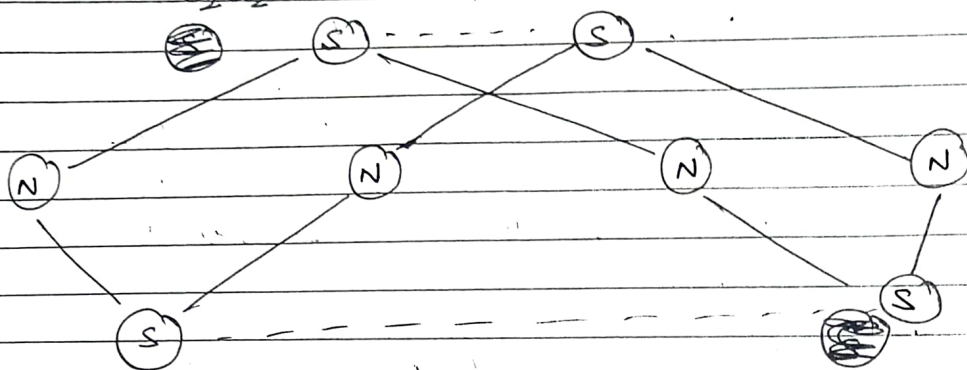
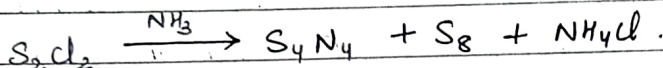


2018

Ques 1) = Discuss the structure of S_4N_4 .

=> Preparation :-



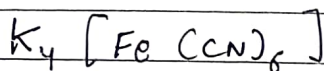
Structure of S_4N_4 .

[also called cradle shaped structure]

Ques 2) = what is Coordination compound.

=> A coordination complex is the product of Lewis Acid - base reaction in which, neutral molecules or anions (called ligands) bond to a central metal atom (or ion) by coordinate covalent bonds.

Example



Potassium hexacyanoferrate (II).

Ques 3) = Give the limitations of CFT.

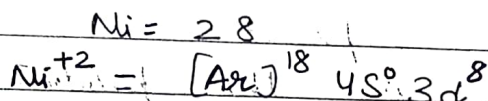
=> 1) The assumption of the interaction b/w Metal-ligand is purely electrostatic and can not said to be realistic.

2) They theory study d-orbitals of a central metal atom but the s and p orbitals are not considered for the study.

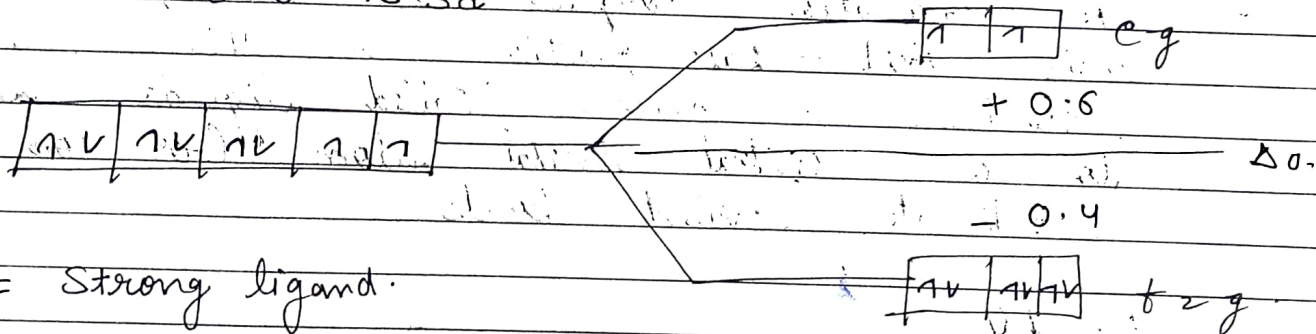
- 3) This theory could not explain the behaviour of some complexes about why some orbitals show large splitting and some show less splitting.
- 4) It cannot explain why H_2O is stronger ligand than OH^- .
- 5) The theory rules out the possibility of having π bonding. This is a serious drawback because π bonding is found in many complexes.
- 6) The theory gives no significance to the orbitals of the ligands.

Ques 4) Calculate the CFSE value of $[Ni(NH_3)_6]^{2+}$

=>



$x + 6(0) = +2$
 $x = +2$



$$\Delta_o = (0.6 \times 2 - 0.4 \times 6) \Delta_o$$

$$= 0.6(2) - 0.4(6) \Delta_o$$

$$= (1.2 - 2.4) \Delta_o$$

$$C.F.S.E = -1.2 \Delta_o$$

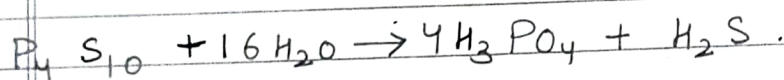
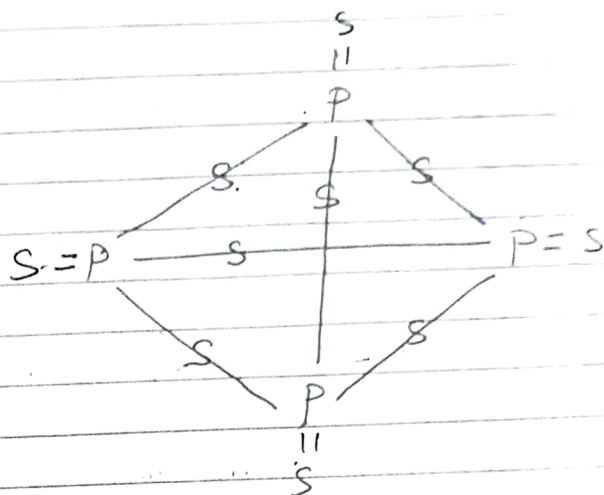
Ques 5> Explain the structure of P_4S_{10} .

No. of P-S-P bonds = 6

No. of P-S bonds = 16

No. of P=S bond = 4

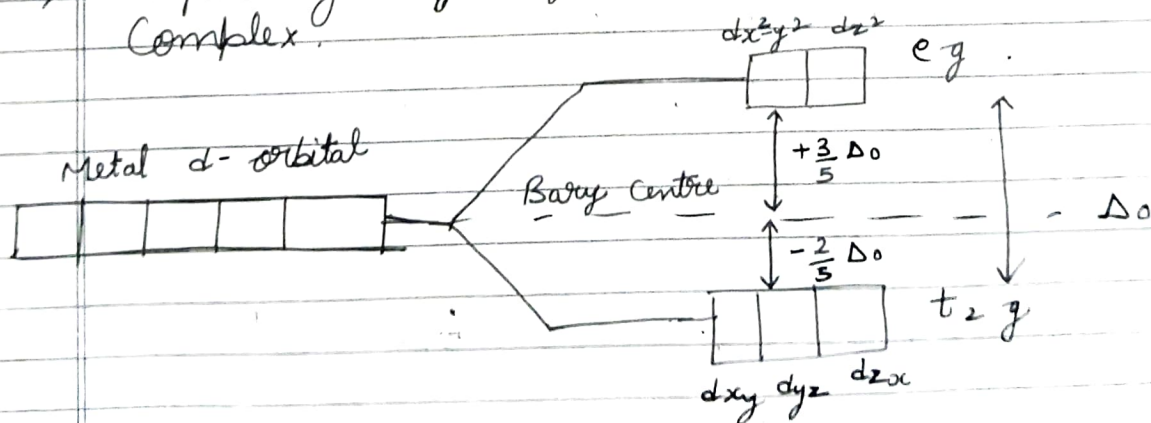
^{31}P - NMR Signals = 1



Ques 6> = Explain the splitting of d-orbitals under octahedral crystal field.

