

INORGANIC CHEMISTRY - I

◎ 18K5CH07

◎ UNIT - III

SUBSTITUTION REACTION IN CO-ORDINATION CHEMISTRY

MECHANISMS OF LIGAND SUBSTITUTION REACTIONS IN OCTAHEDRAL COMPLEXES

These reactions can be classified into different types depending upon the nature of intermediate formed.

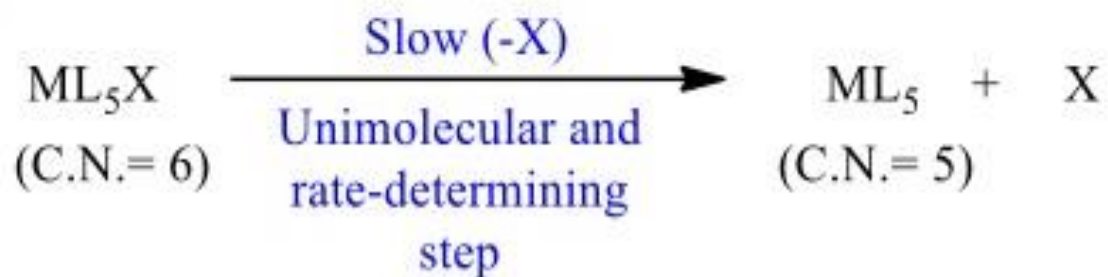
S_N1 or Dissociation mechanism :

- It indicates Unimolecular Nucleophilic Substitution or 1st order.
- M-X bond is fully broken before the formation of M-Y bond.
- Intermediate is detected in the rate determining step in which the central metal has a lower coordination number than it has in the reactant.

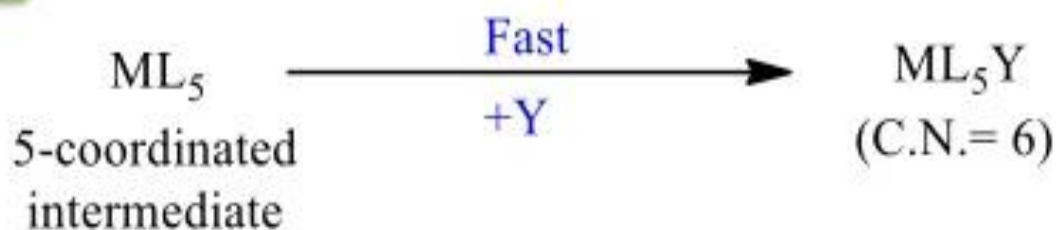


THE TWO STEP MECHANISM

Step 1

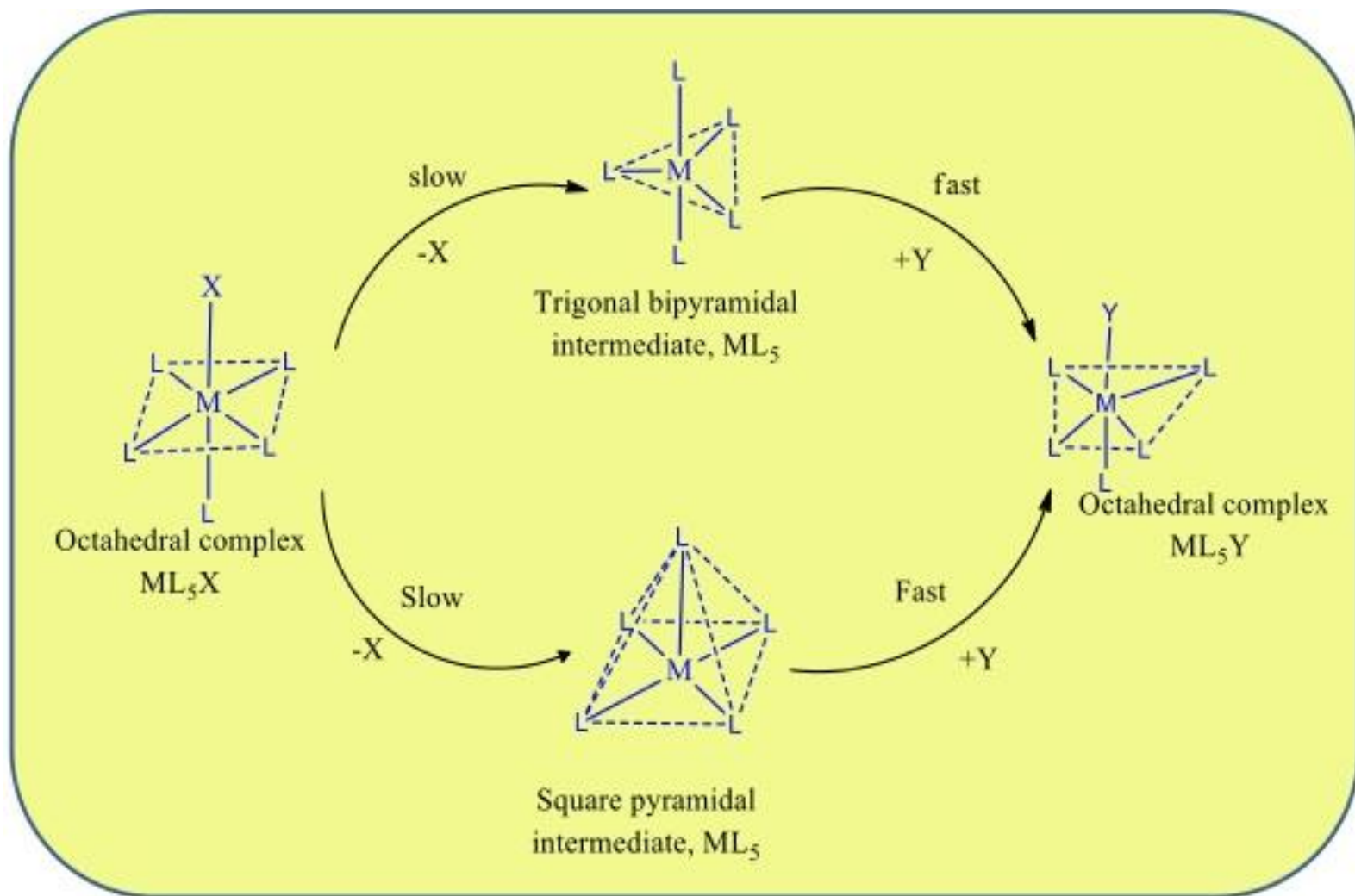


Step 2



$$\text{Rate} = k [\text{ML}_5\text{X}]$$

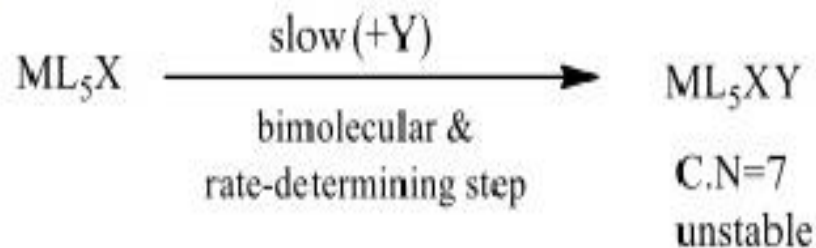
DIAGRAMMATIC REPRESENTATION OF DISSOCIATION



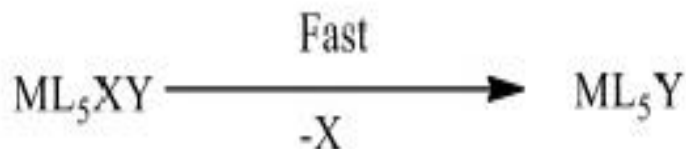
S_N2 OR ASSOCIATION MECHANISM

- Intermediate at the rate-determining step has a higher coordination number than that in the reactant.
- M-Y bond is fully formed before the breaking of M-X bond.
- It is of 2nd order and also involves two steps.

