Coordination & Organometallic Chemistry

Handwritten Notes

COORDINATION CHEMISTRY

Ligand ⇒ The species (molecule or ion) having atleast one lone pair of e^- is called a ligand.

Ligand → Lewis Base
→ Nucleophile

Metal cation ⇒ electron deficient
↓
Lewis acid
↓
Electrophile

Lewis acid + Lewis base ⟶ Addition Product
(Coordinate bond)

$BF_3 + NH_3 \longrightarrow F_3B \leftarrow NH_3$

⇒ A ligand can donates its lone pair of e^-s to the metal cation/atom and form a coordinate bond.

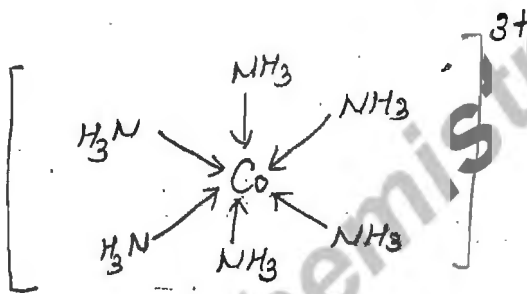
⇒ The compounds in which the ligands are attached to the central metal cation/atom by coordinate bonds are called coordination compounds or complex compounds.

complex ions ⇒ The ions in which a ligand is attached to central metal cation/atom by a coordinate bond are called complex ions./ compounds.

In aqueous solution → The complex compounds retain their properties i.e. they do not lose their identity in aq. soln.

e.g. $[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$

complex ion



Some of the constituent ions lost their properties or identities.

Coordination number ⇒ Number of donor atoms attached to metal cation or atom.

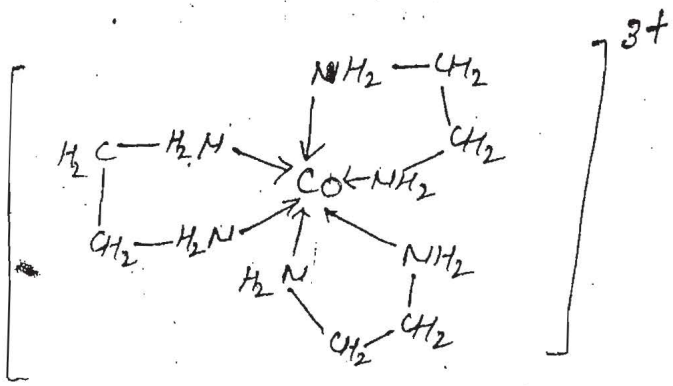
e.g. $[Ag(NH_3)_2]^+$ ⇒ $[Cu(NH_3)_4]^{2+}$ ⇒ $[CoCl_4]^{2-}$

C.N. = 2 C.N. = 4 C.N. = 4

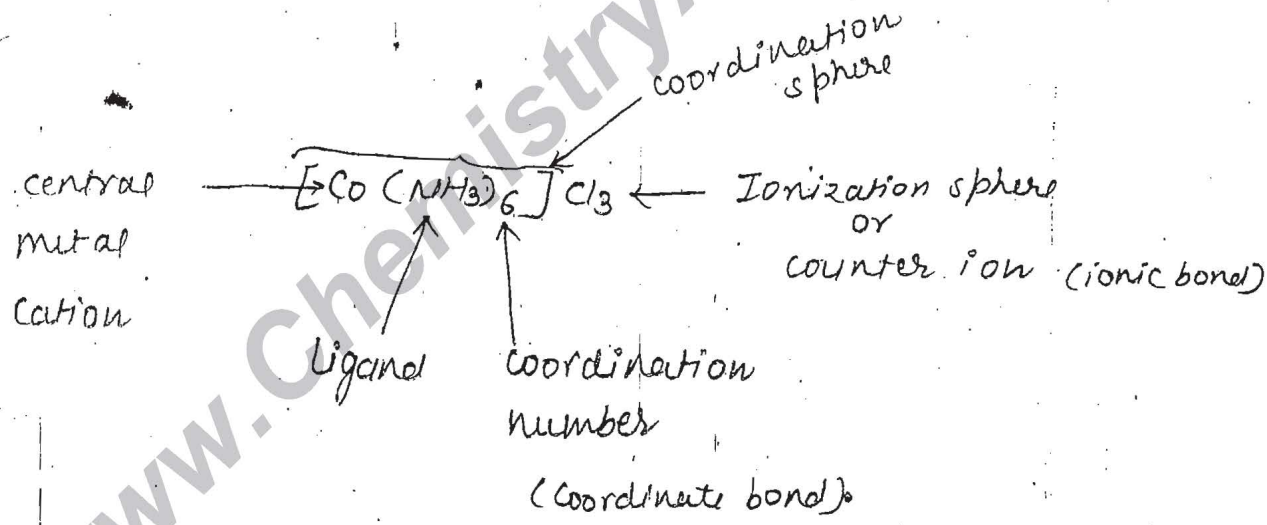
⇒ $[Co(NH_3)_6]^{3+}$ ⇒

C.N. = 6

⇒ $[Co(en)_3]^{3+}$ en ⇒ ethylene diamine → $\ddot{N}H_2-CH_2-CH_2-\ddot{N}H_2$



C.N. = 6



Classification of Ligands ⇒

[I] monodentate Ligands ⇒

dentis → teeth (Greek)

Cut by single tooth i.e. has only one donor atom

① Negative Ligands ⇒

(Old) Name → ends at 'o'

(New) Name → ends at — ide, — ite, — ate $\xrightarrow[+o]{-e}$ — ido, — ito, — ato

• Ex:-

F^-	Fluoro (Fluorido)	New
Cl^-	Chloro (Chlorido)	New
Br^-	Bromo (Bromido)	New
I^-	Iodo	
CH_3COO^-	acetato	
CO_3^{--}	Carbonato	
OH^-	hydroxo	
NO_3^-	Nitrato	
N_3^-	azido	

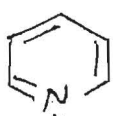
NH_2^-	amido
NH^{2-}	imido
N^{3-}	nitrido
O^{2-}	oxo
O_2^{2-}	peroxo
O_2^-	superoxo
PO_4^{3-}	phosphato
SO_4^{2-}	sulphato
SO_3^{2-}	sulphito
S^{2-}	sulphido
H^-	hydrido
$-NO_2^-$	nitro (or nitrito-N)
$-ONO^-$	Nitrito (or nitrito-O)
CN^-	cyano
CNO^-	cyanato
$-CNS^-$	Thiocyanato (or thiocyanato-S)
$-NCS^-$	isothiocyanato (or thiocyanato-N)
$-S_2O_3^{2-}$	Thiosulphato-S
$-OS_2O_2^{2-}$	Thiosulphato-O

Neutral ligands ⇒

1) $(C_6H_5)_3P$ — triphenyl phosphine

2) $(C_2H_5)_3P$ — triethyl phosphine

3) C_6H_5N or — pyridine



(Py)

4) $CH_3\ddot{N}H_2$ — methylamine

5) $(CH_3)_2NH$ — dimethylamine

6) $(CH_3)_3N$ — trimethylamine

7) $CH_3-\ddot{O}-CH_3$ — dimethyl ether

8) $CH_3\ddot{S}CH_3$ — dimethyl thio ether

9) $\ddot{N}H_3$ — amine

10) $CO:$ — carbonyl

11) $H_2\ddot{O}$ aqua

12) $\ddot{N}O:$ nitrosyl

13) $Me_2\ddot{S}O:$ dimethylsulphoxide (DMSO)

positive ligands ⇒

NO^+ nitrosonium

e.g.

1) $Na_2[Fe(CN)_5NO]$ ↵ [Retheruse E. House Croft – Book]

2) $[Fe(H_2O)_5(NO)]SO_4$ ↵

In the complexes of iron, NO exist in NO^+ form.

[] Bidentate ligands ⇒ having two donor atoms

Examples ⇒

1) $\begin{matrix} COO^- \\ | \\ COO^- \end{matrix}$ oxalato (ox)

2) $NH_2CH_2COO^-$ glycinato (gly)

3) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-CH=\overset{OH}{\overset{|}{C}}-CH_3$

acetyl acetone (keto form) ⇌ (enol form)

$\xrightarrow[\text{(abstract } H^+\text{)}]{NH_3}$ $\xrightarrow{-H^+}$

$CH_3-\overset{O}{\overset{\|}{C}}-CH=\overset{O^-}{\overset{|}{C}}-CH_3$

acetyl acetonato

(acac)

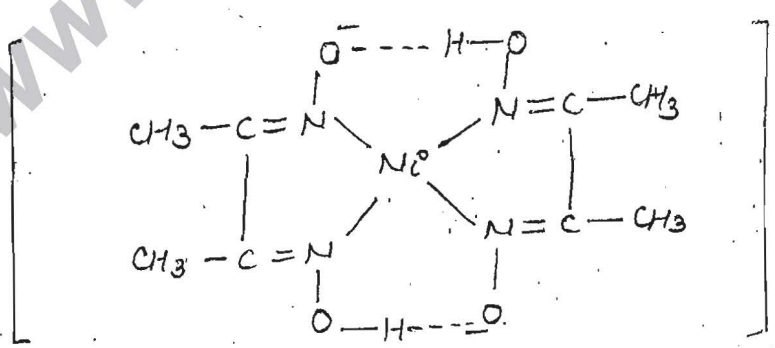
4) $CH_3-C(=N-OH)-H_3C-C=N-OH$ $\xrightarrow{-H^+}$ $CH_3-C(=N-OH)-CH_3-C=N-O^-$

dimethylglyoxime → dimethylglyoximato

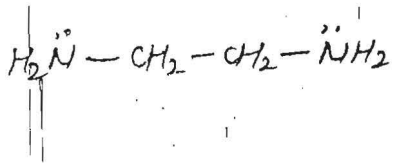
(H_2dmg) (Hdmg)

Estimation of Ni ⇒

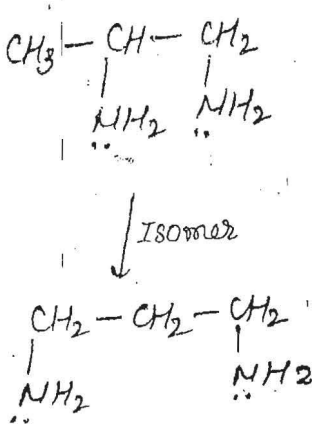
$Ni^{2+} + CH_3-C(=N-OH)-CH_3-C=N-OH \xrightarrow[\text{(abstract } H^+ \rightarrow NH_4^+\text{)}]{NH_3}$



red ppt

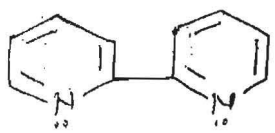
5) 

ethylene diamine (en)

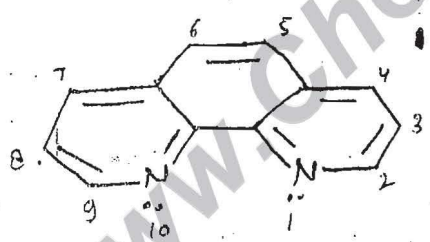
6) 

Propylene diamine (pn)
or
1, 2 - diamino propane

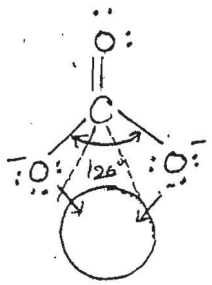
Trimethylene diamine (tn)
or
1, 3 - diamino propane

7) 

bipyridine (bpy or bipy)
or
dipyridine (dpy or dipy)

8) 

o-phenanthroline
or
1, 10 - phenanthroline (phen) or
(o-phen)

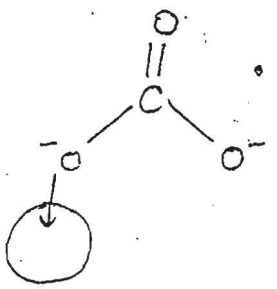


$[Mn(NO_2)_6]^{4-}$

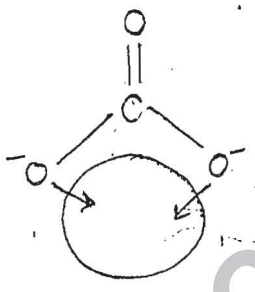
↑ smaller size

[25 Mn]

Both oxygens attached on C-atom can donate lone pair of e⁻ to metal. If the size of metal is small then oxygen atoms will have to come near metal to donate e⁻s. In doing so, bond angle b/w them decreases ⇒ strain ↑ → bond pair repulsion ↑. Therefore only one oxygen atom donates e⁻.



← only one oxygen atom donates lone pair of e⁻ if size of the metal is small.



$(NH_4)_2[Ce(NO_3)_6]^{2-}$ ← ceric ammonium nitrate

C.N = 12

[58 Ce]

larger size

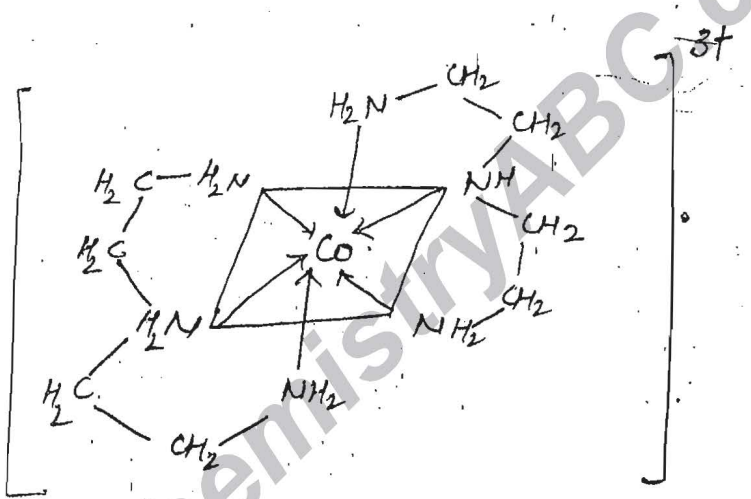
Here size of metal is large enough, therefore it can approach oxygen atoms (both) and oxygen atom will not come to metal, therefore no bond pair - bond pair repulsion will take place. Therefore both the oxygens donate their lone pair of e⁻ and CO_3^{2-} will act as bidentate ligand.

[III] Tridentate ligands ⇒ Three donor atoms

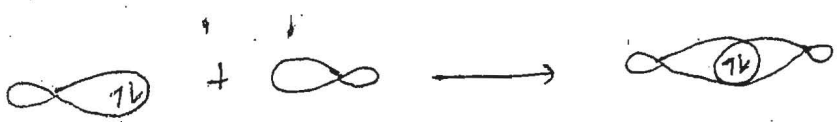
Examples ⇒ $H_2\ddot{N}-CH_2-CH_2-\ddot{N}H-CH_2-CH_2-\ddot{N}H_2$

Diethylenetriamine

$[Co(dien)_2]^{3+}$



Coordinate bond = covalent bond



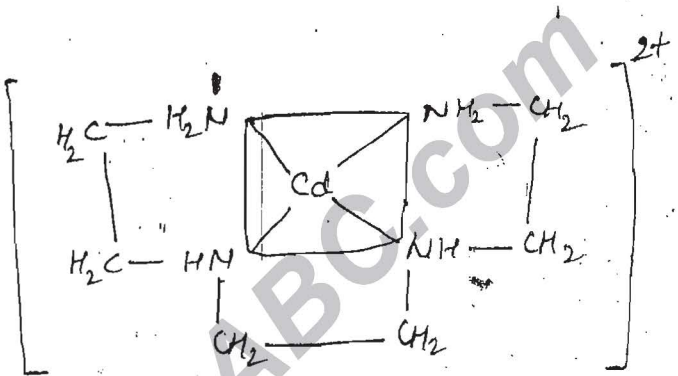
[III] Tetradentate Ligands :-

Example :-

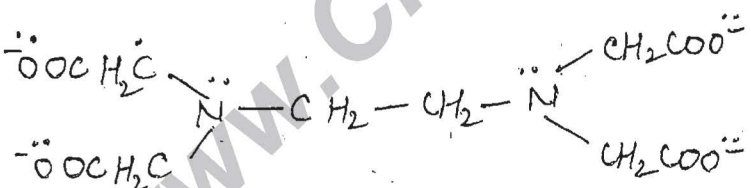
$H_2N - CH_2 - CH_2 - NH - CH_2 - CH_2 - NH - CH_2 - CH_2 - NH_2$

triethylene tetramine (trien)

$[Cd(trien)]^{2+}$



[IV] Pentadentate and hexadentate ligands ⇒



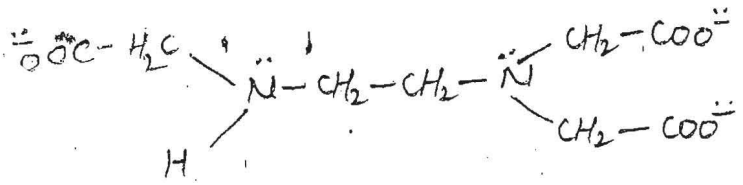
$(edta)^{4-}$

Hexadentate

[Ethylene diamine tetraacetic acid – EDTA]

↓

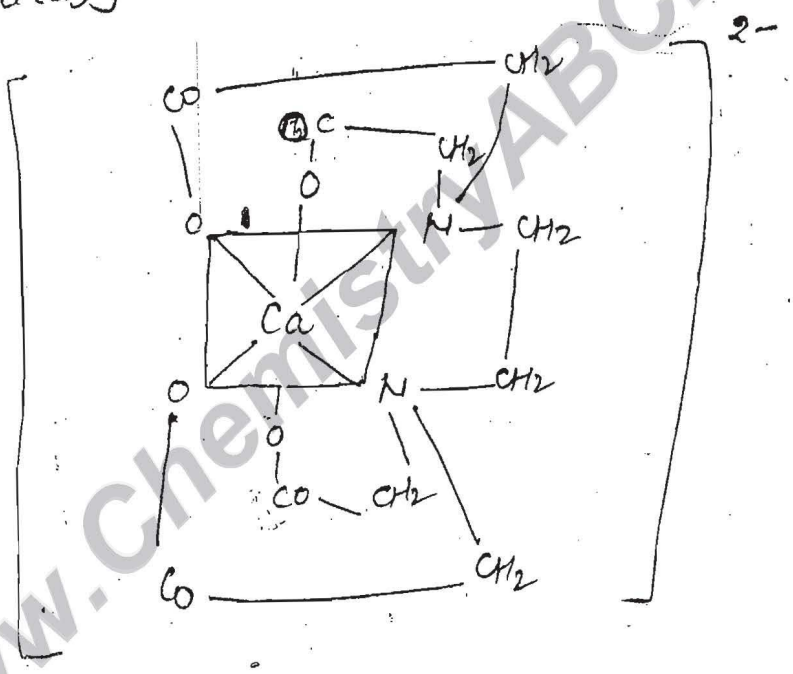
acetate



$(edta)^{4-}$ pentadentate

Ethylenediaminetriacetate

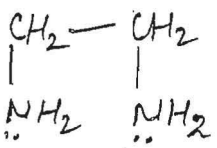
$[Ca(edta)]^{2-}$

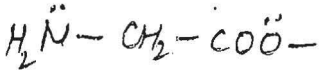


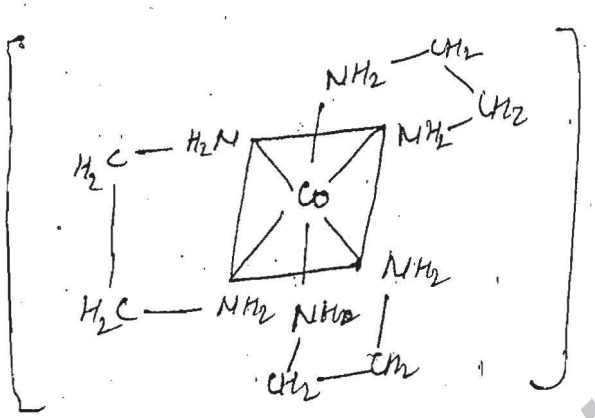
Symmetric and Unsymmetric bidentate ligands

(AA) — Same donor atoms

(AB) — different donor atoms







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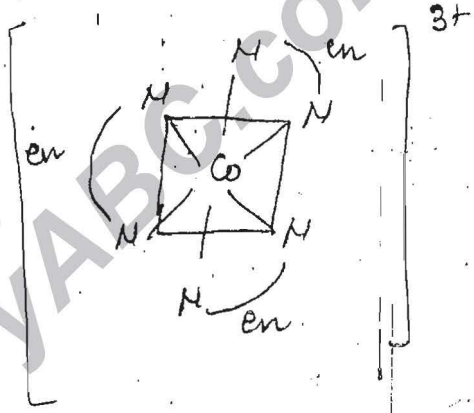

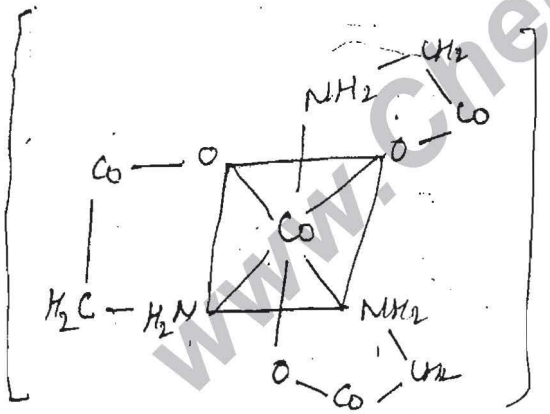

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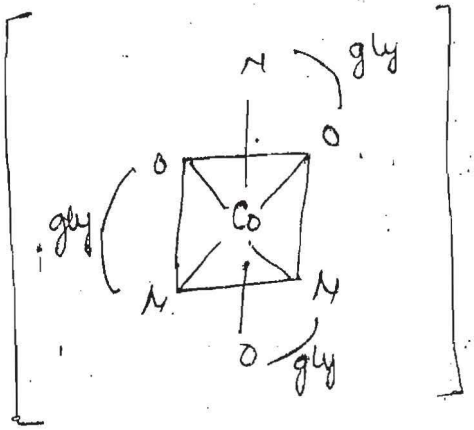
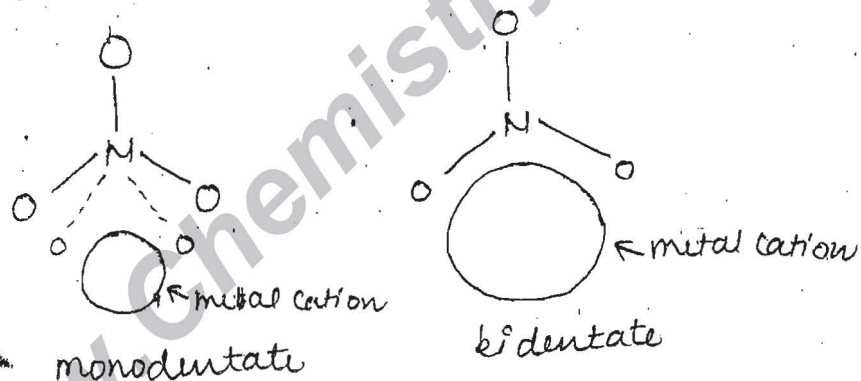


(VI) Flexidentate Ligands ⇒ Ligands that can behave as both monodentate and bidentate ligands.

Examples :- CO_3^{2-} , NO_3^- , SO_4^{2-} , SO_3^{2-}

Smaller metal cation → monodentate

Larger metal cation → bidentate

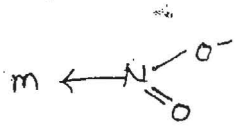


monodentate bidentate

V.V. Imp

(VII) Ambidentate Ligands ⇒ Monodentate ligands having two different donor atoms can coordinate with metal cation by either of the donor atoms.

Ex :- NO_2^- , CNS^- , $S_2O_3^{2-}$



$M \leftarrow SCN^-$

$M \leftarrow NCS^-$

$M \leftarrow S_2O_3^{2-}$

$M \leftarrow O\,S_2O_2^{2-}$

$:C\equiv N:^-$, $:C\equiv O:$, $-C\equiv N-O^-$

cant behave as ambidentate ligand although has two different donor atoms.