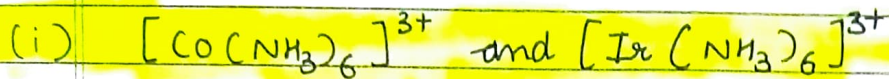
=> The difference of energy b/w the two sets of d-orbitals (in octahedral complexes) is called crystal field splitting energy [CFSE] or Δ_o .

=> Splitting of d-orbital in octahedral complex.



Crystal field splitting energy of octahedral

$$\Delta_o =$$



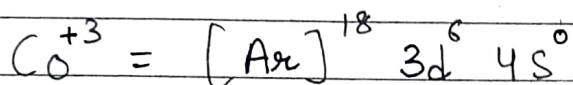
oxidation state of Co

$$x + 6(0) = 3.$$

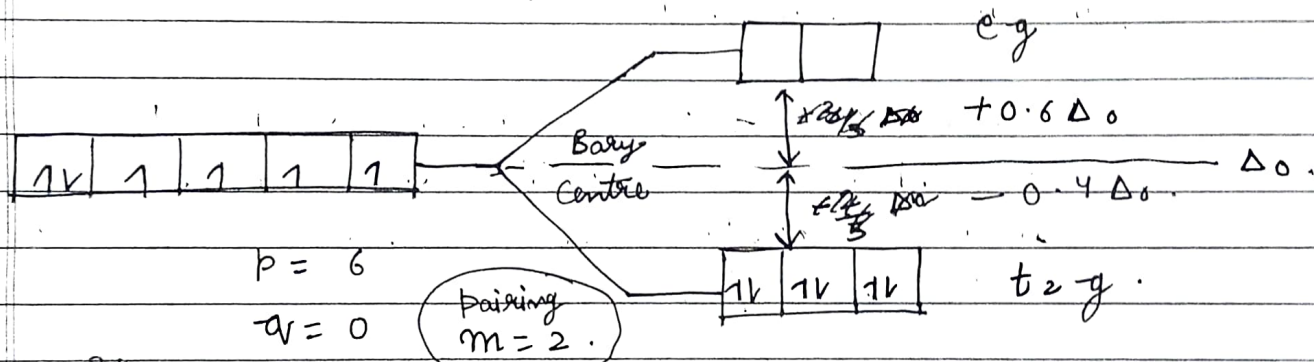
$$x = 3.$$

oxidation state of Co is +3 in $[\text{Co}(\text{NH}_3)_6]^{3+}$

Electronic configuration of Co^{+3} .



Crystal field splitting of $[\text{Co}(\text{NH}_3)_6]^{3+}$



In $[\text{Co}(\text{NH}_3)_6]^{3+}$, NH_3 is strong field ligand then the splitting is very large and its energy is also high.

Crystal field splitting energy.

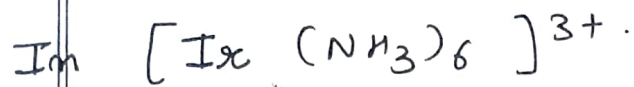
$$\Delta_o = +\frac{3}{5} \Delta_o - \frac{2}{5} \Delta_o$$

or

$$\Delta_o = \left[+0.6 \Delta_o - 0.4 \Delta_o \right] + mP$$

$$= \left[0.6(0) \Delta_o - 0.4(6) \Delta_o \right] + 2P$$

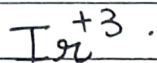
$$\text{C.F.S.E} = -2.4 \Delta_o + 2P$$



oxidation state of Ir is

$$x + 6(0) = +3$$

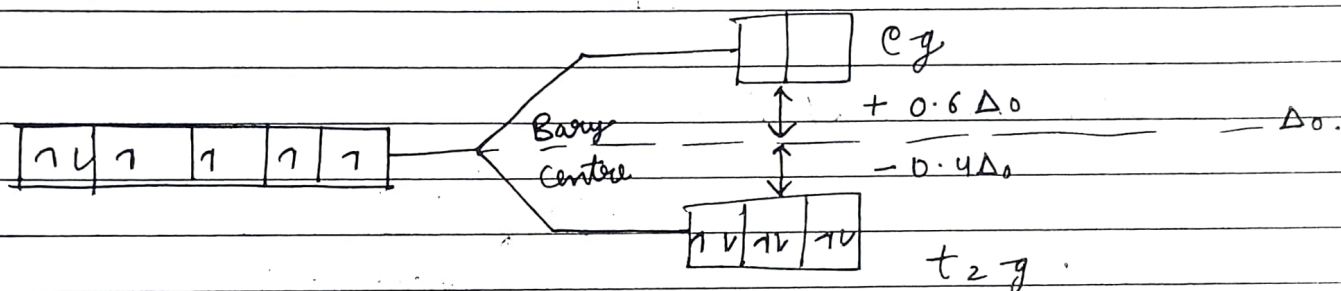
$$x = +3.$$



Electronic Configuration of Ir^{+3} .



Crystal field splitting of $[\text{Ir}(\text{NH}_3)_6]^{3+}$ is.



Here $p = 6$, $q = 0$ pairing $m = 2$

NH_3 is strong field ligand then the splitting is very large and its energy is also high.

C.F.S.E

$$\begin{aligned} \Delta_o &= [+0.6q - 0.4p] \Delta_o + mp \\ &= [+0.6(0) - 0.4(6)] \Delta_o + 2p. \end{aligned}$$

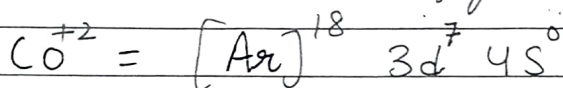
$$\text{C.F.S.E} = -2.4 \Delta_o + 2p.$$

(ii) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ Date: _____In $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

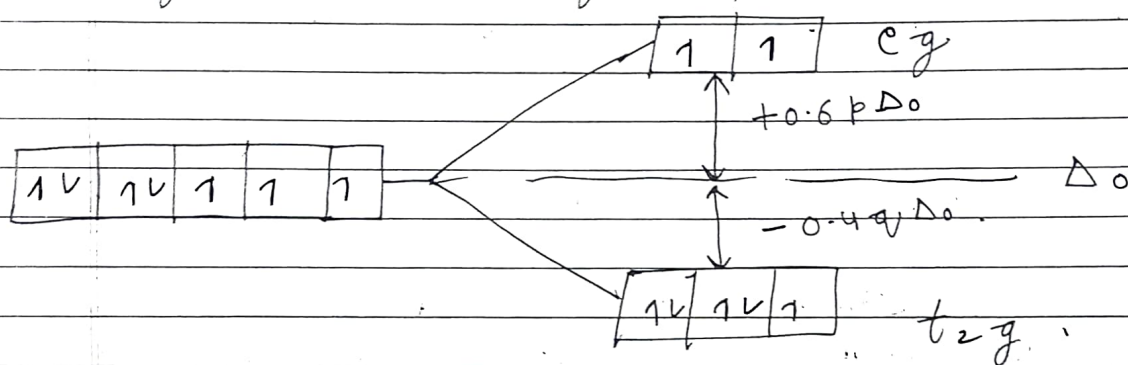
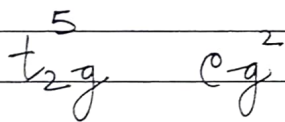
Oxidation state of Co is

$$x + 6(0) = +2$$

$$x = +2$$

Then, Electronic configuration of Co^{+2} 

Crystal field splitting.

