Unit - I

1) Inert complex :- A complex which reacts slowly is called as Inert complex.

2) Labile complex :- A complex which reacts rapidly is called as labile complex.

The Ligand are easily substituted → Labile complex

The Ligand are NOT easily substituted in complex is called as Inert complex.

=> The word inert used indicates only slowness of reaction but not inability to react.

=> The two term inert & labile refers to rates reaction & not related to instability & stability.

According to VBT :-

VBT → It having two types of complex.

VBT

↓ outer orbital complex	↓ Inner orbital complex
Hb → sp^3d^2	Hb → d^2sp^3
(The complex are form in which outer orbitals are involved.)	(The complex which are form in which inner orbitals are involved).

Both are octahedral complex but difference is the involved in orbital is outer & Inner.

ex $[CoF_6]^{-3}$

$x + 6(-1) = -3$

$x - 6 = -3$

$x = -3 + 6$

Co $x = 3$ (0.5)

ex $[Co(CN)_6]^{-3}$

$Co = x + 6(-1) = -3$

$x - 6 = -3$

$x = -3 + 6$

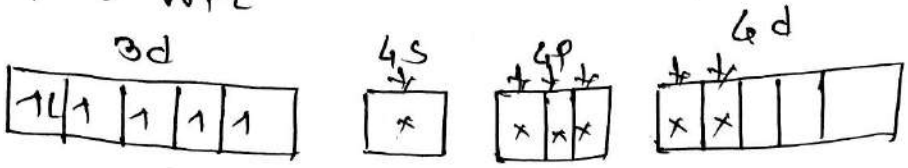
Co $x = 3$ (0.5)

Co^{+3} = outer electronic config

Co^{+3} = $4s^2\ 3d^7$

= t_{2g}^6

F → WFL



F - Strain Heir $\bar{e}$ in empty orbital

∴ Hb = sp^3d^2

↓ It is outer orbital complex

⇒ M-L bond are longer

⇒ M-L bond is weak

⇒ higher in energy

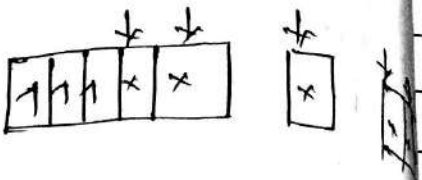
∴ Labile complex

Co^{+3} = outer electronic config

Co^{+3} = $4s^0\ 3d^5$

= t_{2g}^3

CN → SFL



CN - Strain Heir $\bar{e}$ in empty orbital

∴ Hb = d^2sp^3

↓ Inner orbital complex

⇒ M-L bond are shorter

∴ ⇒ M-L bond is strong

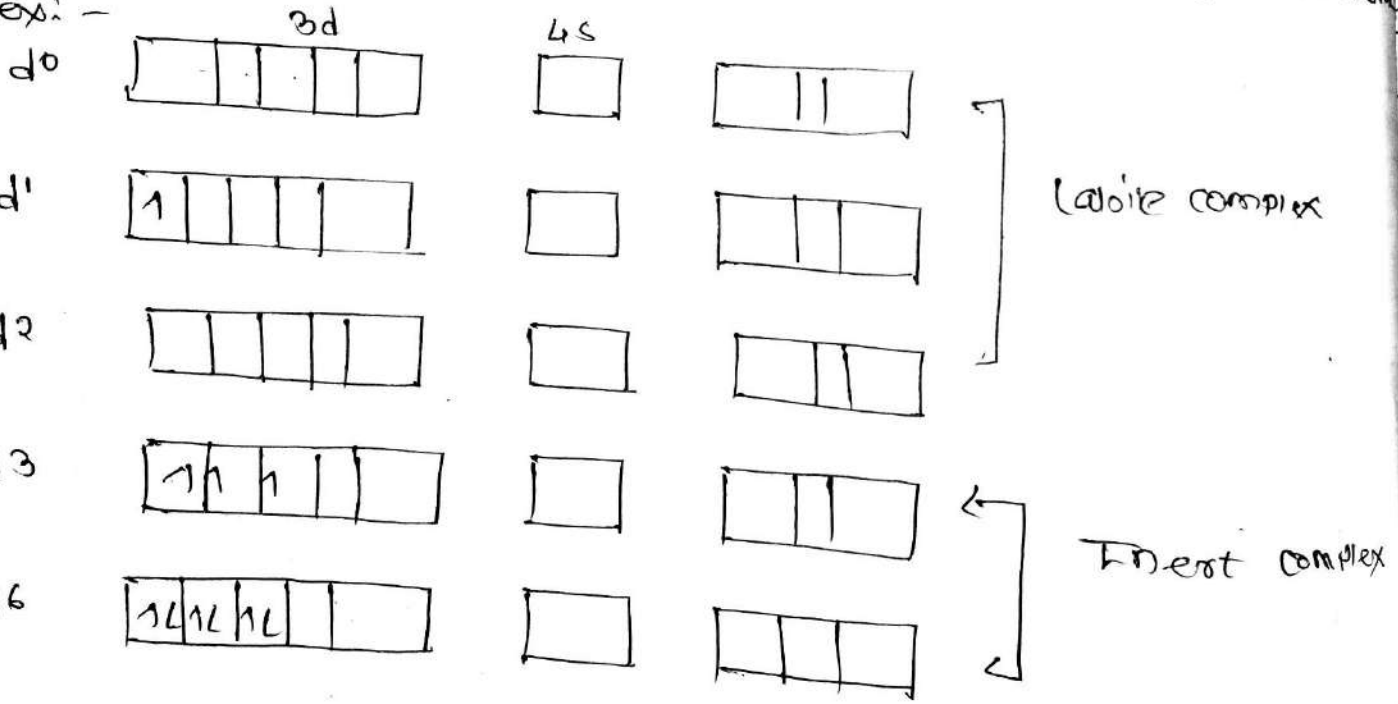
⇒ lower in energy

∴ Inert complex.

⇒ outer orbital complex are labile & it follow S_N1 mech

⇒ Inner orbital complex are Inert & follow S_N2 mechan

ex:-



According to VBT

1) High spin complex are - labile
Low spin complex are - Inert.

High spin ⇒ having more nbr of unpaired e^-
Low spin → having paired e^-.

ex

1	1	1	1	1

Unpaired e^-

1L	1L	1L	1L	1L

Paired e^-

⇒ The complex having strong field ligand → low spin
⇒ The complex having weak field ligand → high spin.

Strong field ligand ⇒ The ligand can results in higher crystal field splitting of d orbital & favour pairing of e^-

weak field ligand :- The ligand can results in a lower crystal field splitting.

ex ⇒ H_2O

M ← O — H → more electronegative atom so there is poor orbital overlap between the e^- pair ono & metal 'd' orbital.

ii) CN - M - CN → The more electropositive C atom is better overlap to M-d orbital.

(thiocyanate)

weak: $I^- < Br^- < SCN^- < Cl^- < S < F^- < OH^-$

ऊन बार स्पिलित क्लासिक स्टील फ्लॉपी फ्लोर

(thiocyanate)

$Ox^{-2} < H_2O < NCS^- < EDTA^{4-}$

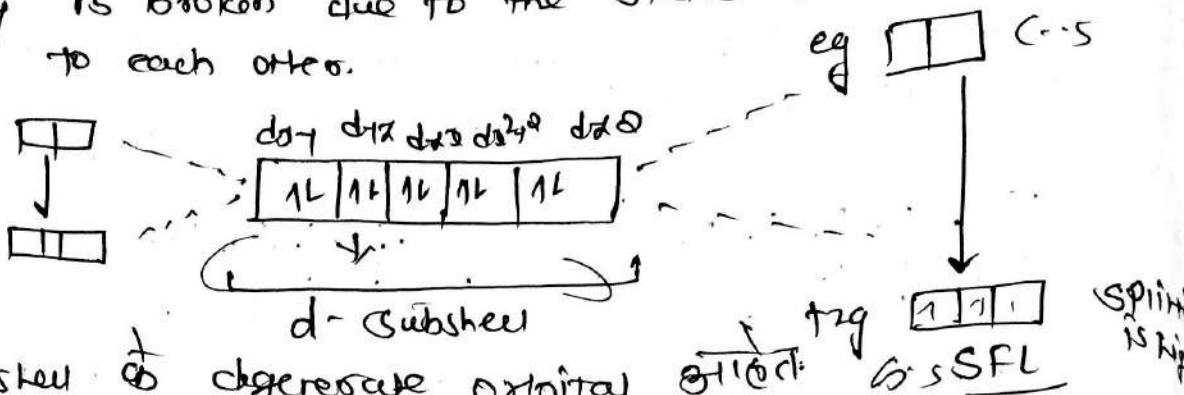
oxalate का पानी से पास जाता हुआ उड़ा

$NH_3 <$ en $< NO_2^- < CN^- < CO$ - strong field ligand.

अमोनिया इन नाइट्रो कैंटीन & को़ल्ड की मिठाई

Generally ligand are Lewis → WFL → Cl, F, I
General ligand are C, N, P → SFL → CN, CO, NC
ligand having N → Intermediate

When the ligand approach the central metal ion d subshell degeneracy is broken due to the static electric field. bcz e⁻ repels to each other.



d-sub-shell ⇒ degenerate orbital ⇒ SFL

When ligand not approaches to central M-d-orbital then it having degenerated but ligand approaches to metal d-orbital then this orbital is splitting.

When the ligand is strong FL then the gap bet. this orbital is high means splitting is high
=> When the ligand is WFL then this gap is low so splitting is low. bcz WFL not overlap to metal.

ex:- ii) $[Fe(H_2O)_6]^{+2}$ iii) $[Co(CNH_3)_6]^{3+}$

Lewis
High spin

Inert
Low spin

eg
t2g

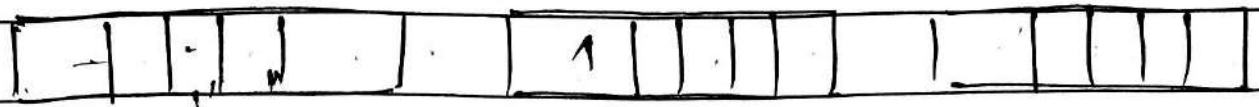
Fe^{+2} → $4s^2 3d^6$
d6

ii] complex that contain at least vacant-d-orbital is labile complex.

ex- Sc+3, Ti+3, V4+

↓

$4s^0 3d^1$ $4s^2 3d^2$ $4s^2 3d^3$ d1



↑ labile

The first three orbital are empty → labile

~~The all~~ according to VBT this first three orbital all orbital are fill then its is Inert complex.