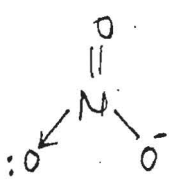
$:C\equiv N:^-$
$:C\equiv O:$
} carbon donates e⁻s because the energy of O_2 is very small (lower than bonding MO), so it cant donate its e⁻s to metal cation becoz the energy of electro+ve metal is very high.

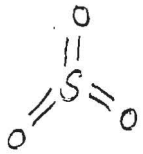
Q⇒ select the ambidentate ligands.

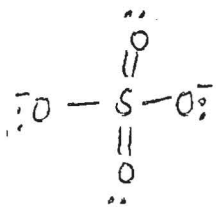
SO_3 , SO_4^{2-} , SO_2 , SO_3^{2-} , ClO_3^- , ClO_4^- , PO_4^{3-} , NO_3^-

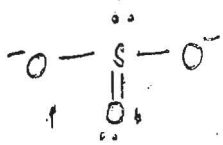
which of the following may acts as ambidentate ligands?

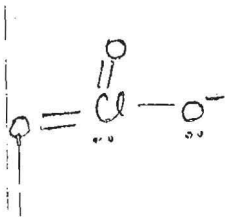
(a) NO_3^- (b) SO_3 (c) SO_4^{2-} (d) SO_3^{2-}











Chelating and macrocyclic ligands ⇒

↓

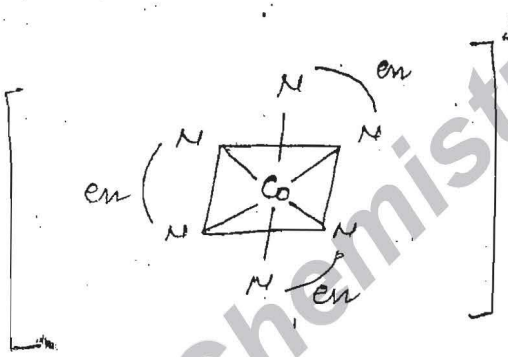
Noncyclic polydentate ligands

(bidentate, tridentate...)

↓

form cyclic compounds

e.g.



macrocyclic ligands :- cyclic ligands.

Ex:- Haemoglobin, myoglobin, chlorophyll

Isomerism

The compounds in which chemical composition is same but arrangement of constituent particles is different are called isomers and this phenomenon is called isomerism.

- Isomerism
  - Structural or constitutional isomerism
    - Ionization Isomerism
    - Linkage "
    - Hydrate "
    - coordination "
    - coordination position "
    - Ligand isomerism
    - Polymerisation isomerism
  - Stereoisomerism
    - Geometrical isomerism
    - optical isomerism

Structural Isomerism ⇒

① Ionization isomerism:-

$[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$

$[Co(NH_3)_5Cl]SO_4$

- $BaCl_2$ → $BaSO_4\downarrow$ white ppt.
- $AgNO_3$ → No ppt.

$[Co(NH_3)_5SO_4]Cl$

- $AgNO_3$ → $AgCl\downarrow$ white ppt
- $BaCl_2$ → no ppt.

$[Co(NH_3)_5Br]SO_4$

- $BaCl_2$ → $BaSO_4\downarrow$ white ppt.
- $AgNO_3$ → No ppt.

$[Co(NH_3)_5SO_4]Br$

- $AgNO_3$ → $AgBr\downarrow$ cream coloured ppt. (Light yellow)
- $BaCl_2$ → No ppt.

$[Co(NH_3)_5I]SO_4$

- $BaCl_2$ → $BaSO_4$ white ppt
- $AgNO_3$ → No ppt.

$[Co(NH_3)_5SO_4]I$

- $AgNO_3$ → AgI yellow ppt
- $BaCl_2$ → No ppt.

② Linkage isomerism ⇒ Shown by ambidentate ligands.

Examples:-

⇒ $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$

⇒ $[Co(NH_3)_5(S_2O_3)]^{+}$ and $[Co(NH_3)_5(OS_2O_2)]^{+}$

⇒ $[Co(NH_3)_5(SCN^-)]^{2+}$ and $[Co(NH_3)_5(NCS)]^{2+}$

③ Hydrate Isomerism ⇒

$CrCl_3 \cdot 6H_2O$

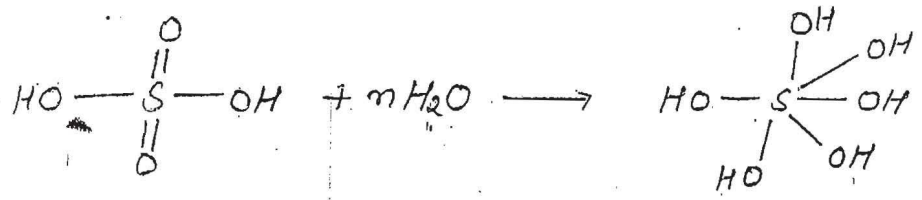
$[Cr(H_2O)_6]Cl_3 \longrightarrow$ Violet colour $\xrightarrow[H_2SO_4]{\text{conc. (dehydrating agent)}}$ No change

$[Cr(H_2O)_5Cl]^{2+}Cl_2 \cdot H_2O \rightarrow$ Light green $\xrightarrow[H_2SO_4]{\text{conc.}} [Cr(H_2O)_5Cl]Cl_2 + H_2O$

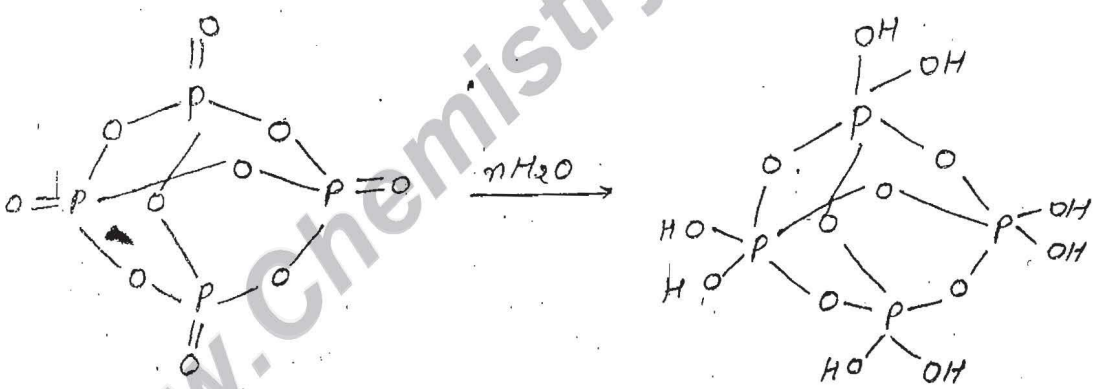
$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O \rightarrow$ dark green $\xrightarrow[H_2SO_4]{\text{conc.}} [Cr(H_2O)_4Cl_2]Cl + 2H_2O$

$[Cr(H_2O)_3Cl_3] \cdot 3H_2O \leftarrow$ not possible to exist [coz there is no +ve charge to bound H_2O]

$[Cr(H_2O)_3Cl_3] \rightarrow$ exist



When H_2SO_4 reacts with H_2O, high amount of energy is released because the reaction is exothermic and here π bond breaks and σ bond forms.



Water is a good reservoir of heat. Therefore H_2SO_4 is added in H_2O, not H_2O in H_2SO_4.

1) $[Cr(H_2O)_6]Cl_3 \xrightarrow{3Ag^+} 3\,AgCl\downarrow$

2) $[Cr(H_2O)_5Cl]Cl_2\cdot H_2O \xrightarrow{2Ag^+} 2\,AgCl\downarrow$

3) $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O \xrightarrow{1Ag^+} AgCl\downarrow$

In estimation of Ag, ① will take $3AgNO_3$ molecule, ② → 2 and ③ → only one.

④ Coordination Isomerism ⇒ exist when cation and anion both are complex ions.

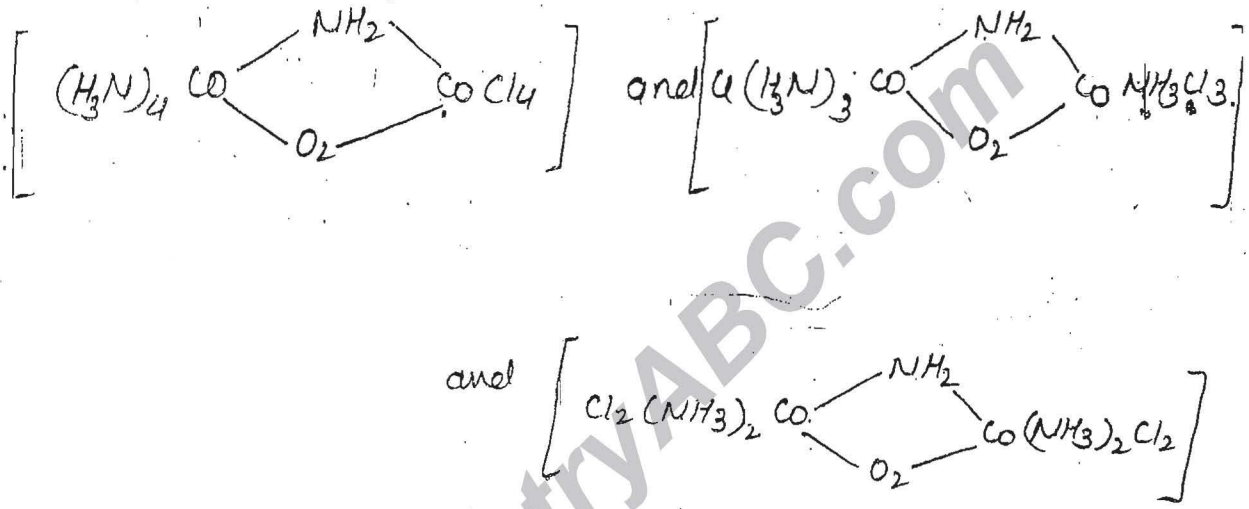
Ex:- $\underbrace{[Co(NH_3)_6]}_{\text{complex cation}}\underbrace{[Cr(CN)_6]}_{\text{complex anion}}$ and $[Cr(NH_3)_6][Co(CN)_6]$

Exchange of one or more or all liganels between 2 complex ions.

Ex:- $[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_3Cl][PtNH_3Cl_3]$

⑤ Coordination position isomerism ⇒ In bridging complexes and there will be exchange of ligands between two metal ions.

Ex:-



⑥ Polymerisation isomerism ⇒ It is not a true isomerism.

Ex:-	Pt	NH_3	Cl	Ratio
$[Pt(NH_3)_2Cl_2]$	1	2	2	
$[Pt(NH_3)_4][PtCl_4]$	2	4	4	1:2:2
$[Pt(NH_3)_3Cl]_2[PtCl_4]$	3	6	6	

Q⇒ which of the following will show ionization isomerism?

ⓐ $[Co^{2+}(NH_3)_5Cl](SCN)$ and $[Co^{2+}(NH_3)_5(SCN)]Cl$

ⓑ $[Cr(NH_3)_4(I)Br]I$ and $[Cr(NH_3)_4ClI]Br$

ⓒ $Fe[Cr(CN)_6]$ and $Cr[Fe(CN)_6]$

(i) a and b only (ii) only a (iii) only b (iv) all

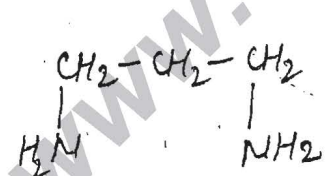
Ans (iv) all

$[Fe[Cr(CN)_6]$ and $Cr[Fe(CN)_6]$ shows ionisation as well as linkage isomerism]

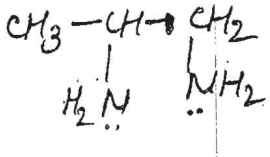
① Ligand isomerism ⇒ Ligand itself exist as isomer

Ex:-

⇒

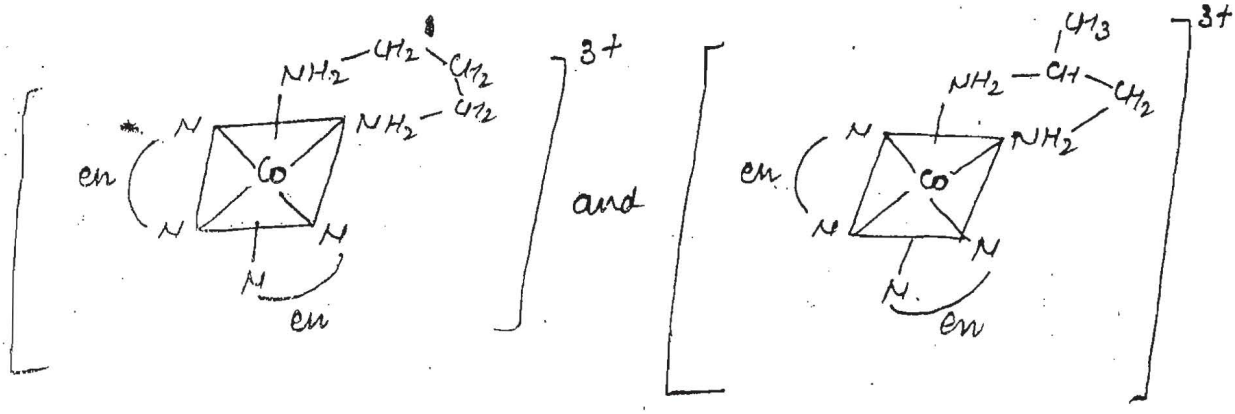


(tn)



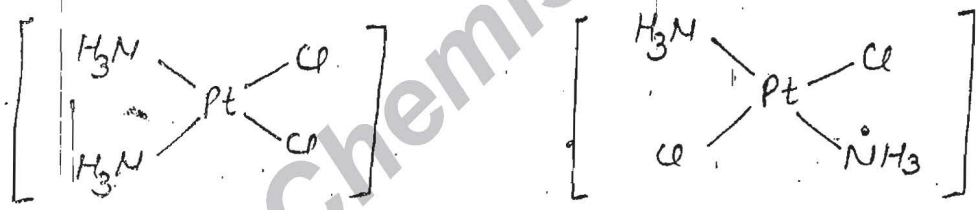
(pn)

⇒ $[Co(en)_2(tn)]^{3+}$ and $[Co(en)_2(pn)]^{3+}$



Stereoisomerism ⇒ same type and same number of atoms coordinated to central metal ion but their spatial arrangement is different.

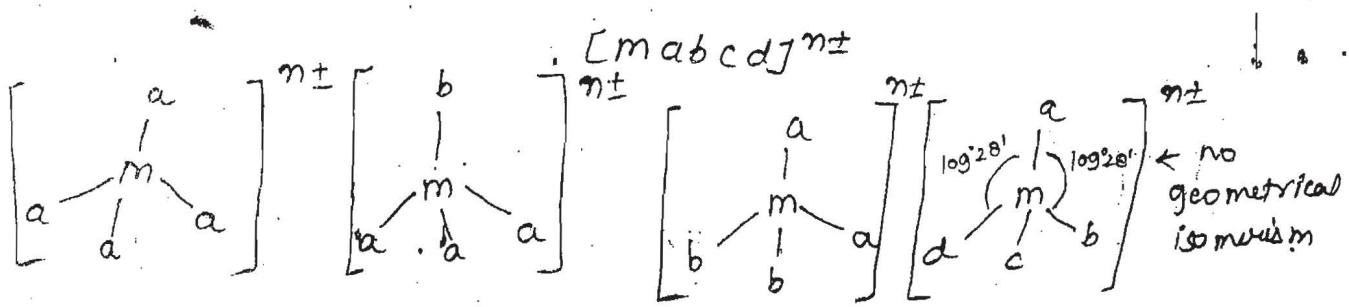
Ex:- $[Pt(NH_3)_2Cl_2]$



Geometrical isomerism ⇒

① Coordination number · 4 ⇒

ⓐ Tetrahidral complexes:- $[ma_4]^{n\pm}$, $[ma_3b]^{n\pm}$, $[ma_2b_2]^{n\pm}$, $[mabcd]^{n\pm}$

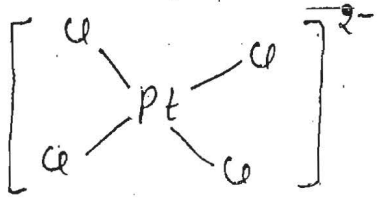


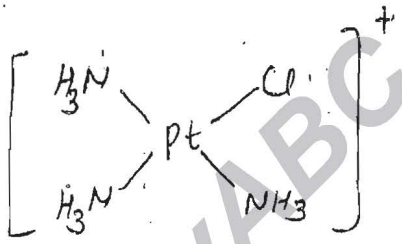
⑥ square planar complexes ⇒

(i) $[Ma_4]^{n\pm}$, $[Ma_3b]^{n\pm}$, $[M(AA)_2]^{n\pm}$

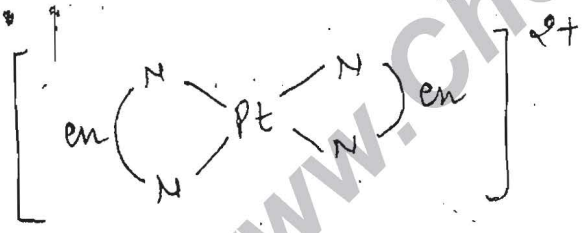
no geometrical isomerism

Ex:- $[PtCl_4]^{2-}$ $[Pt(NH_3)_3Cl]^{+}$

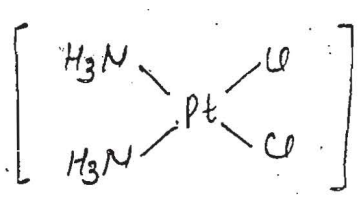




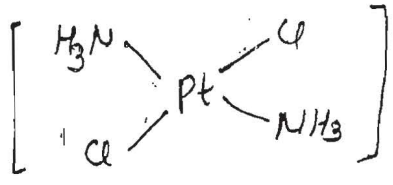
$[Pt(en)_2]^{2+}$



(ii) $[Ma_2b_2]^{n\pm}$ type Ex:- $[Pt(NH_3)_2Cl_2]$

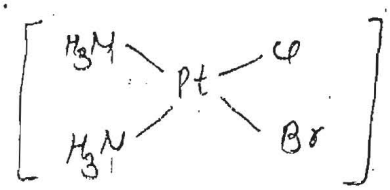


cis

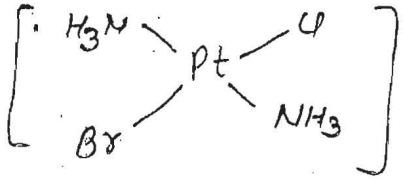


Trans

⇒ $[Pt(NH_3)_2ClBr]$



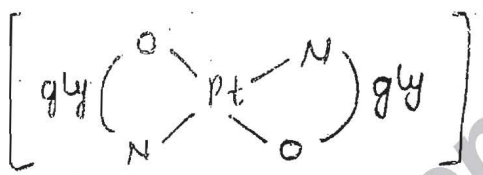
cis



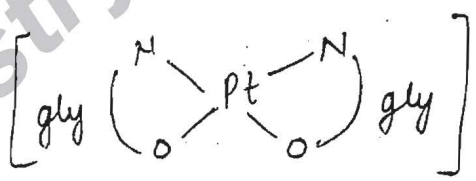
Trans

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

Ex:- $[Pt(gly)_2]$



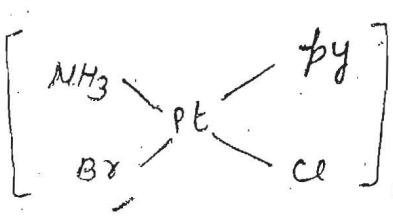
Trans



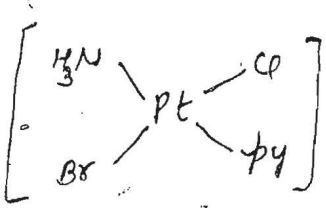
cis

(iv) $[Mabcd]^{n\pm}$ type

Ex:- $[Pt(NH_3)pyBrI]^-$



cis



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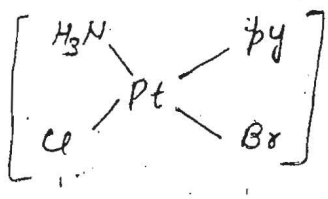


cis

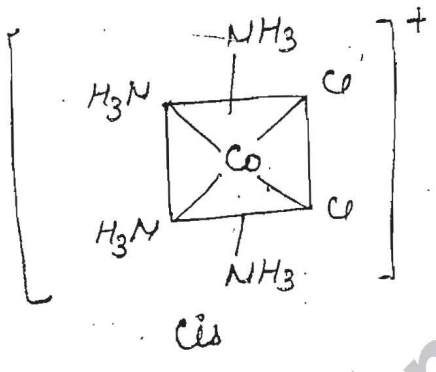
② Coordination no. 6 ⇒

ⓐ Octahedral complexes ⇒

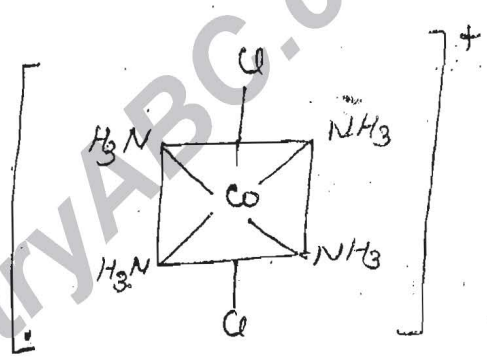
(i) $[ma_6]^{n\pm}$, $[ma_5b]^{n\pm}$, $[M(AA)_3]^{n\pm}$

no geometrical isomerism

(ii) $[ma_4b_2]^{n\pm}$ type Ex:- $[Co(NH_3)_4Cl_2]^+$



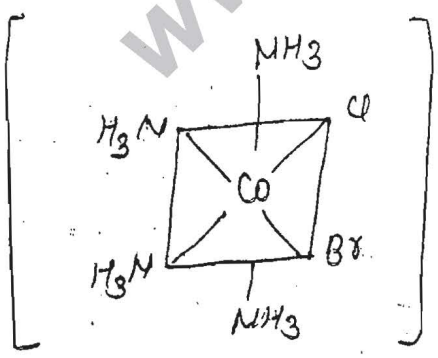
cis



Trans

Two angles are possible → 90°, 180°

(iii) $[ma_4bc]^{n\pm}$ type Ex:- $[Co(NH_3)_4ClBr]^+$



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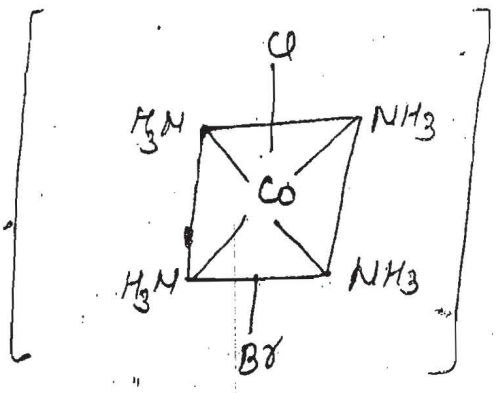
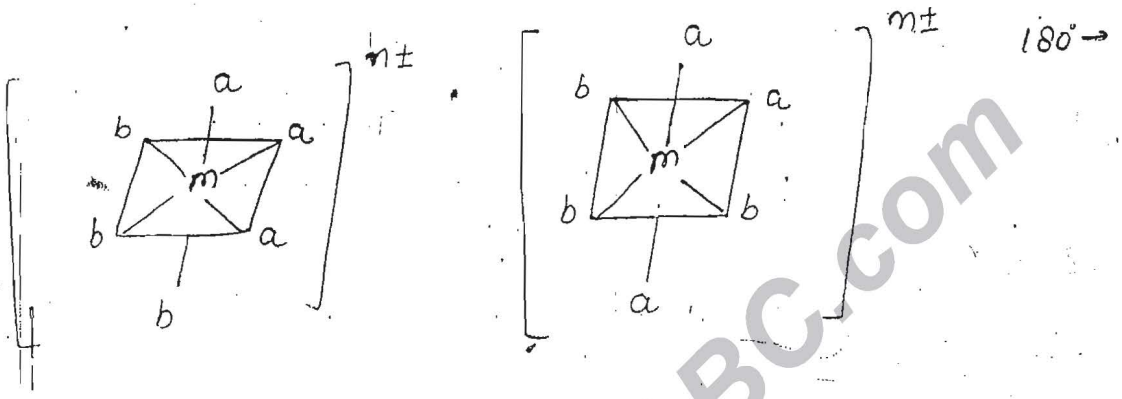


Trans

Geometrical Isomerism ⇒

③ facial and meridional Isomerism ⇒

@ $[ma_3b_3]^{n\pm}$ type.