Here, H_2O is weak ligand then splitting is less.

$$P = 5, \quad q = 2$$

C.F.S.E value for d^7 complex ion (high spin).

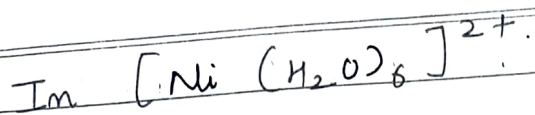
$$= [-0.4P + 0.6q] \Delta_o$$

$$= [-0.4(5) + 0.6(2)] \Delta_o$$

$$= [-2.0 + 1.2] \Delta_o$$

$$= [-0.8 \Delta_o]$$

$$= -0.8 \Delta_o \quad \text{or} \quad -8 Dq$$

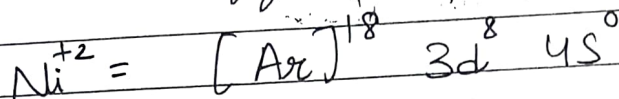


oxidation state of Ni is

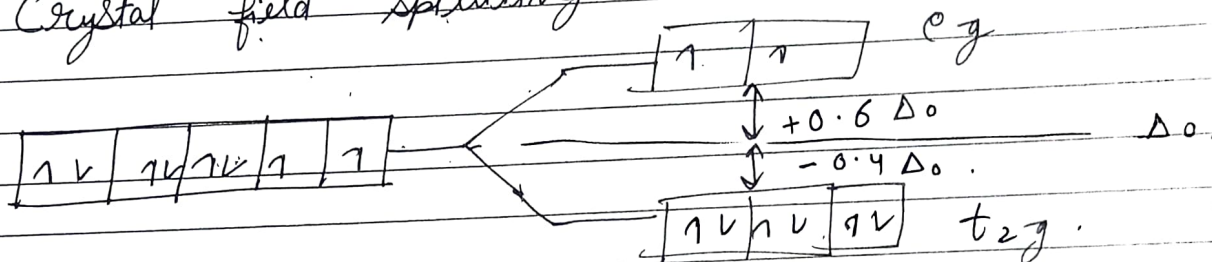
$$x + 6(0) = +2.$$

$$x = +2.$$

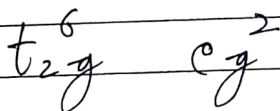
Then, Electronic Configuration of Ni^{+2} .



Crystal field splitting.



Here, H_2O is weak field ligand then splitting is less.



$$P = 6, \quad q = 2.$$

C.F.S.E value for d^8 Complex ion (high spin)

$$= [-0.4 p + 0.6 q] \Delta_o.$$

$$= [-0.4 (6) + 0.6 (2)] \Delta_o.$$

$$= [-2.4 + 1.2] \Delta_o.$$

$$\text{C.F.S.E} = -1.2 \Delta_o \quad \text{or} \quad -12 Dq.$$

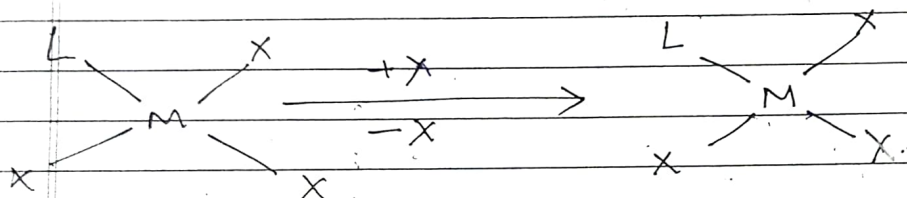
Ques⁷:- what is meant by template effect?

Unit-IV

Trans effect :- The effect of ligand towards substitution on other ligand which is trans to itself.

Ability of the attached group to direct the substitution into a position trans to itself.

(It is in square planar complexes).



π -acceptors

CN, CO, NO, C₂H₄

CN^- , CO , NO , C_2H_4 > Ph_3 > H^- > CH_3^- , C_6H_5^- , NO_2^- , I^- ,

SCN^- , > Br^- > Cl^- > py > RNH_2 , NH_3 > F^- > OH^- > H_2O

(σ donor). Trans effect is nothing but those ligands which are trans directing.

CN^- , CO , NO , C_2H_4 $\rightarrow$ Highly π -acceptors

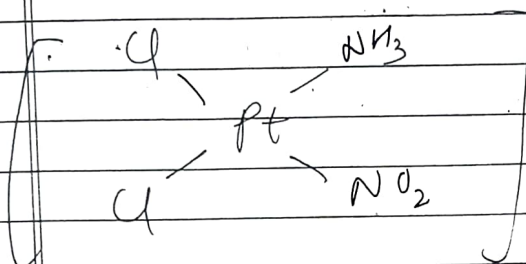
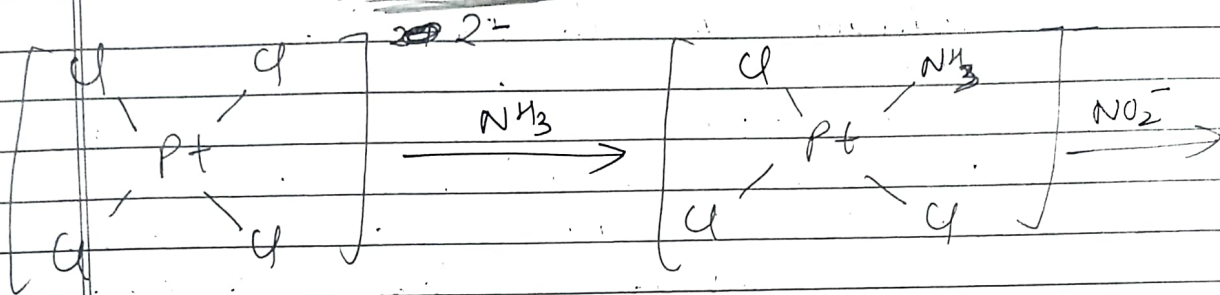
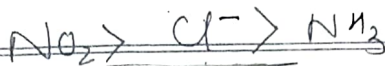
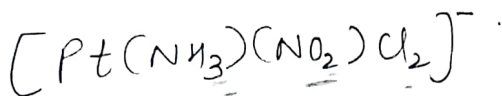
$\rightarrow$ empty π or π^* orbitals, form $d\pi-p\pi$ or $d\pi-d\pi$ bond with metal.

$\rightarrow$ Strong Trans directors.