[V(OH2)6]3+ ii] [Cr(H2O)6]+3

$V = +3 - 4s^2 3d^3$

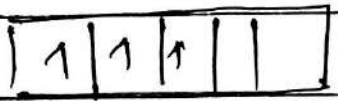
$V = d^2$

d-vacant

labile complex

$Cr = 4s^2 3d^4$

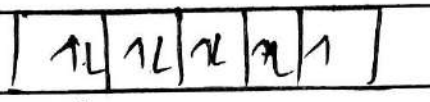
$Cr = d^3$



no vacant orbital - Inert

exception => [Cu(H2O)6]+2 → high spin

$4s^1 3d^{10}$



→ no vacant 'd' orbital but it is labile.

According to VBT d6 (HS) d7 (HS) & d9 octahedral complex have no low lying vacant d-orbital. So it is Inert. But experimentally observed that these complex are labile.

Further, it is observed that the complexes ~~eighter~~ inner orbital ~~or~~ outer are labile if they have vacant low lying unhybridised metal - d orbitals These vacant orbitals act as a point of attack of an incoming ligand.

ex octahedral complexes of d^1, d^2, d^3 metal cations are always inner orbital orbital complexes whether the ligands are weak or strong. ⇒ Labile.

The octahedral complexes of d^8, d^9, d^{10} metal cations are always outer orbital complexes eighter the ligands are strong or weak.

→ d^4, d^5, d^6 & d^7 → metal cation are outer orbital complex if the ligand are weak.

ex:-

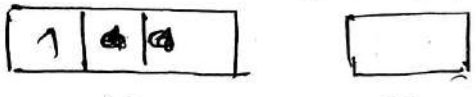
1) $[Ti(H_2O)_6]^{3+}$

$x + 6(0) = 3$

$x = 3$

outer C.C $Ti^{+3} = 4s^2 3d^2$

$CO = d^1$



t_{2g} $\quad$ e_g

It is labile complex

2) $[V(NH_3)_6]^{3+}$

$x + 6(0) = 3$

$x = 3$

outer C.C = $V^{+3} = 4s^2 3d^2$

labile

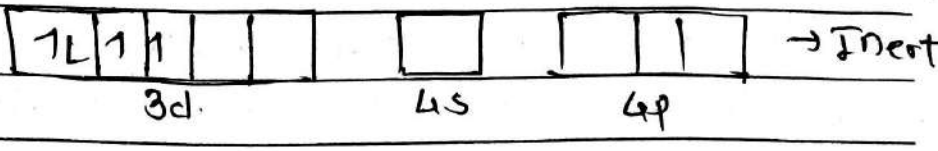
3] $[Cr(CN)_6]$

$x + 6(-1) = -4$ CN - Strong field ligand

$x - 6 = -4$

$x = -4 + 6$

$x = 2$

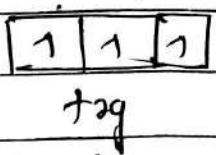


$Cr^{+2} = 4s^1 3d^5$ In Low spin case.

$Cr = d^4$ d^4 - Low spin

when d^4 - High spin

Energy level of 'd' - orbital →



=> when $\bar{e}$ present in eg level Labile complex
then complex is labile complex.

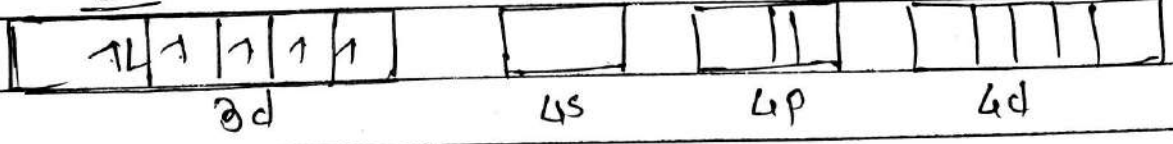
4) $[Fe(H_2O)_6]^{2+}$

$x + 6(0) = +2$ H_2O → WFL → High spin

$x = 2$ more nbr of unpaired $\bar{e}$

$Fe^{+2} = 4s^2 3d^6$

$Fe = \underline{d^6}$



It is a labile complex.

Inert & labile complex :-

First up all lets understand this Inert & labile complex is,

Stability of complex

- kinetically stable
  - labile (ligand are easily subs)
  - inert (ligand are not easily subs)
- Thermodynamically stable
  - β (overall rate const) → means
  - K (stepwise rate const).

ex Something is broken or reduce we have the complex ML6 complex $\xrightarrow{\Delta}$ then give ML5 then ML4 what is the rate of this complex is called as overall rate const.

means the rate of ML6 ⟶ ML4 is overall

⇒ the rate of ML6 ⟶ ML5 is stepwise rate const

ML5 ⟶ ML4

Factors affecting labiility

The labiility depends on the metal - L bond strength

This is M-L bond strength is breakdown & new bond is formed. is substituted.

Now

This M → L

bond is stronger then is not easily substituted so it is inert. & where this is weak then its is easily substituted so it is labile.

charge of ion :- Increases the charge → lesser labiility

1) $[AlF_6]^{3-}$ 2) $[SiF_6]^{-2}$ 3) $[PF_6]^{-1}$

+3 +4 +5

Size of central metal ion ⇒ smaller size → lesser

i) $[Mg(H_2O)_6]^{+2}$ ii) $[Ca(H_2O)_6]^{+2}$ 3) $[Sr(H_2O)_6]^{+2}$

iii) ii) i)

$3p^6 4s^2$

Mg
Ca
Sr ↓ size increases

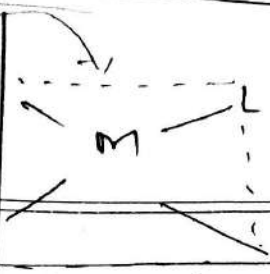
Charge / size ratio :- Increases charge/size ratio → lesser

i) $[Na(H_2O)_6]^{+}$ ii) $[Mg(H_2O)_6]^{+2}$ iii) $[Al(H_2O)_6]^{3+}$

In left to right size ↓ charge/size ratio ↑ So labiility of complex ↓

Geometry :-

1) Tetrahedral / square planar complex are most labile. why bcz



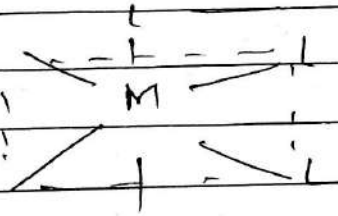
Always talcite why bcz ligand are arranged ion metal on the plane

if square attacking ligand on onside it easily come & attack on upsi-to on plane or downside on the plane.

ii) It is not stericcay crowded bcz metal Open in upside / downside.

iii) favours ligand substitution bcz it is not stericcay crowded so incoming ligand can easily come here.

i] octahedral complex



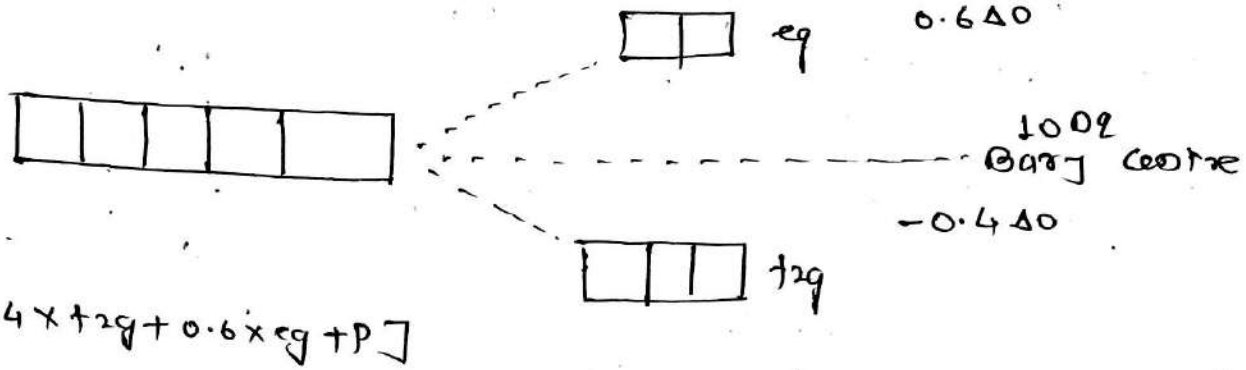
may be talcite or inert

It is stericcay crowded bcz metal covered in all side → so it may be talcite or inert complex depends on electronic configuration & expansion caused between metal orbital & ligand.

According to CFT (Crystal Field Theory)

he Why some complex are high spin & other are low spin
eg. Stability of complex ~~of~~ explain these properties in CFT.

In an octahedral complex, the d-orbitals of the metal cation are split into two sets of different energy, t_{2g} of lower energy & e_g of higher energy.

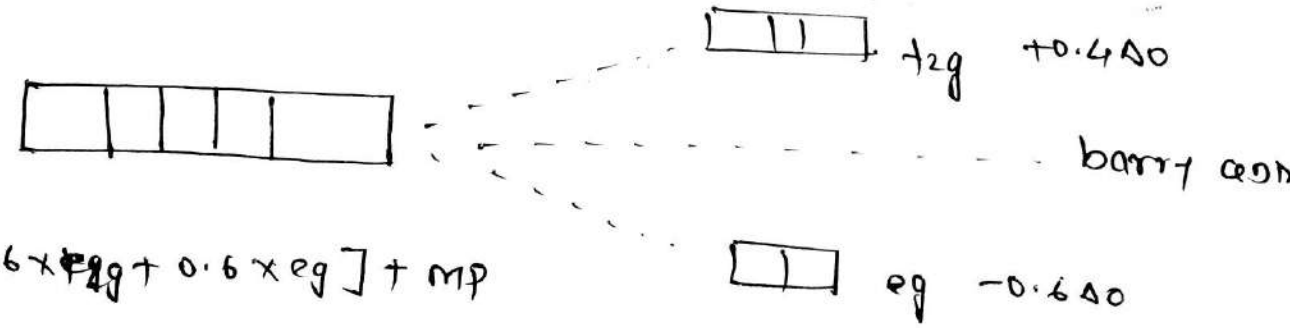


$[-0.4 \times t_{2g} + 0.6 \times e_g + P]$

Crystal Field splitting in octahedral Field

=> The separation between these two sets is equal to Δ_o (10Dq (Differential of quanta)

The t_{2g} set has an energy of $(-0.4\,\Delta o)(-4Dq)$ & e_g set has energy of $+0.6\,\Delta o\ (6Dq)$ relative to barycentre. (-) & (+) sign indicates ↓ & ↑ in energy relative to the barycentre.



