 0.30. LiCl retains the NaCl type lattice in spite of low radius ratio value because of the strong repulsion of Cl$^-$ ions, which are in close proximity. Thus the crystal structure of LiCl is the same as that of LiCl.

Structure of ZnS.

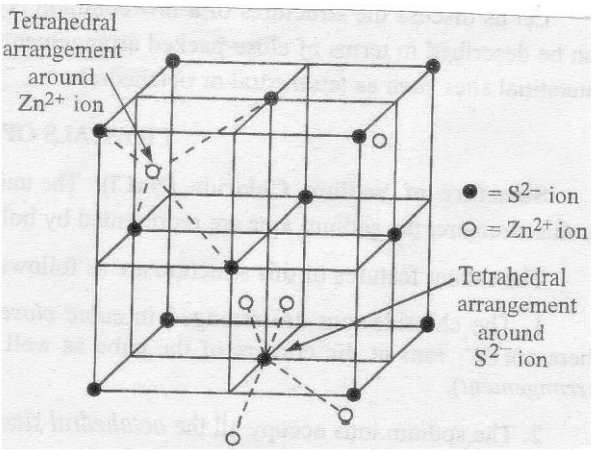
It has two types of crystals.

i) Zinc blende

ii) Wurtzite.

In zinc blende, the ratius ratio is 0.40. so, it should have tetrahedral shape. Each Zn^{2+} is tetrahedral surrounded by four S^{2-} ions and each S^{2-} ion is tetrahedral surrounded by four Zn^{2+} ions. Thus, it has 4:4 coordination. It has cubic close packed structure.

In Wurtzite, Zn^{2+} and S^{2-} ions have hexagonal close packed structure.



5.3 Imperfections in a crystal.

At absolute zero most of the ionic crystals contain well ordered arrangement of constituent ions and hence the crystals have no imperfections or defects. With rise of temperature, one or more of the lattice sites become unoccupied or vacant and this gives rise to a defect in the regular arrangement of he constituent ions of the crystal. The number of such defects per cm^3 at a given temperature T is

$$n = Ne^{-W}/2RT$$

N = total no. of sites per cm^3.

W = work required to produce a defect.

R = Gas constant.

There are two types of defects.

1) Stoichiometric defects

2) Non- Stoichiometric defects.

Stoichiometric defects:

Stoichiometric compounds are the compounds where the ratio of the number of A^+ ion to the number of B- ions is these defects are two types.

i) Schottky defects:

This defect arises when some cations and equal number of anions are missing from their own position and create holes in the lattice since the no. of missing cations is equal to the no. of missing anions, the crystal as a whole remains neutral. This defect in found in compounds which have high coordination number and the radius ratio is not below unity. Ex . alkali metal halides.

A^+ B^- A^+ B^-
B^+ O B^- A^+

A^+ B^- A^+ O

B^- A^+ B^- A^+

ii) Frenkel defect:

This defect arises when one of the ions leaves its position and occupies another one in between other ions in the lattice. Cations usually smaller in size moves and occupies interstitial space since the no. of cations is equal to the no.of anions, the crystal remains neutral. This type of defect is seen in compounds which have low coordination number, radins ratio is low. Ex Ag Br, Zns.

A^+ B^- A^+ B^-

B^- O B^- A^+

A^+ B^- A^+ B^-

B^- A^+ B^- AA^+

Effects of frenkel and schottky defects:

i) In frenkel defect similar charges come closer to each other, which leads to increase in the dielectric constant of the crystal.

ii) In schottky defect, the number of ions in the lattice of the crystal is decreases the density of the ionic solids.

iii) The presence of holes in both types of defects lowers the lattice energy or stability of the crystal.

iv) As a result of both types of defects, the crystal is able to conduct electric current when electric field is applied between the two ends of the crystal.