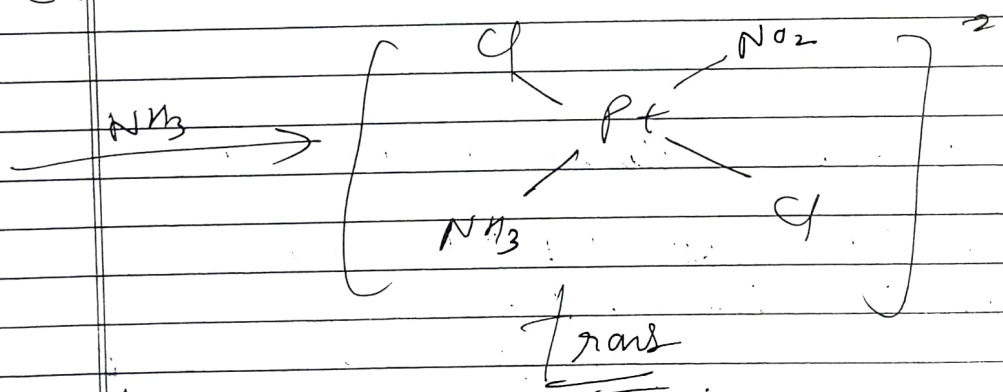
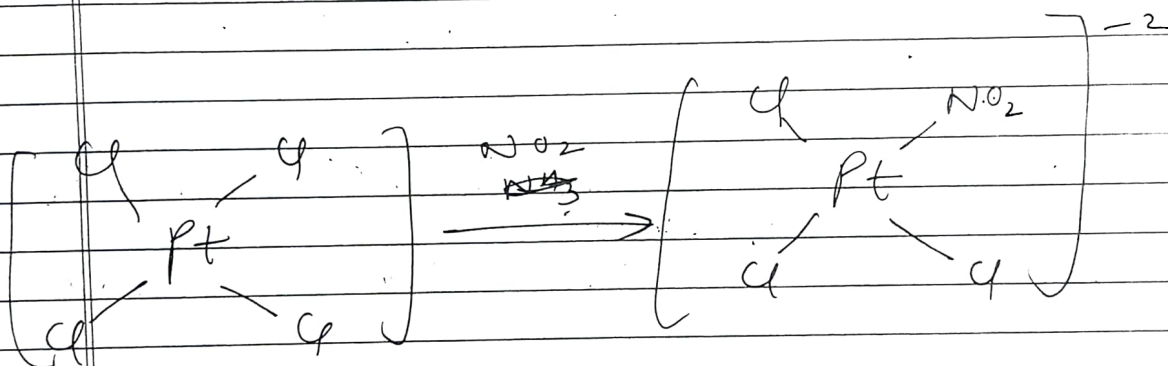
$\Rightarrow$ [strong trans directors promotes Rapid Substitution of ligand trans to itself than it does cis to itself.

Application of Trans-effect.

$\rightarrow$ Most of Trans-effect done on square planar complexes of Pt(II).



Cis



Theories of Trans effect :-

1) Polarisation theory, 2) π -Bonding Theory

Polarization theory :-

apsara

Acc. to this theory the metal ligand bond polarization play a significant role in the trans effect.

This theory was forwarded by 'Grimberg'. according to this theory. When a ligand approach centre metal atom. then the leaving ligand show some polarity effect on the trans position. which leads the trans effect. ligand with sigma donor or pi acceptor produce the metal ligand bond polarity as a Result trans effect observed.

Limitation of Polarization theory :-

- 1> This theory can not explain the formation of cis effect.
- 2> Bond Polarity Concept is not explain the trans effect successfully.
- 3> This theory cannot explain the formation of Back Bonding.

π - Bonding Theory

was given by proposed - Chatt and Orset.

This is the most important theory which explain the trans effect.

Acc. to this concept a ligand with π -c- always prefer the trans effect in the square planar complex under the Substitution Reax.

This is due to the associative mechanism i.e. Substituent Reax of Square Planar Complex involve the

Trigonal bipyramidal intermediate. In the Trigonal bipyramidal species P_i Bonded or P_i .

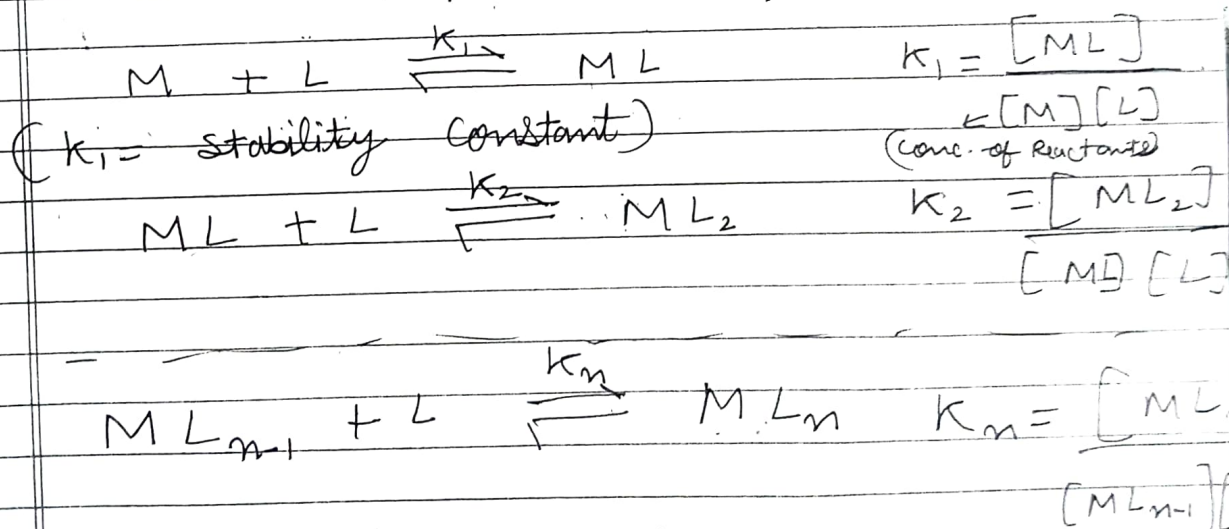
Acceptor ligand always prefer the axial position and the result trans position formed.

Evidence:

- (1) The Stereochemistry of the Reax. favour the P_i $\rightarrow$ P_o bonded theory.
- (2) This theory is also prefer the Reaction kinetics.

unit-2. # Formation Constant and its overall Stability Constant
Stepwise and overall formation constants

$\Rightarrow$ According to L. Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex ML_n may take place by the following n consecutive steps and equilibrium constants



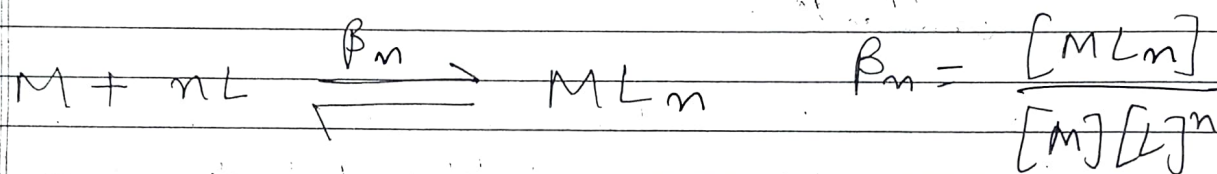
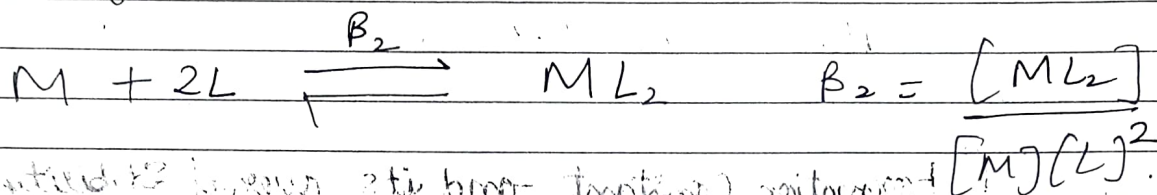
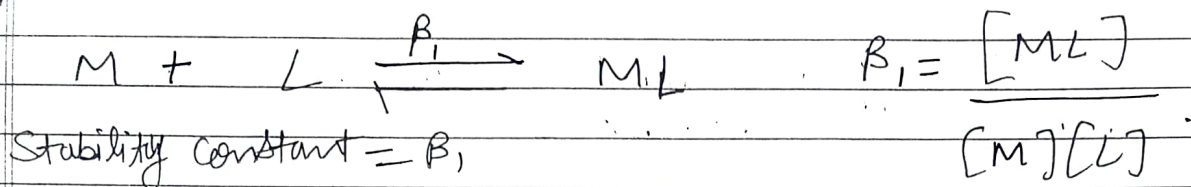
The equilibrium constants $K_1, K_2, \dots, K_n$ are called stepwise formation constants or stepwise stability constants. These constants are also