$[-0.6 \times t_{2g} + 0.6 \times e_g] + MP$

CFSE → Crystal Field stabilization energy means released energy state.

ex → For d^1 C.C → t_{2g} eg°

CFSE = $-0.4 \times 1\Delta o = -0.4\Delta o$

=> The change in crystal field stabilization energy when reacting complex transferred into transition state or intermediate is called as CFAE value.

=> IF CFAE value is zero, negative then complex is Labile.

=> IF CFAE value is positive it require more amount of energy to transform reacting complex into the intermediate i.e complex is Inert.

=> When charge ↑ inertness of complex increases bcz charge streghten the M-L bond & reduces the Lability.

ex => $Cr^{+3} < V^{+2}$

ex. d^1 → Labile — t_{2g} — d^1

d^2 → Labile — t_{2g}^2 — d^8 — Labile

d^3 → Inert — t_{2g}^3 — d^9

d^{10}

d^4 → t.s Inert t_{2g}^4 eg°

H.S Labile t_{2g}^3 eg¹

d^5 → t.s Inert t_{2g}^5 eg°

H.S → Labile t_{2g}^3 eg²

d^6 → t.s → Inert t_{2g}^6 eg°

H.S → Labile t_{2g}^4 eg²

$4s^2 3d^7$

$5s^2 6d^7$

$6s^2 5d^7$

ex =>

1) $[Ti(H_2O)_6]^{3+}$ 2) $[V(H_2O)_6]^{3+}$

Ti = d^1 V = d^2

labile labile

3) $[Mn(H_2O)_6]^{2+}$ 4) $[Mo(H_2O)_6]^{3+}$

Mn = d^5 Mo = d^3

H.S → labile

L.S → Inert Inert

5) $[Pt(H_2O)_6]^{+4}$ $[Mo(H_2O)_6]^{+3}$

$5s^2 5d^2$

$5s^2 4d^2$

5

pt = d6 $5s^2 5d^8$ $5s^1 6d^5$

Inert $6s^1 5d^9$ = d^4

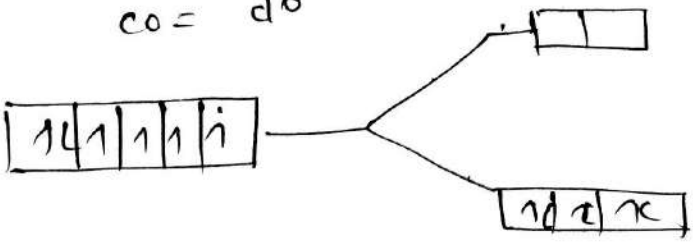
=> Always 4D & 5d series are Inert complex, no matter is SFL & WFL. bcz the 4D & 5D series having size is high so it is more diffused (i.e larger) so these orbitals extend towards ligand & overlap with ligands orbital more effectively & thus a strong M-L bond formed so it is always Inert complex.

=> exception => when Co^{+3} complex with ligand is H_2O, NH_3 → Low spin

ex

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

Co = d^6



→ Inert complex

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

d^1 - Labile

2) $[Cr(CN)_6]^{4}$

Low spin - Inert

high spin - Labile

3) $[Fe(H_2O)_6]^{2+}$

d^6 - H.S - Labile

L.S - Inert

4) $[Mo(H_2O)_6]^{3+}$ ↑42

$5s^1 4d^5$

5) $[Mn(H_2O)_6]^{2+}$

d^5 HS - Labile

LS - Inert

6] $[Pt(H_2O)_6]^{+4}$ ↑78

$6s^1 5d^9$

7] $[Co(H_2O)_6]^{3+}$

Inert

8] $[CoF_6]^{3-}$

$x + 6(-1) = -3$

$x - 6 = -3 \quad -3+6 = 3$

$4s^2 3d^7 = d^6$ Labile

9] $[Ca(EDTA)]^{-2}$ (EDTA: -4)

~~$x + -4 = -2$~~

~~$x = -2 + 4$~~

~~$x = 2$~~

$3p^6 4s^2$

9] $[V(phen)_3]^{3+}$

10] $[Ir Cl_6]^{-2}$ 27 ↑ → 77

$5d^7 6s^2$

d^5 (L.S)

Inert

11] $[Co(NH_3)_5Cl]^{+2}$

~~$x + (0) + 1 = 3$~~

~~$4s^2 3d^7$~~

$x - 1 = 2$

$x = 2 + 1$

$x = 3$ Inert

classmate

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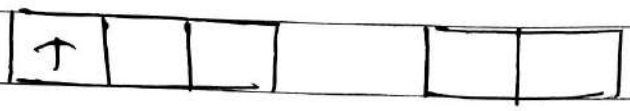
1] $[Ti(H_2O)_6]^{3+}$

$x + 0 \times 6 = 3$

$x = 3$

outer electronic configuration of $Ti = 4s^2 3d^2$

(d1) = labile



t_{2g} eg

t_{2g}^1 t_{2g}^2 d0

2] $[V(H_2O)_6]^{3+}$

$x + 0 \times 6 = 3$

$x + 0 = 3$

$x = 3$

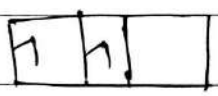
outer electronic configuration of V is $4s^2 3d3$

labile

d2

eg

t_{2g}



3] $[Cr(CN)_6]^{4-}$

$x + (-1 \times 6) = -4$

$x - 6 = -4$

$x = 6 - 4$

$x = 2$

outer electronic configuration of Cr is $= 4s^1 3d^5$

d4 = Inert

1S, HS

t_{2g}^3 eg^1

inert labile

4] $[Mn(H_2O)_6]^{2+}$

$x + 0 \times 6 = 2$

$x = 0 = 2$

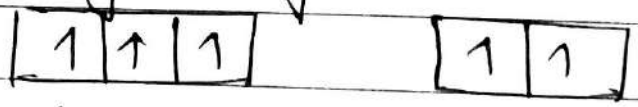
$x = 2$ (Mn)

outer electronic configuration of Mn = $4s^2$

d5 - Inert

- 1S HS

t_{2g}^3 eg^2



inert Labile

5] $[Fe(H_2O)_6]^{2+}$

$x + 0 \times 6 = 2$

$x = 0 = 2$

$x = 2$

Outer electronic configuration of Fe = $4s^2$

d6 = Inert

1S HS

classmate
Date
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Taube's explanation of lability & inertness

According to Taube's the degree of lability & inertness of transition metal complex can be related with the 'd' electronic configuration of metal ion.

Henry taubes discuss about the labile & inert complex. He tell the metal has higher charge is inert.

ex-) M^{+3} is electron deficient so it is lewis acid & ligand is lewis base so greater the interaction between lewis acid & base the complex is inert in nature.

Also higher oxidation state is inert in nature. but their is some exception.

Mo having V oxidation state & Mo(III) is oxidation state according to this Mo(V) is inert but this is labile & Mo(III) is inert.

The smaller the size of metal & greater the interaction between the ligand & more inert of complex.

He found that size of metal atom small charge is equivalent what happen is inert

io Nature. $3s^2 3p^1$

ex →

The complex Al^{3+}, Fe^{3+}, V^{3+} these complex having roughly equal io size & same oxidation state they are inert io nature.

(bcz same charge & radius

Al^{3+}, Fe^{3+}, V^{3+}

equal inert

Cr^{3+} is more inert size & charge is comparable.

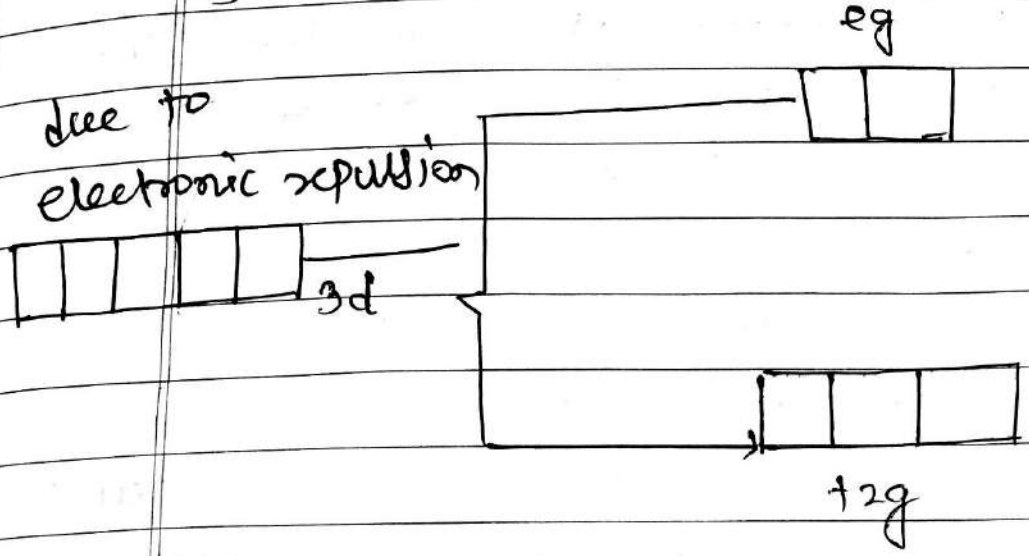
This phenomenon explanation d' electronic configuration.