Examples ⇒ $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_3(NO_2)_3]$

Facial ⇒

① $\angle ama = 90°$

$\angle bmb = 90°$

② Same ligands lie on the corner of a face → facial isomers

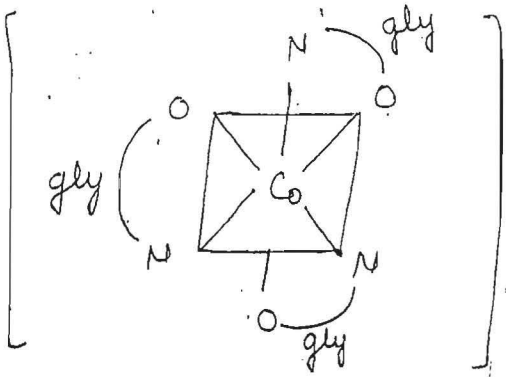
Meridional ⇒

① $\angle ama = 180°, 90°$

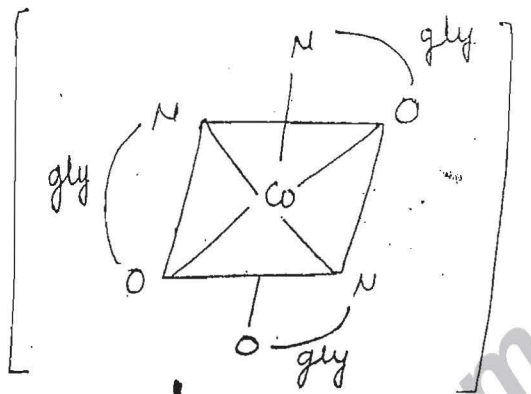
$\angle bmb = 180°, 90°$

② Two same ligands are present on the meridian (largest part of the) of the octahedrally spherical field.

(b) $[M(AB)_3]^{n\pm}$ type Ex:- $[Co(gly)_3]$

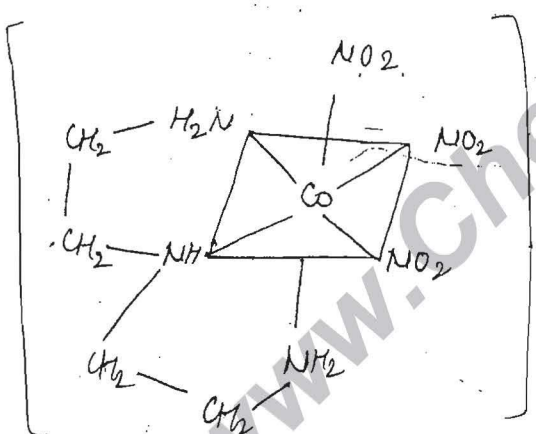


Facial

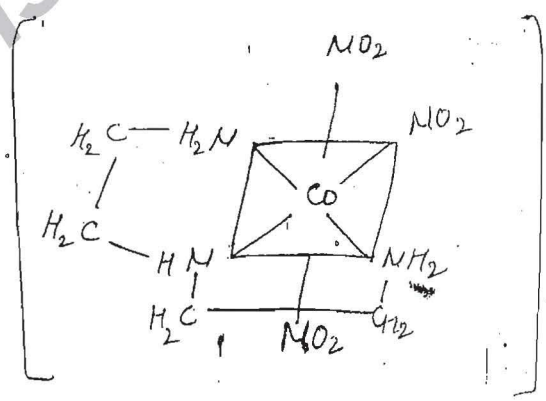


meridional

(c) $[Co(dien)(NO_2)_3]$



Facial



meridional

Q⇒ Which of the following show facial and meridional isomerism?

(i) $[Co(NH_3)_3Cl_3]$

(ii) $[Co(acac)_3]$

(iii) $[Co(dien)_2]^{3+}$

(iv) $[Co(gly)_3]$

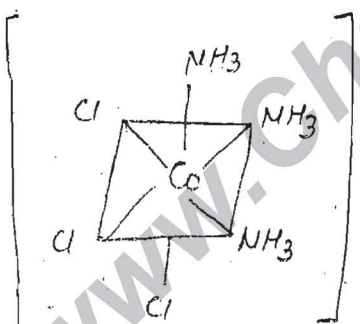
(v) $[Co(dien)(NO_2)_3]$

(a) only (ii) and (iii) (b) only (i), (ii) (iii) and (iv)

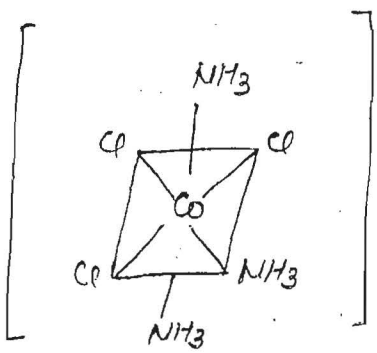
(c) only I, III, IV and V (d) only I, III and II

(d) all

(i)

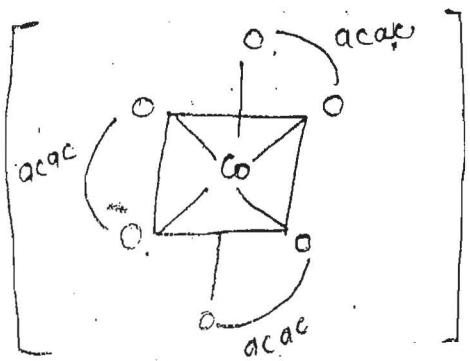


facial



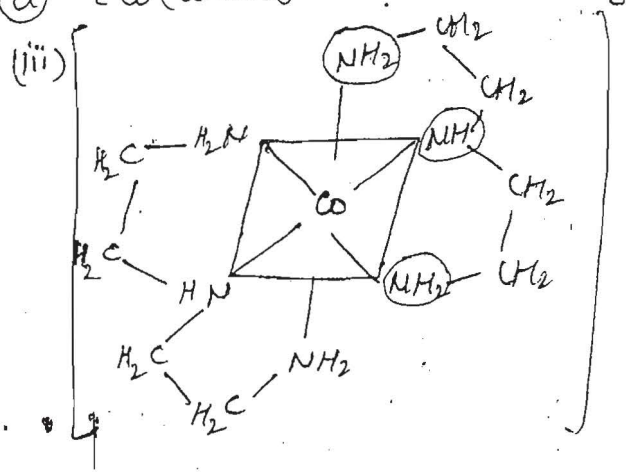
meridional

(ii)

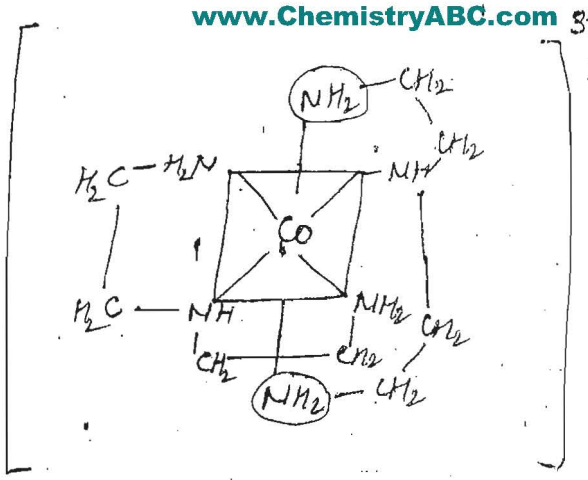


(d) $[Co(dien)_2]^{3+}$

(iii)



Facial

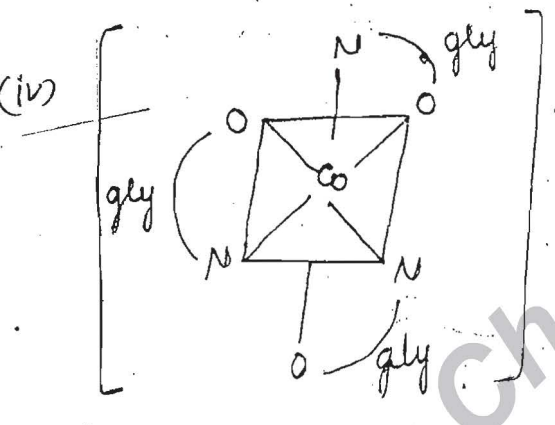


meridional

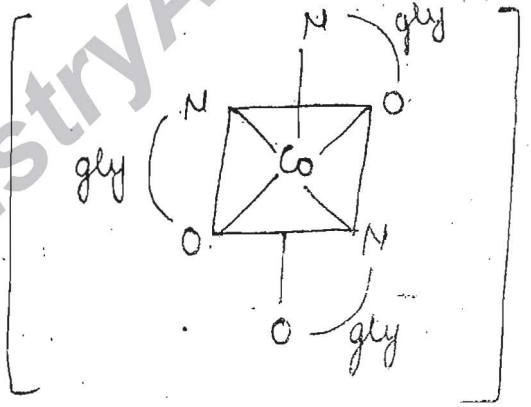
Facial → cis

meridional → Trans

(iv)

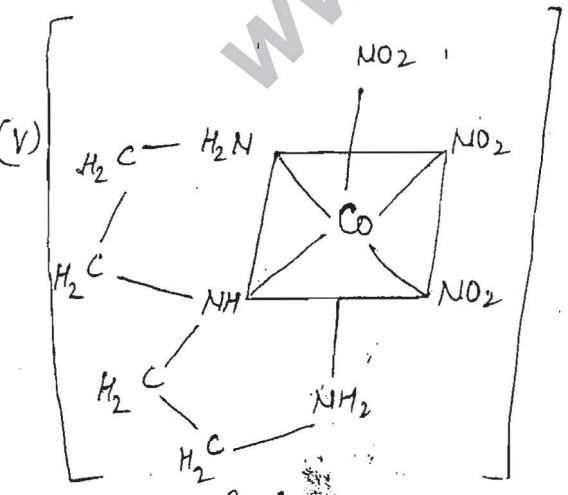


facial

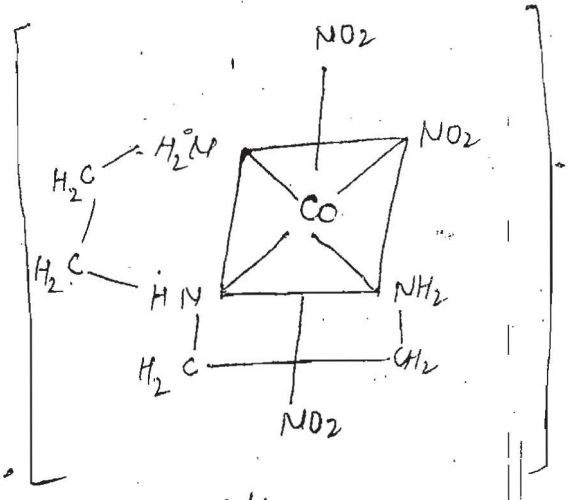


meridional

(v)

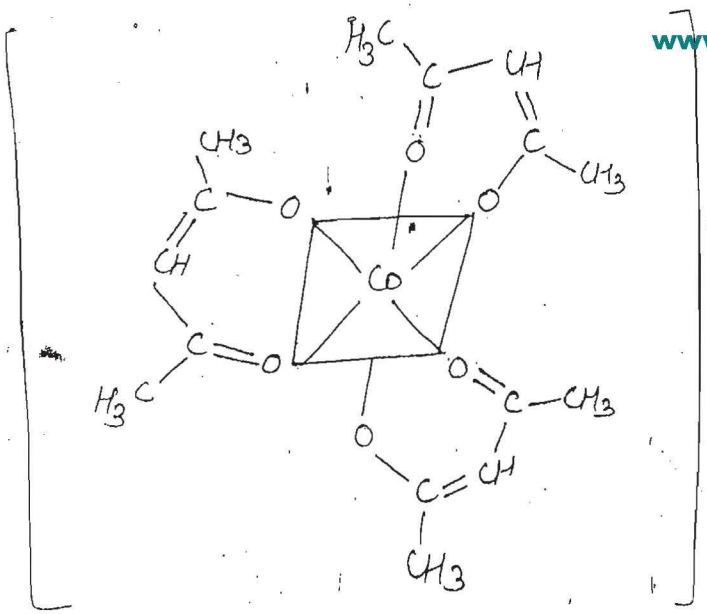


facial

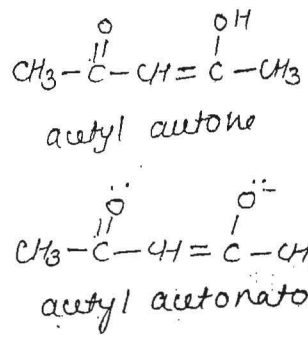


meridional

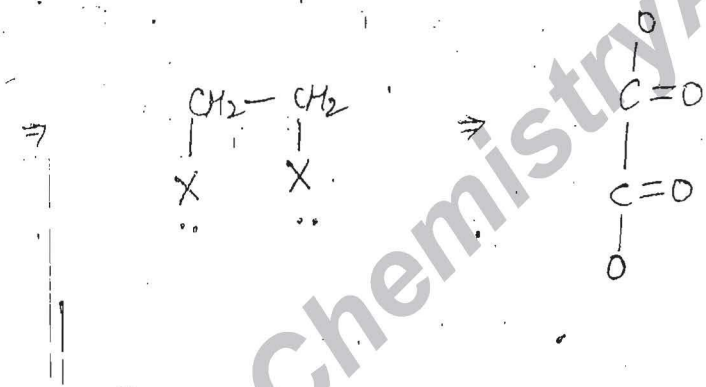
(ii)



$[Co(acac)_3]$



Note ⇒ ^Bidentate ligands ^attached on cis position (i.e. at 90° angle)
Donor atoms of are always
①

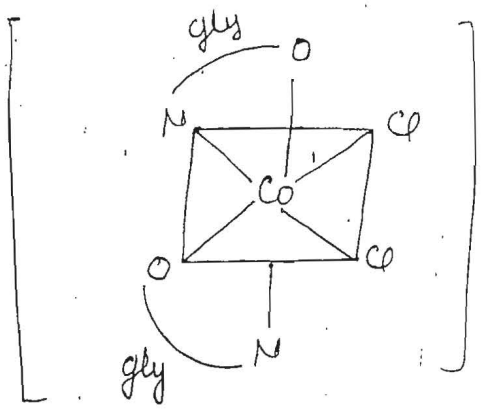


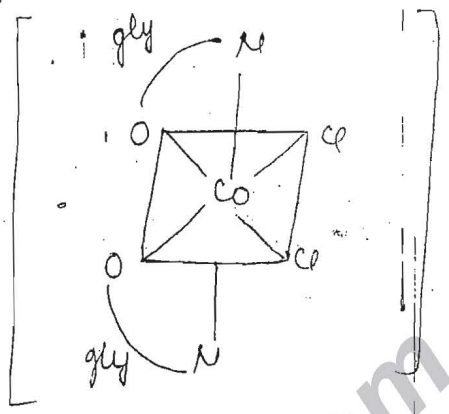
All
② ^Donor atoms of other polydentate ligands can attached at 90° as some of them at 180°.

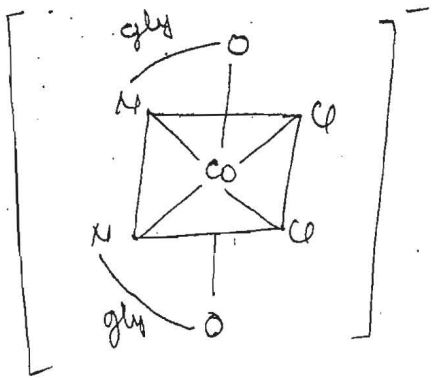
Ex:- (i) $[Co(dien)(NO_2)_3]$ (ii) $[Co(dien)_2]^{3+}$

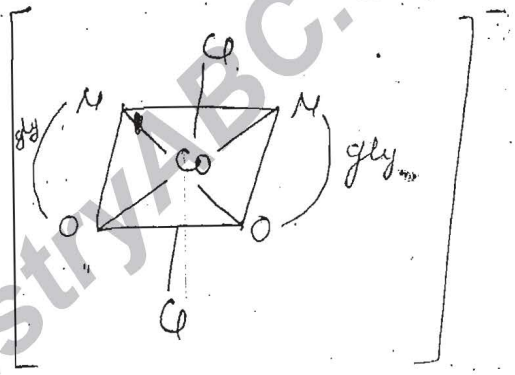
fac & mer.

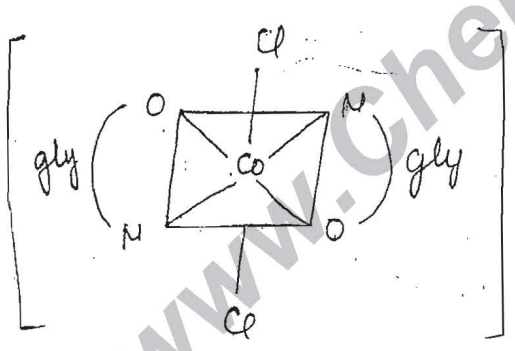
④ $[M(AB)_2a_2]^{n\pm}$ type Ex:- $[Co(gly)_2Cl_2]$







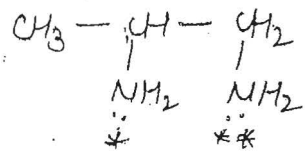




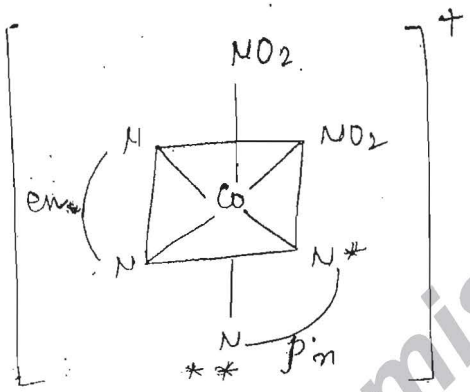
Geometrical isomers = 5

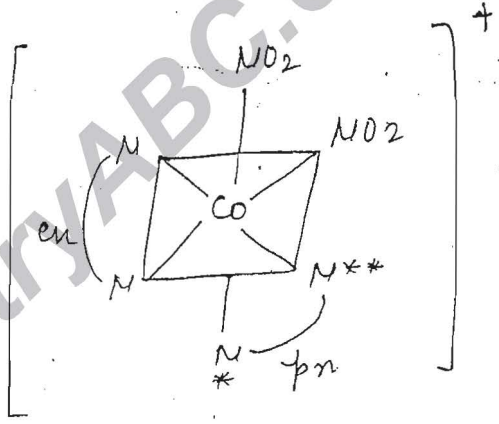
[Here only angle is considered to determine geometrical isomers.]

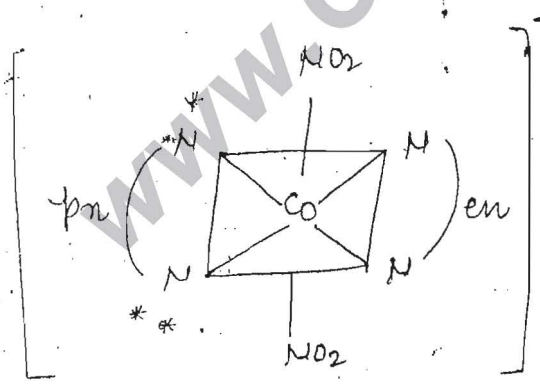
Complexes containing optically active ligands ⇒



Ex:- $\left[Co(en)(pn)(NO_2)_2\right]^+$

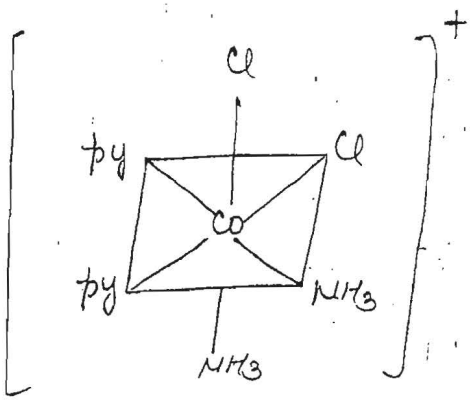


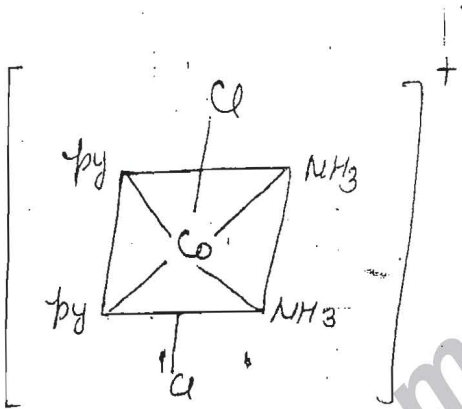


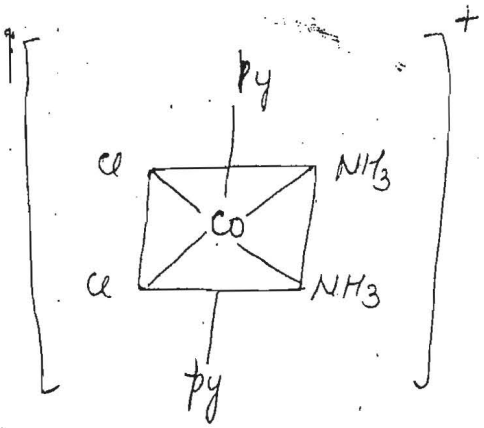


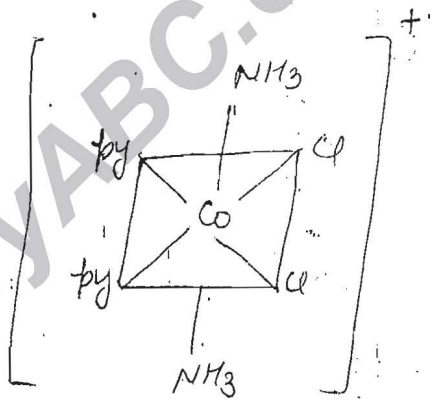
Geometrical isomers = 3

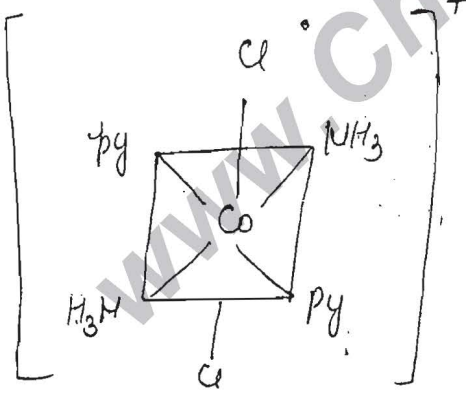
(5) $[ma_2b_2c_2]^{n\pm}$ type Ex:- $[Co(py)_2(NH_3)_2Cl_2]^+$