Step 1

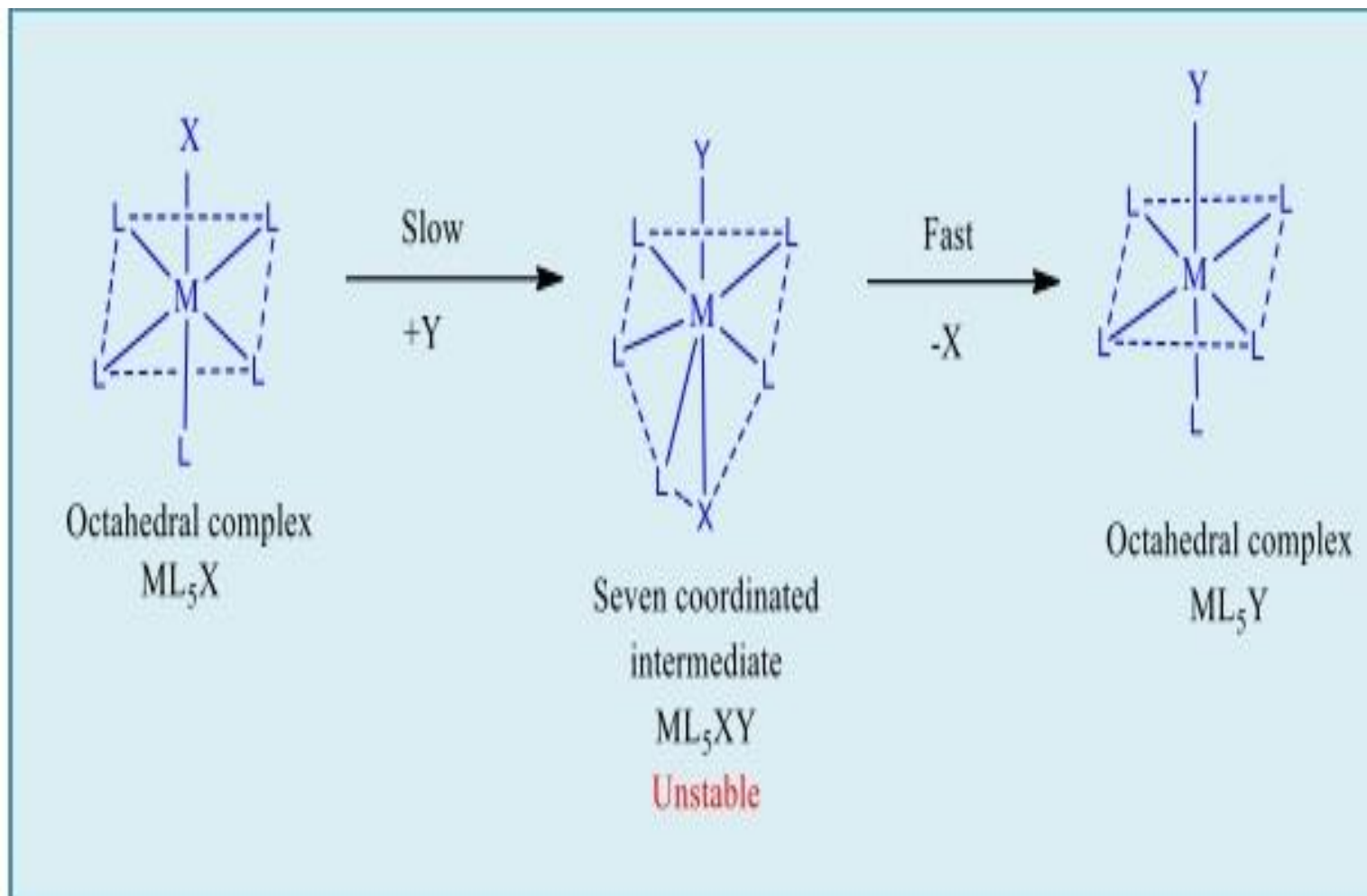


Step 2



$$\text{Rate} = k[\text{ML}_5\text{X}][\text{Y}]$$

DIAGRAMMATIC REPRESENTATION OF ASSOCIATION



HYDROLYSIS REACTIONS

- These are the substitution reactions in which a ligand is replaced by a water molecule or by OH^- groups.
- The reactions in which an aquo complex is formed by the replacement of a ligand by H_2O molecule are called **acid hydrolysis** or **aquation**.
- The reactions in which a hydroxo complex is formed by the replacement of a ligand by OH^- group are called **base hydrolysis**.

ACID HYDROLYSIS

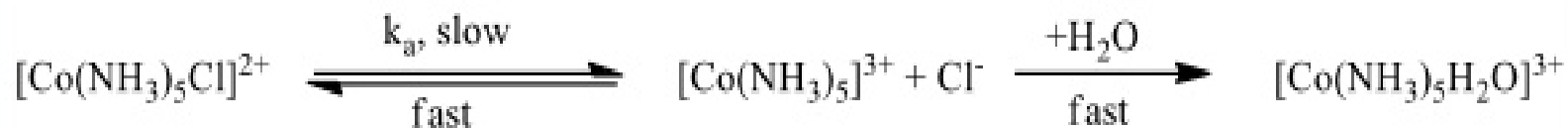
- Occurs in neutral and acid solutions ($\text{pH} < 3$)
- Rate is independent of water molecule



$$\text{Rate} = k[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$$

MECHANISM OF ACID HYDROLYSIS

➤ Dissociative Mechanism



➤ Associative Mechanism



FACTORS AFFECTING ACID HYDROLYSIS

- ▶ Crowding of a reaction centre may favor a dissociative process.
- ▶ Due to inductive effect rate increases. Increasing alkyl substitution will distort the electron density towards the metal atom and favors dissociative process.
- ▶ The rate decreases with increase in the overall charge on the metal. This indicates dissociative process.
- ▶ Ligands possessing lone pair of electron favor dissociative process and ligands which withdraws electron from the metal centers by delocalization of electron pairs favor associative process.

BASE HYDROLYSIS

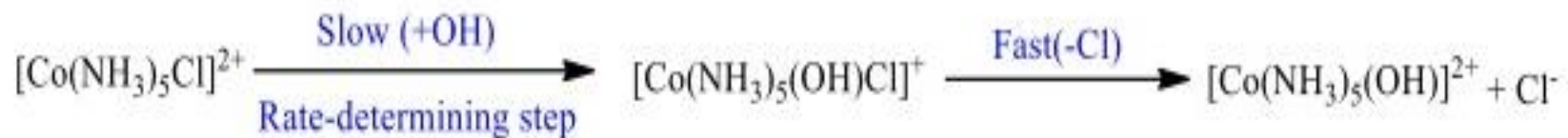
- Occurs in basic solutions ($\text{pH} > 10$).
- Two types of mechanisms in octahedral complexes.
 - S_N2 or Associative mechanism.*
 - S_N1CB or Dissociation mechanism.*

S_N1CB Mechanism is more favored than S_N2 Mechanism

Acid-Base properties of the complexes are more important than the nucleophilic properties of OH^- in S_N1CB Mechanism.

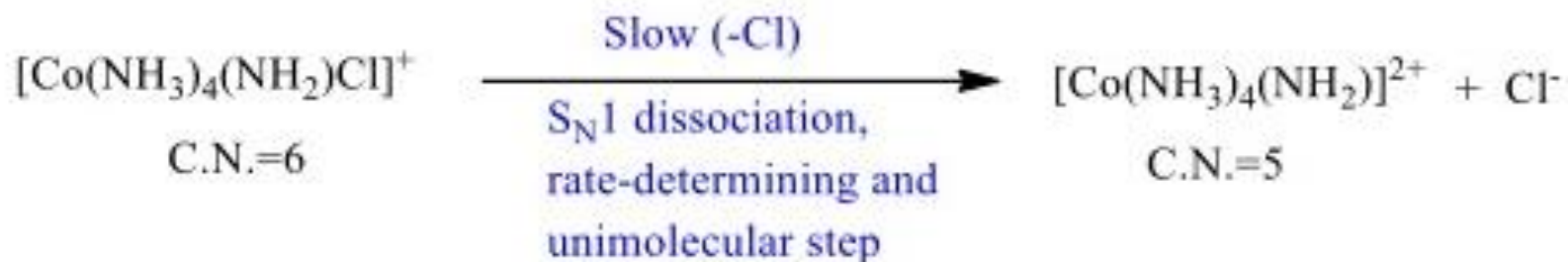
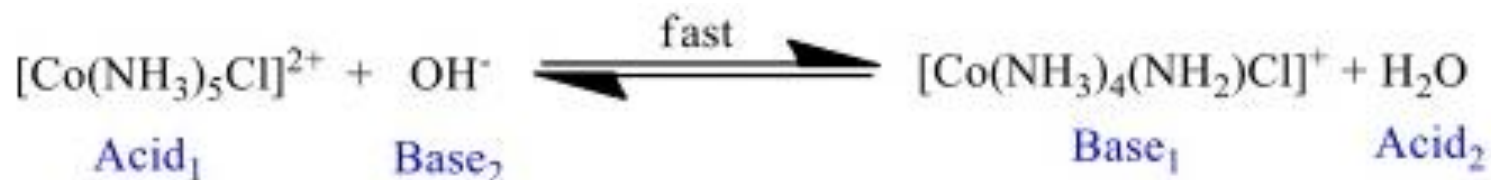
Reactions occurring in non hydroxylic solvents like Dimethyl sulphoxide, can be explained by S_N1CB mechanism but not by S_N2 .