The higher transition element Ru Os, all of them all those complex are inert. bcz the 'd' element are diffused they are toward the outside & hence they diffused to ligand orbital 3d, 4D & 5D orbital

The 4D & 5D orbital are far away from the nucleus & they interact better with orbital of ligand i.e they are more diffused. so stronger bond the ligand. thats why the higher transition

element are inert in nature.

Now. 3D complex octahedral complex of 3D transition element we have eg & t_{2g}



Due to electronic repulsion the 'd' orbital having eg & t_{2g} orbital.

t_{2g} having lower energy & eg having higher energy.

Some $\bar{e}$ in eg orbital it is labile complex why bcs it is higher in energy & some character of antibonding character so e^- present in eg- orbital then it is acts as antibonding orbital so it is labile in nature is always.

$\bar{e}$ present in antibonding orbital then energy of the complex is higher it can

easy substituted by ligand so it is labile in nature.

Now in t_{2g} orbital if more than three e^- then the complex is inert & less than three then it is labile complex. in t_{2g} orbital.

The reason is when the ligand is approaching to metal so if there are more than three e^- in t_{2g} they repel to ligand bcs they obtained as inertness

we have less than three e^- in t_{2g} orbital they are not repel to ligand so the complex is labile.

If complex is substituted by ligand Totally substituted in reaction within one minute at 25oc then the complex is labile & more than one minute in 25°c then the complex is inert. some scientist & Taubes explain this point.

(4) Ligand Substitution reaction

The substitution of one or more ligand in complex by another ligand, is called ligand substitution reaction.

ex $[MLSx]^{n+} + y^- \longrightarrow [MLSy]^{n+} + x$

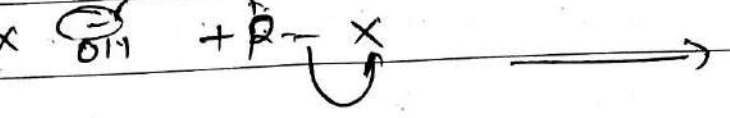
In this reaction the ligand x is replaced by another ligand 'y'.

ex $[Co(H_2O)_6]^{3+} + CN^- \rightleftharpoons [Co(H_2O)_5CN]^{2+} + H_2O$

(5) SN1 or dissociation Mechanism

(Substitution reaction -> The atom or group or atom are replaced by another atom).

(Nucleophilic substitution reaction)

ex 

(Nucleophile- $\bar{O}H$, H_2O, $\ddot{N}H_2$, $R\ddot{N}$, R-Mg-X)

(electrophile- lewis acid) NO_2^+, $C\bar{O}$,

S - substitution

N - Nucleophilic

1 - Unimolecular

Dissociation Mechanism -> The mechanism which describes the which comp can interchange the ligand.

The incoming ligand occupies of the centre of central metal ion in Nucleophilic substitution reaction in octahedral comp is show as,

Coctahedral comp means six ligand are symmetrically arranged in central metal atom.

ex -> $[Fe(CN)_6]^{2+}$

(6) $ML_5X + Y \longrightarrow ML_5Y + X$

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It has two step.

Step-I :

It is slow & rate determine step. (slow - It determines overall reaction) in the step a is lost & five co-ordinate activated complex are formed.

$ML_5X \xrightarrow[RDS,]{slow} ML_5$

CN = 6 (octahedral)

CN = 5 (Square pyramidal, ~~Pentagonal~~ bipyramidal Trigonal)

The metal ligand bond broken in this step & is reaction is unimolecular. this reaction involves only one reactant species ML_5X to give activated complex ML_5

The ML_5 is e^- deficient it is Square Pyramidal or trigonal Bipyramidal (five e^- pair).

$ML_5X \xrightarrow[RDS, unimolecular]{slow} ML_5$

CN = 6 octahedral — CN = 5

(7)

The ML_5X is dissociative in this step. So the name is dissociation mechanism.

Step - II

In the second step Five-cordinated intermediate having less stability It is attached by Nucleophile to give ML_6Y.

$ML_5 + Y \longrightarrow ML_5Y$

$CN = 5 \qquad CN = 6$

This step is fast & activation energy is ...
The rate of overall reaction depend on conin of of ML_5X & not on 'y'. So reaction is first order with respect to ML_5X & [illegible] order with respect to y.

$\therefore$ Rate of reaction $k = [ML_5X]$

combining the above two step can show formation of ML_5Y as,

$ML_5X \xrightarrow[RDS]{slow} ML_5 \xrightarrow{+Y} [ML_5Y]$

$CN = 6 \qquad C = 5 \qquad CN = 6$

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ex

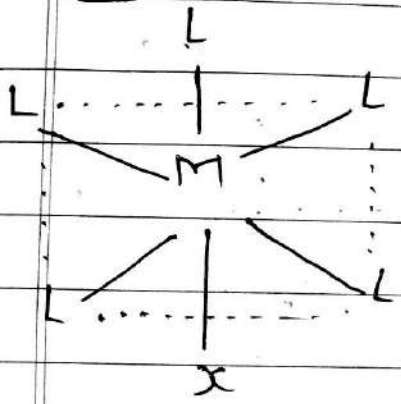
$[Cr(H_2O)_6]^{3+}$ —slow→ $[Cr(H_2O)_5]^{3+}$ $+H_2O$

$[Cr(H_2O)_5]^{3+}$ —$-CN^-$, Fast→ $[Cr(H_2O)_5CN]^{2+}$.

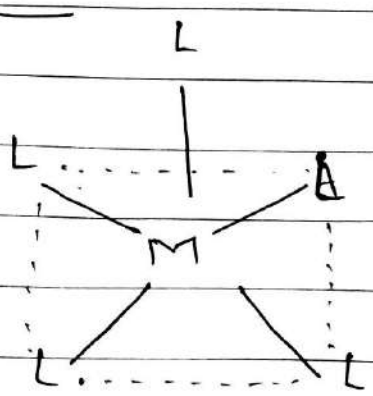
CN = 6

Energy profile diagram

Step- I

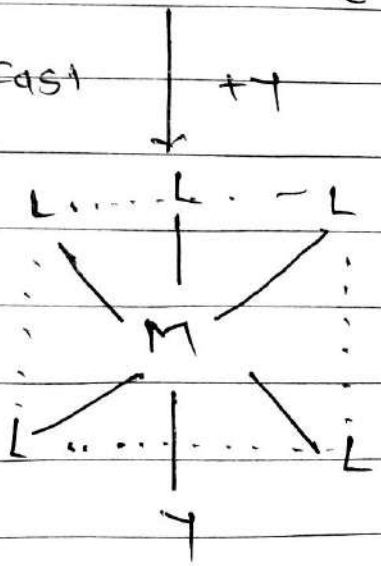


x —slow→



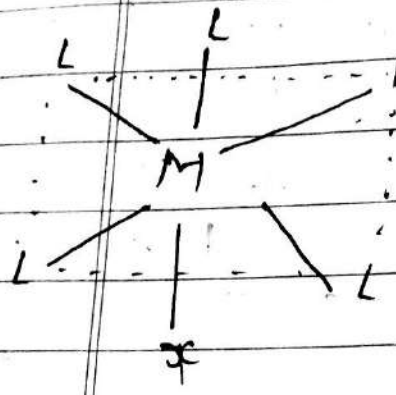
Square pyramidal intermediate (CN=5)

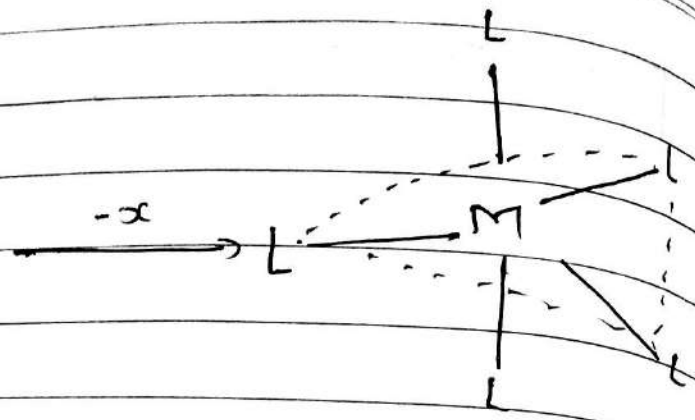
Fast, $+Y$



(9)

Step - II

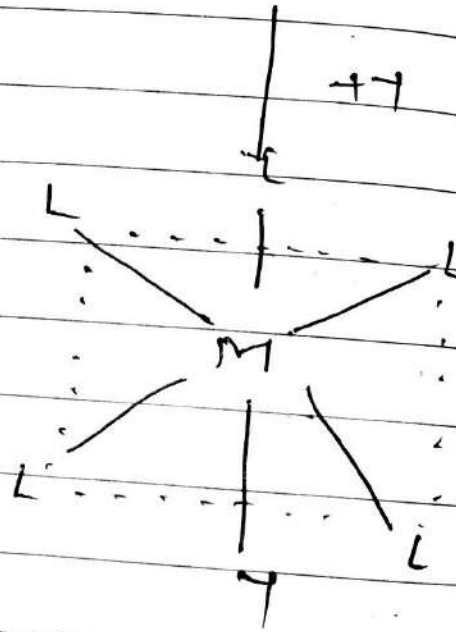




intermediate

(Trigonal bipyramidal

CN = 5)



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S_N2 Mechanism

S - Substitution
N - Nucleophilic
2 - Bimolecular

Association Mechanism

The reaction involves also two step.
Step-I - It is a slow rate determining step in which incoming is attached to MLSx to form seven co-ordinated unstable intermediate having pentagonal bipyramidal geometry etc.
It is metal ligand bond formation step.

$$MLSx \xrightarrow[\text{slow, RDS}]{+Y} \underset{C=7}{MLSxY} \xrightarrow{-x} \underset{CN=6}{MLSY}$$

two types of geometry
The rate of this reaction involves bimolecular bcs the concentration of this reaction depend two reactant MLSx & Y are taking part in this step hence it is so second order reaction i.e first order incoming ligand nucleophile Y' .'.

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Rate of reaction = $k [MLSx] [Y]$

To this step 'Y' is associated with MLSx to form MLSxY thus the same association mechanism is given to it.