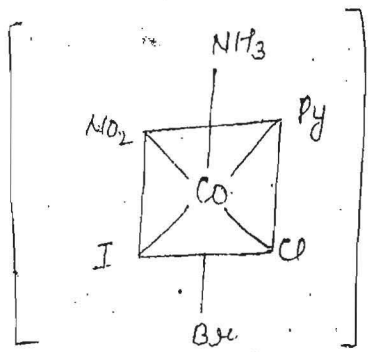




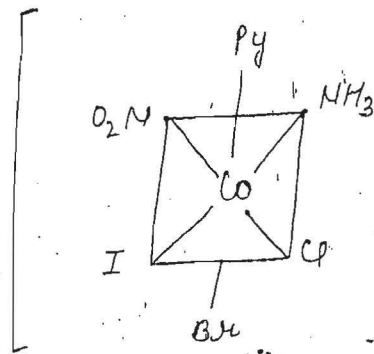


⑥ $[Mabcdef]^{n\pm}$ type ⇒ Ex:- $[Co(NH_3)(Py)(Cl)(Br)(I)(NO_2)]^-$

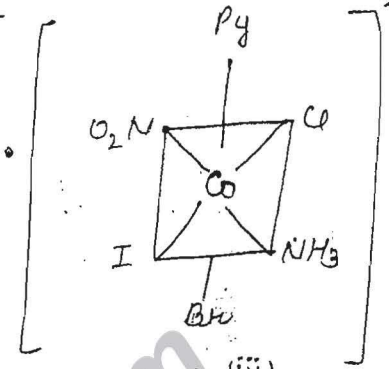
15 geometrical isomers



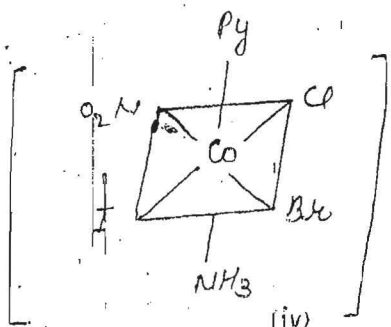
(i)



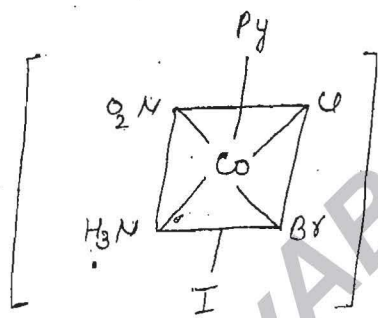
(ii)



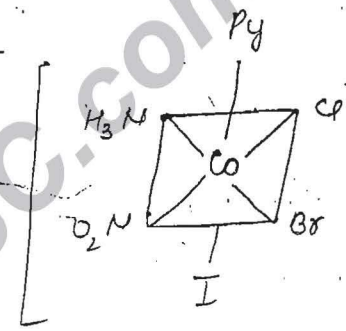
(iii)



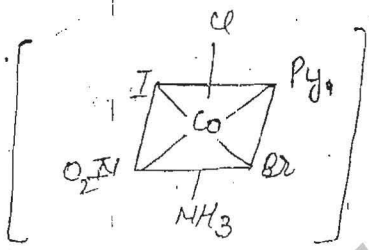
(iv)



(v)

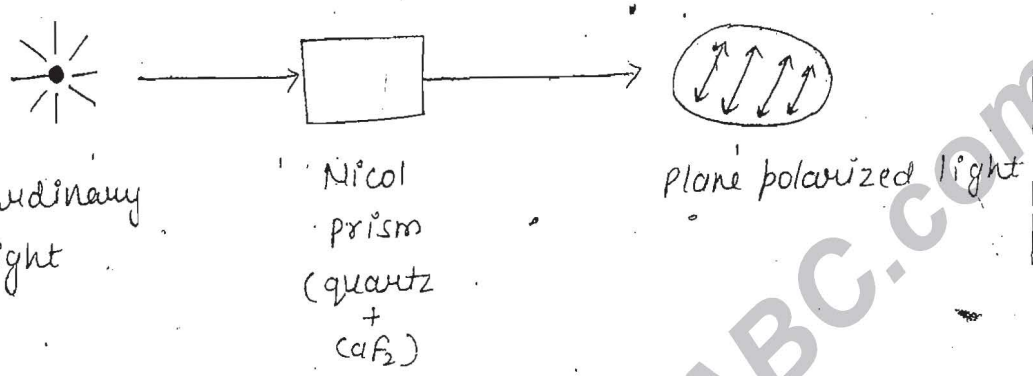


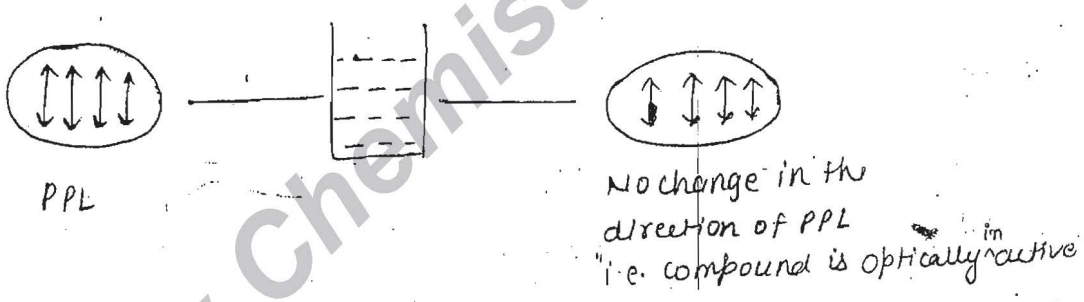
X

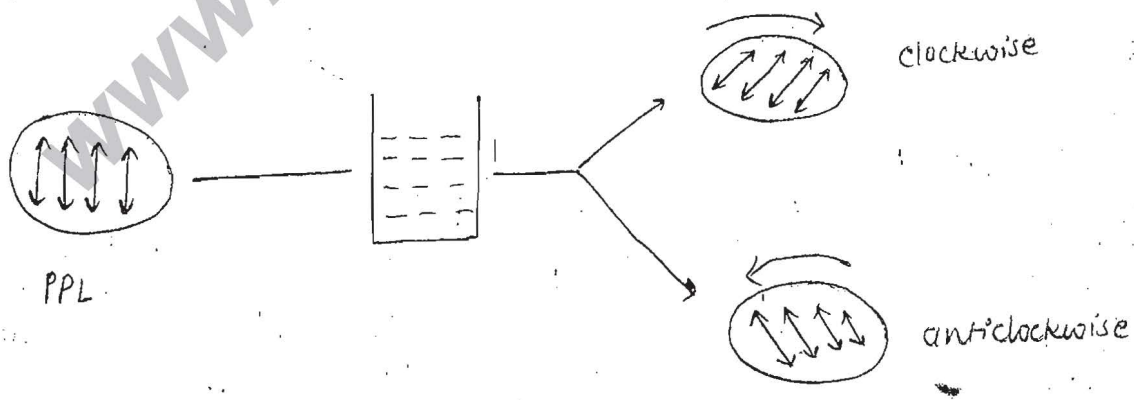


(vi)

Optical Isomerism ⇒ The isomers which rotate plane polarized light (i.e. are optically active) are called optical isomers.







⇒ The compound which rotate PPL in clockwise or right direction ⟶ dextrorotatory (d° or +)

⇒ The compound which rotate PPL in anticlockwise or Left side ⟶ laevorotatory (l° or −)

⇒ If no change in the direction of PPL ⟶ optically inactive

The compounds (or isomers) or enantiomers which are mirror image of each other but non superimposable on each other are called optical isomers.

Chiral ⟶ Cheir ⟶ Handedness
(Ky-ral)

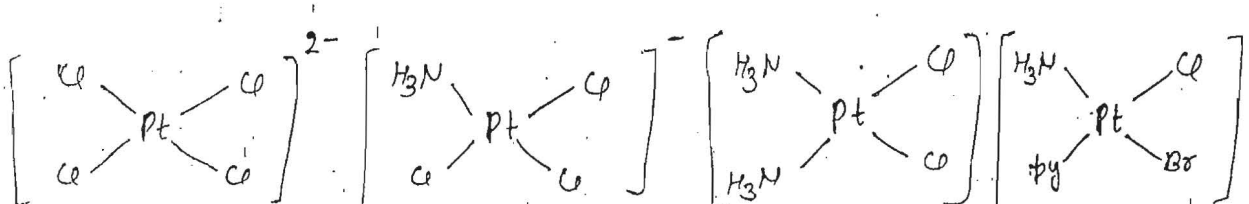
Examples:-

① coordination no-4 ⇒

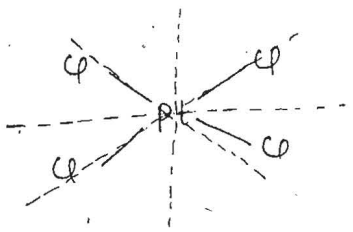
ⓐ Square planar complexes ⇒ In general, square planar complexes are optically inactive.

e.g. $[PtCl_4]^{2-}$, $[Pt(NH_3)Cl_3]^-$ OR $[Pt(NH_3)_3Cl]^+$, $[Pt(NH_3)_2Cl_2]$

$[Pt(NH_3)(Py)(Cl)(Br)]$



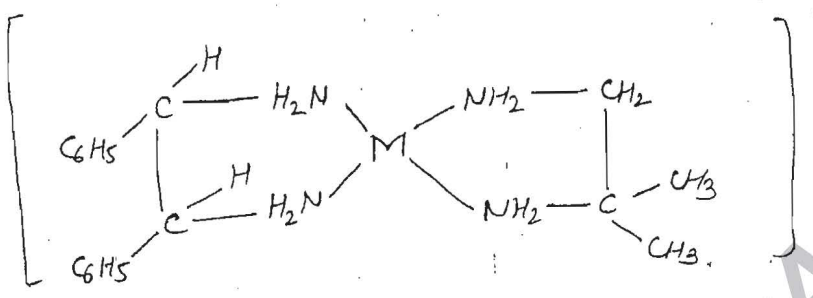
All these have plane of symmetry ⟶ optically inactive



5-plane of symmetry

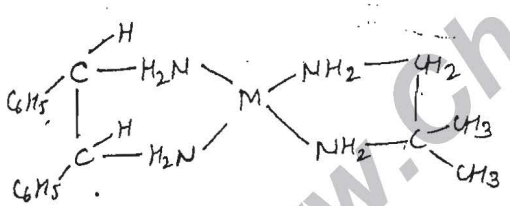
[There are 5 plane of symmetry. We will have to check all the 5 in determining optical activity of a compound.]

Examples showing optical activity ⇒

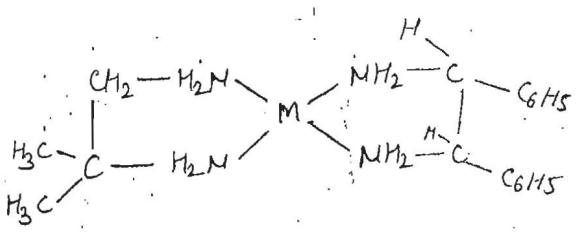
① 

← No plane of symmetry
↓
Optically active

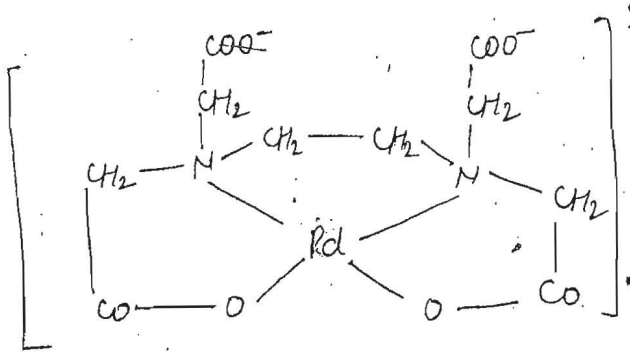
M = Pt or Pd



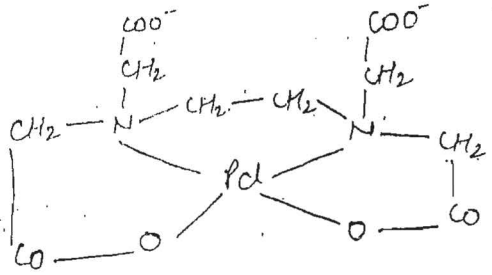
d

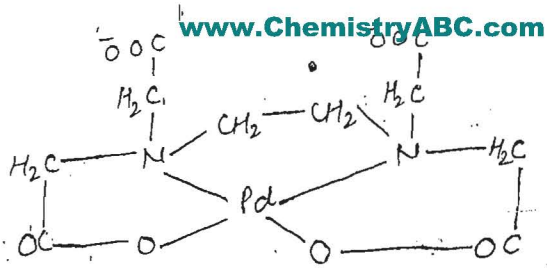


l

② 

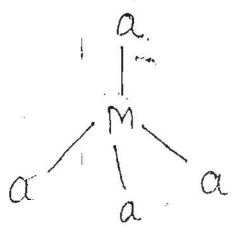
← $[Pd(edta)]^{2-}$



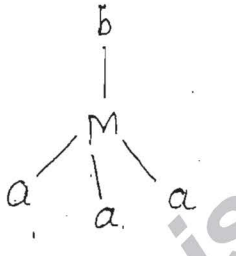


$[Pd(edta)]^{2-}$ & $[Pd(edta)]^{2+}$ always form square planar complexes.

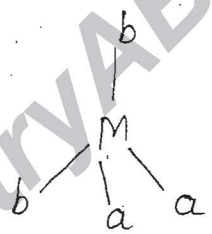
(b) Tetrahedral complexes ⇒



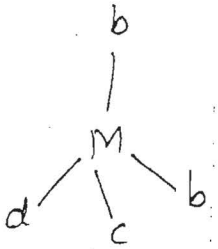
optically inactive



optically inactive

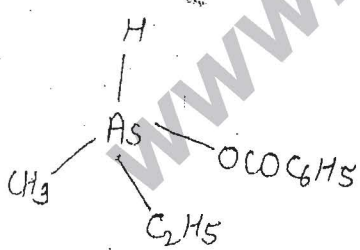


optically inactive



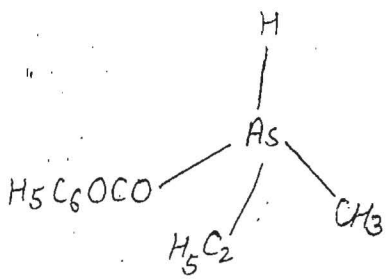
optically active

Examples :-

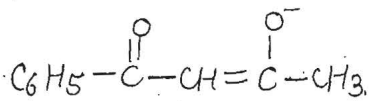


optically active

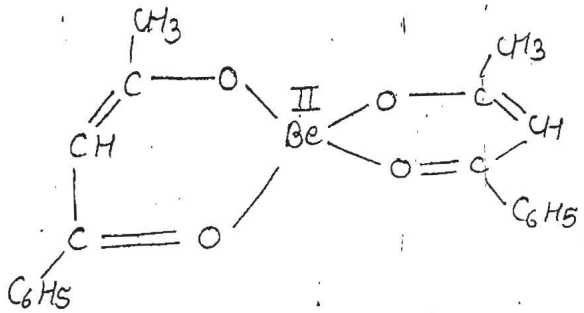
d

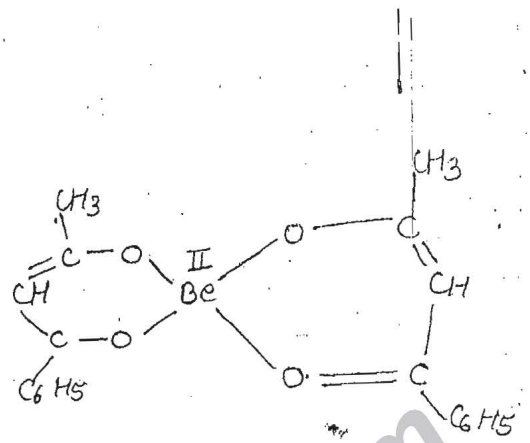


l



Benzoyl acetonato





d l

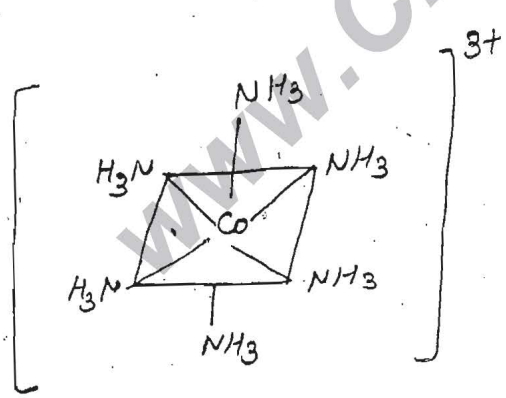
optically active

[No plane of symmetry due to asymmetry of rings and $-C_6H_5$ gp.]

19/08/13

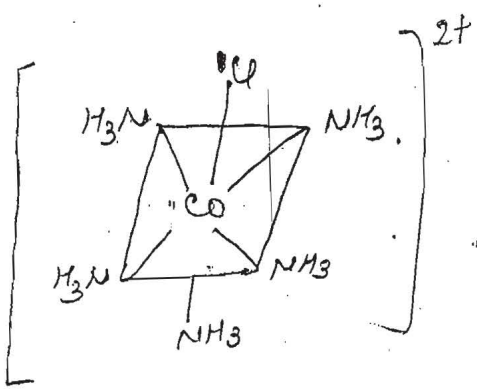
© octahedral complexes ⇒

① $[Ma_6]^{n\pm}$, $[ma_5b]^{n\pm}$ ex:- $[Co(NH_3)_6]^{3+}$ ex:- $[Co(NH_3)_5Cl]^{2+}$



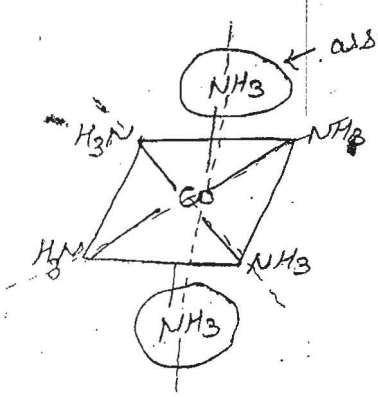
optically inactive

5 plane of symmetry



optically inactive

4 plane of symmetry



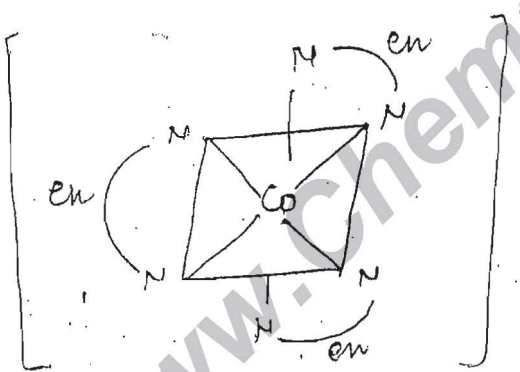
[The groups or atom from which plane is passing are left because they are bisecting like balls which have two equal halves having plane of symmetry The atoms or groups which are reflected are considered.]

No. of geometrical isomers = 0

No. of optical isomers = 0

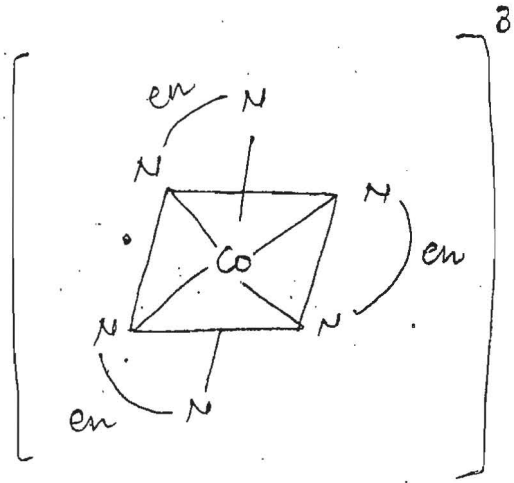
Total stereoisomers = 0

② $[M(AA)_3]^{n\pm}$ type Ex:- $[Co(en)_3]^{3+}$ (en = ethylenediamine)



No plane of symmetry
optically active

d



l

If in any complex, there are 3 rings, there will be no plane of symmetry and compound will be optically active.

Condition ⇒ ligand must be bidentate.

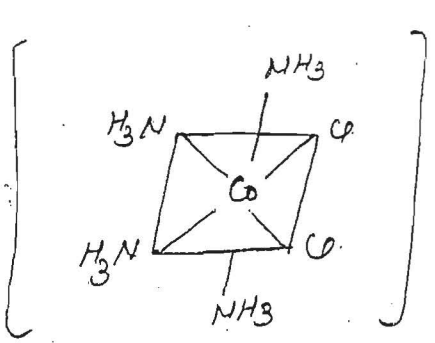
If there are 2 rings one above the plane and another below the plane, there will be no plane of symmetry and compound will be optically active.