S_N2 OR ASSOCIATIVE MECHANISM



$$\text{Rate} = k[\text{Co(NH}_3)_5\text{Cl]}^{2+} [\text{OH}^-]$$

S_N1CB OR DISSOCIATIVE MECHANISM



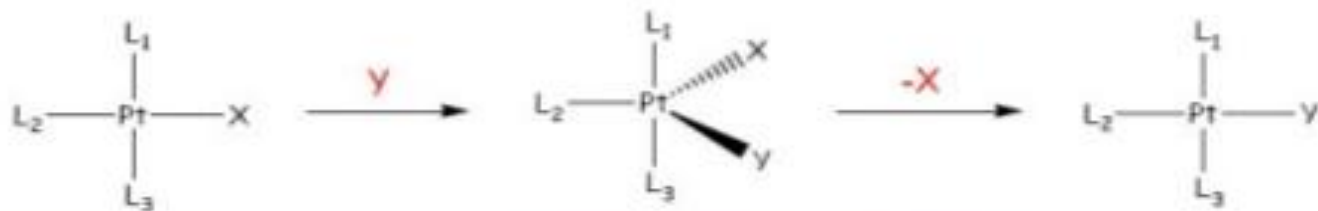
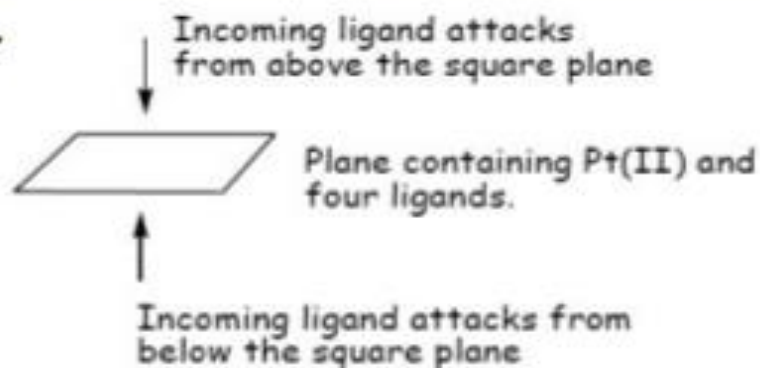
- Rate = $k_1[\text{CB}]$; where CB= Conjugate Base ,

$$[\text{CB}] = \frac{K [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} [\text{OH}^-]}{[\text{H}_2\text{O}]}$$

LIGAND SUBSTITUTION IN SQUARE PLANAR COMPLEXES

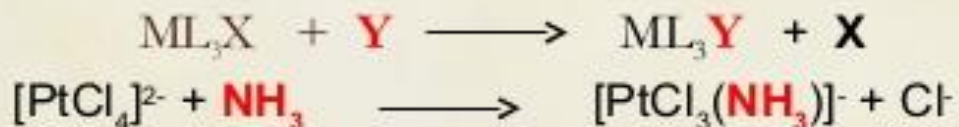


Mechanism:



Initial attack by the entering group at a square planar Pt(II) centre is **from above or below the plane**. Nucleophile **Y** then coordinates to give a **trigonal bipyramidal intermediate** species which loses X with **retention of stereochemistry**).

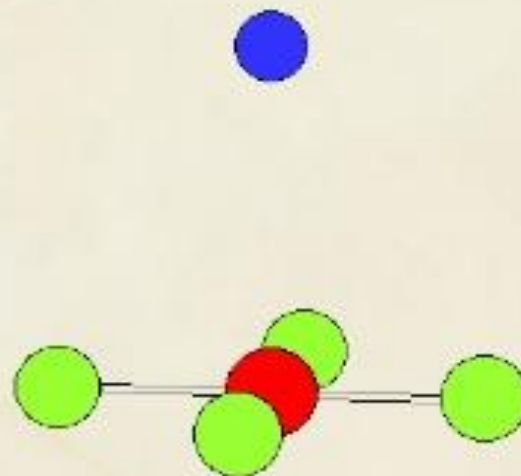
ASSOCIATIVE MECHANISM



The incoming ligand (colored blue) approaches a vacant axial site of the square planar complex to form a square pyramidal intermediate (or transition state).

Intramolecular rearrangement via a **trigonal bipyramid** generates a different **square pyramidal** structure with the incoming ligand now in the basal plane. (This motion is closely related to **Berry Pseudorotation**).

The reaction is completed by the leaving group departing from an axial site with the **stereochemistry being retained during the substitution process**.



FACTORS WHICH AFFECT THE RATE OF SUSTITUTION

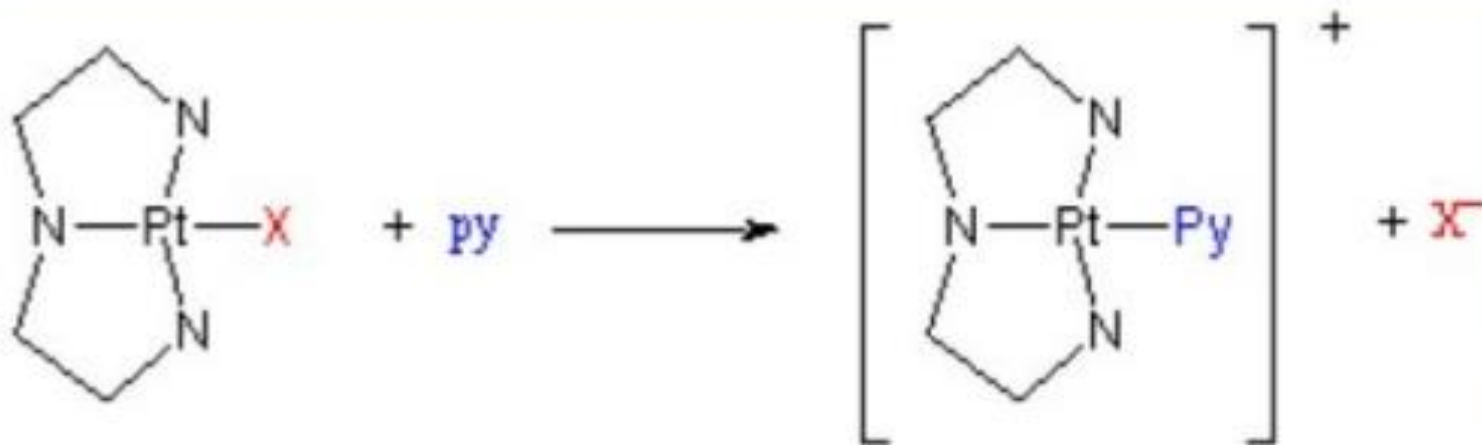
- 1) Role of the entering group
- 2) Role of the leaving group
- 3) Effect of the Metal Center
- 4) The *trans* effect

Role of the Entering Group:

- The rate of substitution is proportional to the nucleophilicity of entering group
i.e. for most reactions of Pt(II), the rate constant increases in the order
: H₂O < NH₃ = py < Br < I < CN
- The ordering is consistent with **Pt(II)** being a soft metal center.

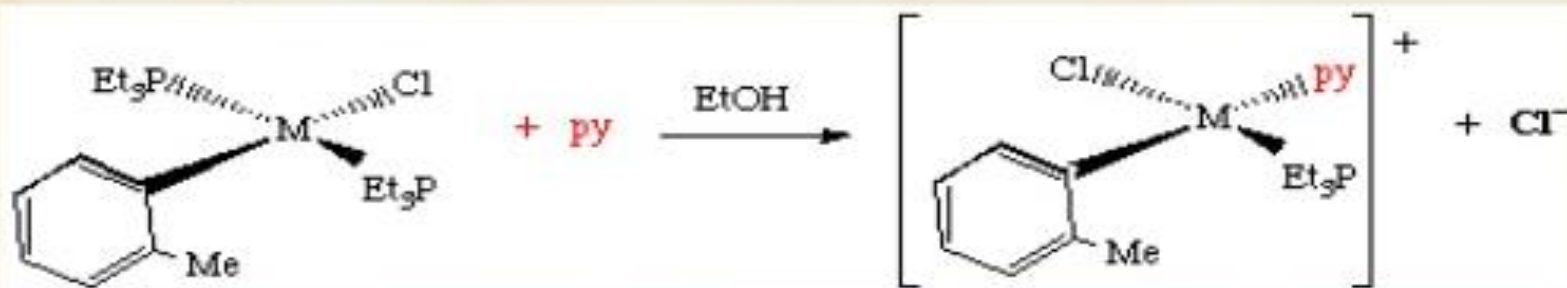
THE ROLE OF THE LEAVING GROUP

- $[\text{Pt}(\text{dien})\text{X}]^+ + \text{py} \longrightarrow [\text{Pt}(\text{dien})(\text{py})]^+ + \text{X}^-$
- In H_2O at 25°C the sequence of lability is : $\text{H}_2\text{O} > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{N}_3^- > \text{SCN}^- > \text{NO}_2^- > \text{CN}^-$
a spread of over 10^6 in rate across series.



EFFECT OF THE METAL CENTER

- The order of reactivity of a series of isovalent ions is: Ni(II) > Pd(II) >> Pt(II)
- This order of reactivity is the same order as the tendency to form 5-coordinate complexes.
- More readily is the formation of a 5-coordinate intermediate complex, the greater is the stabilization of the transition state and so the greater is the bimolecular rate enhancement.