expressed as $\log_{10} k_1, \log_{10} k_2 \dots \log_{10} k_n$ respectively.

Date: _____

overall formation constant.

The formation of complex ML_n may also be expressed as below :-



The equilibrium constants $\beta_1, \beta_2 \dots \beta_n$ are called overall formation constants or overall stability constants. These constants are also expressed as $\log_{10} \beta_1, \log_{10} \beta_2 \dots \log_{10} \beta_n$ respectively.

Relation b/w stepwise and overall formation constant :-

Stepwise and overall formation constants are related to one another. For example let us consider the expression for β_3 viz.

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

~~Multip~~

→ Multiplying numerator and denominator by $[ML][ML_2]$

$$\Rightarrow \beta_3 = \frac{[ML_3]}{[M][L]^3} \times \frac{[ML][ML_2]}{[ML][ML_2]}$$

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

$$\Rightarrow \beta_3 = \frac{[ML]}{[M][L]} \times \frac{[ML_2]}{[M][L]} \times \frac{[ML_3]}{[ML_2][L]}$$

$$\Rightarrow \beta_3 = k_1 \times k_2 \times k_3 \dots$$

or

$$\boxed{\beta_3 = k_1 \cdot k_2 \cdot k_3 \dots k_n} \quad \text{--- (1)}$$

$$\boxed{\log_{10} \beta_3 = \log_{10} k_1 + \log_{10} k_2 + \log_{10} k_3 \dots \log_{10} k_n}$$

From eqn (1) it is evident that the overall formation constant (β_n) is equal to the product of the stepwise formation constants. (2)

Ques = Brief-out Various boranes.

⇒ Boranes are the type of cluster compound which are formed by the combination of boron and hydrogen.

⇒ Hypercloso-boranes → General formula is $B_n H_m$.

If $n=2$.



1> closo-Boranes :- Cage like structure.
General formula is $B_n H_{n+2}$.

2> Nido-Boranes :- Nest like structure.
General formula = $B_n H_{n+4}$.

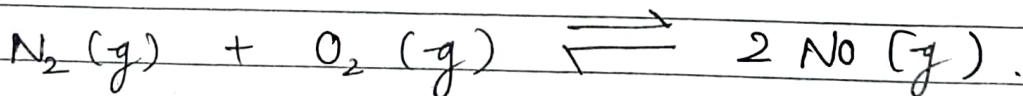
3> Arachno-Boranes :- Spider web like structure
General formula = $B_n H_{n+6}$.

4> Hypo-Boranes :- Net like structure
General formula = $B_n H_n$.

Ques = Define Le chatlier law:-

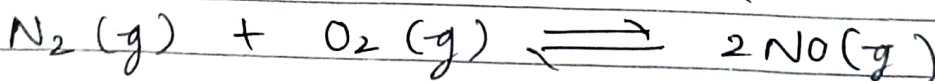
Ans = It states that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium.

Example :- (Add more Reactant)



Reaction Shifts Right →

(Add more Product)



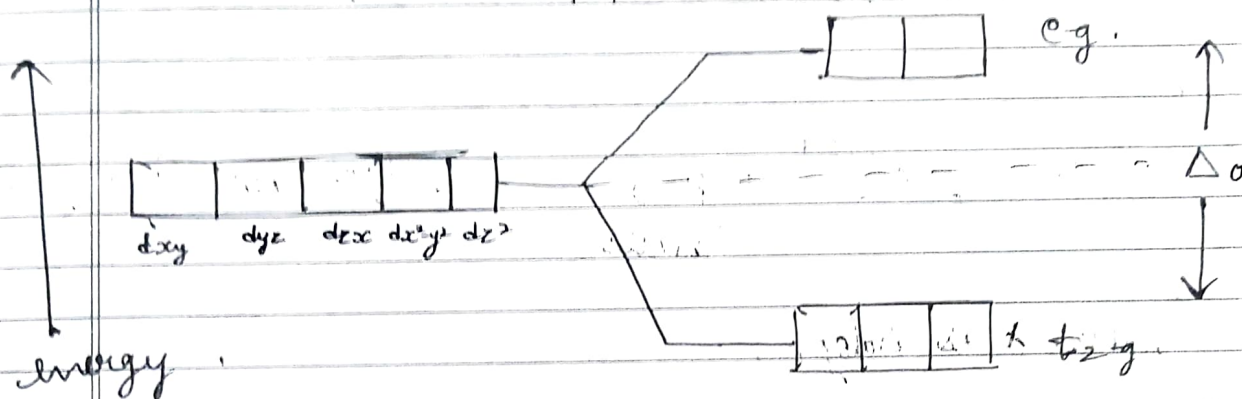
Reaction shifts left



Ques = What is meant by CFT?

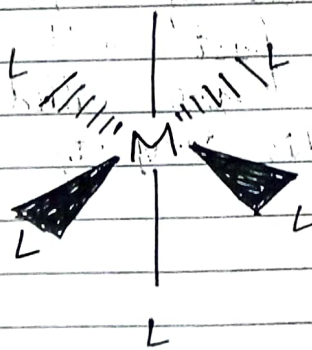
The CFT stands for Crystal field theory. It describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands.

Crystal field splitting in octahedral complex.

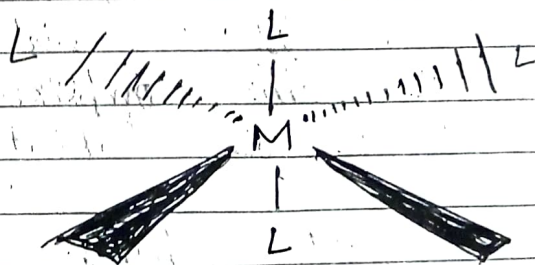


Ques = Explain Jahn-Teller distortion.

⇒ The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy. This distortion is typically observed among octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds.



Elongated



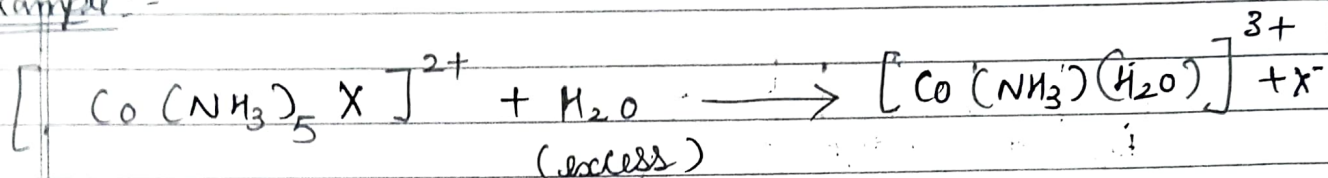
Compressed.