Step - II

In this step the ligand x from MLSxY to form MLSY

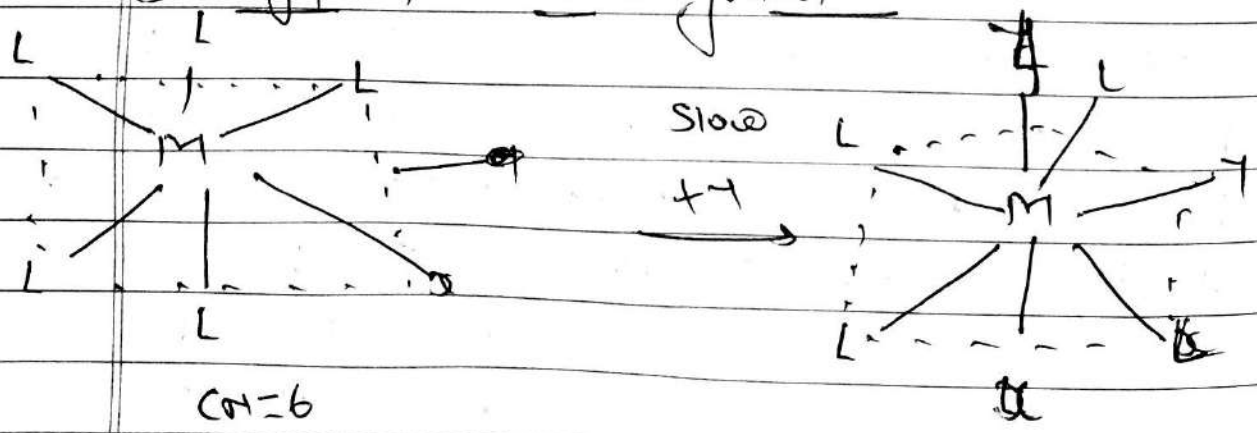
This is fast step.

$$MLSx + Y \xrightarrow[-x]{\text{Fast}} MLSY$$

Both step can be shown as,

$$MLSx \xrightarrow[RDS]{\text{Slow (+Y)}} MLSxY \xrightarrow[-x]{\text{Fast}} MLSY$$

Energy profile diagram



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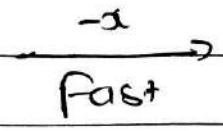
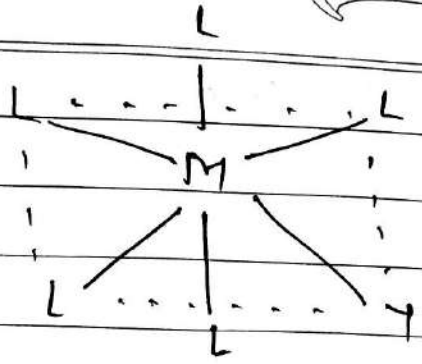
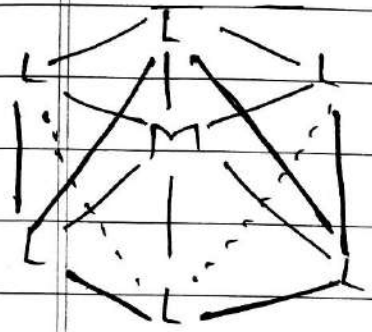


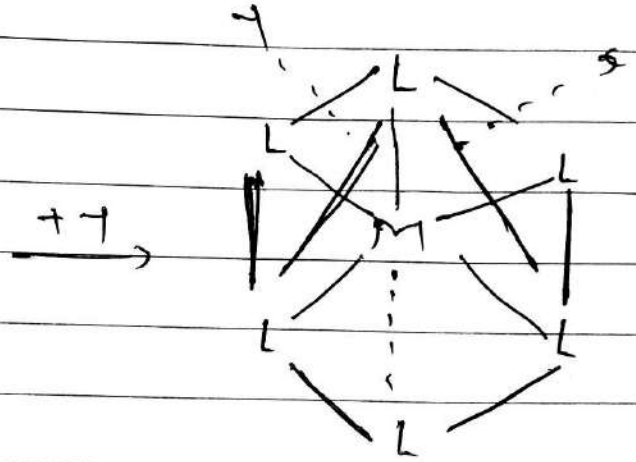


CN = 6

octahedral

Step - II



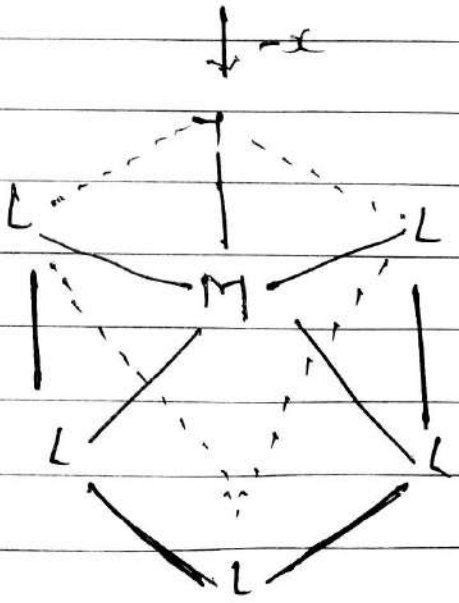


octahedral wedge

it give two types of geometry

1] pentagonal geometry

2) octahedral wedge



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SN1cB Mechanism

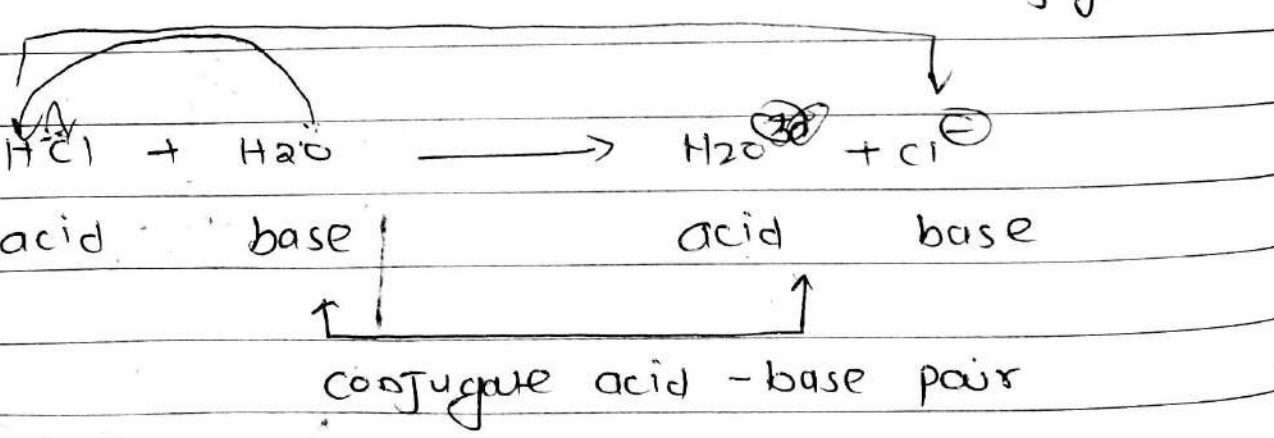
It is a substitution nucleophilic unimolecular conjugate base mechanism.
This mechanism which proposed by Garrik

SN1cB std For
S- substitution
N- nucleophilic
1- unimolecular
cB- conjugate base

C| conjugate base → It is Bronsted - lowry acid-base theory. acid → is a substance which donate proton & base is substance which accept proton)

conjugate acid base, concept

ex



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conjugate acid is formed when a base gain H^+ ion or loses an OH^- ions. it make more acidic.

A conjugate base is formed when an acid loses H^+ ion or gains an.

Applying this mechanism the complex

$[Co(NH_3)_5^-)Cl]^{2+}$ which behavie as brownsted acid is changed into its brownsted base. i.e $[Co(NH_3)_4(NH_2)Cl]^+$

ex

$$[Co(NH_3)_5)Cl]^{2+} + OH^- \longrightarrow [Co(NH_3)_4(NH_2)Cl]^+ + H_2O$$

Acid base base acid

conjugate acid base pair. conjugate acid

The complex which are not having not such proton on non-leaving group react slowly with OH^- ions

ex

$[Co(CN)_5Br]^{3-}$ hydrolysis slow $[Co(CN)_5OH]^{3-}$

$[Co(py)_4Cl_2]^+$ hydrolysis slow

- Lie is the ~~prese~~ absence of acidic proton
SN1CB mechanism is not possible.
- hence, The ~~base~~ acid base properties of
complexes are more imp in the rate
reaction than the nucleophilic properti
of $OH^{\ominus}$ ions.

ex

ii) The reaction of $[Co(en)_2(NO_2)Cl]^{+}$ bis(ethylenediamine)nitro co
NO_2^- gives $[Co(en)_2(NO_2)_2]^{+}$ with
non-aqueous solvent (DMSO) have
following mechanism.

$$[Co(en)_2(NO_2)Cl]^{+} \xrightarrow{\text{slow}} [Co(en)_2(NO_2)]^{++}$$

CN = 6 CN = 5

$$[Co(en)_2(NO_2)]^{++} \xrightarrow{\text{Fast}} [Co(en)_2(NO_2)_2]^{+}$$

CN = 5

rate slow

The addition of small amount of ~~OH⁻~~ ~~reduces~~ the $t_{1/2}$ / $t_{1/2}$ = 5-6 hours but addition of small amount of OH^- reduces the $t_{1/2}$ to a few seconds. it increases the rate.

The catalytic action of OH^- in non-

(common name ⇒ ethylenediamine chloro nitro)

aqueous medium can be explained in SN1CB mechanism is below.

$$[Co(en)_2NO_2Cl]^{+} + OH^{\ominus} \xrightarrow[DMSO]{Fast} [Co(en)_2(NO_2)]^{2+}$$

Acid base base Acid H_2O

$[Co(en)(en-H)NO_2Cl]$

(en-H) ethylene diamine from which $H^{\oplus}$ ion have been removed.