M (II)

Ni $k = 33 \text{ M}^{-1} \text{ sec}^{-1}$

Pd $k = 0.58 \text{ M}^{-1} \text{ sec}^{-1}$

Pt $k = 6.7 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$

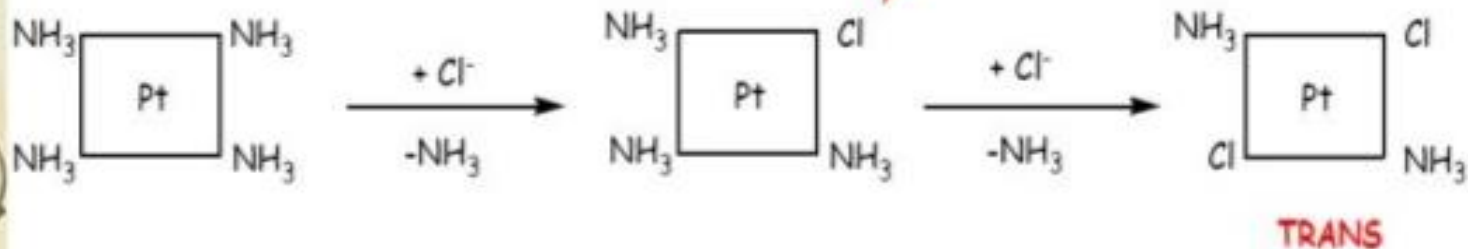
TRANS EFFECT

- The *trans* effect is best defined as the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it.
- **Or** The ability of a ligand in a square planar complex to direct the replacement of the ligand *trans* to it.
- It was recognized by Werner (1893) and elaborated by Chernuyayev (1926).
- By comparing a large number of reaction rates Langford and Grey set up a trans directing series.
- In the trans-directing series, the ligands are arranged in the increasing order of trans effect as follows:
$$\text{H}_2\text{O} < \text{OH}^- < \text{F}^- \approx \text{RNH}_2 \approx \text{py} \approx \text{NH}_3 < \text{Cl}^- < \text{Br}^- < \text{SCN}^- \approx \text{I}^- \\ \approx \text{NO}_2^- \approx \text{C}_6\text{H}_5^- < \text{SC}(\text{NH}_2)_2 \approx \text{CH}_3^- < \text{NO} \approx \text{H}^- \approx \text{PR}_3 < \\ \text{C}_2\text{H}_4 \approx \text{CN}^- \approx \text{CO}$$

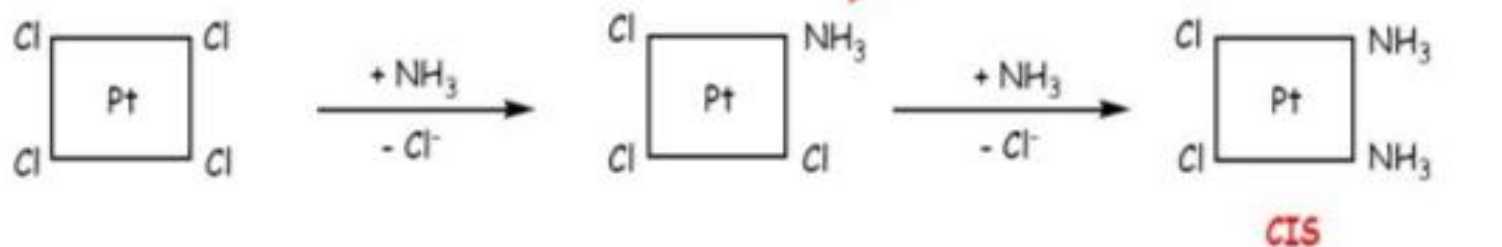
APPLICATION OF TRANS EFFECT

1. Synthesis of isomers of $Pt(NH_3)_2Cl_2$

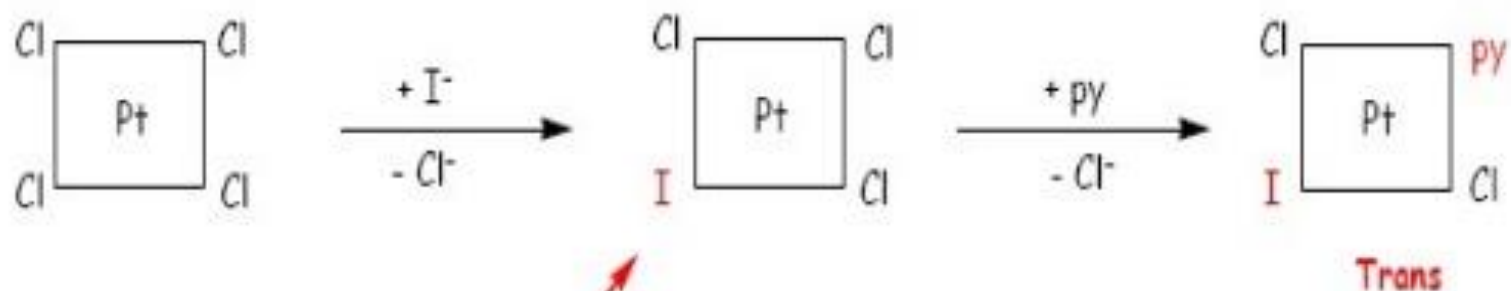
Reaction 1



Reaction 2

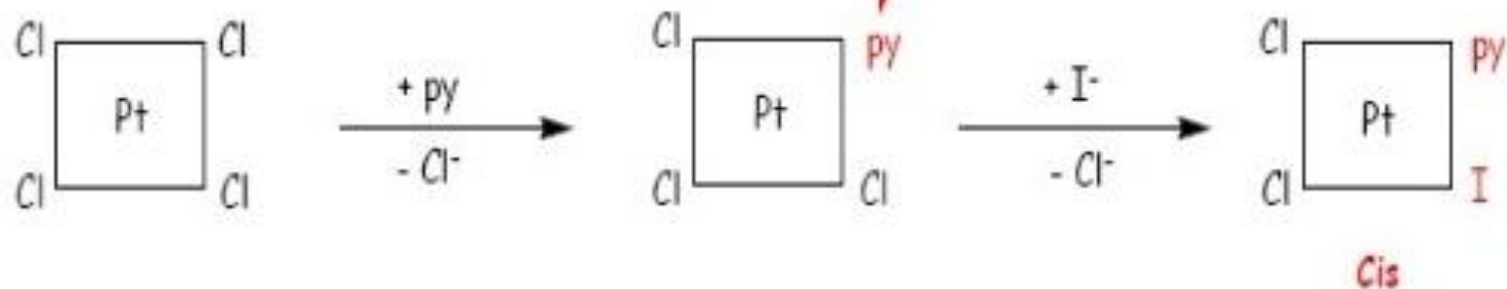


PREPARATION OF CIS AND TRANS ISOMERS



higher than Cl^- in the trans directing series, directs py trans to it

lower than Cl^- in the trans directing series, Cl^- directs I trans to py



APPLICATION OF CO-ORDINATION COMPOUNDS

- ◉ **DETECTION OF K⁺ ION:** K⁺ form a complex with sodium hexanitritocobaltate(III). Formation of this potassium hexanitritocobaltate complex is used for the gravimetric estimation of K⁺.
- ◉ **Separation of Cu²⁺ and Cd²⁺** in second group is done by adding KCN solution. The sulphides of both metals form complexes and go into solution, hydrogen sulphide is passed. Cd²⁺ alone is precipitated, it can be separated by filtration.
- ◉ **ESTIMATION OF NICKEL:** Ni²⁺ forms a bis(dimethylglyoximate) nickel(II) complex with dimethyl glyoxime. It is scarlet red in colour. Formation of this complex is used for the gravimetric estimation of Ni²⁺ in solution.
- ◉ **ESTIMATION OF ALUMINIUM:** Al³⁺ forms a trisoxinatoaluminium complex with oxine. Formation of this complex is used for the gravimetric estimation Al³⁺ of in solution

BIOLOGICALLY IMPORTANT CO-ORDINATION COMPOUNDS

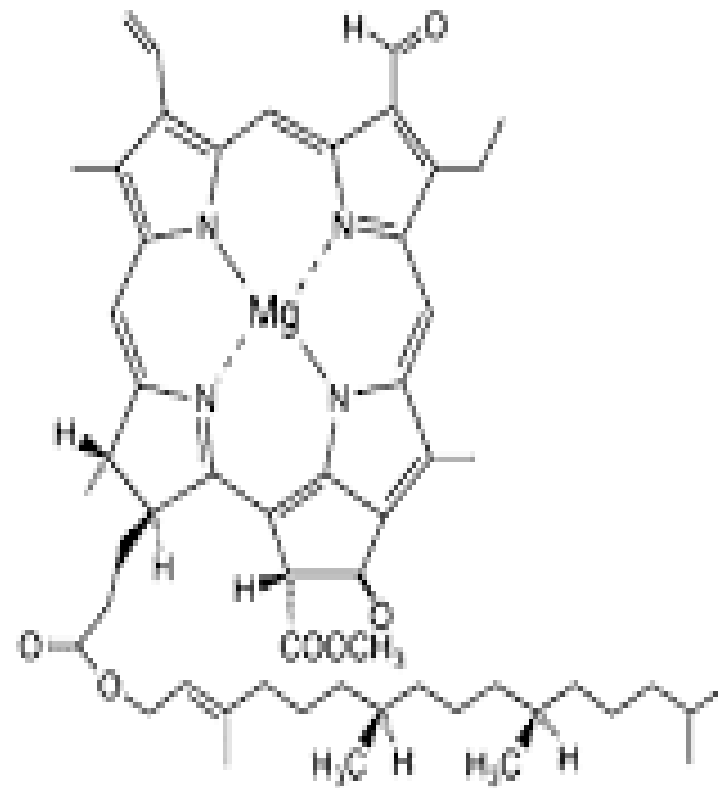
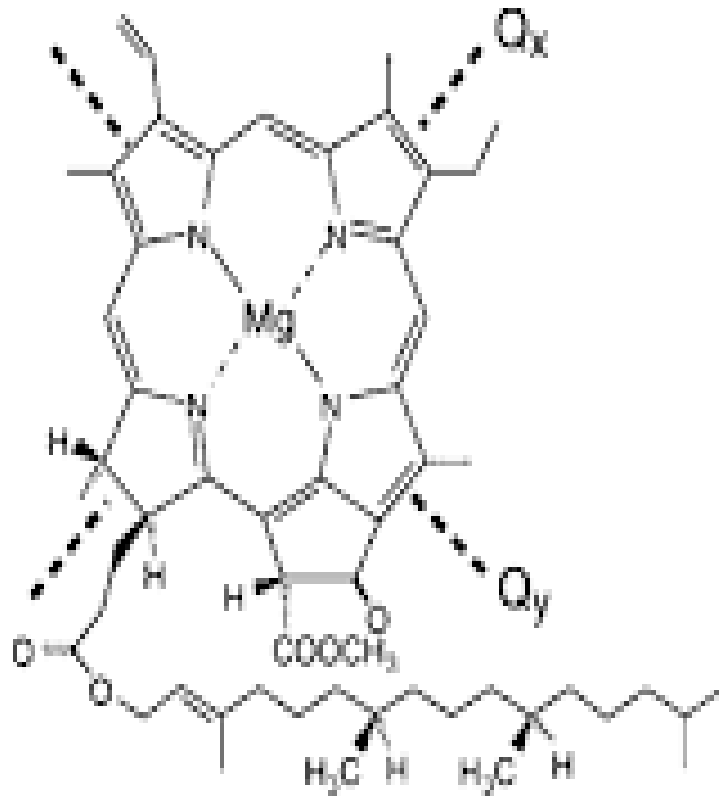
CHLOROPHYLL

Chlorophyll is magnesium porphyrin complex, present in green plants, It consists of two distinct but chemically related chlorophyll –a and chlorophyll –b substances.