No. of geometrical isomers = 0

No. of optical isomers = 2

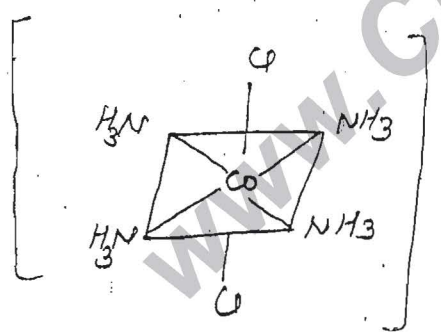
Total stereoisomers = 2

③ $[Ma_4b_2]^{n\pm}$ type Ex:- $[Co(NH_3)_4Cl_2]^+$



← optically inactive
(plane of symmetry is present)

cis



← optically inactive
(plane of symmetry is present)

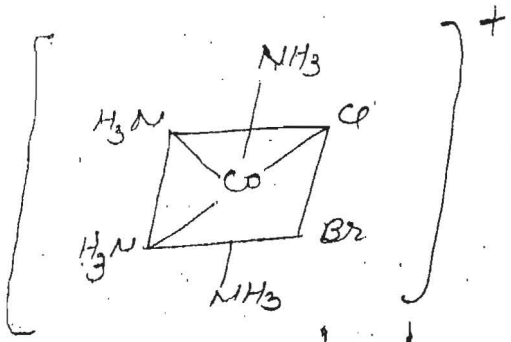
Trans

No. of geometrical isomers = 2

No. of optical isomers = 0

Total stereoisomers = 2

④ $[Ma_4bc]^{n\pm}$ type Ex:- $[Co(NH_3)_4ClBr]^+$

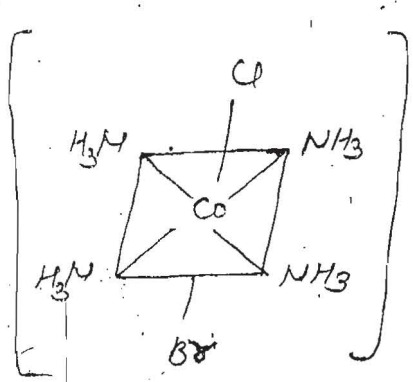


No. of geometrical isomers = 2

No. of optical isomers = 0

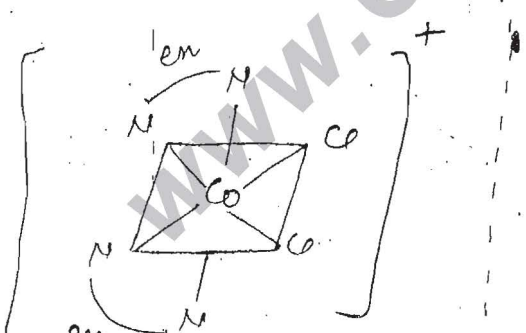
Total stereoisomers = 2

cis (optically inactive)

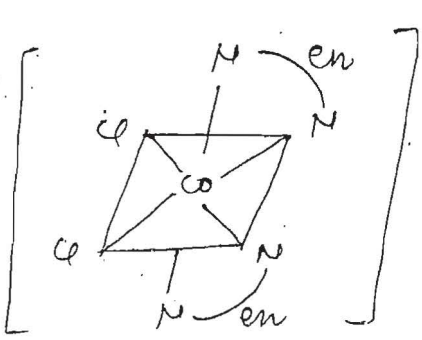


Trans (optically inactive)

⑤ $[M(AA)_2a_2]^{n\pm}$ type ex:- $[Co(en)_2Cl_2]^+$

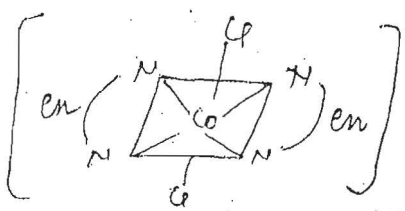


cis - d

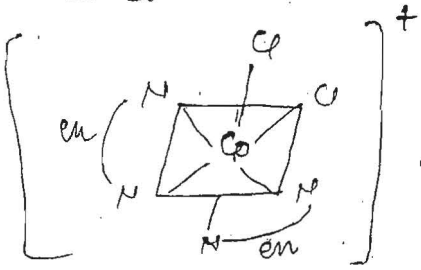


← two rings, one is above the plane while another below the plane → optically active

cis - l ||| ← identical / similar



Trans optically inactive

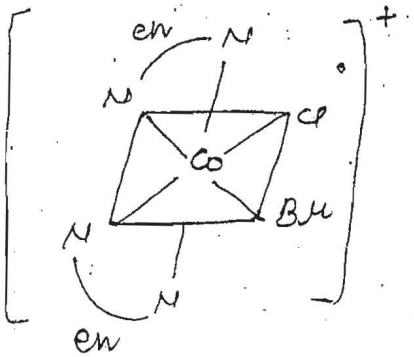


No. of geometrical isomers = 2

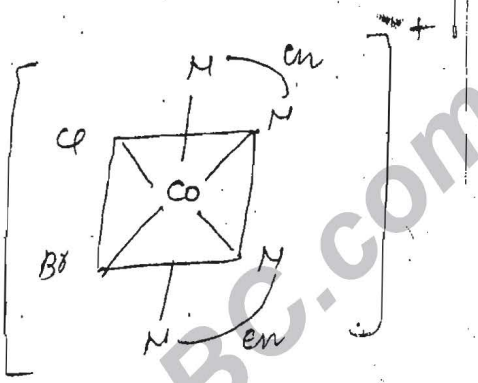
No. of optical isomers = 2

Total stereoisomers = 3

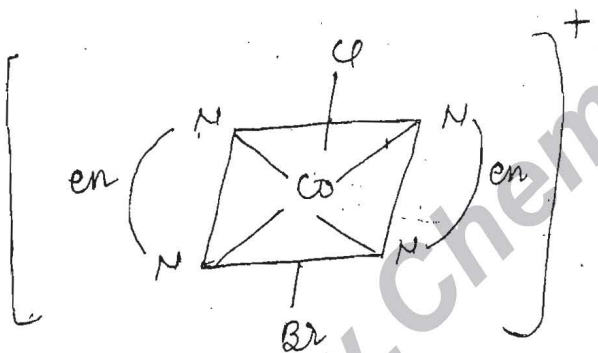
(6) $[Co(en)_2 Cl Br]^+$.



cis-d



cis-l



Trans (plane of symmetry present)

No. of geometrical isomers = 2

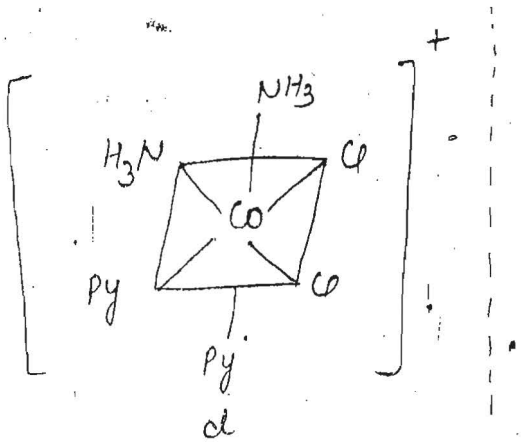
No. of optical isomers = 2

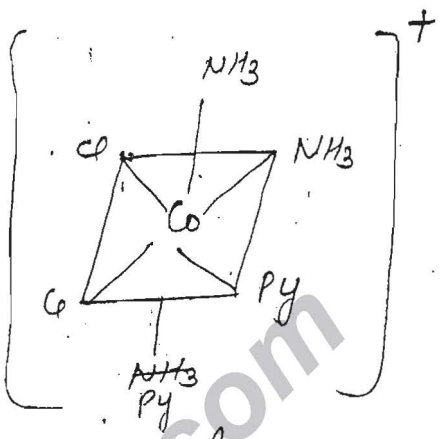
Total stereoisomers = 3

In counting optical isomers, both cis-d and cis-l are counted while in counting geometrical isomers one cis that either 'd' or 'l' is counted because geometrically both are same.

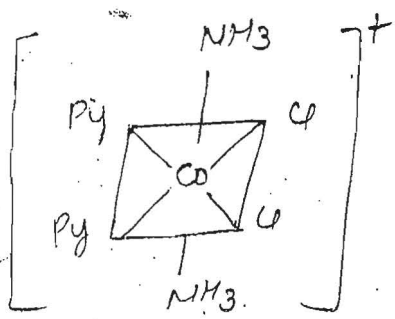
⑦ $[Ma_2b_2c_2]^{n\pm}$ type. Ex:- $[Co(NH_3)_2(Py)_2Cl_2]^+$

(i)





(ii)



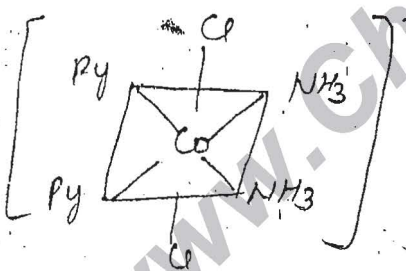
No. of geometrical isomers = 5

Optical isomers = 2

Total stereo isomers = 6

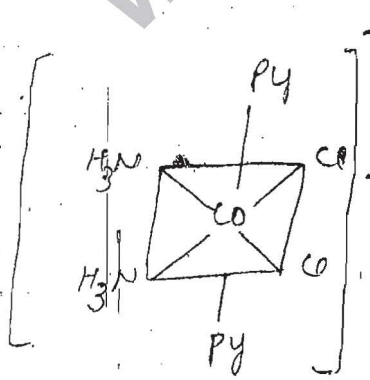
optically inactive (plane of symmetry)

(iii)



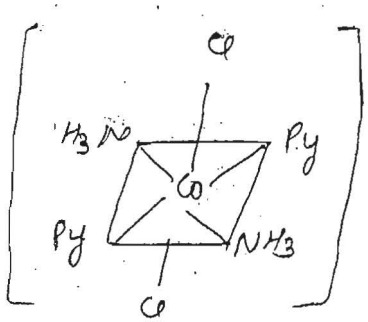
← optically inactive (plane of symmetry)

(iv)



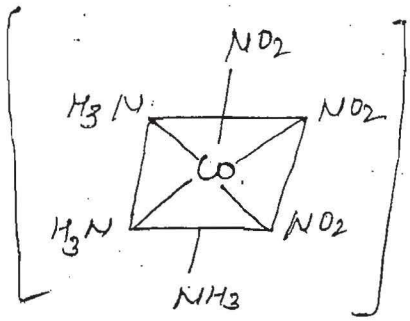
← optically inactive (plane of Symmetry)

(v)



← plane of symmetry (optically inactive)

⑧ $[Ma_3b_3]^{n\pm}$ type Ex:- $[Co(NH_3)_3(NO_2)_3]$

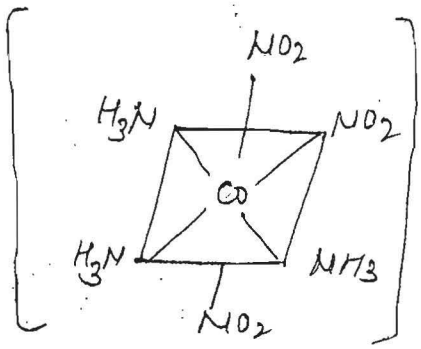


No. of geometrical isomers = 2

No. of optical isomers = 0

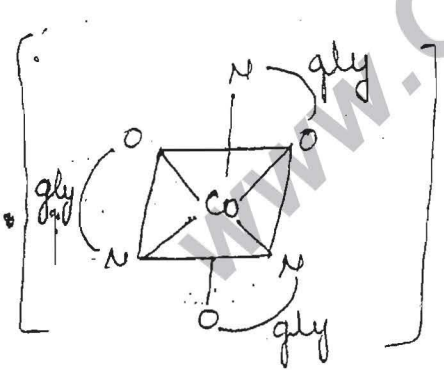
Total stereoisomers = 2

Facial (plane of symmetry → optically inactive)

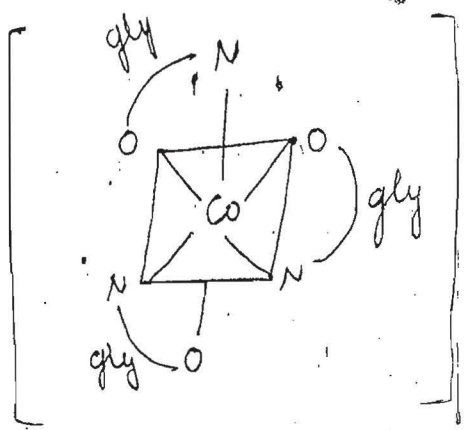


Meridional (plane of symmetry → optically inactive)

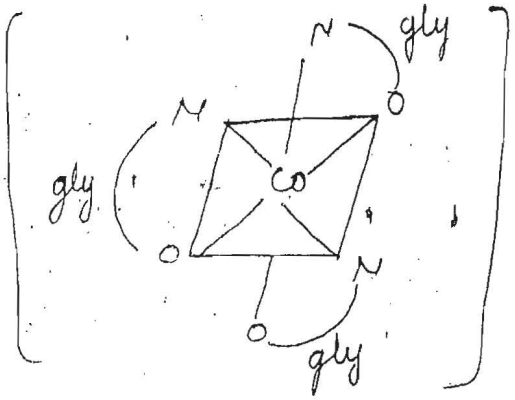
⑨ $[M(AB)_3]^{n\pm}$ type Ex:- $[Co(gly)_3]$



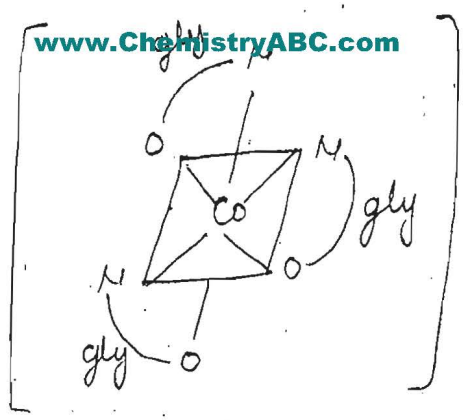
cis-d



cis-l



Trans-d



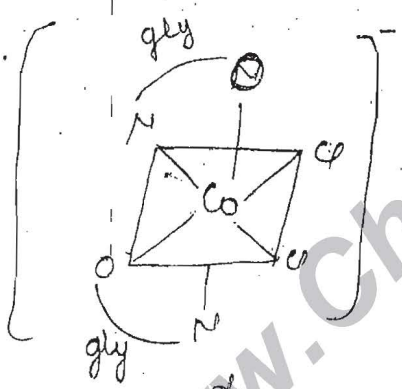
Trans-l

No. of geometrical isomers = 2

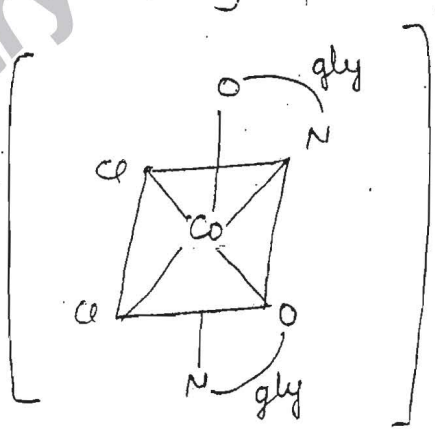
No. of optical isomers = 4

Total no. of stereoisomers = 4

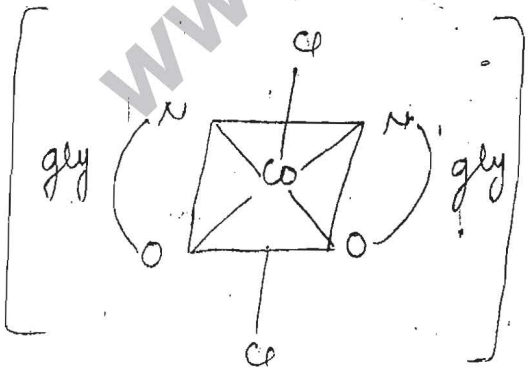
(10) $M(AB)_2C_2]^{n\pm}$ type Ex:- $[Co(gly)_2Cl_2]^-$



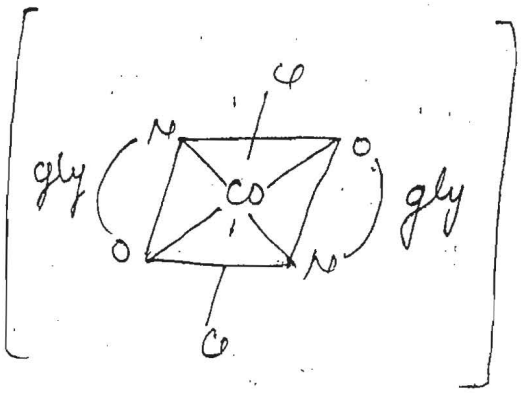
d



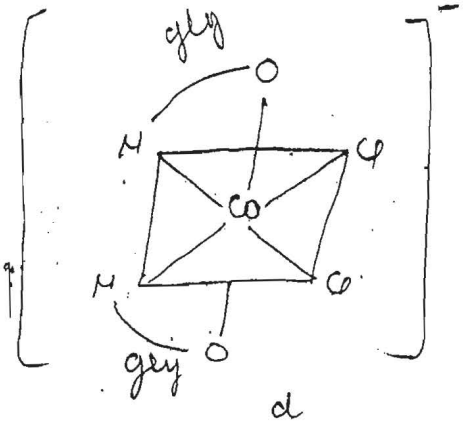
l



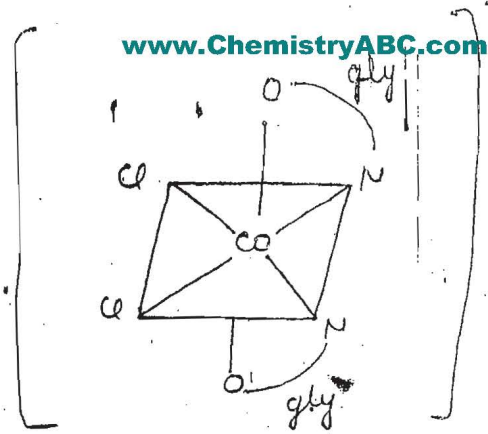
optically inactive



optically inactive



d



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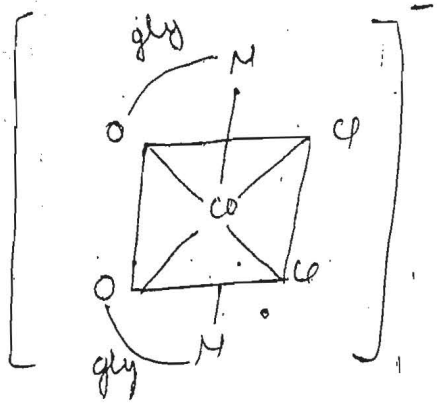

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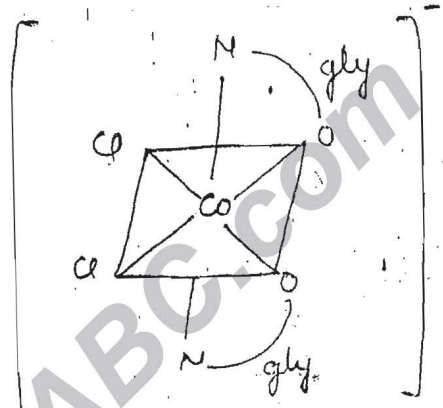
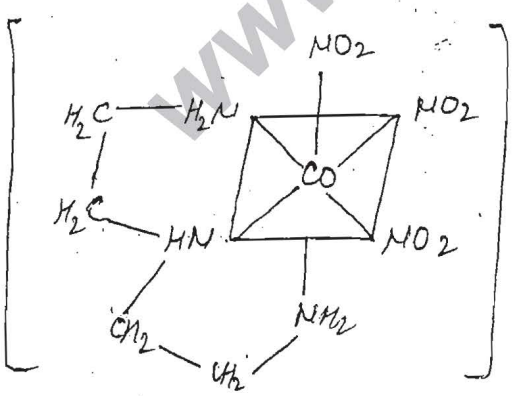


l

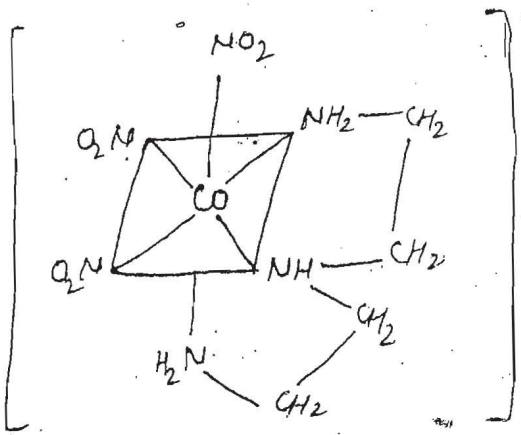
Total stereo isomers = Geometrical + $\frac{1}{2}$ of the optical isomers

This formula is applied where geometrical isomers exist.

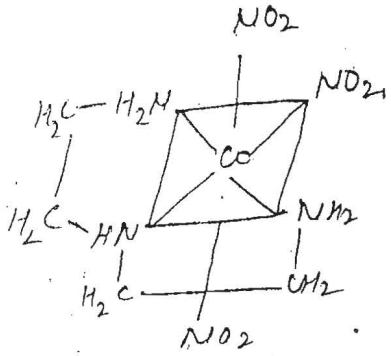
(11) $[Co(dien)(NO_2)_3]$ [dien → diethylenetriammine]



facial-d
optically active



facial-l



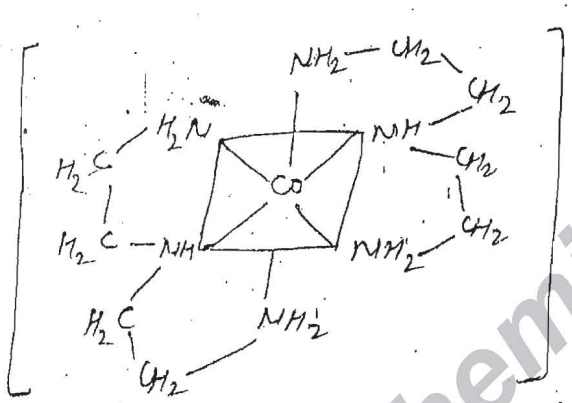
meridional
optically inactive

No. of geometrical isomers = 2

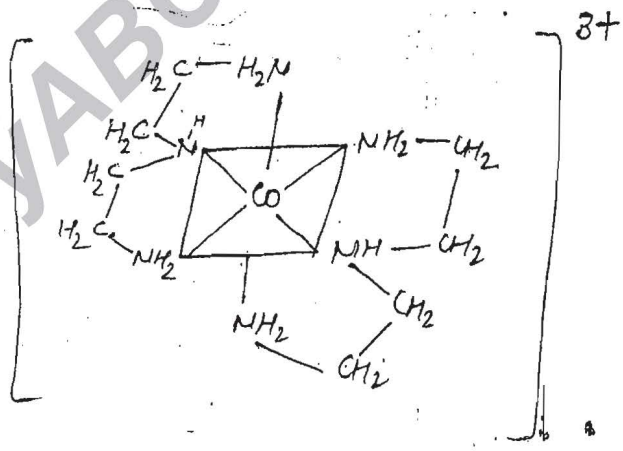
optical = 2

Total = 3

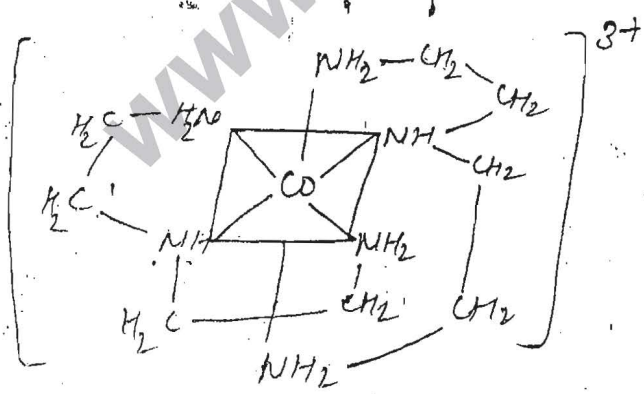
(12) $[Co(dien)_2]^{3+}$



facial - optically active
d



facial - l



meridional → optically inactive

No. of geometrical isomers = 2

optical = 2

Total = 3

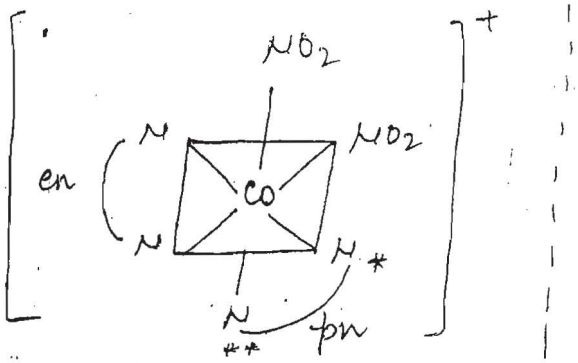
(•) Complexes containing one optically active ligand

Examples ⇒

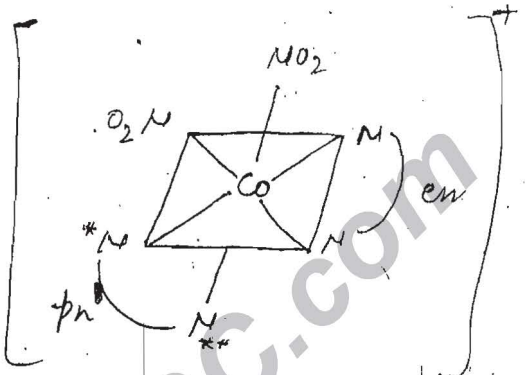
① $[Co(pn)(en)(NO_2)_2]^+$

$CH_3-CH(NH_2)-CH_2(NH_2)$ ← optically active

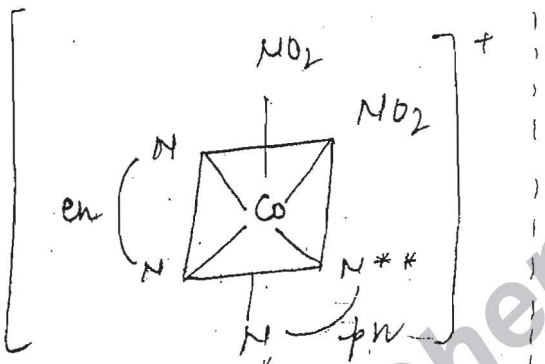
(propylene diamine)