The dissociation of Co-Cl bond from conjugate base $[Co(en)(en-H)(NO_2)Cl]$ is easy due to presence of NH π-bonding group i.e not present in complex $[Co(en)_2NO_2Cl]^{+}$

$$[Co(en)(en-H)NO_2Cl] \xrightarrow[DMSO]{Slow} [Co(en)(en-H)(NO_2)]^{+} + Cl^{\ominus}$$

CN = 6

$$[Co(en)(en-H)(NO_2)]^{+} + NO_2^{-} \xrightarrow[DMSO]{Fast} [(Co)(en)(en-H)(NO_2)_2] \longrightarrow (i)$$

$$[Co(en)(en-H)(NO_2)_2] + H_2O \xrightarrow[DMSO]{Fast} [Co(en)_2(NO_2)_2]^{+} + OH^{\ominus} \longrightarrow (ii)$$

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Hence,
The rate of equation (1) is comparately slow than (2).

Hence,
simple S_N1 or S_N2 mechanism are unable to explain the catalytic action of OH^- or base in base hydrolysis This can be explained on the basis of S_N1CB mechanism only.

Addition of H_2O_2 increases the rate of base hydrolysis bcs,

$H_2O_2 + OH^\ominus \longrightarrow H_2O + HO_2^-$

The HO_2^- is better nucleophile than OH^- which help S_N1CB mechanism.

(15) (15)

Anation reaction →

is a substitution reaction in which one or more water ligand in a complex are replaced by anion.

ex

i) $[Co(NH_3)_5(H_2O)]^{3+} + X^\ominus \longrightarrow [Co(NH_3)_5X]^{2}$

ii) $[Cu(CN)_5(H_2O)]^{3+} + X^\ominus \longrightarrow [CuCCN)_5(H_2O]^{2}$

1

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Anation reaction are II nd order reaction as it is dependent on both the complex & anion.

$$[Co(NH_3)_5H_2O]^{3+} \xrightarrow[-H_2O]{\text{slow}} [Co(NH_3)_5]^{3+} \xrightarrow{\text{fast}} [Co(NH_3)_5X]^{2+}$$

$X^{\ominus}$

is this mechanism there is equilibrium between aquo complex i.e $[Co(NH_3)_5H_2O]^{3+}$ & five co-ordinate intermediate.

The rate of formation of $[Co(NH_3)_5X]^{2+}$ is independent on x^- as the anion competes with the solvent (H_2O) for the formation of active intermediate.

if concentration of five is very high then rate of replacement of water dose not depend on anion $x^{\ominus}$

- At a such high concentration of x^- the rate of formation of $[Co(NH_3)_5X]^{2+}$ should be equal to the rate of formation of intermediate i.e $[Co(NH_3)_5]$ a large nbr of -ve ligand (X^-) effect the anions reaction for the complex of the

anion reaction.

$[Co(NH_3)_5 H_2O]^{3+} \xrightarrow[-H_2O]{+X^-} [Co(NH_3)_5X]^{}$

---

(6) Electron- Transfer reaction

There are the reactions in which the oxidation state of some atom may change by the transfer of an e^- from one atom to the other.

ex

$4Al + 3O_2 \longrightarrow 2Al_2O_3$

(0) 3(0) (+3) (-2)

In these example each oxygen atom has gained two e^-, & each aluminium has lost three electrons.

in the aluminium - oxygen example, the aluminium was oxidised & the oxygen was reduced bcs they electron transfer reaction involves simultaneously oxidation & reduction. These reaction are called redox reaction.

oxidising agent → is sub that causes oxidation by accepting e^-, reducing agent → is substance causes reduction by losing e^-.

gain of e^- is reduced

ex ii) $Mg + O_2 \longrightarrow Mg^{2+}[O]^{2-}$

oxidation nbr decreases

↓ oxidised (oxidation nbr increase)

in this reaction when magnesium is burnt in air to give magnesium oxide so oxygen it gets oxidised to magnesium oxide (MgO) in the formation MgO. two e^- from mgo are transferred to oxygen atom

The process of transfer of e^- is described as redox process.

Simultaneously oxidation & reduction taking part in reaction is called Redox reaction.

ex

oxidised $2e^-$ or

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

reducing agent oxidising

oxidised $-2e^-$ reduced $+2e^-$

in this reaction zinc atoms lose e^- & & are oxidised to (Zn^{2+}) where,

(Cu^{2+}) gains e^- & are reduced to copper atom.

Thus, cupric ions acts as oxidising agent & zinc atom are acts as reducing agent.

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e⁻ gained : oxidation nbr decreases.

oxidant + e⁻ —reduction→ product

reductant —oxidation→ product + e⁻

(electron lost : oxidation nbr increases.

electron Transfer reaction can be divided into two main types.

a) outer sphere reaction

b) Inner sphere reaction or ligand reaction ~~can be divided into two main types.~~

bridged activated complex reaction.

(17) a) outer - sphere mechanism →

e⁻

The transfer from one reactant to another reactant i.e from oxidant to reductant & co-ordination sphere remain unaffected.

ex $[Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+} \rightarrow$

oxidised reduced

$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+}$

The central metal ion + the attached ligand of co-ordination comp

for e⁻ transfer to takes place the energies of the participating electronic orbitals must be same & this is possible only when metal ligand length of the two reacting complexes are equal.

These two complex come to each other & form precursors complex (simply reaction between oxidation & reduction are attach. is called precussors complex.

ex

O + R ——→ O ------ R

ii) This process is occured in critical conin which is given by Frank-condon principle states that.

(He suggest that Principle state that changing in bond length i.e elongation of compression this bcs Frank-condo principle states that,

The e⁻ transfer only takes place when bond length of interacting species same.

The bond length of two complex i.e

has same bond length. but there is shorter in length of one is compress in length.

- In order to understood the Franck-codon principle, the transfer of an e^- from $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ is considered.

$$[{}^{*}Fe^{2+}(CN)_6]^{4-} + [Fe^{3+}(CN)_6]^{3-} \longrightarrow$$

ferrocyanide ion — low-spin inert — $Fe^{2+} \rightarrow d^6$ — $(t_{2g}^6\ e_g^0)$ — Fe-C bond longer

ferricyanide ion — inert — $Fe^{3+} \rightarrow d^5$ — $(t_{2g}^5\ e_g^0)$ — Fe-C bond shorter

$$[{}^{*}Fe^{3+}(CN)_6]^{3-} + [Fe^{2+}(CN)_6]^{4-}$$

Fe-C bond longer — Fe-C bonds sh

Both Fe (II) & Fe (III) complexes are inert. the loss or exchange of CN^- or any ligand substitution reaction is very fast.

Both reactant are inert so that the close approach of metal atoms is not possible & therefore the e⁻ transfers must be takes place by tunneling outer-sphere mechanism.

1) Both complexes undergoes substitution reaction more slowly than the rate of e⁻-transfer. that means e⁻ transfer is much faster than substitution reaction. that why e⁻ transfer first & substitution reaction is close not takes place.

2) Electron transfer from reductant to oxidant when complex come closer to each other & distance between the metal is min. (what happen

ex →

oxidant + reductant ⟹ ox || red

ler. ~~one~~ their are two complexes one is ~~reduced~~ oxidised & one is reduced what will happen then come to each other & distance between these two complexes are min. & the complex is ~~so~~ known as precussors complex.

Activation of precurssors complex takes place

Precussors complex activates 4 recognisation of solvent molecule recognisation mean (C means solvent molecule around the precursors complex get recognise → It means they organise they transfer the charge one to each & change in bond length is changes.

why this is happining → bcs of Frank-Codon principle he tell e^- transfer only takes place when the bond length of complex are similar.

ex (metal bond length are similar).

$$[Fe(CN)_6]^{4-} + [Fe(CN)_6]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Fe(CN)_6]^{4-}$$

Fe^{2+} Fe^{3+} Fe^{2+}

The metal-ligand bond of these complex are similar, (not equal but similar) (so e^- transfer).

why solvent molecules recognise bus they organise then transfer the e^- in

ox + red → ox II red

from reductant to oxidant so reductant lose e^- & gain (+) charge & oxidant give (-) charge.
so Reductant are Reducing agent & oxidant means oxidising agent.

metal - ligand changes bcs of elongation & compression of bond length.

Step III → Ion pair dissociates into product the precursors complex is not dissociates to oxidant & reductant so overall then it converted into

oxidisation

$$ox + Red \longrightarrow O^{\ominus} + R^{\oplus}$$

reduction

so oxidising get (-) charge & reducing get (+) charge.

3-5-19

Features →

1) some reactants are should be kinetically inert.

2) If both reactant are inert w.r.t ligand exchange then close approach of metal ions is impossible then e^- transfer transfer takes place by tunneling or outer sphere mechanism

Shielded → Decrases the nucleus pull on the outer electrons. (blocking the nuclear charge)

ex $[M(CN)_6]^{m+} + [N(CN)_6]^{n+}$

consider two complexes are inert then that means ligand not move ~~bcs of~~ so they can not come to each other so the minimum distance is obtained they will not transfer the e^- is not takes place so e^- transfer takes place by the tunneling.

- The rate of e^- transfer depends upon the ability of e^- to tunned through ligand.

- e^- transfer is very fast when both complexes are low spin & if transfer is from $t_{2g}(red) \rightarrow t_{2g}(ox)$ why the e^- is very fast bcs they are not directly to ligand the t_{2g} is not shielded to ligand so e^- transfer to $t_{2g} \rightarrow t_{2g}$ they dont have tunnel out bcs they have less shielded

if e^- present in e_g orbital then what happen ~~eigand~~around in e_g orbital it is difficult ~~difficult~~ to tunnel out so it is ~~easier~~ in transfer the ligand.

π- acceptor ligand → will donate density to the metal atom.

- Rate of e^- transfer is much faster in the complexes having π- acceptor ligand like (CN⁻, BPy, phenthere). than those having σ- donar ligand like (H_2O, NH_3) etc.
- if (ONO)⁻ is having π- acceptor ligand then e^- transfer is much fast than the σ- donar ligand bcz. π- acceptor ligand is tunneling to antibonding orbital (bcs of e^- tunneling to π- acceptor ligand but this not takes place in σ- donar ligand so e^- transfer in π- acceptor ligand.

- Since π- acceptor ligand have π* vacant orbitals they accept e^- being transferred & can pass them to recieving metal ion. σ- donar ligands cannot do so.

$$M(R^-) \longrightarrow M(O)$$

reductant → oxidant

the e^- go to the π- antibonding orbital to the π- acceptor ligand.