BIOLOGICAL IMPORTANCE

Its presence is essential for photosynthesis in plants. it can capture and transmit the light energy for chemical reaction taking place in photosynthesis. Mg^{2+} ions act as a source of phosphorescence which is responsible for making the light energy available for photosynthesis.

STRUCTURE OF CHLOROPHYLL a AND b



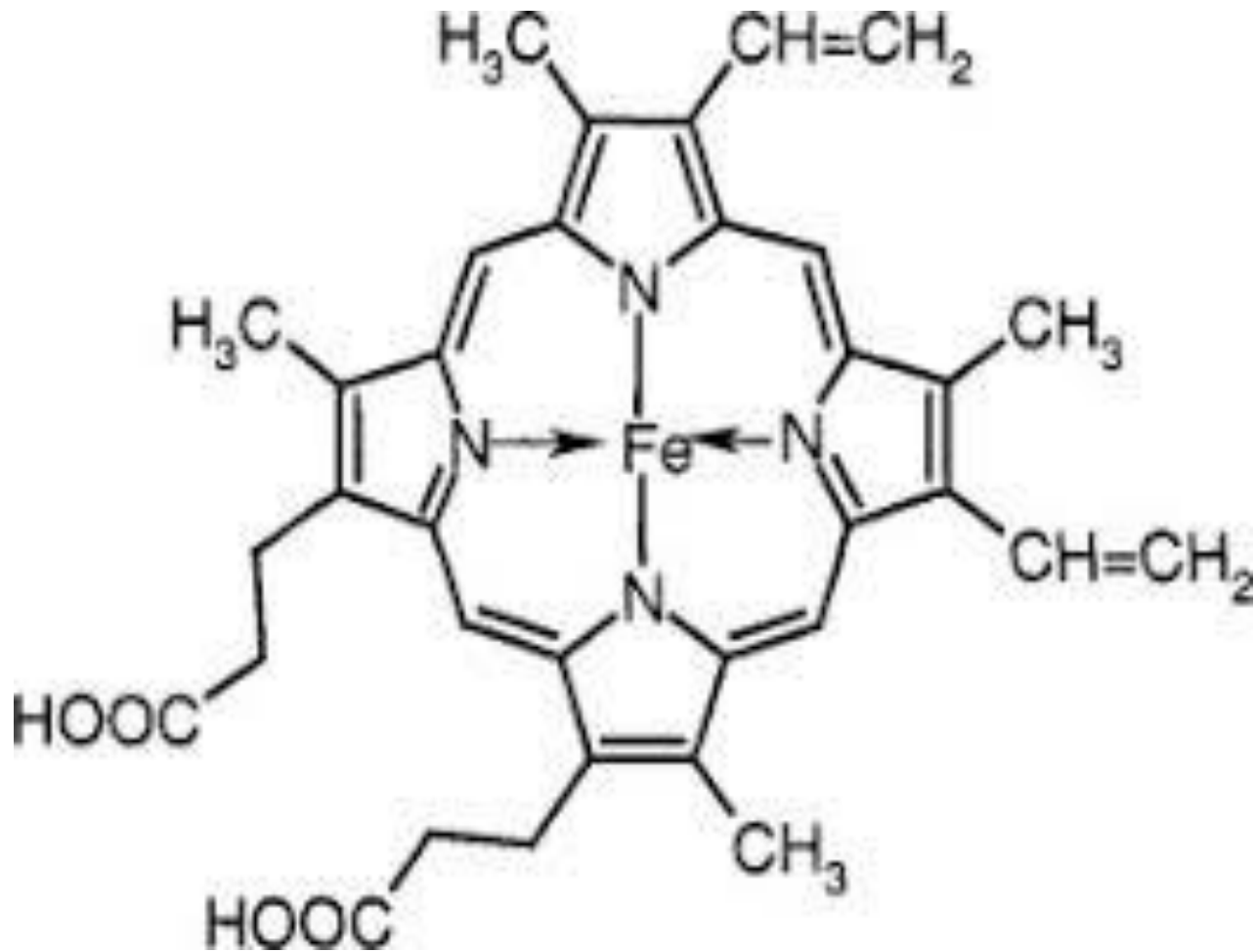
HAEMOGLOBIN

- It is a conjugated protein the protein part being globin and the prosthetic group being heme. It is presented in red cells of blood.

BIOLOGICAL IMPORTANCE

- It forms the main constituent of blood.

STRUCTURE OF HAEMOGLOBIN



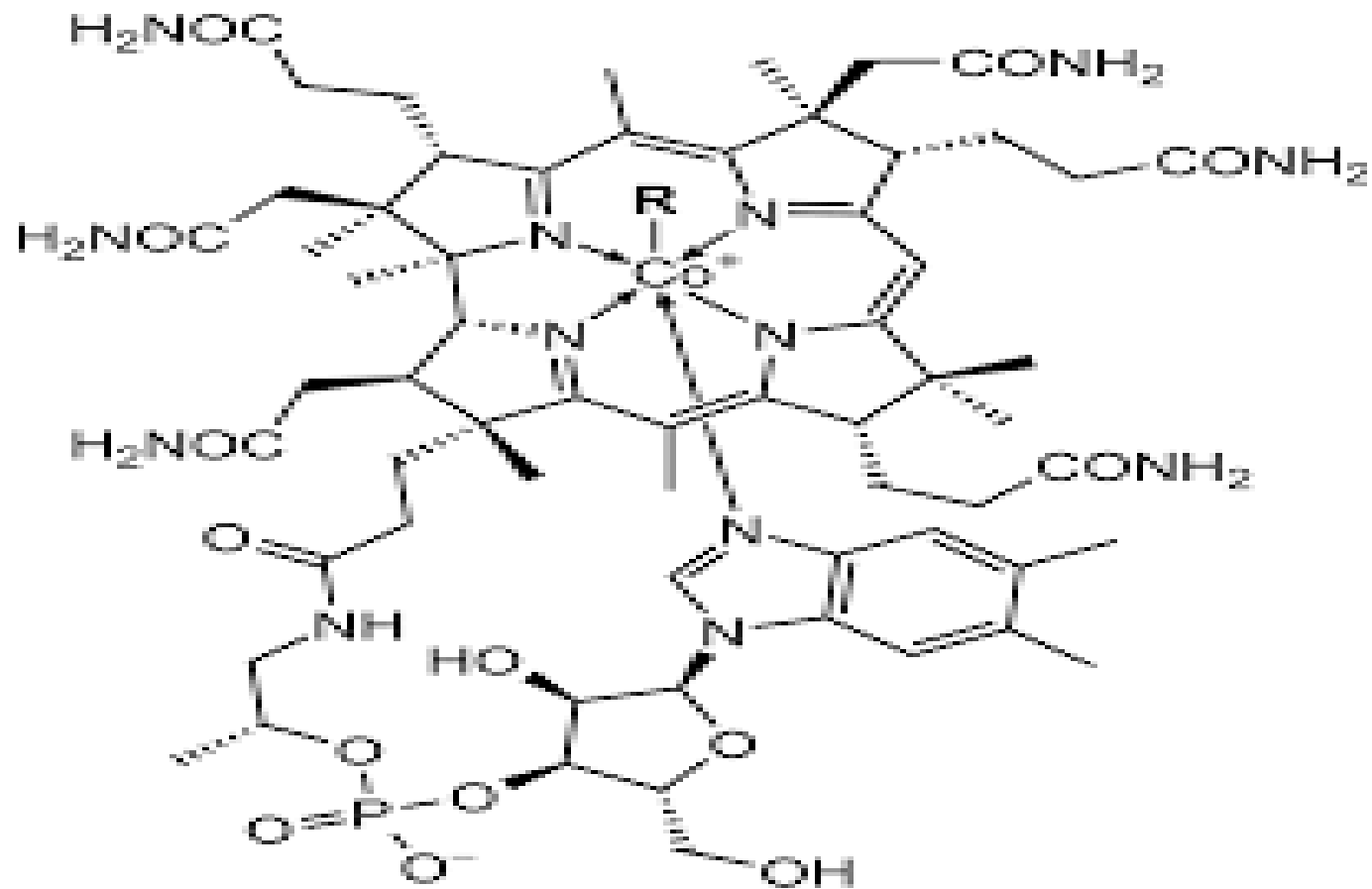
VITAMIN B₁₂

- ⊙ It is an octahedral complex of Co^{3+} , it contains corrin ring co-ordinated by four nitrogen atoms, the fifth position is filled by an benzimidazole nitrogen, sixth by a CN^- .