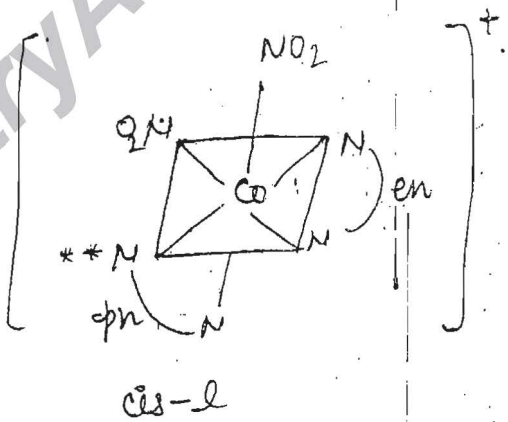
cis-d



cis-l



cis-d

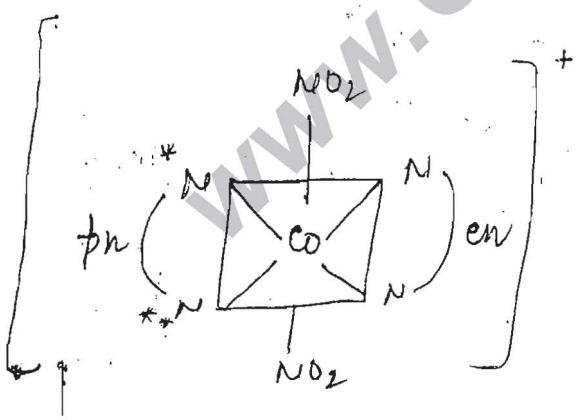


cis-l

No. of geometrical isomers = 3

No. of optical isomers = 4

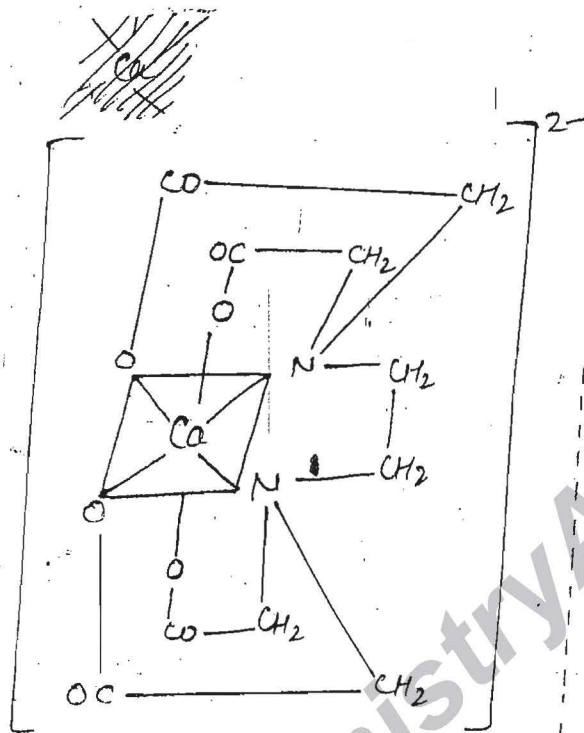
Total Stereoisomers = 5



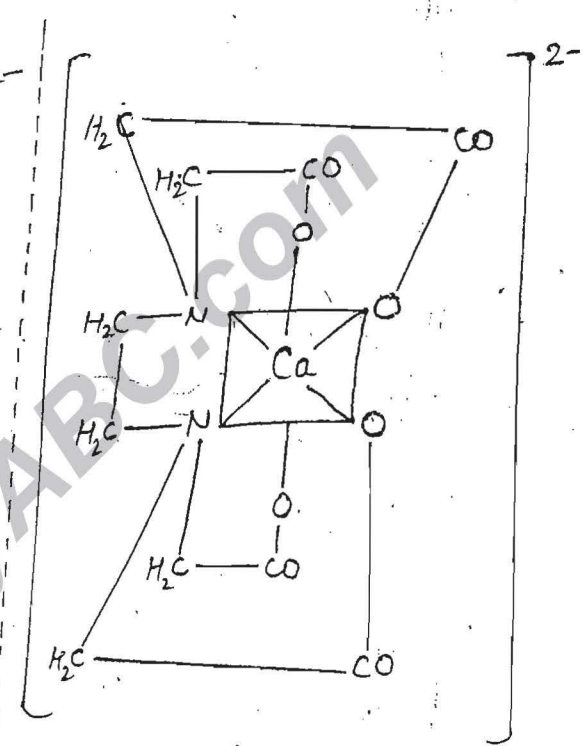
Trans-optically inactive

(This complex should be optically active because 'pn' ligand present in this complex is optically active, therefore whole compound should be optically active but it is not universally accepted.]

② $[Ca(edta)]^{2-}$



d



l

To distinguish cis and trans isomers ⇒

① Dipole moment ⇒

Trans → $\mu = 0$

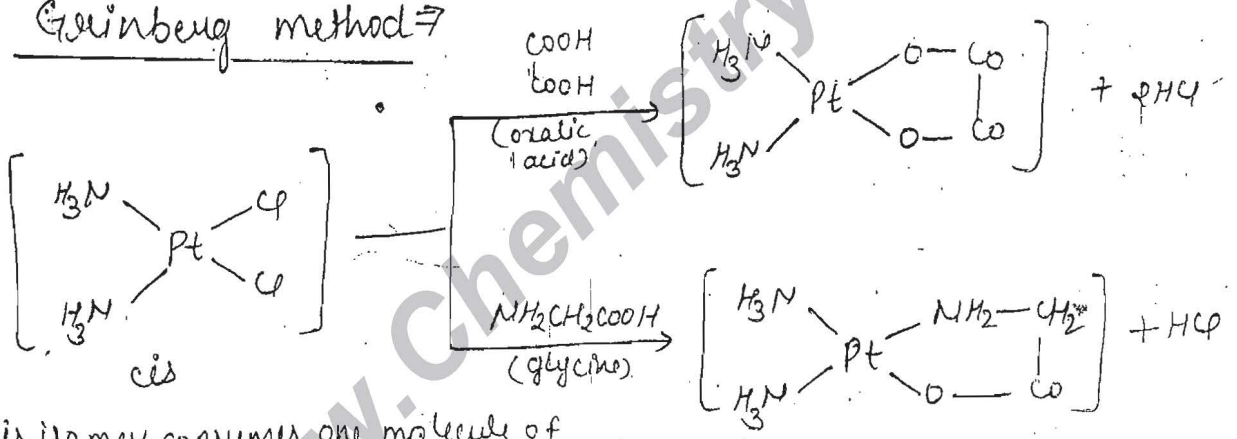
cis → $\mu = +ve$

② IR spectroscopy ⇒

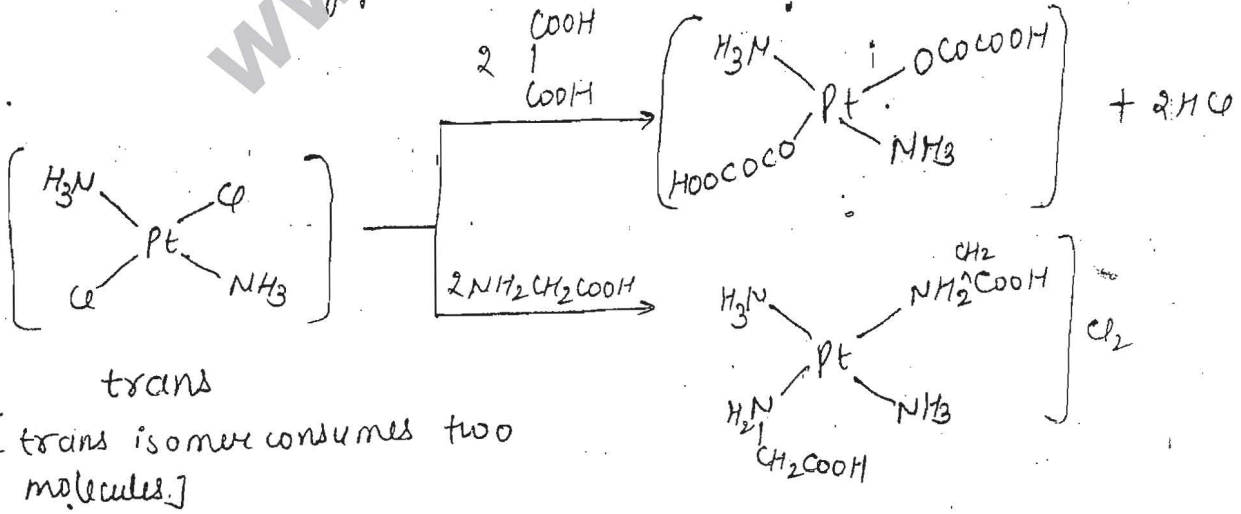
permanent dipole moment → IR active

③ X-rays structure determination ⇒

④ Grinberg method ⇒



[cis isomer consumes one molecule of oxalic acid and glycine.]



[trans isomer consumes two molecules.]

IUPAC Nomenclature

• [Name of cation should be written before the name of anion.]

① complexes containing complex cations ⇒

NOMENCLATURE

Ex:- (i) $[Co(NH_3)_6]^{3+}Cl_3$ ← anion

complex cation

Hexaamine cobalt (III) chloride

• [There should be space between the name of cation and anion.]

(ii) $[Co(NH_3)_2(Py)_2Cl_2]Cl$

Diaminedichloro dipyridine cobalt (III) chloride

or

Diamminedichlorobis(pyridine) cobalt(III) chloride

(iii) $[Co(NH_3)_4(CH_3NH_2)_2]Cl_3$

Tetraamine bis (methyl amine) Cobalt (III) chloride

(iv) $[Co(NH_3)_5(CH_3)_2NH]Cl_3$

pentaammine dimethylamine cobalt (III) chloride

② complexes containing complex anions ⇒

Examples ⇒ (i) $K_4[Fe(CN)_6]$

↑ cation, complex anion

Potassium hexacyanoferrate (II)

(ii) $Na_3[Fe(CN)_5(NO)]$

+1 coz NO exist as +1 in Fe compounds

$+3 + x + 5(-1) + 0 = 0$

$x = +1$

Sodium pentacyanonitrosyl ferrate (II)

(3) complexes containing complex cations and complex anions ⇒

Examples :- (i) $\underbrace{[Pt(NH_3)_4]}_{\text{complex cation}}\ \underbrace{[PtCl_4]}_{\text{complex anion}}$

tetraammineplatinum (II) tetrachloroplatinate (II)

(ii) $[Pt(NH_3)_4Cl_2]\ [PtCl_4]$

tetraammine dichloroplatinum (IV) tetrachloroplatinate (II)

Note ⇒ Pd^{2+}, Pt^{2+} → square planar complexes

Pt^{4+} → octahedral

Common oxidation states in complexes-

Cr = +2, +3

Mn = +2, +3

Fe = +2, +3

Co = +2, +3

Ni = +2, (+3) ← rarely

Pt = +2, +4

Any metal does not form any complex with zero oxidation state.

⇒ $[Pt(NH_3)_4]^{+1}$ $[Pt(Cl)_4]^{-1}$ $[Pt(NH_3)_4]^{+2}$ $[Pt(Cl)_4]^{-2}$

$x+0=+1$ $x-4=-1$ $x+0=+2$ $x-4=-2$

$x=+1$ $x=+3$ $x=+2$ $x=+2$

$[Pt(NH_3)_4]^{+3}$ $[PtCl_4]^{3-}$ $[Pt(NH_3)_4]^{4+}$ $[PtCl_4]^{4-}$

$x+0=+3$ $x-4=-3$ $x+0=+4$ $x-4=-4$,

$x=+3$ $x=+1$ $x=+4$ $x=0$

⇒ $[Pt(NH_3)_4Cl_2]^{+1}$ $[PtCl_4]^{-1}$ $[Pt(NH_3)_4Cl_2]^{+2}$ $[PtCl_4]^{-2}$

$x+0-2=+1$ $x-4=-1$ $x+0-2=+2$ $x-4=+2$

$x=+3$ $x=+3$ $x=+4$ $x=+2$

$[\overset{(+3)}{\square}\ \overset{(-3)}{\square}] \rightarrow x=+5, x=+1$ $[\overset{+4}{\square}\ \overset{-4}{\square}] \rightarrow x=+6, x=0$

$[Pt(NH_3)_4Cl_2]^{+3}$ $[PtCl_4]^{-3}$ $[Pt(NH_3)_4Cl_2]^{+4}$ $[PtCl_4]^{-4}$

$x-2=+3$ $x-4=-3$ $x-2=+4$ $x-4=-4$

$x=+5$ $x=+1$ $x=+6$ $x=0$

⇒ $[Pt(NH_3)_2Cl_2]$ $[Pt(NH_3)_2Cl_2]$

not exist

2 $[Pt^{+2}(NH_3)_2Cl_2]$

exist

$Ca_3(PO_4)_2$ $\quad +2 \quad -3$

(iii) $[Cr(NH_3)_6]_4[Co(CN)_6]_3$ $\quad +3 \quad -4$

$x - 6 = -4 \Rightarrow x = +2$

hexaammine chromium (III) hexacyano cobaltate (II)

(iv) $[Cr(NH_3)_6][Co(CN)_6]$

hexaammine chromium (III) hexacyanocobaltate (III)

(v) $[Co(NH_3)_6][Cr(NH_3)(CN)_5]$

hexaammine cobalt (II) ammine pentacyano chromium (III)

22/08/13

(4) Bridged complexes ⇒

i) $\left[(NH_3)_4Co\begin{matrix}\diagup NH_2 \diagdown \\ \diagdown OH \diagup\end{matrix}Co(NH_3)_4\right]^{4+}$

tetraammine cobalt (III)-μ-amido-μ-hydroxotetraammine cobalt (III)

$0 + x - 1 - 1 + y + 0 = +4$

$x + y = 6$

$x = 2$, $y = 4$ | OR | $x = 4$, $y = 2$ | OR | $x = 3$, $y = 3$

OR μ-amido-μ-hydroxo octaammine dicobalt (III)

OR μ-amido-μ-hydroxo bis [tetraammine cobalt (III)] } These nomenclature is used when complex is symmetrical

(ii) $\left[Cl(NH_3)_3 Co \begin{matrix} NH_2 \\ O_2 \end{matrix} Co(NH_3)Cl_3 \right]$

triammine chlorocobalt (III) -μ-amido-μ-superoxo ammine trichlorocobalt (III)

If O_2 is present as peroxo-

$-1+0+x-1-2_1+y-3=0$

$x+y=+7$

$\times \begin{cases} x=3, y=4 \\ x=2, y=5 \end{cases}$

If O_2 is present as superoxo

$-1+0+x-1-1+y-3=0$

$x+y=6$

$x=+3, y=+3$ ✓

[This combination of oxidation states is possible, hence O_2 is present as 'superoxo' in above bridged complex.]

(iii) $\left[Cl_2(NH_3)_2 Co \begin{matrix} NH_3 \\ O_2 \end{matrix} Co(NH_3)_2 Cl_2 \right]$

diammine dichloro cobalt (III)-μ-amido-μ-superoxo diammine-dichloro cobalt (III)

OR

μ-amido-μ-superoxo tetraammine tetrachloro dicobalt (III)

OR

μ-amido-μ-superoxo bis {diammine dichloro cobalt (III)}

⑤ complexes containing hydrated water molecules

Ex:- (i) $[Co(NH_3)_6]Cl_3 \cdot 2H_2O$

hexamminecobalt (III) chloride dihydrate

(ii) $[Cr(H_2O)_6]Cl_3$

$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ → pentaaqua chloro chromium (III) chloride monohydrate

$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ → tetraaqua dichloro chromium (III) chloride dihydrate

$1\frac{1}{2}\ H_2O$ → sesqui hydrate

$(O)_2$ → diono

O_2, O_2, O_2 → either dioxygen or peroxo or superoxo

Theories of coordination compounds ⇒

IMPORTANT

1. Werner's Theory
2. Valence Bond Theory (VBT)
3. Crystal field Theory
4. Ligand field theory or molecular orbital theory

1. Werner's Theory

Two types of valencies –

(i) Primary valency
(ii) Secondary valency

(i) Primary valency :–

* oxidation state of the central atom
* It is satisfied only by nigative ligands
* Non-directional → can't decide geometry of the compounds
* Ionisable

(ii) Secondary valency :–

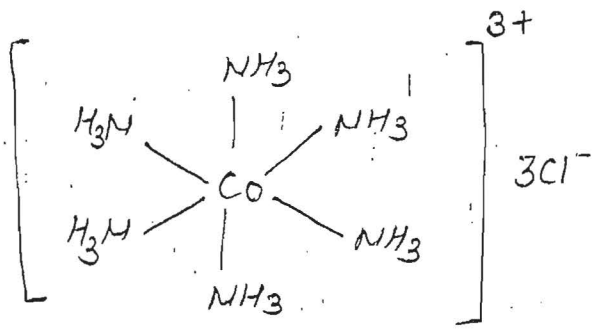
* Coordination no. of the central metal ion

  Satisfied by either neutral or –ve ligands or sometimes by both
* directional → deci. of the geometry of the compound.
* Non-ionisable

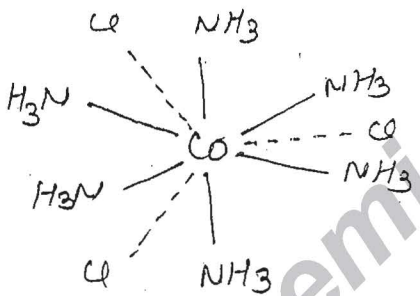
Primary valency is represented by ------

Secondary " " " ——————

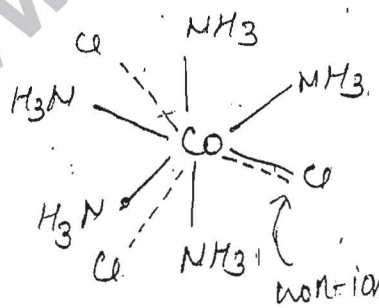
Example:- $CoCl_3 . 6NH_3$, $[Co^{+3}(NH_3)_6]Cl_3$



$[Co^{+3}(NH_3)_6]Cl_3$

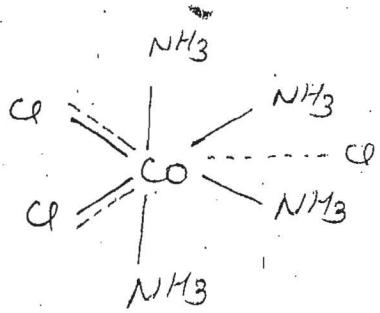


$[Co^{+3}(NH_3)_5Cl]Cl_2$

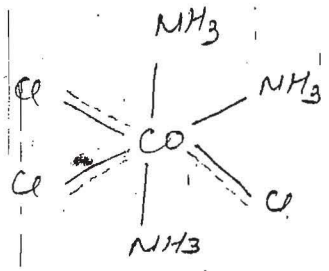


non-ionisable Cl [becoz it is bonded through coordinate bond which is non-ionisable]

$[Co^{+3}(NH_3)_4Cl_2]Cl$



$[Co^{+3}(NH_3)_3Cl_3]$



size of metal small

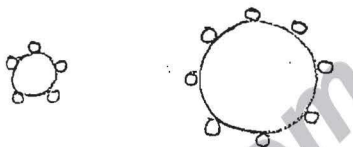
↓

low coordination no.

size of metal large

↓

high coordination no.



Evidence in favour of Werner's theory ⇒

① Molar conductance ⇒

★ depends on the charges on cation and anion

Higher the charge - more will be the molar conductance

Example:-

$[Co(NH_3)_6]Cl_3 > [Co(NH_3)_5Cl]Cl_2 > [Co(NH_3)_4Cl_2]Cl > [Co(NH_3)_3Cl_3]$

$(+3,-1)$ $(+2,-1)$ $(+1,-1)$ $0,0$

$[Co(NH_3)_5Cl]SO_4 > [Co(NH_3)_5SO_4]Cl$

$(+2,-2)$ $(+1,-1)$

② Cryoscopic measurement ⇒ (depression in freezing point)

↓

a colligative property

↓

depends only on the no. of particles

depression in freezing point increases with increase in no. of particles.

$[Co(NH_3)_6]Cl_3$ > $[Co(NH_3)_5Cl]Cl_2$ > $[Co(NH_3)_4Cl_2]Cl$ > $[Co(NH_3)_3Cl_3]$

No. of particles: 4 > 3 > 2 > 1

← Increasing order of depression in freezing point

depression in freezing point = Freezing point of the solvent − freezing point of the soln.

for 1 mole – order of freezing point

$[Co(NH_3)_6]Cl_3 < [Co(NH_3)_5Cl]Cl_2 < [Co(NH_3)_4Cl_2]Cl < [Co(NH_3)_3Cl_3]$

Abnormal behaviour of solutes –

		1 atm press^r	
	water	0°C	(Freezing point)
1 mole	sucrose	f.p. −ve	decreases
2 mole	sucrose	f.p. −ve	

1 mole $NaCl \longrightarrow Na^+ + Cl^-$

1 mole NaCl = 2 mole solute

↓

$Na^+ + Cl^-$

2 mole

Q ⇒ 0.2 mole of $[Co(NH_3)_6]Cl_3$ is dissolved in 500gm water. Calculate depression in freezing point. ($K_f = 0.56$)

$$\Delta T_f = K_f \times m$$
$$= 0.56 \times 0.4$$
$$= 0.224$$

$[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$

1 → 4

Total ions = 4

or $i = 4$

$$\Delta T_f = i \times m \times k_f = 4 \times \frac{0.2 \times 1000}{500} \times 0.56$$

$$= 0.896\ ^\circ C$$

Strong electrolytes

Salts except $HgCl_2$, CdI_2 etc.

HCl

H_2SO_4

$NaOH$, KOH

Weak electrolytes

CH_3COOH ·

HCl ✗ } not weak electrolytes as ionised 100%.
H_2SO_4 ✗ }

NH_4OH ·

$NaOH$, KOH ✗

③ Precipitation :-

$[Co(NH_3)_6]Cl_3 \xrightarrow{+3Ag^+} 3AgCl\downarrow$

$[Co(NH_3)_5Cl]Cl_2 \xrightarrow{+2Ag^+} 2AgCl\downarrow$

$[Co(NH_3)_4Cl_2]Cl \xrightarrow{+Ag^+} AgCl\downarrow$

$[Co(NH_3)_3Cl_3] \xrightarrow{+Ag^+}$ No ppt.

Limitations :-

① Could not explain the magnetic properties.

② Could not explain colour and electronic spectra

③ Could not explain the nature of ligands

④ could not explain the pairing of electrons in presence of some ligands

⑤ Could not explain the electronic distribution in the complexes.

$Co^{3+} \rightarrow 3d^6$ | ↿⇂ | 1 | 1 | 1 | 1 |

VALENCE BOND THEORY

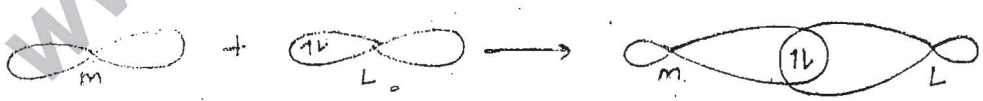
(2) Valence Bond Theory (VBT)

Given by 'Pauling.'

Postulates ⇒ :

(1) Metal cation or atom should have empty s, p and/or d-orbitals for the accomodation of e^-s donated by the ligands.

(2) Empty orbitals of the metal cation or atom are hybridised and the empty hybrid orbitals overlap with the filled orbitals of the ligands and as a result coordinate or covalent bond is formed.



(3) Ligands

- strong ligands → strong σ donor → Ex:- CO, CN^-, NO etc
- weak ligands → weak σ donor → Ex:- R^-, Cl^-, Br^-, I^-, H_2O etc

(4) Strong ligands have the tendency to pair up the electrons in metal orbitals where as weak ligands have no such tendency.

(5) Complexes having one or more unpaired electrons are paramagnetic and the complexes having no unpaired electrons are diamagnetic.

magnetic moment –

$$\mu = \sqrt{n(n+2)} \text{ Bohr magneton}$$

n = no. of unpaired electrons

(6) • octahedral complexes → sp^3d^2 hybridisation
→ d^2sp^3 hybridisation

⇒ In sp^3d^2 hybrid., d-orbitals of outermost shell i.e. n^{th} shell are used, therefore these are called outer orbital complex.