- Rate of e^- transfer is slow if it is from eg (reductant) ⟶ eg (ox)

ex → H.S Co^{+2} (d^7) ⟶ L.S Co^{+3} (d^6)

$$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$$

ligand classified sigma donar when co-ordinated to metal. (Pi-bond is Form).

why bcs they shielded orbital like e⁻ density is higher so it is e⁻ can not tunnel through eg orbital to reduce to oxidant.

when e⁻ transfer is slow when it is high spin complex & low spin complex

eg →

Co^{+2} (d^7) ⟶ L.S Co^{+3} (d^6)

H.S ↿ ↿ (Homo) — — (Lumo)

↿ ↿ ↿ ↿ ↿ ↿

$t_{2g}^5 e_g^2$ $t_{2g}^6 e_g^0$

if e⁻ transfer is Homo to Lumo then H.S eg to eg. H.S e⁻ configuration to L.S electronic configuration is slow.

why slow e⁻ transfer in Homo to Lumo to eg to eg bcs the eg orbital is shielded so e⁻ density is low e⁻ tunned through the ligand so transfer of e⁻ is low. & difficult so it is slow.

to form one single sigma bond.

- Cross reaction is faster than self exchange.

i) $[Fe(CN)_4]^{4-} + [Mo(CN)_8]^{3-} \rightarrow$

Fe2+ Mo+5

$[Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$

ii) $[Mn(CN)_6]^{3-} + [Mn(CN)_6]^{4-} \rightarrow [Mn(CN)_6]^{4-} + [Mo(CN)_6]^{3-}$

Mn+3 Mn+2 Mn+2 Mn+4 Mn+3

- when metal are different means cross when e^- is taking place Fe to Mo so it is different so called cross reaction.

- when e^- transfer is taking place in same metal then called self - exchange reaction

- spin Forbidden reaction will be slow bcs bcs require more activation energy.

Characteristics

Condition for outer sphere mechanism (fast)

1) Inert complex
2) C.s of $t_{2g} \rightarrow t_{2g}$ (e^- transfer)
3) complex has π- acceptor ligand (CN^-, py)
CN^- is good for outer sphere mech.
4) cross reaction.
5) Spin allowed

outer sphere mechanism is again classified into two types.

1] Complementary electron transfer reaction

The oxidant & reductant change their oxidation state by an equal number of units.

ex

$Sn^{2+} + Tl^{+3} \longrightarrow Sn^{4+} + Tl^{+}$

2] Non-complementary electron transfer reaction

when the numbers of electrons gained or lose are different. Then called non-complementary reaction.

ex $Tl^{3+} + 2Fe^{2+} \longrightarrow Tl^{+}(aq) + 2Fe^{3+}$

oxidant reductant reductant oxidant

19-8-19 (19)

Inner Sphere Mechanism

electron transfer through bridging ligand.

- Inner sphere mechanism occurs through generally have one inert & one labile reactant.
- The inert reactant has a co-ordinated ligand which is capable of forming a bridg

ex 1) $[Cr(H_2O)_6]^{2+}$ + $[Co(NH_3)_6]^{3+}$ → $[Cr(H_2O)_6]^{3+}$ + $[Co(NH_3)_6]^{2+}$

~~labile~~ inert

see, the reactant $[Cr(H_2O)_6]^{2+}$ is a labile complex ion & can easily lose a H_2O molecules. & the oxidant $[Co(NH_3)_6]^{3+}$ is an inert complex with no co-ordinate ligand capable of forming a bridge with the reductant. So electron transfer in the example cannot occurs through inner sphere mechanism & the rate of electron transfer would be slow.

ex $[Cr(H_2O)_6]^{2+}$ + $[Co(NH_3)_5(H_2O)]^{3+}$ ⟶

$[Cr(H_2O)_6]^{3+}$ + $[Co(NH_3)_5(H_2O)]^{2+}$

The oxidant $[Co(NH_3)_5(H_2O)]^{3+}$ is a bridging ligand → (Cl, Br, I, F^-, OH^-, CN^-, N_3^-)

orbital overlap between e^- pair on O & d-orbital.

(20) ioert but the co-ordinated H_2O is a capable of forming a bridge, through a very weak one, with the reductant leading to the formation of the intermediate bridge-complex - $[(H_2O)_5 Cr-(H_2O)-CO(NH_3)_5]^{5+}$

The formation of an aqua-bridge has been established by H_2O exchange studies. So reaction proceeds through inner sphere mechanism & is much faster than the reaction CO).

ex $[Cr(H_2O)_6]^{2+} + [CO(NH_3)_5(OH)]^{2+} \longrightarrow [Cr(H_2O)_5(OH)]^{2+} + [CO(NH_3)_5(H_2O)]$

The reaction $[CO(NH_3)_5(OH)]^{2+}$ has a co-ordinated OH^- - ligand which is capable of forming a strong bridge with the reductant leading to formation of the bridge intermediate

$[(H_2O)_5 Cr-\overset{H}{O}-CO(NH_3)_5X]$ since

OH bridge is stronger (i.e stabler) than aqua bridge, the energy of activation required to form OH - bridge intermediate

would be less than required for the formation of aqua- bridge intermediate.
∴ through inner sphere mechanism is more facile than reaction (b).

ex $[Co(NH_3)_5Cl]^{3+}$ (III, inert) + $[Cr(H_2O)_6]^{2+}$ (II, labile) →

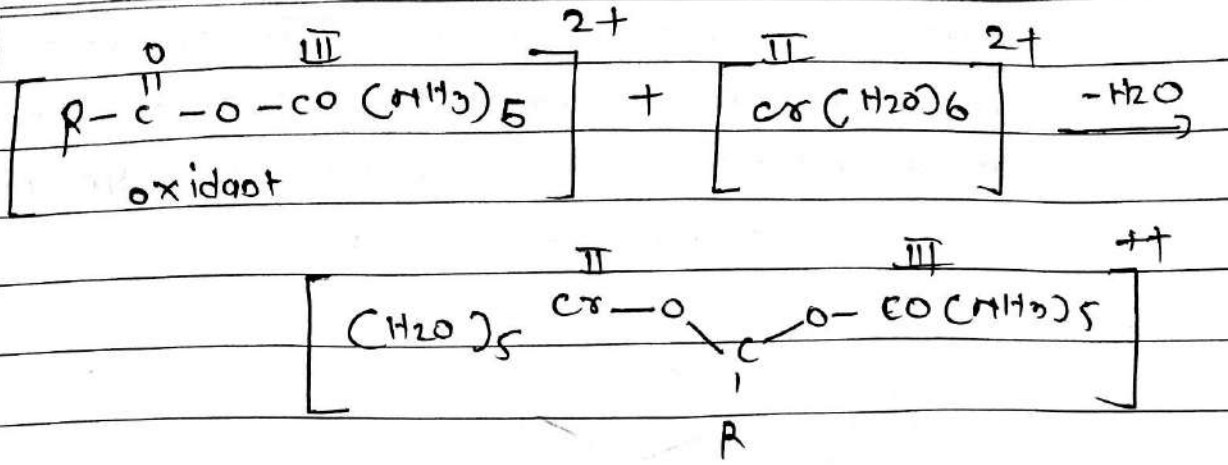
$[(NH_3)_5Co-Cl-Cr(H_2O)_5]$ → $[Co(NH_3)_5]^{2+}$ + ...

so in this reaction Cr is a bridging ligand
It is labile what happen in this ex the complex is labile the co-ordination nbr is (6) what happen the Cl is substituted by bridges the Cr then so one of the water molecules remove co-ordination nbr also six. bcs Cl is substituted by water

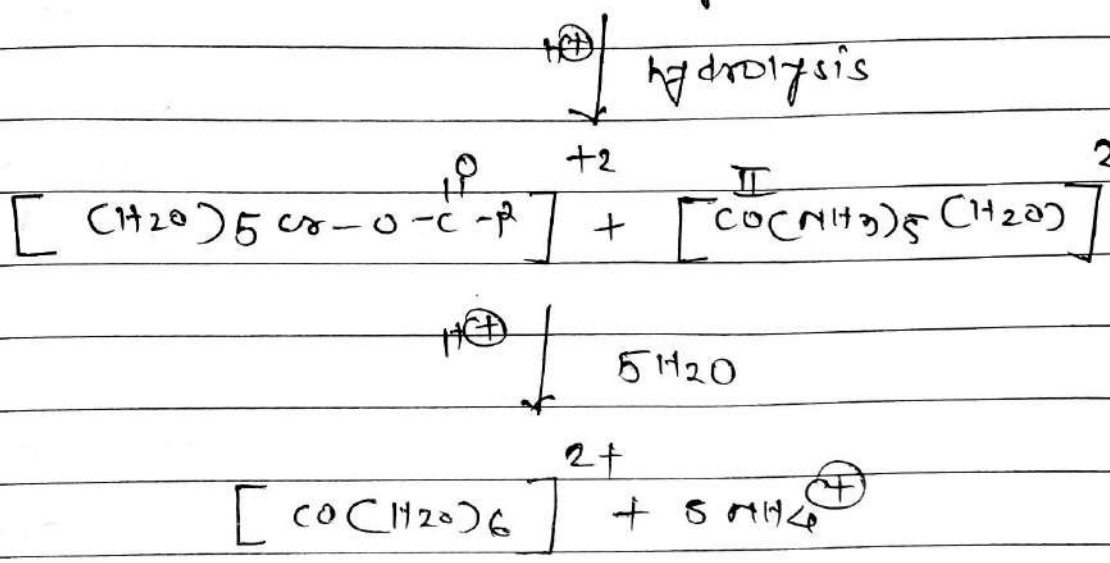
- when substitution is only happining when complexes are labile. when the complex is not labile then Cl is not bridges to Cr so then the reaction is not takes place by inner sphere mechanism. bcs they not form bridges.

$[Cr(H_2O)_5Cl]^{2+}$

ex



Activated bridge complex



COOR group form a bridge between the oxidant & reductant so that the reaction is occurs through the inner sphere mech.