Non – stoichiometric Defects:

In non- stoichiometric compounds the ratio of the no.of A^+ ions to the no. of B^- ions is not a whole number. There is excess of positive ions or negative ions which leads to defect in the crystal. These defects are of two types.

i) Metal excess defects

ii) ii) Non- Metal excess defects.

i) Metal excess defects:

This defect occurs due to the presence of excess of positive ions which occurs in two ways. One is the negative ion missing from its real position, leaving a hole and this hole is occupied by an extra free electron. Another way is an extra positive ion occupies a position in the lattice and to maintain the electrical neutrality, an electron occupies a position in the lattice.

Consequences:

1) Due to the presence of free electons, these crystals conduct electricity to

   some extent. Since the no.of free electrons are less, they conduct small amount of electricity.

2) Due to the presence of free electrons, the compounds having such type of defects are generally coloured. Nonstoichiometic Nacl is yellow, zinc oxide is yellow when hot and white when cold.

$A^+ \ B^- \ A^+ \ B^-$	$A^+ \ B^- \ A^+ \ B^-$
$B^- \ A^- \ e^- \ A^+$	$B^+ \ A^+ \ B^- \ A^+$
	A^+
$A^+ \ B^- \ A^+ \ B^-$	$A^+ \ B^- \ A^+ \ B^-$
$B^- \ A^+ \ B^- \ A^+$	$B^- \ A^+ \ B^- \ A^+$

ii) Non metal excess defects:

This defect is produced by the presence of excess of negative ions which is achieved by one of the two ways. One is one of the positive ions is missing from its position, to keep the crystal neutral, another cation acquires an extra positive charge. Another way is an extra negative ion occupies a position in the lattice, one of the adjacent cation acquired an extra positive charge, which is not possible.

$A^+ \ B^- \ A^+ \ B^-$
$B^- \ O \ B^- \ A^+$
$A^{2+} \ B^- \ A^+ \ B^-$
$B^- \ A^+ \ B^- \ A^+$

Consequences:

i) Conversion of A^+ to A^{2+} takes place through the movement of an electron from A^+ to A^{2+} ie there is movement of positive holes. Hence, the crystal having this type of defects is seen in semi conductors.

5.4 Symmetry elements and symmetry operations symmetry elements:

When a ball is cut into halves, they are identical. So the ball possess symmetry elements an object is symmetrical if it can take up more than one equivalent orientation. For example, H_2. When it is rotated through 180^0, both cannot be distinguished from each other.

Symmetry operations:

Symmetry operation is the process carried out on the molecule which brings it from the original orientation to another equivalent orientation. It can be a reflection or rotation, which performed within the molecule. There should be at least one point in the molecule. Which is unaffected by all symmetry operations. The following table gives the symmetry operation performed using the symmetry element.

Symmetry elements	**Symmetry operation**	**Symbol**
Plane of symmetry	Reflection	σ
Centre of symmetry	Inversion	I
Proper axis of symmetry	Rotation	Cn
Improper axis of symmetry	Rotation followed by reflection (or) Reflection followed by rotation	Sn
Identity		E

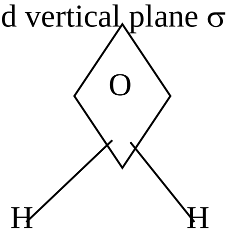
Reflection:σ

Reflection is the symmetry operation performed using plane of symmetry. Where plane of symmetry is the imaginary plane which divides the molecule into two halves so that one half is the mirror image of the other half.

There are 3 types of planes of symmetry.

a) The plane passing through the principal axis and one of the subsidiary axis. Is called vertical plane σh. (Ex) H_2O, H_2S,SO_2, NH_3

b)



c) The plane perpendicular to the principal axis is called horizontal plane, oh. (EX) H_2,N_2,Co_2

H-H

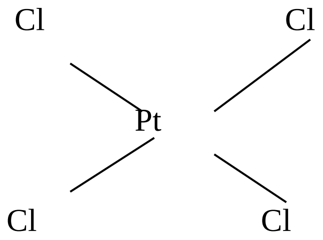
N ≡ N

d) The plane passing through the principal axis but passing in between two subsidiary axes is called dihedral plane, σ d.