BIOLOGICAL IMPORTANCE

- ⊙ The deficiency of vit-B₁₂ causes pernicious anemia which is accompanied by degradation of the spinal cord.

STRUCTURE OF VITAMIN B₁₂



R = 5'-deoxyadenosyl, CH₃, OH, CN

UNIT - IV

METAL CARBONYLS

CONTENTS

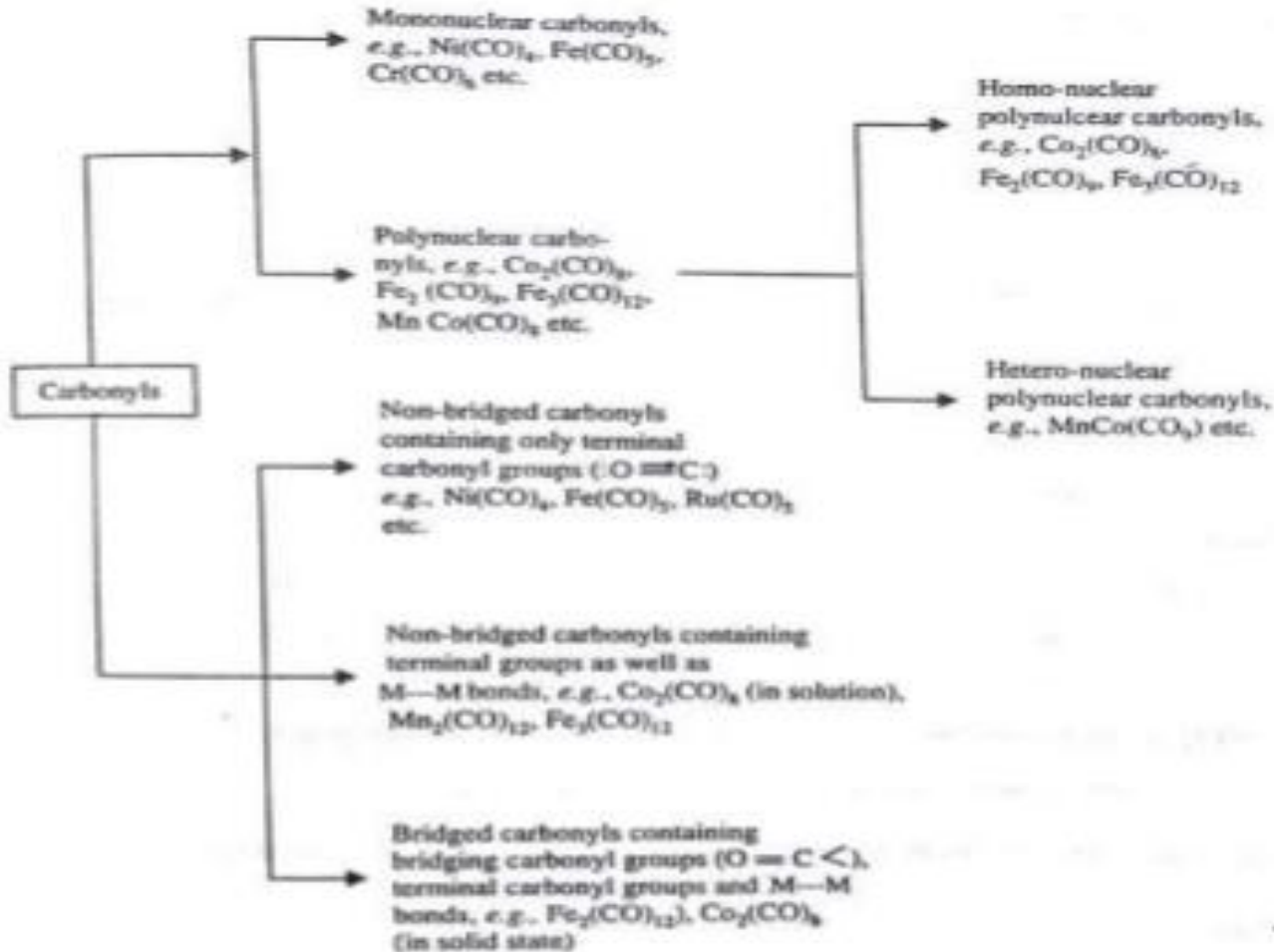
- INTRODUCTION
- CLASSIFICATION
- PREPARATION & PROPERTIES
- STRUCTURE & BONDING
- APPLICATIONS

INTRODUCTION

- Metal carbonyls are coordination complexes of transition metals with carbon monoxide ligands in **low oxidation state**. In this ,CO ligands acts as neutral ligands
- Metal carbonyl compounds were first synthesized in by **Paul Schützenberger** in 1868 by passing chlorine and carbon monoxide over platinum black, where **dicarbonyldichloroplatinum ($\text{Pt}(\text{CO})_2\text{Cl}_2$)** was formed.
- Although many compounds were produced, they couldn't be fully characterized until the development of X-ray diffraction, and IR and NMR spectroscopy.
- In general, these compounds obey the "**18 electron rule**."
- Normally **dimagnetics**.
- Monomerics are **colourless** where polymeric are coloured.
- Poor conductors of electricity & Sublimated at low temp
- Soluble in organic solvents.

CLASSIFICATION

Classification of carbonyls



PREPARATION

1. Direct reaction of metal with carbon monoxide



2. Reduction of metal salts and oxides



3. Preparation of dinuclear carbonyls from mononuclear carbonyls (Photolysis and thermolysis)



CHEMICAL PROPERTIES

1.CO substitution



2.REDUCTIONS



3.Nucleophilic attack at CO



4. With electrophiles



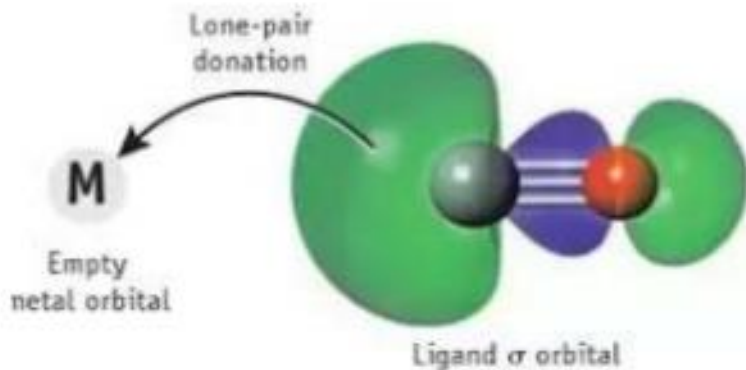
METAL - CARBON BOND

Formation of σ -bond:

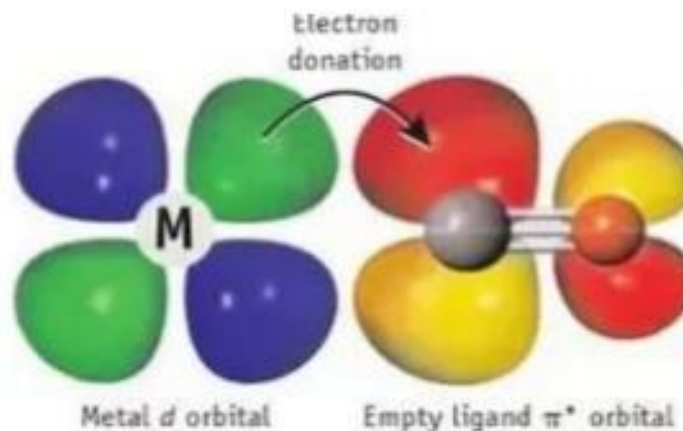
The overlapping of empty hybrid orbital on metal atom with the filled hybrid orbital on carbon atom of carbon monoxide molecule through lone pair electrons results into the formation of a $M \leftarrow CO$ σ -bond.

Formation of π -bond by back donation:

This bond is formed because of overlapping of filled $d\pi$ orbitals or hybrid $dp\pi$ orbitals of metal atom with antibonding π orbitals on CO molecule.



Ligand to metal sigma bonding.
Donation of CO lone pair to empty orbital on M.



Metal to ligand pi bonding.
Donation of electrons from filled M d orbital to empty π^* antibonding orbital on CO.