⇒ In d^2sp^3 hybrid. d-orbitals of penultimate shell i.e. innershell or $(n-1)^{th}$ shell are involved in hybridisation, therefore these are called Inner orbital complexes

- Tetrahedral complexes → sp^3 hybridisation
- Square planer complexes → dsp^2 hybridisation

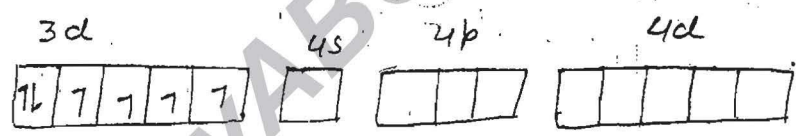
Octahedral complexes:-

① $[Co F_6]^{3-}$ $\mu = 4.92$ B.M. , F^- → weak ligand

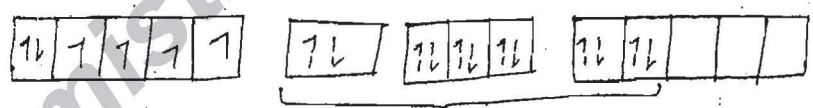
$_{27}Co \rightarrow 3d^7 4s^2$

$Co^{3+} \rightarrow 3d^6$

Co^{3+} in free state



Co^{3+} in $[CoF_6]^{3-}$



sp^3d^2 hybridisation

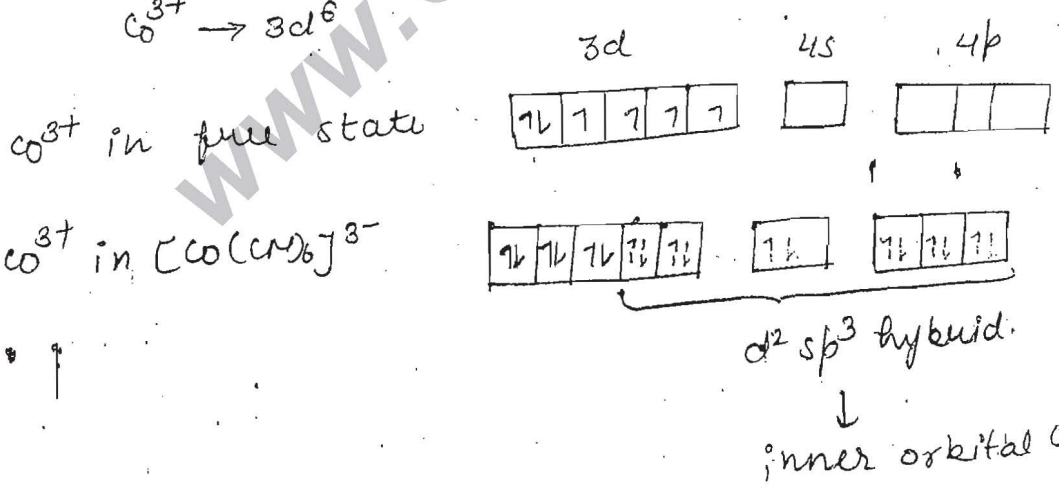
↓

octahedral complex

No. of unpaired e⁻ (n)	Calculated magnetic moment (u skin only) (in B.M.) $\mu = \sqrt{n(n+2)}$
1	$\sqrt{1(1+2)} = \sqrt{3} = 1.73$
2	$\sqrt{2(2+2)} = \sqrt{8} = 2.87$
3	$\sqrt{3(3+2)} = \sqrt{15} = 3.89$
4	$\sqrt{4(4+2)} = \sqrt{24} = 4.90$
5	$\sqrt{5(5+2)} = \sqrt{35} = 5.92$

(2) $[Co(CN)_6]^{3-}$ $\mu = 0$ CN^- → strong ligand

$Co^{3+} \rightarrow 3d^6$



③ $[V(NH_3)_6]^{3+}$

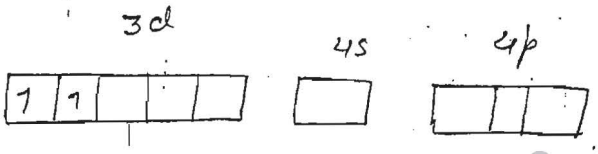
~~NH_3~~ → ~~strong~~ Ligand

NH_3 → moderate ligand

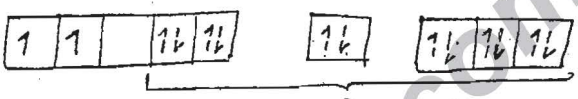
$_{23}V \longrightarrow 3d^3 4s^2$

$V^{3+} \longrightarrow 3d^2$

V^{3+} in free state



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



d^2sp^3

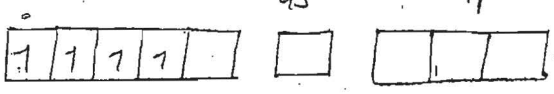
e⁻ are not paired because a/c to Hund's rule e⁻ can't paired until one e⁻ take place in all degenerate orbital.

④ $[Cr(CN)_6]^{4-}$

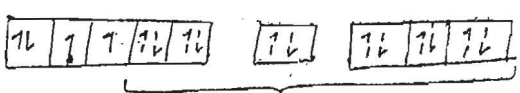
CN^- → strong ligand

$_{24}Cr \rightarrow 3d^5 4s^1$ $\quad Cr^{2+} \rightarrow 3d^4 4s^0$

Cr^{2+} in free state



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

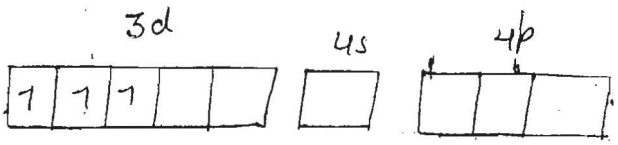


d^2sp^3 hybrid → Inner orbital complex

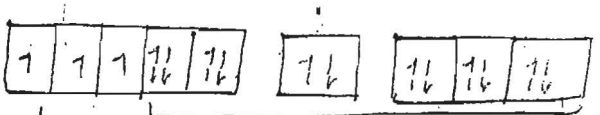
$[Cu(CN)_6]^{3-}$ $CN^- \rightarrow$ strong ligand.

$_{24}Cu \rightarrow 3d^5 4s^1$ $Cu^{3+} \rightarrow 3d^3 4s^0$

Cu^{3+} in free state



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



(no pairing due to degeneracy) d^2sp^3 hybridisation

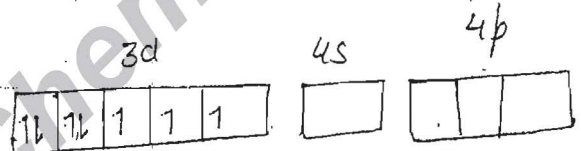
↓

inner orbital complex

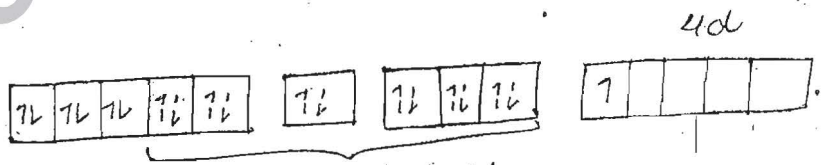
$[Co(CN)_6]^{4-}$ $CN^- \rightarrow$ strong ligand $\mu = 1.73$ B.M.

$_{27}Co \rightarrow 3d^7 4s^2$, $Co^{+2} \rightarrow 3d^7$

Co^{+2} in free state



Co^{+2} in $[Co(CN)_6]^{4-}$



d^2sp^3 hybrid.

Inner orbital complex

Cobalt is strong reducing agent because it excludes its e- present in 4d orbital very easily.

$[Fe(H_2O)_5(NO)]^{2+}$ $H_2O \rightarrow$ weak ligand $\mu = 3.98 B.M.$

$NO^+ \rightarrow$ strong ligand

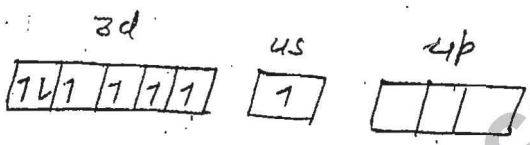
$x + 0 + 1 = +2$

$x = +1$

$_{26}Fe \rightarrow 3d^6 4s^2$

$Fe^+ \rightarrow 3d^6 4s^1$

Fe^+ in free state



Fe^+ in $[Fe(H_2O)_6NO]^{2+}$

Three unpaired electrons

sp^3d^2 hybridisation

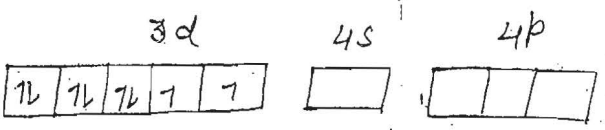
1 pairing is due to strong NO ligand.

Tetrahedral complexes :- Hybridisation sp^3

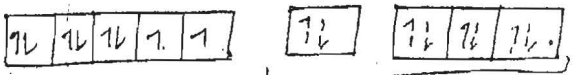
Ex:- $[NiCl_4]^{2-}$ $\quad Cl^- \rightarrow$ weak ligand

$_{28}Ni \rightarrow 3d^8 4s^2$, $Ni^{2+} \rightarrow 3d^8$.

Ni^{2+} in free state



Ni^{2+} in $[NiCl_4]^{2-}$



sp^3 hybridisation

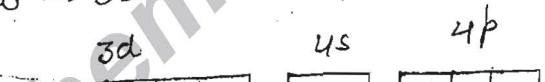
↓

Tetrahedral complex

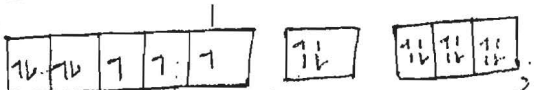
$[CoCl_4]^{2-}$ $\quad Cl^- \rightarrow$ weak ligand

$_{27}Co \rightarrow 3d^7 4s^2$, $Co^{2+} \rightarrow 3d^7$

Co^{2+} in free state



Co^{2+} in $[CoCl_4]^{2-}$



sp^3 hybridisation

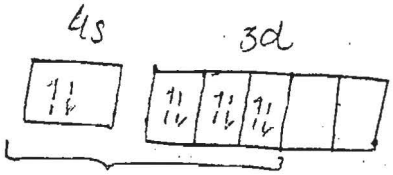
↓

Tetrahedral complex

MnO_4^- :-

$_{25}Mn \rightarrow 3d^5 4s^2$, $Mn^{+7} \rightarrow 3d^0 4s^0$

Mn^{+7} in free state MnO_4^- ion



sd^3 hybridisation

(s, d_{xy}, d_{yz}, d_{zx})

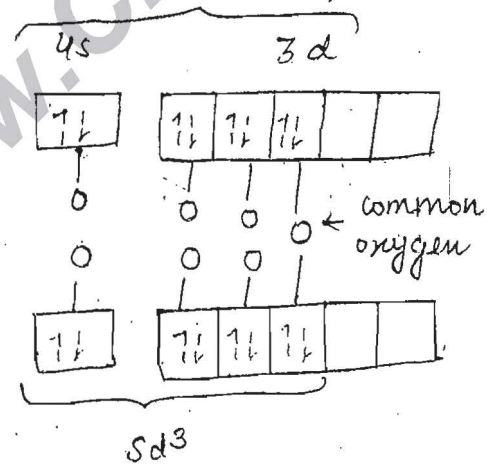
[In MnO_4^-, Mn exist in +7 oxidation state and its 3d and 4s orbitals are empty. Hence, 4s orbital can penetrate into 3d orbital, resulting lowering in energy of 4s orbital. Therefore, in MnO_4^-, sd^3 hybridisation takes place.]

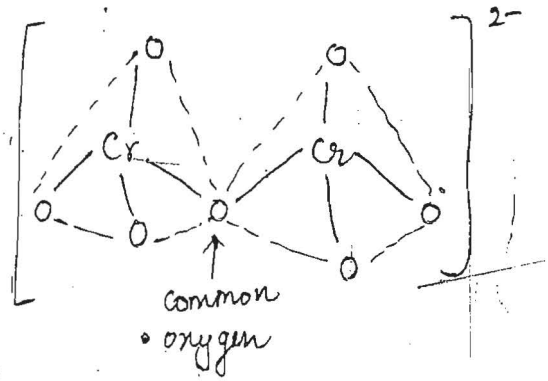
CrO_4^{2-} :-

$_{24}Cr \rightarrow 3d^5 4s^1$

$Cr^{+6} \rightarrow 4s^0 3d^0$

sd^3



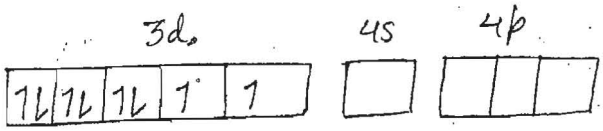


Square planar complexes :- Hybridisation

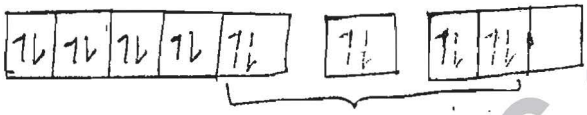
Ex:- $[Ni(CN)_4]^{2-}$ CN^- → strong ligand

$Ni^{2+} \longrightarrow 3d^8$

Ni^{2+} in free state



Ni^{2+} in $[Ni(CN)_4]^{2-}$



dsp^2 hybridisation

↓

square planar

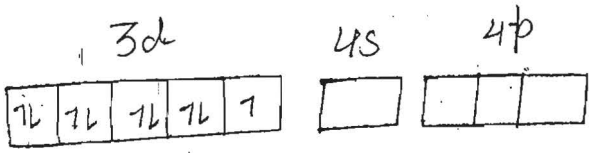
v. imp v. imp

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

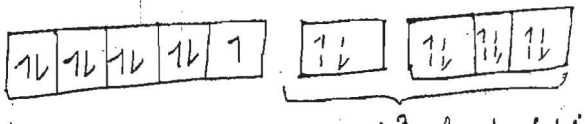
$_{29}Cu \rightarrow 3d^{10}\ 4s^1$

$Cu^{2+} \rightarrow 3d^9\ 4s^0$

Cu^{2+} in free state



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



sp^3 - hybridisation

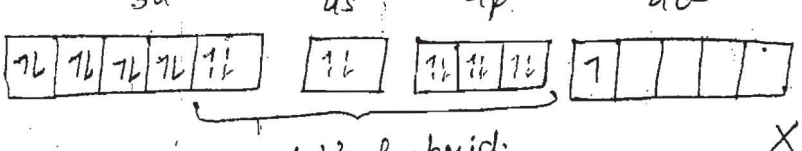
↓

tetrahedral

According to ESR and X-ray spectroscopy it is square planar.

Therefore, VBT failed in case of above complex.

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



dsp^2 hybrid.

X

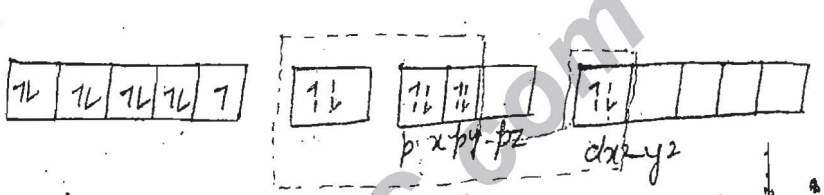
[Excitation of e⁻ from 3d → 4d orbital is not possible here because Cu is not a reducing agent.]

$[Cu(NH_3)_4]^{2+} \longrightarrow [Cu(NH_3)_4]^{3+}$

not exist

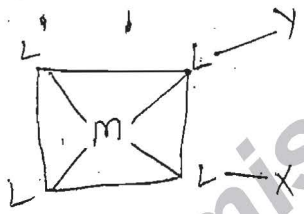
Huggin concept ⇒

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



sp^2d - hybridisation

[pz orbital is not participating because it is not in plane].



XY-plane

25/08/13,

Limitations of VBT ⇒

① It could not explain the structure of some compounds like $[Cu(NH_3)_4]^{2+}$, $[Cu(CN)_4]^{2-}$ etc.

② It could not explain the nature of liganels (whether the ligand is strong or weak).

③ It could not explain why pairing of e⁻ occurs in presence of strong ligand.

(4) It could not explain effect of temp^{r} on magnetic properties.

(5) It could not explain colour and electronic spectra of complexes.

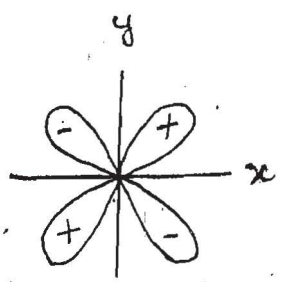
(3) Crystal Field Theory (CFT)

⇒ Given by Bethe and van Vlack.

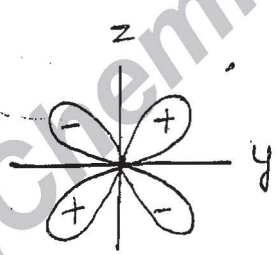
⇒ First applied for ionic crystal, therefore it is called as crystal field theory.

Shape of d-orbitals ⇒

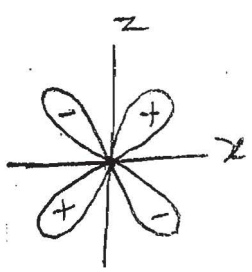
dxy, dyz, dzx, dx^2-y^2, dz^2



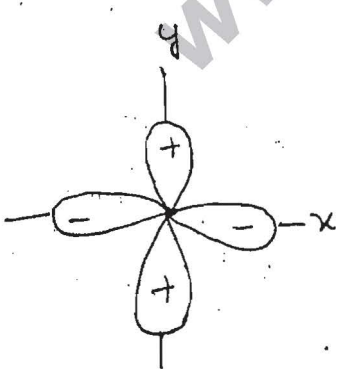
dxy



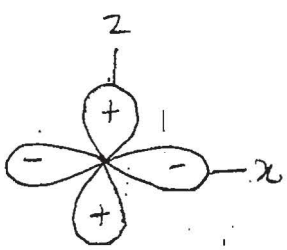
dyz



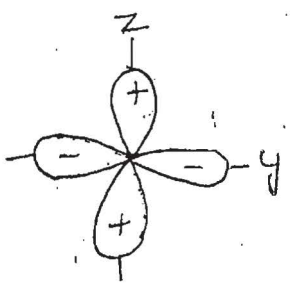
dzx



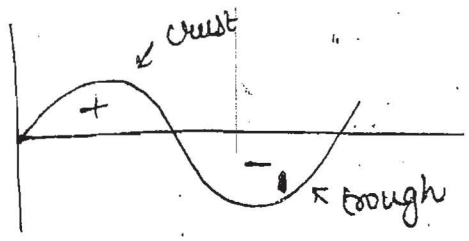
dx^2-y^2

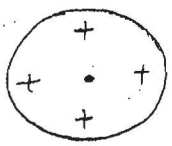


dz^2-x^2

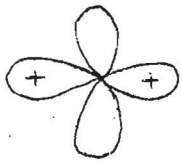


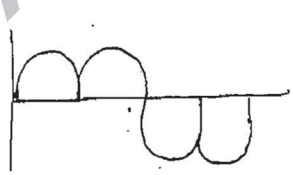
dz^2-y^2



s  gerade

p  ungerade

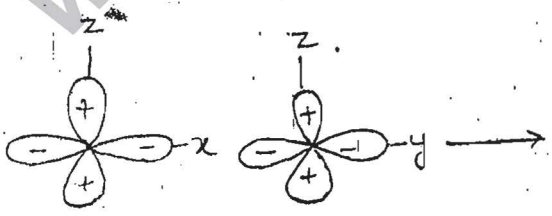
d  gerade

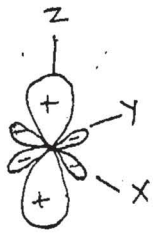


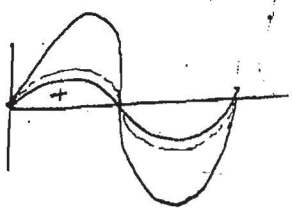
f → u

g → g

h → u







$d_{z^2-x^2}$ $d_{z^2-y^2}$

dependent

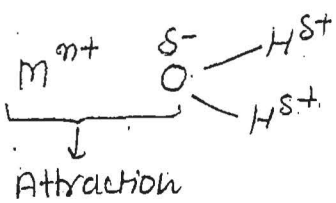
$d_{2z^2-x^2-y^2} \equiv d_{z^2}$

Postulates ⇒

① Ligands → negative Ligands → Point Charges (F^-, Cl^-)
Ligands → Neutral Ligands → Point dipoles or dipoles (NH_3, H_2O)

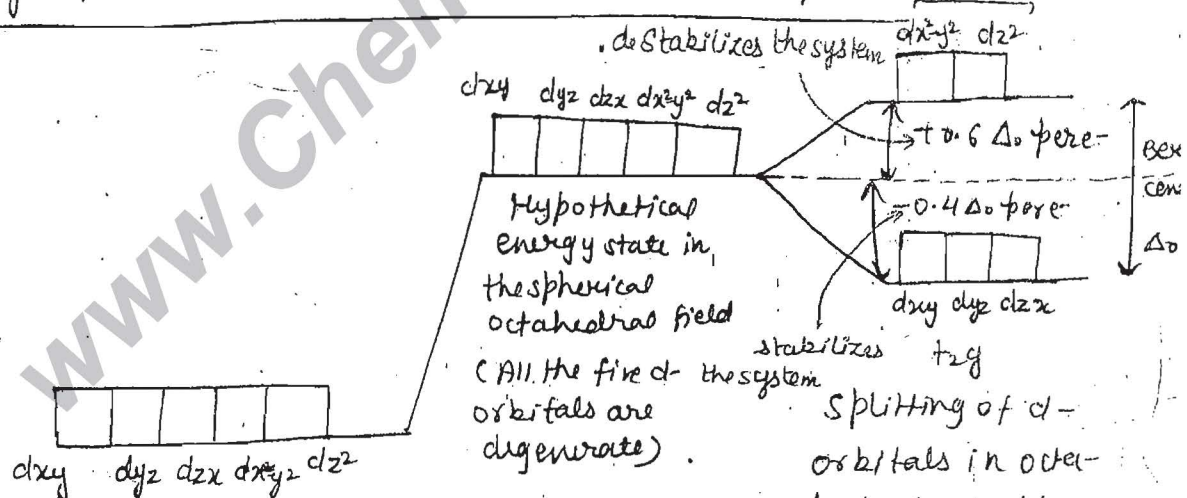
② Ionic bond b/w the metal cation & Ligand. (No overlapping of orbitals)

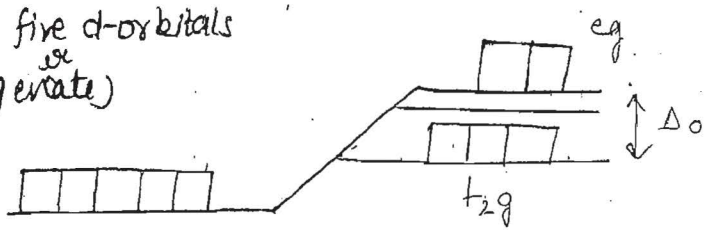
③ Negative end of the Ligands approaches the metal cation.



④ Splitting of d-orbitals in the presence of Ligands.