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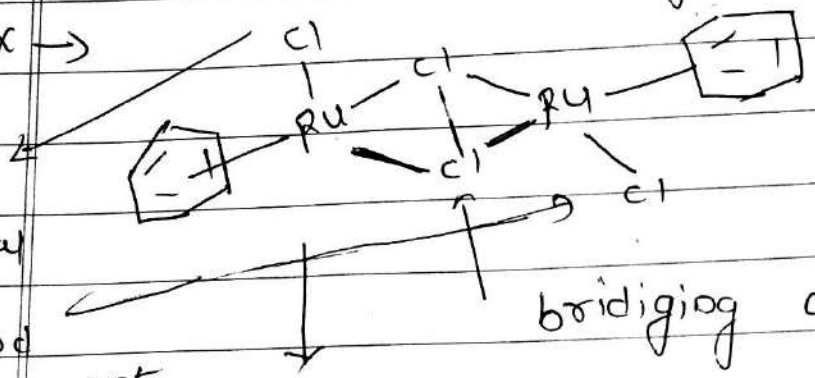
(bridging ligand means → In co-ordination chemistry the ligand that connect two or more atoms, usually metal ions. the ligand may be atomic or polyatomic.

ex →



terminal Cl⊖ ligand ↓ (ligand are not bridging)

bridging chloride ligand

see this example benzene ruthenium complex two Cl ligand are terminal & two are bridging.

see, the ligand is transfer (not always) then, the complex is inner sphere mechanism.

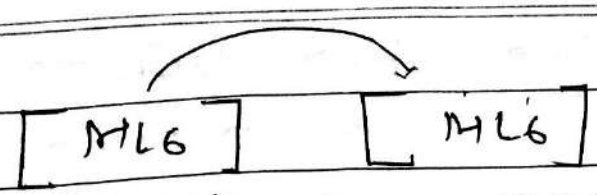
example,

Bridging ligand,

OH^-	CO^-	Br^-
O^{2-}	Cl^-	I^-
NH_2^-	H Hydride SH^- Thiol	
N^{2-}	CN^-	

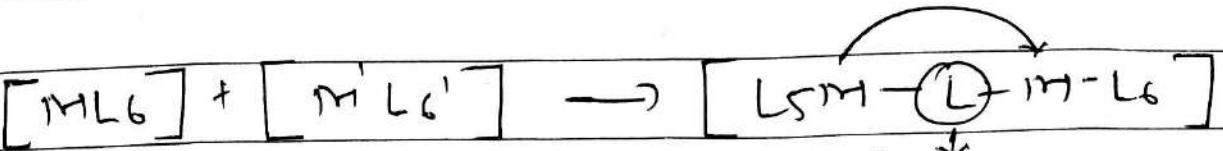
why this is called outer & inner sphere, (see) example, the sphere, is nothing but bracket

e^- Transfer



metal ligand complex the e^- transfer in one complex i.e one sphere to another sphere then it is outer sphere mechanism.

another example,



inside the transfer in e^- so it is called inner sphere mechanism & happing the bridging - ligand.

(few ligand are not briding ligand → H_2O).

ex →

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \xrightarrow{aq.} [Co(H_2O)_6]^{2+} + 5NH_4 + Cl^-$$

Bridging

$3d^7 4s^2$

eg. $[Co(NH_3)_5Cl]^{+2}$ $[Cr(H_2O)_6]^{2+}$

d^6 - high spin d^4 - High spin

Inert Labile

$t_{2g}^6 e_g$ ↑↓ ↑↓ ↑↓ $t_{2g}^3 e_g^1$ ↑ ↑ ↑

In aqueous medium this $(H_2O)_6$ is attacked to cobalt & Cl is transfered to Cr to give $[Cr(H_2O)_5Cl] + NH_4^+$ is coming out

Mechanism →

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow$$

$$[(H_3N)_5Co^{+3}-Cl-Cr^{+2}(H_2O)_5] + H_2O$$

↓ charge transfer

$$[(H_3N)_5Co^{+2}-Cl-Cr^{+3}(H_2O)_5]$$

d^7 lose d^3

Labile

$$[Co(NH_3)_5]^{+2} + [Cr(H_2O)_5-Cl]^{+3}$$

NOW

↓ $+H_2O$ left out

$$[Co(NH_3)_5H_2O]^{2+}$$

↓ hydrolysis (rapid)

$$[Co(H_2O)_6]^{2+} + 5\,NH_4$$

weak Field ligand → F, Cl, OH, H2O
strong Field ligand → NH3, CN, NO, CO
depend on splitting.

Co has +3 oxidation state & one water molecules go out bcs the complex is labile see, Cl is briding ligand & oxidation nbr of Co & Cr is (+3, +2) total is +4 next, charge transfer is takes place then only inside sphere Cr is giving one e⁻ to Co so Co changes so (+2 & Cr is +3) so Co +2 is d7 - L.S & Cr +3 - d3. H.S

↓ ↓

1

↑↑ ↑↑ ↑↑ labile ↑↑↑ inert

so Co is labile & break the bond close e⁻ so unsaturation co-ordination form). So give

$[Co(NH_3)_5]^{+3} + [Cr(H_2O)_5 - Cl]^{+2}$

↓

complex is unsaturated & water molecules is left out to form complex $[Co(NH_3)_5 H_2O]^{2+}$

then hydrolysis give $[Co(H_2O)_6] + 5NH_4^+$

Inner sphere mechanism without ligand transfer

$$[IrCl_6]^{2-} + [Cr(H_2O)_6]^{2+} \longrightarrow$$

Ir: +4, Cr: 0

6-2 = 4

5d7 6s2 → 5d5 (L.S) Inert

Cr: 4s2 3d4 → 3d4 (H.S) labile

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$$[IrCl_6]^{3-} + [Cr(H_2O)_6]^{3+}$$

5D & 4D are 100 spin so it is Inert. & 3d4 are labile. oxidation state has Ir - +4 & Cr is +2. Briding ligand is Cl. see Mech. two react & Form.

Mechanism →

$$[Cl_5Ir^{+4} - Cl - Cr^{+2}(H_2O)_5]^{0} + H_2O$$

↓ e^- transfer

$$[Cl_5Ir^{+3} - Cl - Cr^{+3}(H_2O)_5]$$

↓ break

Ir^{+3} is d4 so inert Cr^{+3} so inert both are inert so not bond form this bond break.

$$[IrCl_6]^{+3} + [Cr(H_2O)_5]^{+3}$$

↓

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

Join

Consider the reaction given below.

i) $[Cr(NH_3)_5(NCS)]^{2+}$ $[Cr(H_2O)_6]^{2+}$ →

oxidant reducement

$[(H_3N)_5Cr-NCS-Cr(H_2O)_5]^{4+}$

$[(H_3N)_5Cr-NCS-Cr(H_2O)_5]^{4+}$ $\xrightarrow{\text{hydrolysis}}$

~~$[(H_3N)_5Cr-N-N-N-Cr(H_2O)_5]^{4+}$~~

$[Cr(NH_3)_5(H_2O)]^{2+} + [Cr(H_2O)_5(NCS)]^{2+}$

ii)

$[(Cr(NH_3)_5N_3]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow$

oxidant reductant

$[(H_3N)_5Cr-N-N-N-Cr(H_2O)_5]^{4+}$

$(H_3N)_5Cr-N-N-N-Cr(H_2O)_5]^{4+}$ $\xrightarrow{\text{hydrolysis}}$

$[Cr(NH_3)_5(H_2O)]^{2+} + [Cr(H_2O)_5N_3]^{2+}$

The e^- transfer reaction in example (II) is found to be faster than (I).

The bridged transition state of reaction (i) is less stable & hence would require more energy for its formation compared to the energy required for the formation of the bridged transition state of reaction (ii) As a result.

the $\bar{e}$ transfer reaction (ii) is faster than (i). The Cr-NCS-Cr bridge is less stable bcs S-Cr linkage is weaker than N-Cr linkage where, Cr-N-N-N-Cr bridge is more stable as it acquires greater stability through resonance.

The observed energy of activation (E_a) for all the above mentioned $\bar{e}$ transfer reaction is found to be very low (3-4 kcal) & entropy change (ΔS) is found to be -ve

if a dissociative step, like the one shown,

$$[Cr(NH_3)X]^{2+} \longrightarrow [Co(NH_3)_5]^{3+} + X^{\ominus}$$

The RDS in these reaction, the energy of activation have been high $\Delta S = (S_{product} - S_{reactant})$ been the

it is clear above that in $\bar{e}$ transfer reaction occuring through inner sphere mech an atom or group is also transferred from one complex ion to another.

$[ML_6]^{n+} + [ML_6]^{n+}$ outer

$[ML_6] + [ML_6] \rightarrow [ML_5 \overset{L}{} ML_5]$

Difference between outer sphere & inner sphere mechanism

i) outer sphere mechanism occurs through the complex are inert but inner sphere mechanism one reactant is inert & one is labile.

ii) outer sphere electron transfer occurs between complexes that do not undergo substitution. No new bonds are broken or formed. inner sphere electron transfer occurs between complexes via a bridging ligand.

iii) outer sphere mechanism occurs through tunneling mechanism. & inner sphere mechanism occurs through activated bridged ligand.

iv) e^- transfer with no change of coordination in outer mechanism. in inner sphere mech. e^- transfer through briding ligand.

v) in outer sphere mechanism the e^- transfer between ions of the same metal is fast if M-L distances in the reductant & the oxidant are very nearly the same. Electron transfer reactions occuring through

inner sphere mechanism are faster than similar reactions occuring through outer sphere mechanism.

vi) In outer sphere mechanism the e^- transfer is fast if the e^- are able to reach the surface of the complex either through unsaturation or through conjugation.
The e^- transfer is increases in inner sphere if the bridging ligand has unsaturation or extended conjugation in its structure.

vii) In outer sphere e^- transfer depend upon the polarising power of central metal ion.

viii) In inner sphere e^- transfer also increases with increase in the nucleophilic character of the briding ligand.
In outer sphere e^- transfer is fast if e^- transferred is present in a t_{2g} orbital & is slow if its present in e_g orbital.

ix) Electron transfer is fast in outer sphere when complexes having π- acceptor ligand.