Ques: What is meant by Acid hydrolysis?

Ans: In Acid hydrolysis reaction:-

In such reactions an aqua complex is formed by the replacement of a ligand by H_2O molecules. These reactions occur in neutral and Acid solution. ($pH < 3$).

Example:-



(where X is halogen).

Inert and Labile Complexes

1) Labile Complexes:-

The Metal Complexes in which the rate of ligand displacement reactions is very fast and hence show high reactivity are called as labile complexes, and this property is termed as lability.

2) Inert Complexes:- ^{slow}

The Metal Complexes in which the rate of ligand displacement reactions is very slow and hence show low reactivity are called inert complexes, and this property

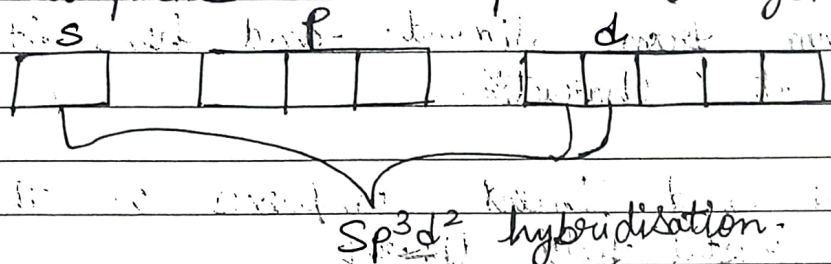
is termed as inertness.

⇒ Labile and inert complexes on the basis of Valence Bond theory (VBT).

According to the Valence Bond theory of chemical bonding octahedral metal complexes can be divided into two types:-

1) Outer orbital complexes

These complexes have sp^3d^2 hybridisation.

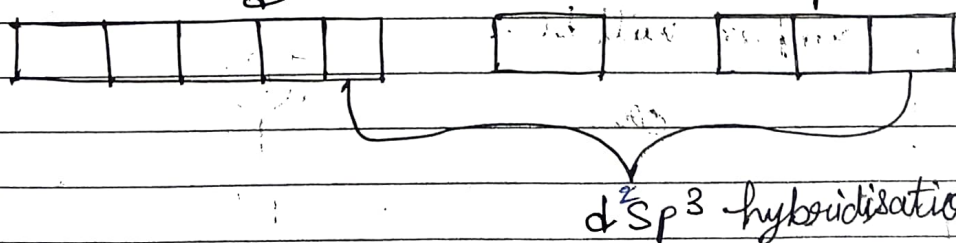


The bond in sp^3d^2 hybridisation complex is weak. therefore, they show labile character.

⇒ Example:- octahedral complexes of Mn^{2+} , Fe^{2+} show fast ligand displacement.

2) Inner orbital complexes

These complexes have d^2sp^3 hybridisation.



These ~~These~~ This ~~is~~ d^2sp^3 ~~can~~ hybridized complex can form both inert and labile complexes.

$\Rightarrow d^2sp^3$ hybridized Complex Show Labile Complex.

when one orbital should be empty in d_x, d_y, d_z . So that it can accept electron pair and can form seven coordinated intermediate. which is necessary step for ligand displacement.

$\Rightarrow d^2sp^3$ hybridized Complex Show inert Complex.

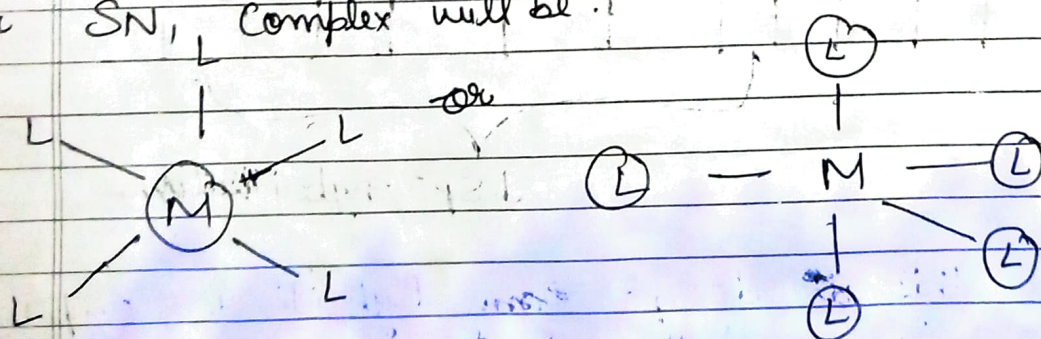
~~when one orbital should be empty in~~
when all d_{xy}, d_{yz}, d_{xz} orbitals contain at least one electron, it will not accept electron from ligand and hence it ~~shows~~ shows inert character.

$\Rightarrow$ Labile and Inert Complexes on the bases of crystal field theory

octahedral complexes react either by SN^1 ~~or~~ or SN^2 mechanism in which the intermediate are five and seven-coordinated species respectively.

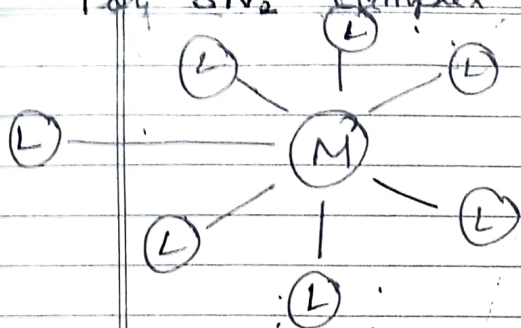
In both cases, the symmetry of the complex is lowered down and due to this change in crystal field symmetry, the crystal field stabilization energy (CFSE) value also changes.

For SN_1 complex will be:



Coordination no. = 5

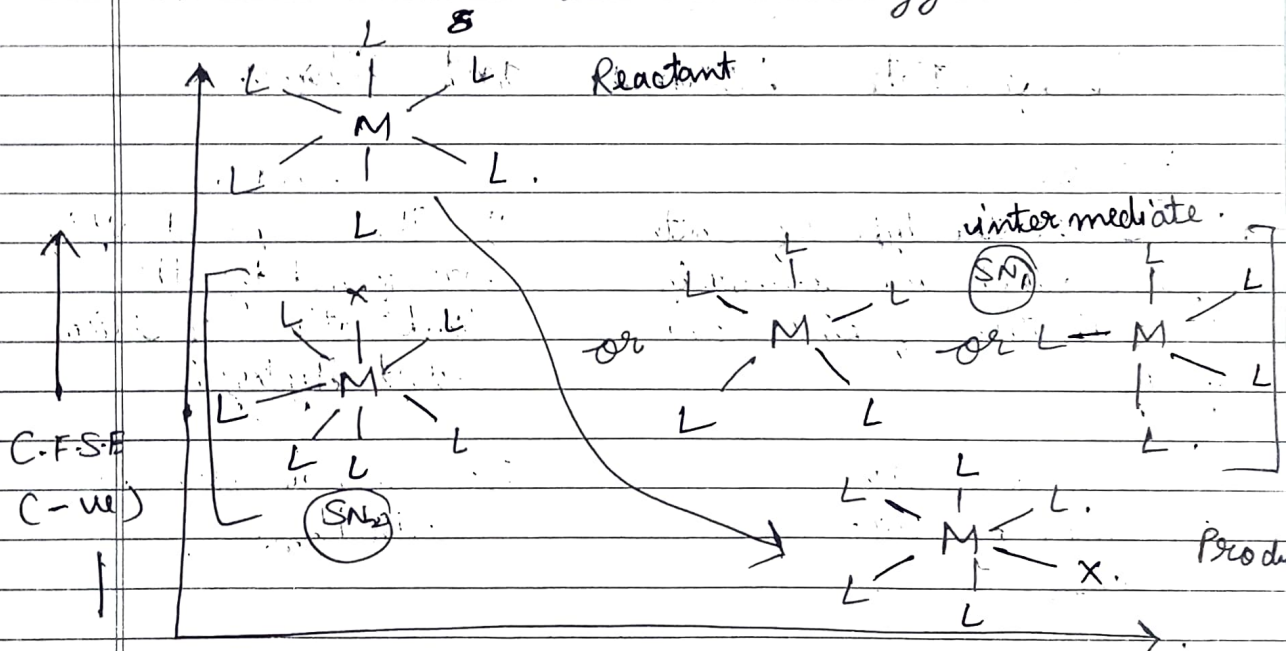
For SN_2 Complex will be.



Coordination no :- 7

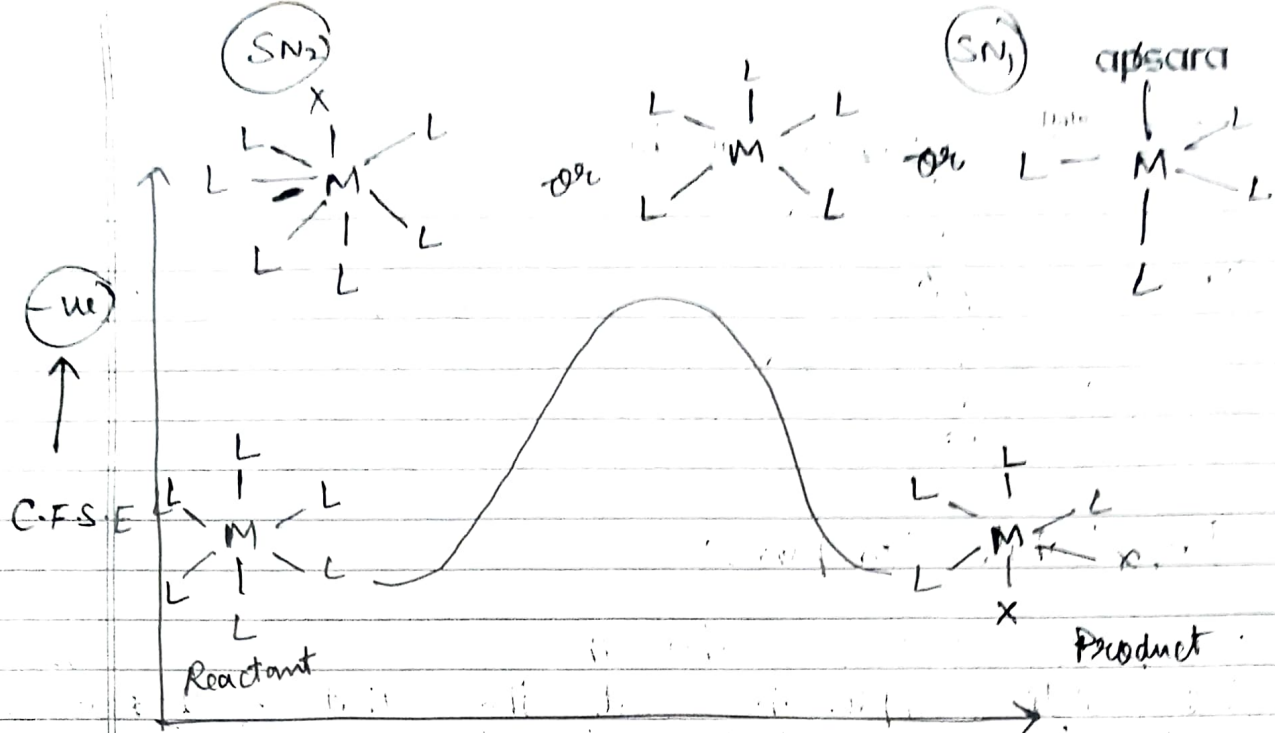
For Labile Complex :-

If the CFSE value for the five or seven membered intermediate complex is greater than that of the reactant the complex will be of labile nature as there is zero activation energy barrier.



For inert Complex :-

If the CFSE value for the 5 or 7 membered intermediate complex is less than that of the Reactant, the metal complex will be of inert nature as loss of CFSE will become the activation energy barrier.



Differentiate Boranes and Silanes

Boranes

1) Boranes are the type of cluster compound which are formed by the combination of Boron and Hydrogen.

2) General formulae
 $B_n H_{n+4}$ and
 $B_n H_{n+6}$

3) Diboranes are toxic gases with sweet smell.

4) Diborane reacts with water to form Boric Acid.

5) Diborane is used as a Rocket propellant.

Silanes

1) The compound which are formed by the combination of Silicon and Hydrogen.

2) General formula
 $Si_n H_{2n+2}$

3) Silane is toxic gas with repulsive smell.

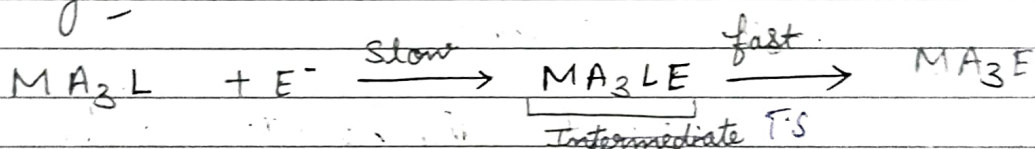
4) Silane does not react with water.

5) Silanes are used to make fiberglass.

Ligand Displacement Mechanism in Square-Planar Complexes

⇒ The ligand displacement reaction is nucleophilic substitution reaction in which the ligand of the complex is displaced by the another ligand.

⇒ The ligand displacement is favourable in square planar because the C.N. is 4. it means the steric hindrance is low then the change of ligand of complex displaced by another ligand.



SN_2 mechanism is followed due to low steric hindrance.

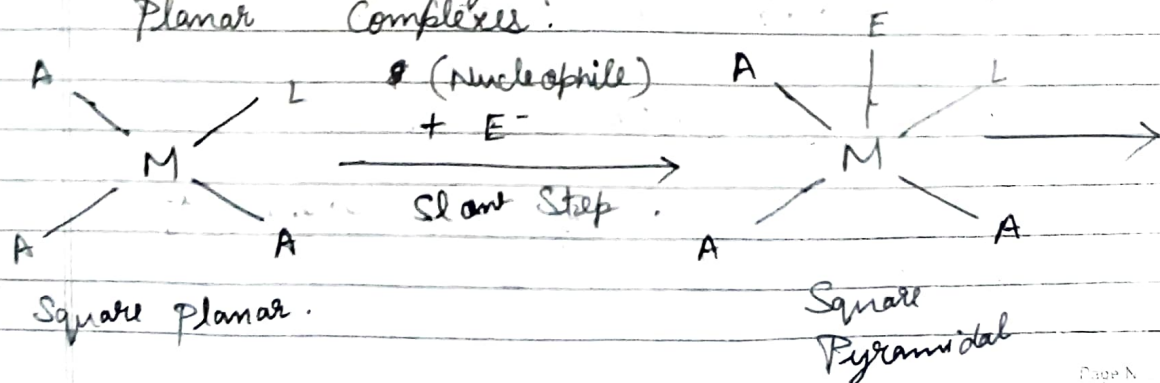
In ligand displacement reaction the geometry of MA_3L ^{Complex} is same after nucleophilic substitution reaction.