(Ex) $AlCl_4^-$

Inversion, I:

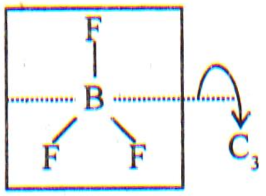
Inversion is the symmetry operation carried out using centre of symmetry. Centre of symmetry is defined as an imaginary point which if a line is drawn to one end of the molecule and extends to other end of the molecule, meets equivalent atoms. Ex:$[PtCl_4]^{2-}$ C_2H_4

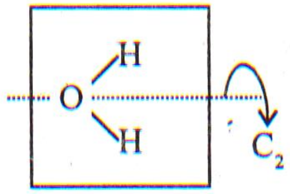


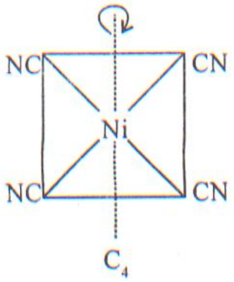
Rotation, Cn:

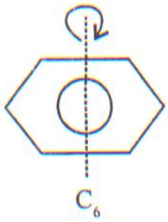
Rotation is the symmetry operation carried out using proper axis of symmetry Axis of symmetry is defined as an imaginary axis through which if a molecule is rotated through $360^0/n$, the molecule is represented more than once.

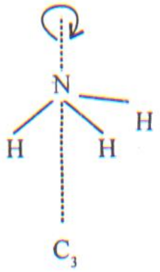
Figures







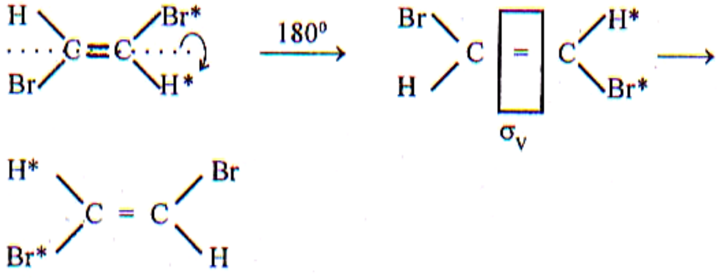




Rotation followed by reflection, Sn,

This is the symmetry operation done by rotation followed by reflection or reflection followed by rotation. Both operations are done.

Figures



Identity (E)

This is an operation which brings back the molecule to the original orientation.

Point group:

It is simplest rotation which gives information about the number of symmetry operations possible on the molecule.

Point group of:

i) H_2

a) The principal axis is $C\infty$

b) There is a C_2 axis perpendicular t the principal axis. $C\infty$

c) It has horizontal plane of symmetry.

d) The point group is $(C\infty+C_2) = D\infty$. $D\infty$ with σh gives $D\infty h$.

ii) HCl

a) The principal a x is $c\infty$

b) There is no C_2 axis perpendicular to $C\infty$

c) It has ∞ no.of vertical planes of symmetry.

d) Hence the point group is $C\infty\mu$.

Linear molecules with equal halves have the point group $D_{\infty h}$ and without equal halves has the point group $C\infty V$.

iii) Co_2.

Co_2 is a linear molecule with equal halves. Hence the point in $D\infty$ h as discussed in H_2.

iv) H_2O

a) The principal axis is C_2

b) There is no C_2 axis perpendicular to the principal axis.

c) It has 2 vertical planes of symmetry.

d) The point group is $C_2 + 2\sigma u = C2V$

v) NH_3

a) The principal axis is C_3

b) There is no C_2 axis perpendicular to the principal axis.

c) It has 3 vertical planes of symmetry.

d) The point group is $C_3 + 3_{\sigma V} = C2V$

vi) BF_3

a) The principal axis is C_3

b) There is no 3 C_2 axis perpendicular to the principal axis.

c) It has 3 σμ's and 1 oh

d) The point group is $C_3 + C_2 = D_3$ (D_3+ 1oh) D_3h

vii) CH_2Cl_2

a) The principal axis is C_3

b) There is no 3 C_2 axis perpendiculars to the principal axis.