Structure of Ni(CO)₄

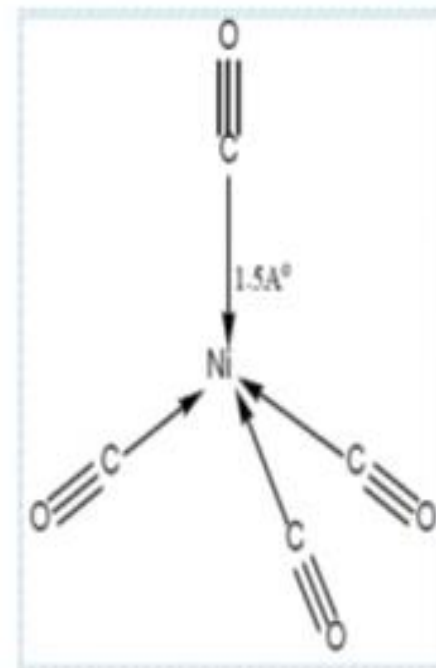
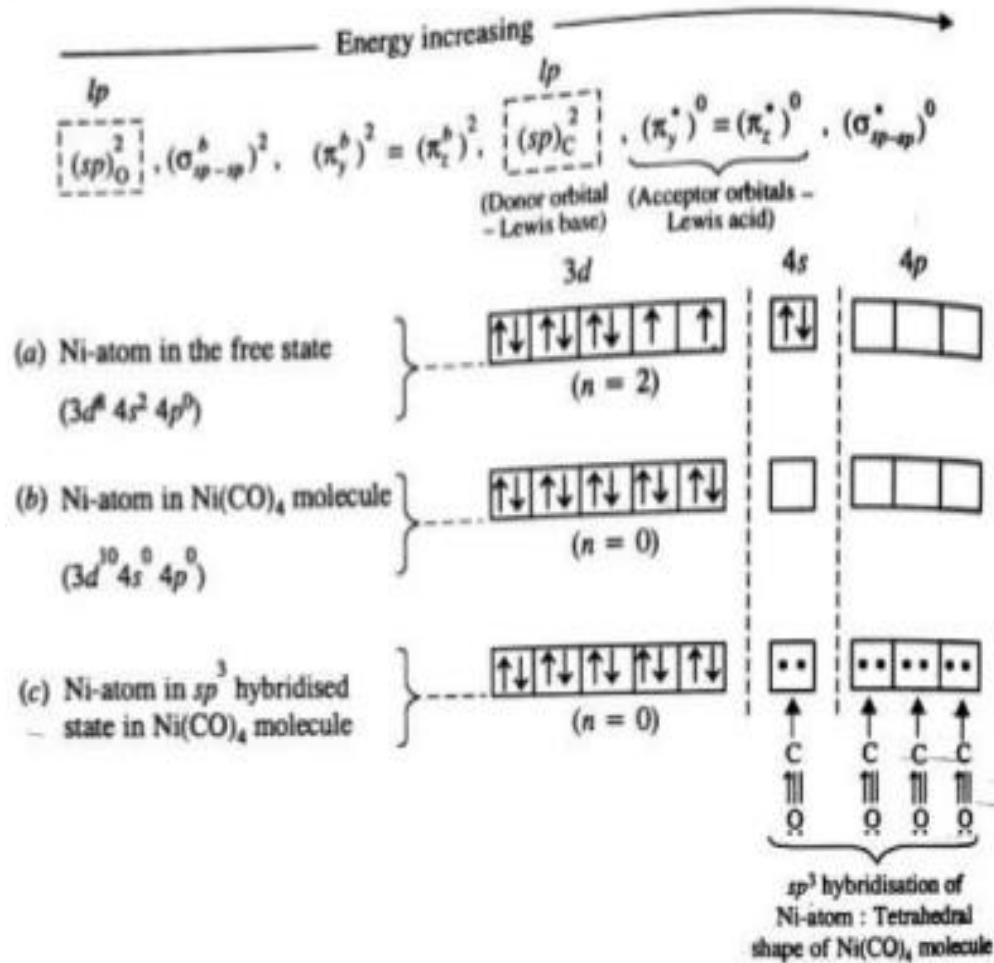
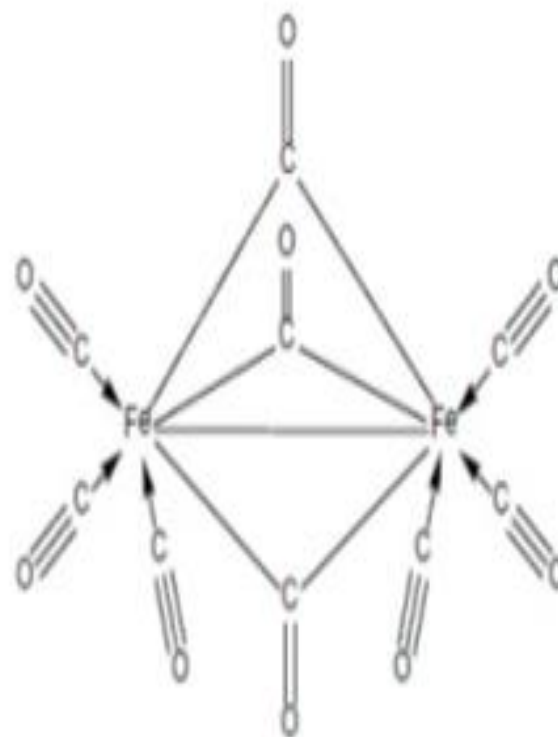
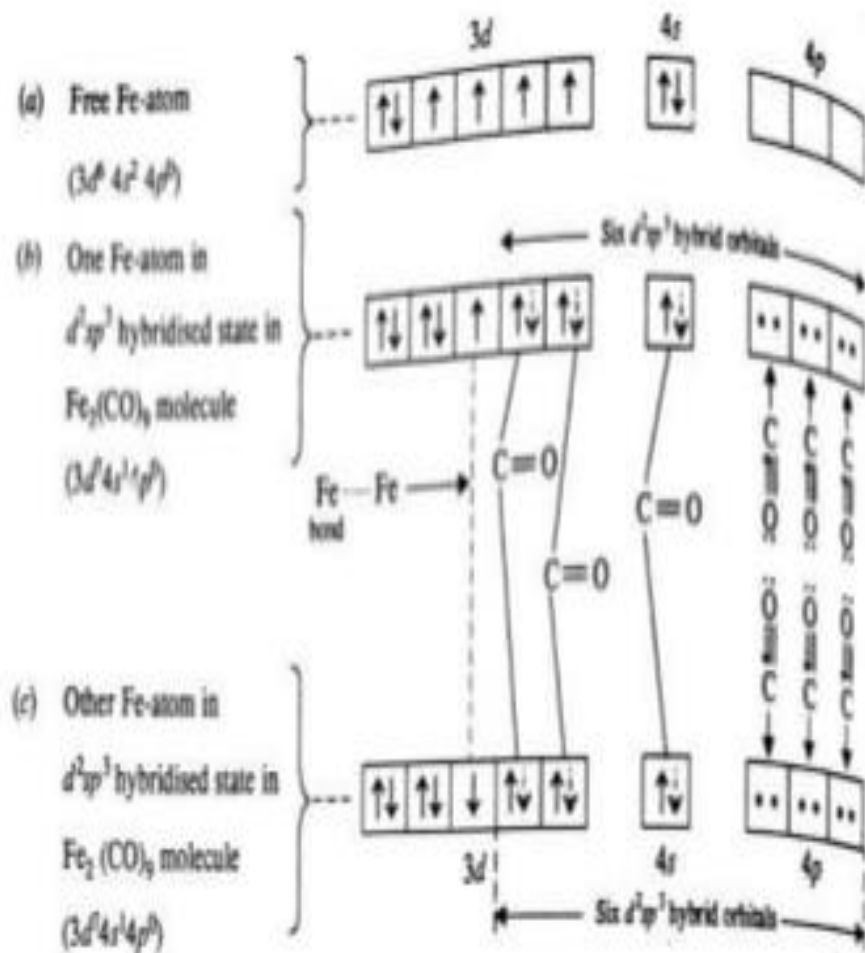


Figure: Tetrahedral structure of nickel tetracarbonyl.

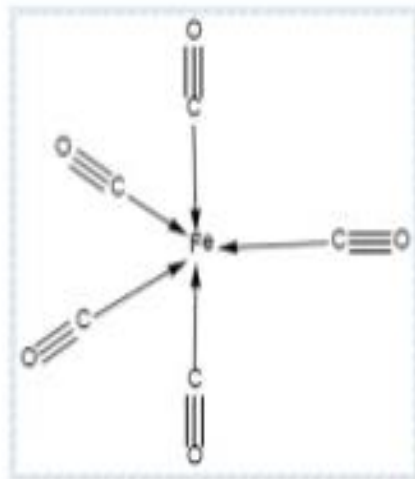
Structure of $\text{Fe}_2(\text{CO})_9$



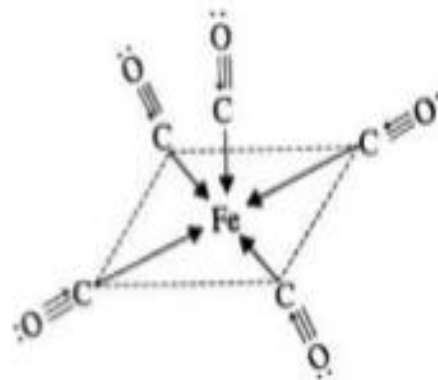
APPLICATIONS

1. DETERMINATION OF GEOMETRY OF CARBONYLS :-

Calculating no of IR active bands with Raman active bands and then tally with no of bands predicted theoretically