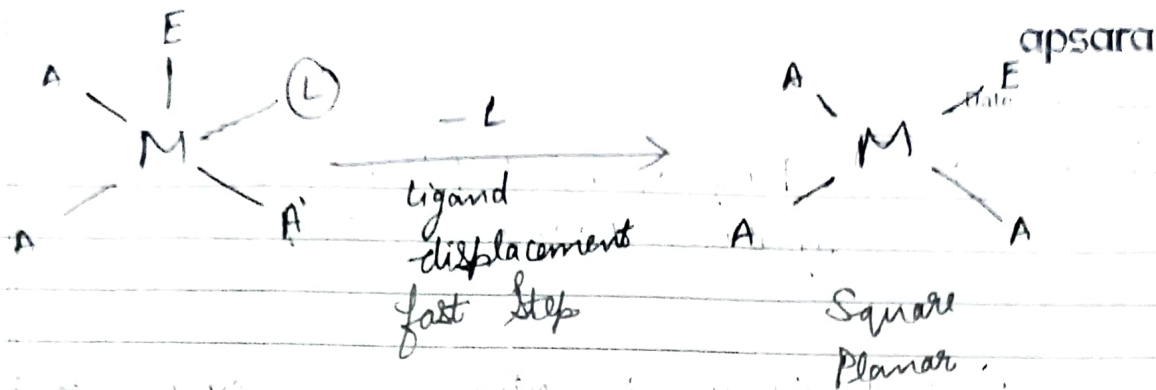
$$\text{Rate} = k [MA_3L][E^-]$$

order of reaction = 2.

It follows 2nd order kinetics.

⇒ Mechanism of ligand displacement in square-planar complexes:

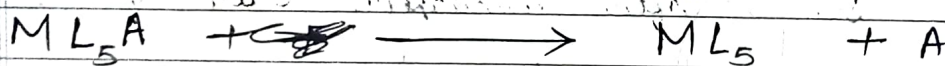




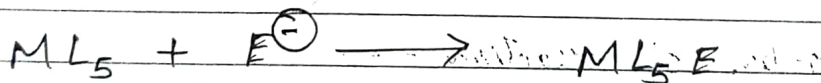
⇒ The ligand displacement reaction in octahedral complex is not much favourable because the C. No. of octahedral complex is 6. It means its steric hindrance is high. So, the ligand displacement reaction take place not easily. Here S_N1 mechanism follow because of high steric hindrance.

The General ligand displacement reaction. In S_N1 , the reaction take place in two steps.

Step I



Step II



Rate of the reaction is

$$\text{Rate} = k [ML_5A]$$

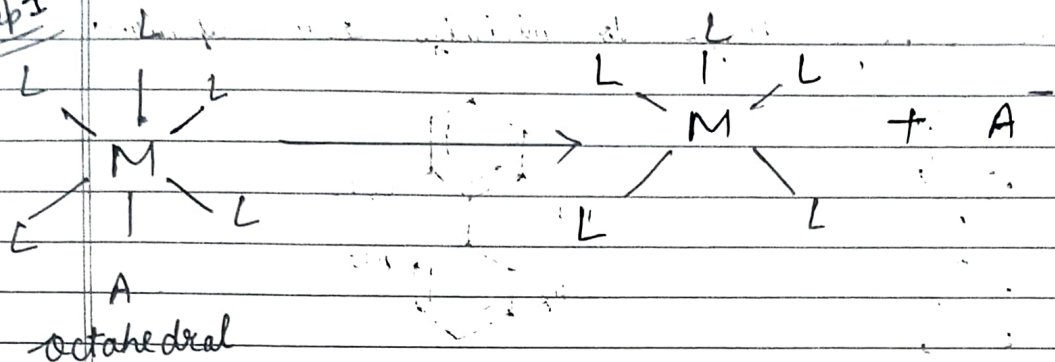
order of reaction is 1.

The Reactivity ~~of S_N1 order of~~ order of kinetics is 1.

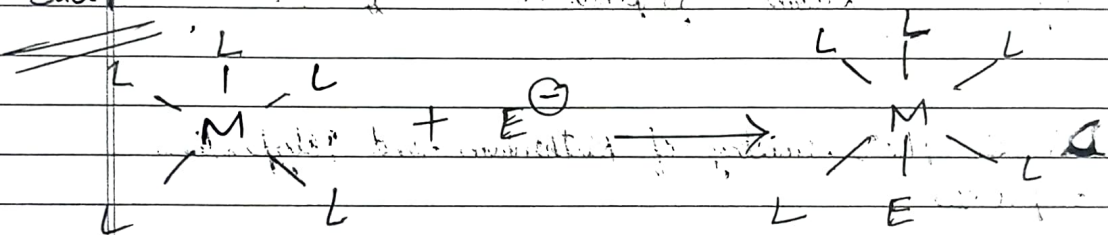
The Mechanism of octahedral Complex

Date: _____

Step I



Step II



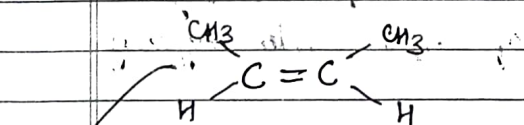
Steric effect :-

The substituent effect caused by σ -cloud repulsion of bulky group when they are close to each other is called steric effect.

Some Examples of Cis and trans

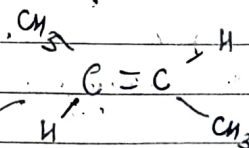
(1) Stability of cis and trans :-

In general cis structure is less stable than trans structure due to more steric repulsion present in cis form.



Steric Repulsion
exist (Less Stable)

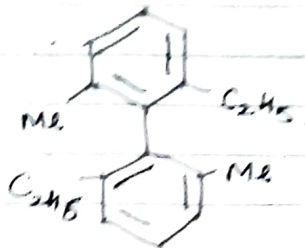
Bulky group (CH_3) in
same side



Less steric repulsion
(More Stable).

Bulky group in opposite side
(CH_3).

③ Plane of Rings changes to minimize steric repulsion.



To minimize steric repulsion one ring rotate about other going and become perpendicular to its.

Discuss Photochemistry of Ruthenium and Polypyridine Complexes

→ The Ruthenium (II) Polypyridine are the most

⇒ The Ruthenium (II) Polypyridine are the most popular systems.

⇒ These compounds strongly emit visible light in fluid solution.

⇒ The compounds are thermally very stable in aqueous solutions.

⇒ These compounds are capable of participating in oxidation-reduction reactions (as both +2 and +3 oxidation states are stable in solution).

⇒ These compounds are used as photocatalyst.
Example:- Decomposition of H_2O into hydrogen and oxygen.

Example:-