c) It has 3σv's and 1 oh

d) Hence the point group is $C_3 + C_2 = D_3$ (D_3+ 1oh) D_3h

viii) $[PtCl_4]^{2-}$

a) The principal axis is C_3

b) There are no 3 C_2 axis perpendiculars to the principal axis.

c) It has 3σμ's and 1 oh

d) The point group is $C_3 + C_2 = D_3$ (D_3+ 1oh) D_3h

ix) PCl_5

a) The principal axis is C_3

b) There are no 3 C_2 axis perpendiculars to the principal axis.

c) It has 3σμ's and 1 oh

e) The point group is $C_3 + C_2 = D_3$ (D_3+ 1oh) D_3h

x) Cis (Pt $(NH_3)_2Cl_2$)

a) The principal axis is C_3

b) There are no 3 C_2 axis perpendiculars to the principal axis.

c) It has 3σv's and 1 oh

a) The point group is C_3 +σv = C_{2V}

xi) Trans (Pt $(NH_3)_2Cl_2$)

a) The principal axis is C_2

b) There is Centre of symmetry

c) In addition, it has 1 oh.

d) Hence the point grou is C_2 h.

5.5 Magnetic properties of molecules.

When a substance is placed between the poles of a magnet, it interacts with the applied magnetic field, such substances are said to have magnetic behaviour.

Magnetic susceptibility

The force f acting between two magnetic poles of strength p_1 and p_2 separated by a distance r is given by

$$F = P_1P_2/qr^2$$

Where q in the magnetic permeability.

The total magnetic moment per unit volume induced by a field of strength H is I. If a substance is placed in a magnetic field of strength H, the flux B is given by

$$B = H + 4\Pi I$$

The ration B/H is the magnetic permeability of the material. Intensity of magnetization is directly proportional to the field strength.

$$I \alpha H; I = KH$$

$$B/H = I + 4\prod I/H = 1 + 4\prod K.$$

k is called the magnetic susceptibility per unit volume and is independent of field strength.

Types of magnetic behaviour.

Substances for which the magnetic permeability is less than one are called diamagnetic substance and those for which it is slightly greater than one are called paramagnetic substances. The magnetic lines of force prefer to pass through vacuum rather than through the diamagnetic substance. Such substances tend to move from the stronger part of the magnetic field to the weaker part. the field induced in a diamagnetic substance is opposite to the external field. The lines of force have greater tendency to pars through a paramagnetic substance than through vacuum. The substance tends to move from weaker prt to the stronger part of the applied field.

In a few cases, q is very large. Such substances are called ferromagnetic.

Diamagnetism

Diamagnetism is a function of distribution of electron density within an atom, ion or a molecule. It arises from the interaction of the applied field with filled electron orbits. In a diamagnetic material, the effects of individual electrons are mutually neutralized, where the electrons are completely paired. The diamagnetic effect is produced by the orbital motion of the electrons. The orbital motion of electrons is disturbed by the applied field. The diamagnetic effect is a function of the quantum numbers of the electrons. It depends on the nature of the electron orbitals.

The orbital angular momentum of an electron of an atom depends on the quantum number. It is given by the expression √L (L+1) h/2Π. Therefore the magnetic moment due to the orbital motion of the electron can motion of the electron can be expressed as:

$$\mu_L = \frac{eh}{4\pi mc}\sqrt{l(l+1)}$$

$\frac{eh}{4\pi mc}$ is a constant and is a unit for expressing the magnetic moments of atoms and molecules. This unit is called Bohr magneton, μ_B

$$\mu_B = \frac{eh}{4\pi mc}$$

Where h= planck's constant, m= mass of the electron

C = Velocity of lights

Examples of diamagnetic ions:

H^-, Li^+, Ba^{2+}, Cu^+, Ga^+, Ge^{2+}

The magnetic susceptibility of diamagnetic substances is independent of temperature. It is the same for a substance in the gas and liquid states. Most of the organic molecules are diamagnetic because they do not contain spin free electrons.