TBP structure of $\text{Fe}(\text{CO})_5$



Square pyramidal structure of $\text{Fe}(\text{CO})_5$ molecule

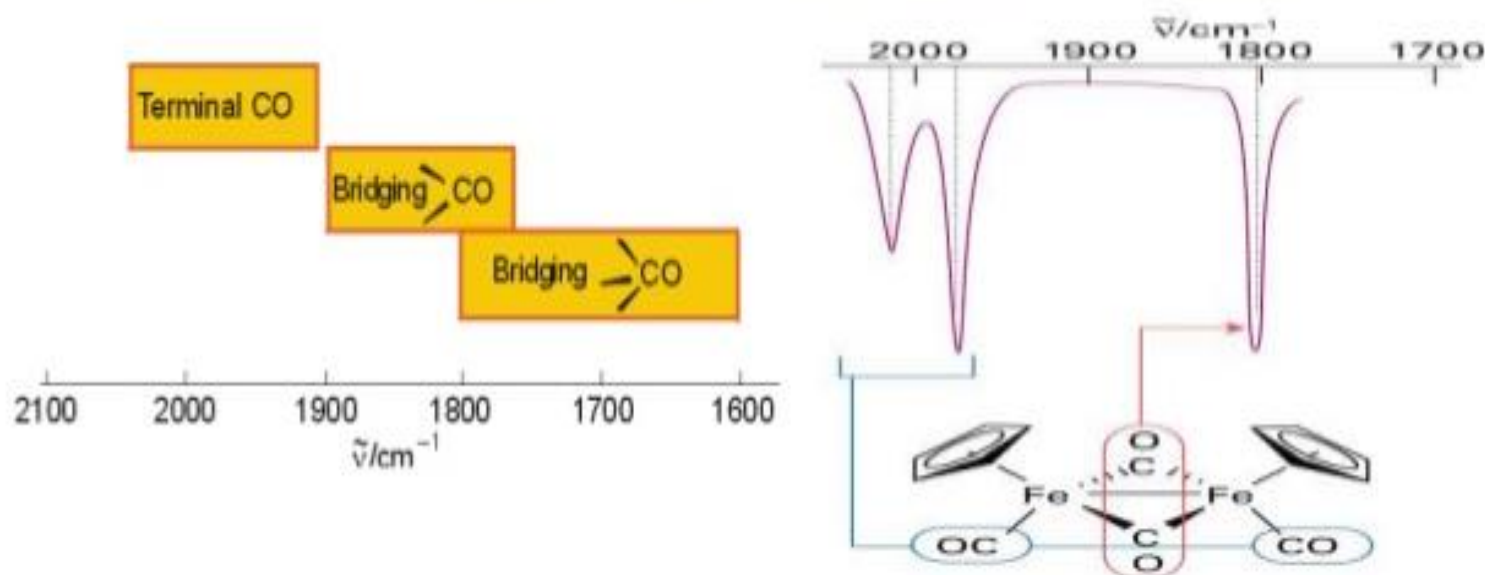
2. DETERMINATION OF BOND ORDER:-

2. To determine the bond order (B.O.) of ligated CO, It has been seen that I.R. absorption frequency of ligated CO is directly proportional to its B.O. In other words the I.R. absorption band due to the stretching vibration of ligated CO with a higher B.O. would occur at a higher frequency and the I.R. absorption band of ligated CO with a lower B.O. would occur at a lower frequency. Since the absorption frequency for free CO is equal to 2250 cm^{-1} while that for ligated CO lies between $2220\text{--}1700\text{ cm}^{-1}$, ligated CO has lower B.O. The lower B.O. is due to the transfer of metal $d\pi$ electrons into the π^* orbitals of ligated CO. Let us study the following examples.

Metal carbonyl :	$[\text{V}(\text{CO})_6]^-$	$\text{Cr}(\text{CO})_6$	$[\text{Mn}(\text{CO})_6]^+$
Charge on metal carbonyl :	—	0	+
Absorption frequency for CO (cm^{-1}) :	1860	1980	2090

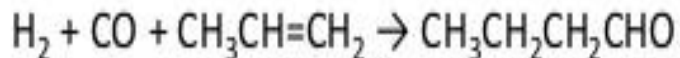
Since the presence of positive charge on $[\text{Mn}(\text{CO})_6]^+$ restricts the flow of metal $d\pi$ electrons into the π^* orbitals of CO, the B.O. of CO increases. Due to the increase in B.O., the absorption band of ligated CO occurs at higher frequency ($=2090\text{ cm}^{-1}$).

3. DETERMINATION OF TERMINAL & BRIDGING CARBONYL GROUP:-



SOME OTHER APPLICATIONS

- Ligand. Metal carbonyls are useful in organic synthesis and as catalysts or catalyst
- Precursors in homogeneous catalysis, such as hydroformylation and Reppe chemistry.



Dicobalt octacarbonyl acts as catalyst

- In the Mond process, nickel carbonyl is used to produce pure nickel.
- In organometallic chemistry, metal carbonyls serve as precursors for the preparation of other organometallic complexes.
- Metal carbonyls are toxic by skin contact, inhalation or ingestion, in part because of their ability to carbonylate hemoglobin to give carboxyhemoglobin, which prevents the binding of O_2 . That is why precaution is used before using it.

METAL NITROSYLS

- Organometallic compounds containing nitric oxide as ligand are termed as metal nitrosyl complexes.

CLASSIFICATION

EAN

T
Stable
electro

NITROSYL CHLORIDE

Nitrosyl chloride

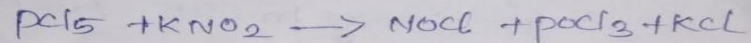
(2)

PREPARATION:

1. NO and Cl_2 combine directly in bright sunlight or in the presence of animal charcoal at 40 we get NOCl

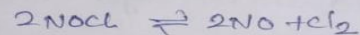


2. When PCl_5 is treated with KNO_2 we get



PROPERTIES:

1. Stability: It is stable, above 160°C it decomposes into NO and Cl_2

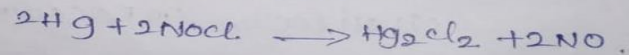


2. With water: It is decomposed by water easily.



3. With metals:

It attacks many other metals forming metallic chlorides.

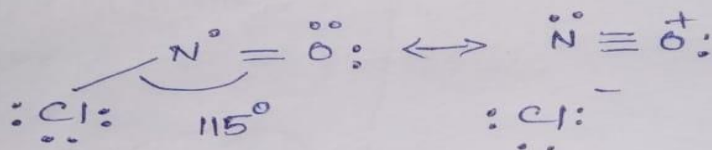


Uses: It is used to identify the presence and number of double bonds in a molecule.

STRUCTURE

STRUCTURE:-

Electron diffraction studies have a shown that NOCl molecule is bent. The bond distances are $N-O = 1.14 \text{ \AA}$, $N-Cl = 1.95 \text{ \AA}$. The O-N-Cl bond angle is 115° . The bond distance of N-Cl 1.95 \AA is relatively high.



(a) Covalent structure

(b) Ionic structure.



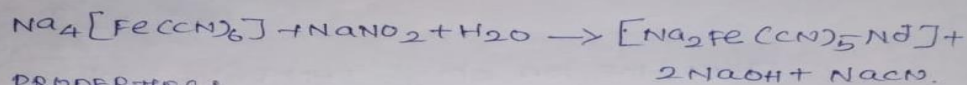
The covalent structure of NOCl is V shaped. N is in a state of sp^3 hybridisation. The unhybridised p orbital of O-atom. one of the sp^2 hybridised orbitals is occupied by a lone pair of electron.

SODIUM NITROPRUSSIDE

sodium nitroprusside $\text{Na}_2[\text{Fe}^{2+}(\text{CN})_5(\text{NO})]$ (4)

PREPARATION.

NaNO_2 is treated with $\text{Na}_4[\text{Fe}(\text{CN})_6]$



PROPERTIES:

1. It exists as ruby red rhombic crystals soluble in water.
2. It gives a flesh colour with silver nitrate
$$2\text{AgNO}_3 + \text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \rightarrow \text{Ag}_2[\text{Fe}(\text{CN})_5(\text{NO})] + 2\text{NaNO}_3$$
3. Aldehydes and ketones containing $>\text{C}=\text{O}$ group give deep red colour with sodium nitroprusside and excess NaOH .

STRUCTURE:

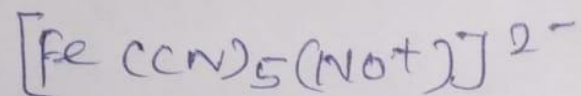
$[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ was thought to contain Fe in +2 oxidation state. But Pauling (1931) and Sidgwick (1934) suggested that one electron from NO group enters the valency shell of Fe^{2+} ion converting it to Fe^{2+} so NO acquires one positive charge. This NO⁺ ion is co-ordinated to Fe^{2+} ion. This idea is supported by the fact that $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ is diamagnetic whereas $\text{Na}_3[\text{Fe}(\text{CN})_6]$ is paramagnetic. It has an octahedral structure with Fe^{2+} ion in the centre of the octahedron.

Uses:

- i) It is used to detect the presence of sulphide in qualitative analysis.
- ii) It is used to detect the presence of aldehydes and ketones containing $>\text{C}=\text{O}$ group.

EAN RULE

EAN Rule as applied to nitroprusside ion



$$\text{Fe}^{2+} = 24$$

$$5\text{CN} = 10$$

$$\text{NO}^+ = \frac{2}{36} (\text{Kr})$$

Thus the ion obeys EAN Rule and so is stable. The molecule contains no unpaired electrons. So it is diamagnetic.

THANK YOU