Paramagnetism

Paramagnetic property in shown by a substance when the magnetic effects of the individual electrons are not mutually neutralized. Thus, paramagnetism is associated with the presence of either unpaired electrons or an incomplete electronic level. Free sodium atom, nitric oxide and ions with partly filled shells are paramagnetic. All free radicals are paramagnetic, since each contains an unpaired electron. Paramagnetism depends upon temperatures. The presence of odd number of electrons to characteristic of paramagnetic substance. Lack of electron pairing in an even-electron system will lead to paramagnetism. The spin and orbital motions of the electrons are the sources of magnetic moment. The total magnetic moment of a molecule has two components, the spin contribution and the orbital contribution. Both types of motion are responsible for paramagnetism.

If the orbital contribution and the spin contribution do not interact with each other, than the two can be considered separately.

Orbital contribution, $\mu_L = \sqrt{L(L+1)}\ B.M$

Spin contribution,

$$\mu_S = g\sqrt{L(L+1)}\ B.M$$

$$g = Lande\ splitting\ \ factor$$

$$\therefore\ = 2\ for\ a\ \ free\ electron$$

$$\mu = \sqrt{4S(S+1) + L(L+1)}$$

Magnetic moment is directly related to the number of unpaired electrons.

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

The magnetic susceptibility of paramagnetic substances varies with temperature.

This is given by the curie Law,

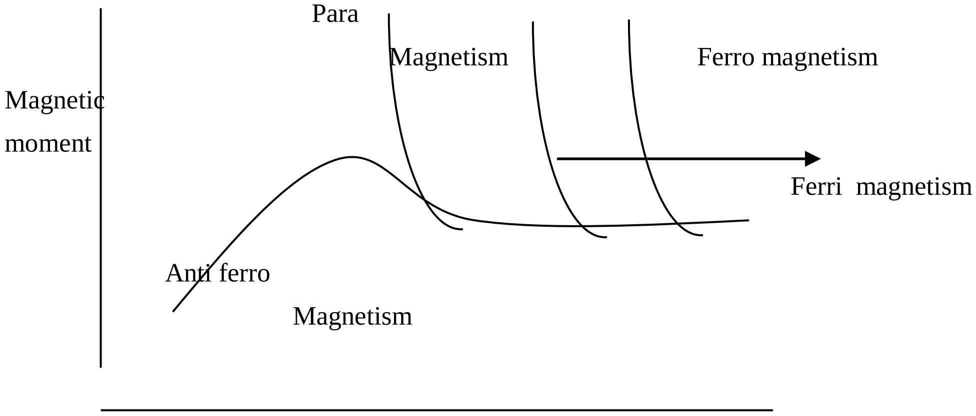
$$\chi_m = \propto_m + {}^{C}\!/_{T}$$

$\propto_m$ and C are constants for a given substance. C is the curie constant.

Temperature and magnetic Behaviour

Diamagnetism is independent of temperatures. Paramagnetism is temperature dependent. But does not depend on the strength of the applied field.

Figures



The temperature dependence of paramagnetism is denoted by the curie law,

$X_m{}^{Corr} = C/T$

Where C is curie constant, T is the absolute temperature X_m corr represents the susceptibility after correction for diamagnetism and temperature independent paramagnetism.

A graph is drawn by plotting 1/Xm with T. A straight line passing through the origin should be obtained for some substances, such lines are obtained. For some others, the lives do not pass. Through the origin for such substances, a modified form of Curie Law is given which is curie-Weiss Law.

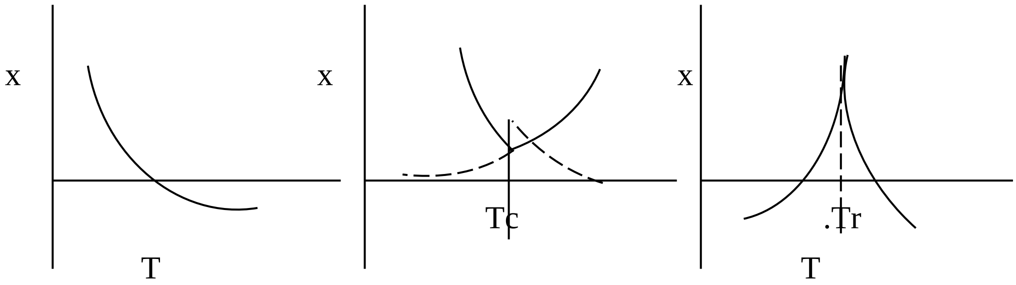
$$\chi_M{}^{Corr} = \frac{C}{T - Q}$$

θ is called the Weiss constant. This correction arises due to the mutual interaction of magnetic dipoles in the substance and also interaction with the applied field.

The molar magnetic susceptibility of a substance containing independent atoms, ions or molecules, the magnetic moment μ varies with temperature which is given by

Ferromagnetism and anti ferromagnetism

A group is drawn by plotting Xm VsT.



In the case of paramagnetism magnetic susceptibility decreases with increase in temperature. In ferromagnetic substances, there is a discontinuity in the trend at some temperature. This temperature in the trend at some temperature. This temperature is called the curie temperature, Tc. Above Tc, the magnetic behaviour obeys the curie law, ie it is a simple paramagnetic property.

Below Tc there is a steep increase in susceptibility. This is characteristic of ferromagnetic substances. The anti ferromagnetic substances, behave like a simple paramagnetic system upto a particular temperature, the susceptibility increases with decrease in temperature. Below a particular temperature called the Neel temperature. T_N, the susceptibility drops sharply.

Both ferro and anti ferromagnetic properties are due to inter ionic interactions. In an anti ferromagnetic system, the moments of the ions in the lattice tend to align themselves so as to cancel each other leading to a sharp decrease in susceptibility. Above T_N, thermal agitations prevent effective alignment. Below T_N, anti-parallel alignments become effective and therefore the susceptibility is diminished. In a ferromagnetic system, the moments of separate ions tend to align themselves parallel and thus reinforce one another. Above T_c, thermal energies are more or less able to randomize the orientations. Below T_c, the tendency of alignment gets controlled hence susceptibility increase much more rapidly with decreasing temperature.

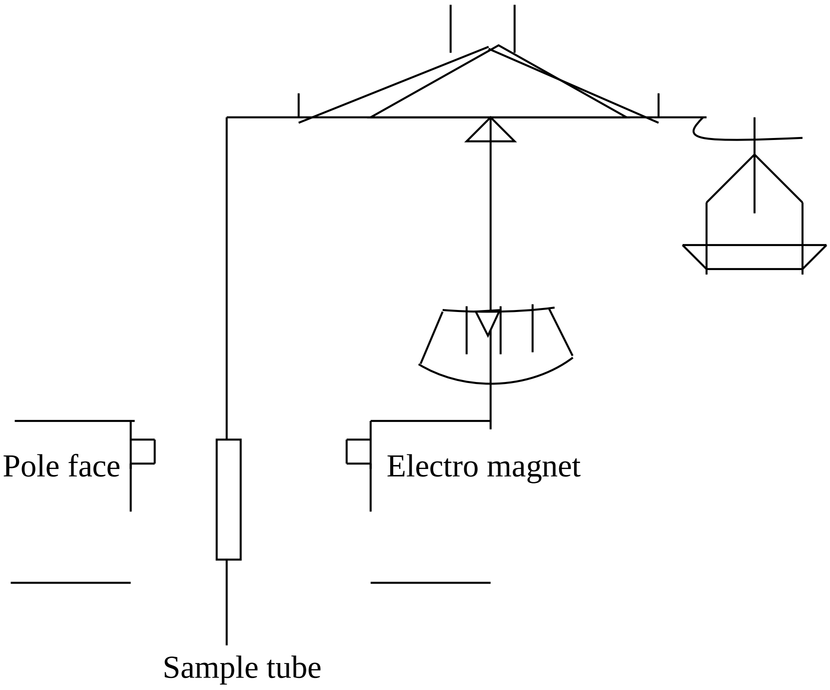
↑↑↑↑↑↑↑↑↑↑ Ferromagnet

↑↓↑↓↑↓↑↓↑↓ Anti ferro magnet

Temperature-independent paramagnetism

IN substances which contains unpaired electrons and no unpaired electrons, a weak paramagnetism which is independent of temperature is possible. It resembles diamagnetism. This magnetism is not due to any magnetic dipole existing in the molecule, but due to dipole induced by the field.

Determination of magnetic moment using Guoy Balance.



Guoy Balance is a modified analytical balance. A long thin sample tube can be hung from the left pan book, through a hole in the bottom of the balance. The sample tube is filled uniformly with the substance and is suspended between the pole pieces of a magnet. The sample tube is weighed first with the field and then without the field. A substance of known volume susceptibility is uses as the reference standard.$CuSo_4$, $5H_2O$ or an aqueous solution of nickel chloride are used as the standard substances.

The apparent of weight of the substance is greater in the presence of a magnetic field than in the absence.

This difference is weight which due to the force to draw the substance into the magnetic field. The difference in weight Δw is given by

$\Delta w = (k-kr)\ H^2\ A/2$

H = Strength of the magnetic field

A = Cross sectional area of the sample tube.

Using the equation

$$X_m = N\ \alpha + \frac{N}{3KT}\ \beta^2\ \mu^2$$

X_m determined at different temperature, μ is determined from the solpe of the plot of X_m Vs 1/T , N is the Avagadro Number. α is the diamagnetic constant, k is the Bolzmann constant, T is the absolute temperature, B is bohr magneton.

Applications of magnetic measurements.

i) From the magnetic moment values, the no.of unpaired electrons and the valency of the metal in a compound can be calculated.

ii) Certain organic molecules like hexapheylethane dissociate into free radical fragments, which have unpaired electrons. Measurement of susceptibility of such molecules ins solution can be used to interpret the degree of dissociation.

iii) The bond type and the configuration of a metal complex can be understood from the magnetic moment values.

iv) Magnetic moment values can be used to detect association and polymerization in certain species.

v) Some chemical reactions involve change in the magnetic moment of certain ions or molecules. Such reactions can be followed by measuring the change in the magnetic moment of the system.

Questions:

1) Explain Band Theory.
2) Based on Band Theory, explain the properties of metal, non metals and semiconductors.
3) Derive Bragg's Law.
4) Discuss the structure of Nacl.
5) Explain stoichiometric and non-stoichiometic defects.
6) Define elements of symmetry.
7) Arrive at the point group of H_2O, NH_3, and BF_3.

8) How does magnetic behaviour vary with temperature?

9) What are the applications of magnetic moments?

10) Having the magnetic moment determined using Guoy Balance.

References

1. Wahid U.Malik, G.D, Tuli, RD. Madan, selected topics in Inorganic Chemistry, S.Chand & Co.
2. Puri, Sharma, Pathawia, Textbook of Inorganic chemistry, Vishal publications.
3. R. Gopalan, P.S. Subramanian, K. Rengarajan, elements of Analytical chemistry., S.Chand & co.
4. V. Venkateswaran, R. Veerasamy. A.R. kulandaivel, Basic principles of practical chemistry, S. Chand & co.
5. R.D. Madan, Modern Inorganic Chemistry, S.Chand &Co.
6. B.K Sharma, H. Kaur, Air pollution, Goel publishing House.
7. S.S. Dara,m A text book of environmental chemistry and pollution control, S. Chand &co.
8. G.S. Sodhi, Fundamental concepts of environmental chemistry, Narosa publishing House.
9. R.C. Mehrotra, A. Singh, organometallic chemistry, Wiley Eastern ltd.,
10. F.A Cotton, Group theory.

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