Splitting of d-orbitals in octahedral complexes ⇒

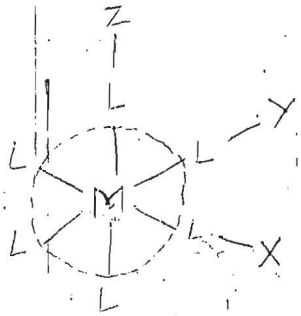


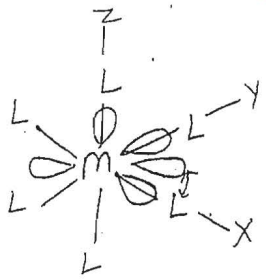


+0.6 Δ_o or 6 Dq

-0.4 Δ_o or -4 Dq

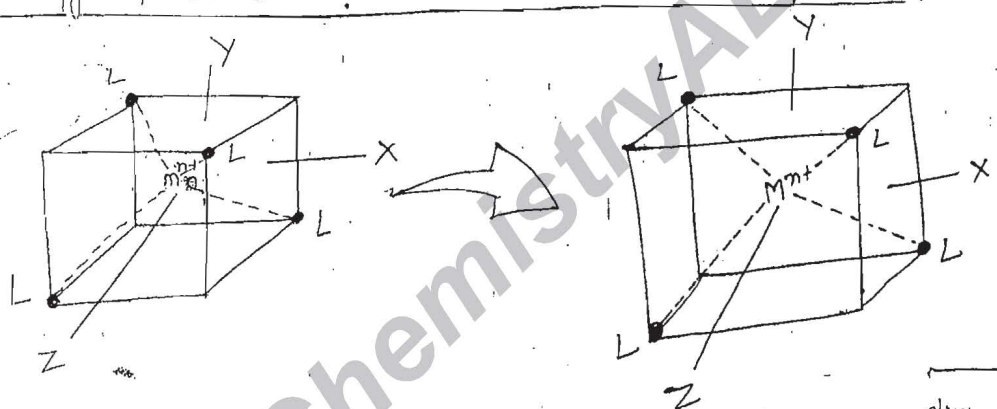
Δ_o = 10 Dq

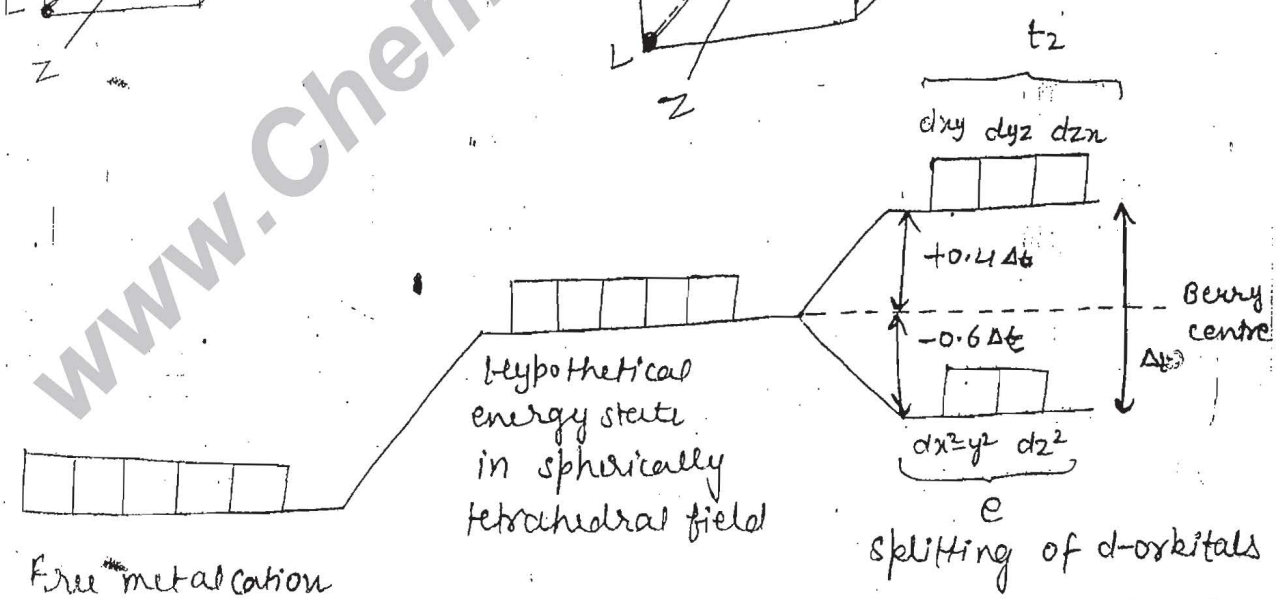




The separation of d-orbitals into 2 different energy levels is called crystal field splitting and the separation or gap between two ~~orbitals~~ energy states (t_{2g} & e_g) is called crystal field stabilization energy.

Splitting of d-orbitals in tetrahedral complexes ⇒





$$\Delta t \approx \frac{4}{9} \Delta_o$$

distance b/w d_{xy}, d_{yz}, d_{zx} orbitals and the ligand $= \frac{a}{2}$

diagonal of face $= a\sqrt{2}$

distance b/w force $d_{x^2-y^2}$, d_{z^2} and ligand $= \frac{a\sqrt{2}}{2}$

$$\Delta t \approx \frac{4}{9}\Delta_o = 0.45\,\Delta_o$$

Reasons of low Δt in tetrahedral complexes than octahedral complexes ⇒

① No. of ligands are $\frac{2}{3}$rd of the octahedral complex.

$$6 \times \frac{2}{3} = 4$$

② In case of octahedral bis complexes the ligands $d_{x^2-y^2}$ axis is present at approx. 'a' distance to the ligand while in tetrahedral complexes, $d_{x^2-y^2}$ do orbital is present at $\frac{a\sqrt{2}}{2}$ distance apart from ligand which is equivalent to $\frac{2}{3}$ as-

$$\frac{a\sqrt{2}}{2} = \frac{a \times 1.414}{2} = a \times 0.7 \approx a \times \frac{2}{3}$$

Therefore the overall decrease of energy of tetrahedral complexes as compared to octahedral complexes is-

$$\frac{2}{3} \times \frac{2}{3} = \frac{4}{9}$$

($\frac{2}{3}$: due to no. of ligand; $\frac{2}{3}$: due to distance of $d_{x^2-y^2}$ orbital)

Factors affecting magnitude of Δ ⇒

① Nature of metal :-

(a) oxidation state ⇒ Higher the oxidation state, more will be the magnitude of Δ.

e.g. $[Co(NH_3)_6]^{3+}$ > $[Co(NH_3)_6]^{2+}$

Higher the oxidation state of metal → more it will attract ligand → more will be splitting

(b) Principle quantum number of d-orbitals ⇒

Δ_o increases by 30–50% on moving 3d to 4d and further increases by 30–50% on moving 4d to 5d series in a group.

Δ_o increase

3d ——(by 30–50%)——→ 4d ——(30–50%)——→ 5d

Co^{3+}

Rh^{3+} ↓ Δ_o

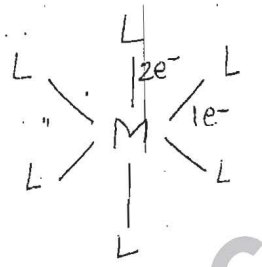
Ir^{3+}

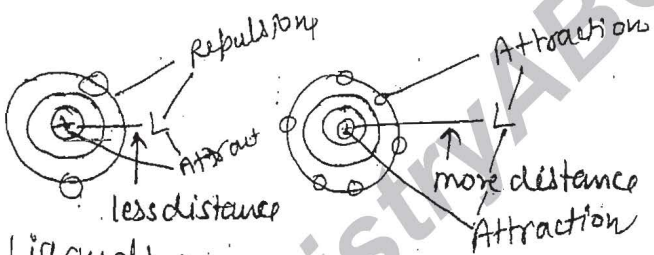
On moving down in a group, the size of the element (cation here) increases, therefore shielding effect of nucleus decreases and ligand can approach more to the cation, resulting in more splitting.

© No. of d-electrons ⇒

$$\Delta_o \propto \frac{1}{\text{d-electrons}}$$

$d^9 \rightarrow t_{2g}^6 \; eg^3$





② Nature of the ligands ⇒

Spectrochemical series ⇒ Arrangement of ligands in the increasing order of their crystal field splitting power.

weak end

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^- < F^- < OX < OH^- < H_2O < NCS^-$

moderate strong ligand

weak ← → strong

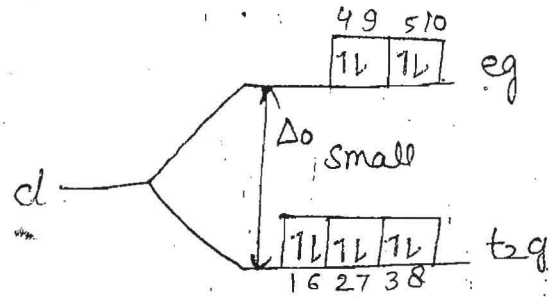
$< NH_3, py < en, pn, tn < bpy, phen < NO_2^- < CH_3^-, C_6H_5^-$

$< R_3P < CN^- < CO < NO$ strong end

26/08/13

Electron distribution in octahedral complexes ⇒

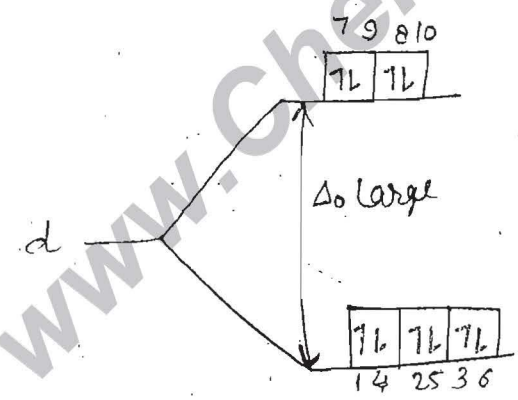
① Weak ligand, or weak ligand complexes ⇒



energy of t_{2g} and eg comparable

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

② Strong field or strong ligand complexes ⇒

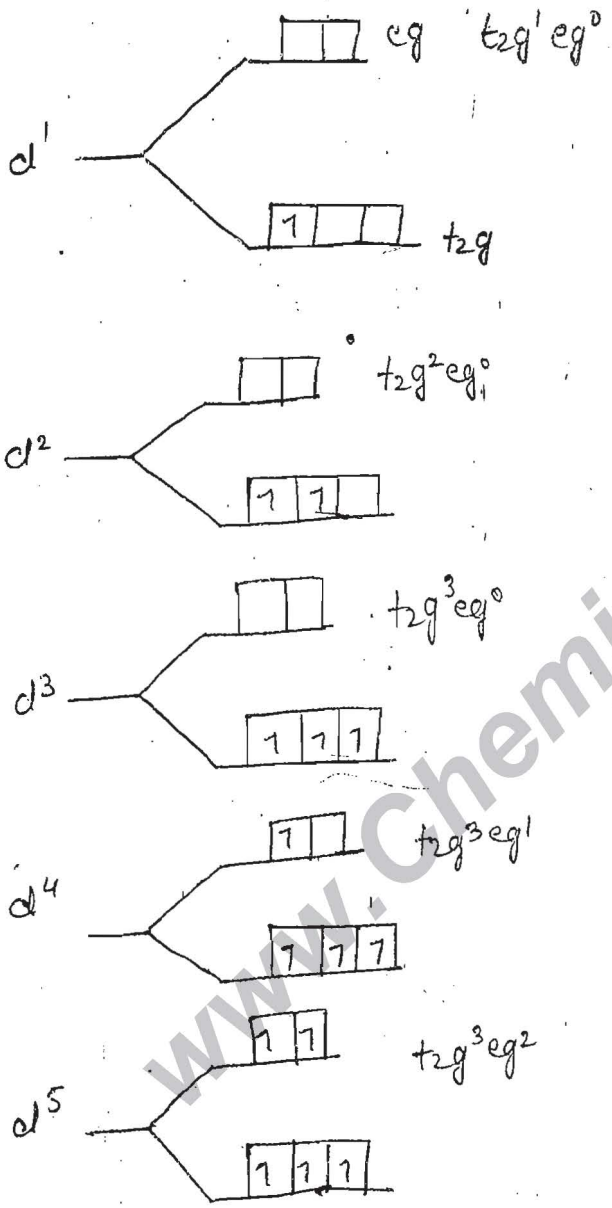


large energy difference between t_{2g} and eg

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

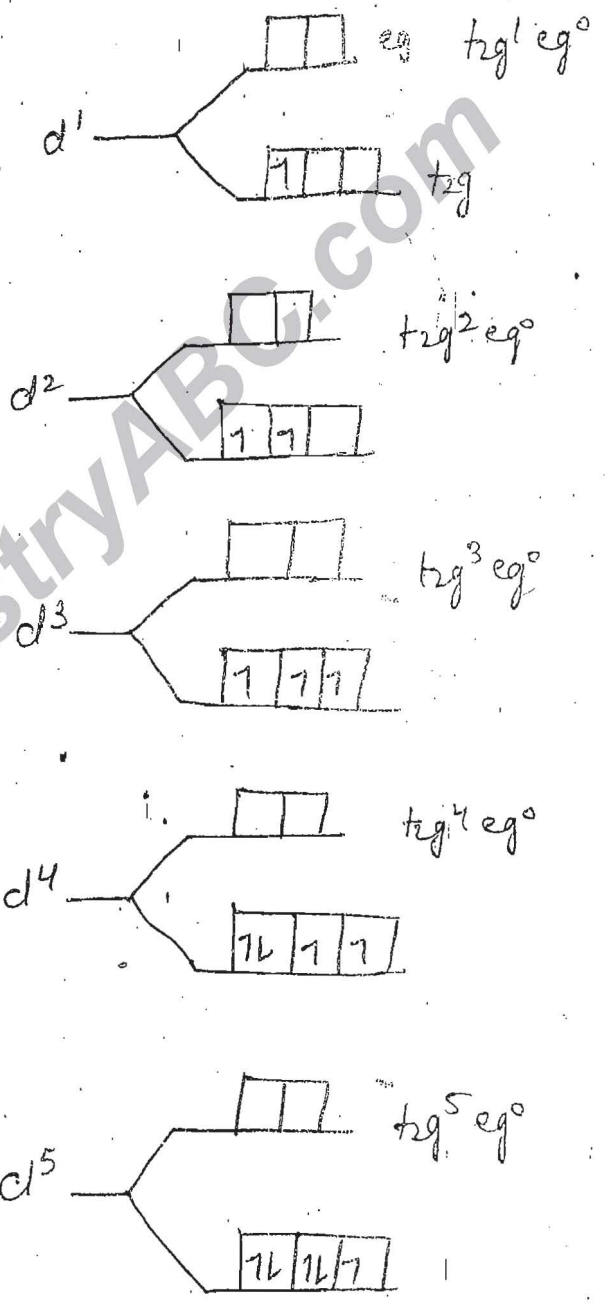
High spin or
Spin free complexes

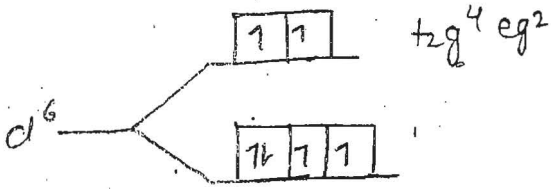
* No pairing of e⁻s
(weak field complexes)

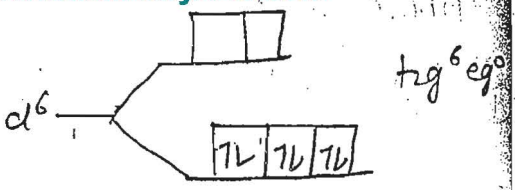


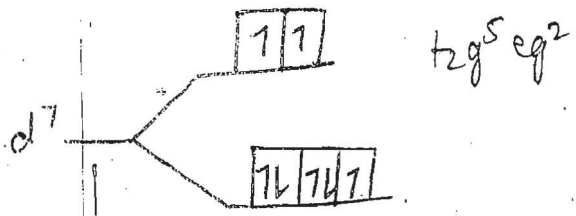
Low spin or spin
paired complexes

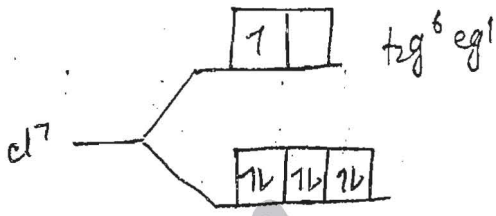
pairing of e⁻s
(strong field complexes)

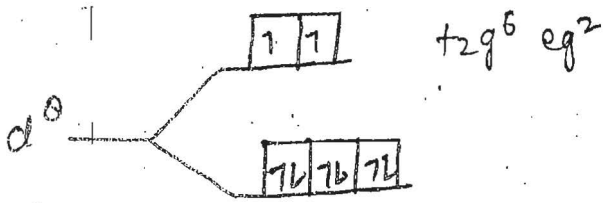


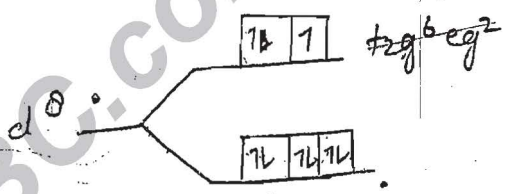


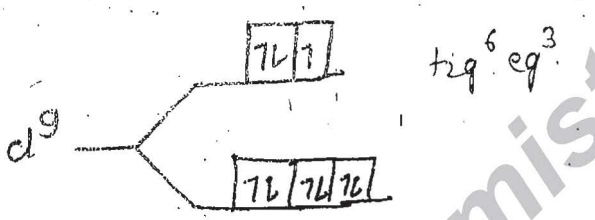


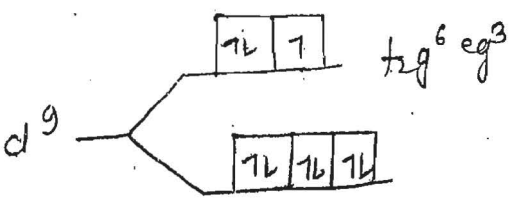


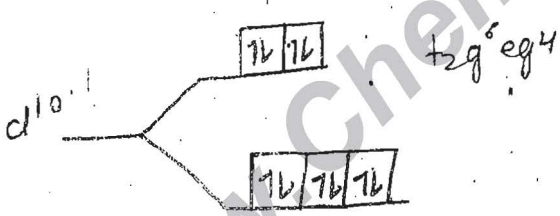


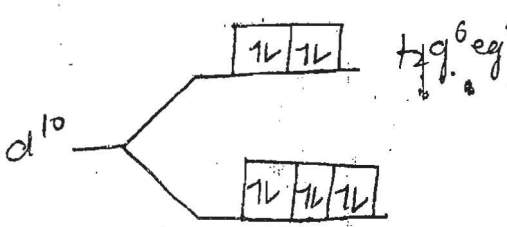












d^4, d^5, d^6, d^7 → HS → weak ligand

→ LS → strong ligand

d^1, d^2, d^3 → complexes

d^8, d^9, d^{10} → complexes

Above electron distribution is valid for

① only 3d series elements

② for +2, +3 oxidation states

③ +4 oxidation state → how skin complexes.

whether the ligand is strong or weak

④ Co^{3+} forms LS complexes with most of the ligands except halides

⑤ 4d and 5d series transition metals in +3 oxidation state form LS complexes whether the ligand are weak or strong.

⑥ +2 oxidation of 5d series – LS

+2 " " " 4d series – LS (in general)

eg · ① $K_2[NiF_6]$ → $_{28}Ni$ = $_{25}Mn^{3+}$ = $3d^5 4s^2$ $3d^8 4s^2$

$3d^6 \rightarrow t_{2g}^6 e_g^0$

② $[Co(H_2O)_6]^{3+} \rightarrow Co^{3+} \rightarrow 3d^6 \rightarrow t_{2g}^6 e_g^0$

③ $[Co(NH_3)_6]^{2+} \rightarrow Co^{2+} \rightarrow 3d^7 \rightarrow t_{2g}^5 e_g^2$ ← low o.s. no pairing

④ $[Rh(H_2O)_6]^{3+} \rightarrow 4d^6 \rightarrow t_{2g}^6 e_g^0$

⑤ $[IrF_6]^{3-}$ → $5d^6 \rightarrow t_{2g}^6 e_g^0$

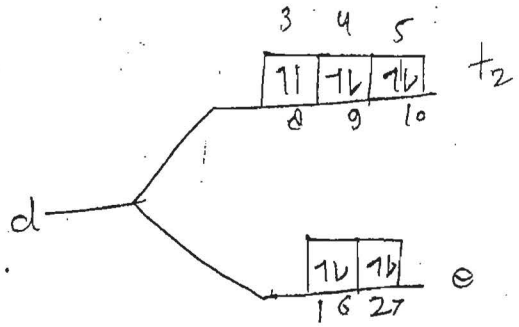
⑥ $[Fe(CN)_6]^{4-}$ → $3d^6 \rightarrow t_{2g}^6 e_g^0$

⑦ $[Fe(CN)_6]^{3-}$ $3d^5 \rightarrow t_{2g}^5 e_g^0$

Electron distribution in tetrahedral complexes ⇒

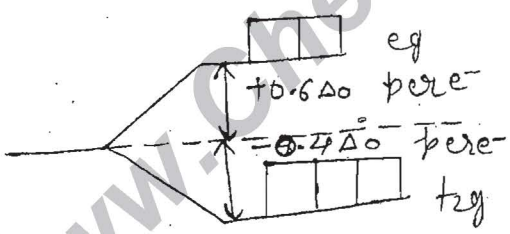
Tetrahedral complexes are high spin complexes.

$$\Delta t = \frac{4}{9}\Delta o$$



1. $e^{1,2} \longrightarrow t_2^{3,4,5} \longrightarrow e^{6,7} \longrightarrow t_2^{8,9,10}$

Crystal field stabilization energy in octahedral complexes ⇒



$d^1 \longrightarrow t_{2g}^1\ eg^0$ CFSE $= -0.4\Delta o$

$d^2 \longrightarrow t_{2g}^2\ eg^0$ $= -0.4 \times 2\ \Delta o$

$= -0.8\ \Delta o$

$d^3 \longrightarrow t_{2g}^3\ eg^0$ $= -0.4 \times 3$

$= -1.2\ \Delta o$

d^4 (HS) → $t_{2g}^3\ eg^1$

CFSE = $[-0.4 \times 3 + 0.6 \times 1]\ \Delta_o$

= $-0.6\ \Delta_o$

d^4 (LS) → $t_{2g}^4\ eg^0$

CFSE = $-0.4 \times 4\ \Delta_o + 1P$

= $-1.6\ \Delta_o + P$

$d^n = t_{2g}^p\ eg^q$

resultant → experimental

$$\boxed{CFSE = \underbrace{[-0.4p + 0.6q]\Delta_o}_{\text{Theoretical}} + mP}$$

Theoretical → actual CFSE → exact CFSE

P = pairing energy or mean pairing energy → energy required for pairing electrons

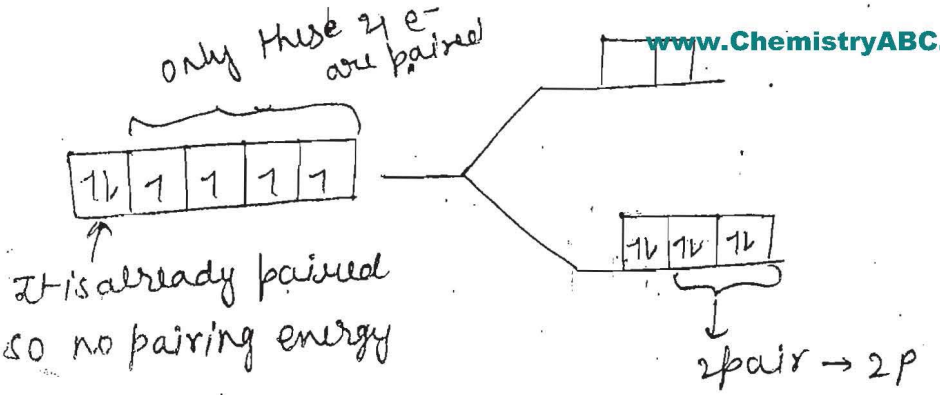
m = no. of paired electrons caused by the ligands or (occurs during the complex formation)

d^6 (LS) → $t_{2g}^6\ eg^0 + 3P$ ✗

$-0.4 \times 6 + 0.6 \times 0$

$-2.4 + 3P$

[no pairing energy in high spin complexes.]

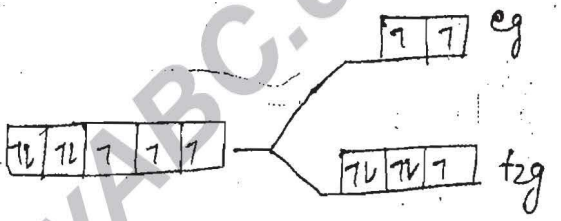


$-0.4 \times 6 + 0.6 \times 0 + 2P$

$-2.4 + 2P$ ✓

Q ⇒ d^7 HS $\rightarrow t_{2g}^5\ eg^2$

CFSE = ?



$-0.4 \times 5 + 0.6 \times 2 = -02.0 + 1.2$

$= -0.8\Delta_o$

(a) $-\frac{4}{5}\Delta o + 3P$

✓ (b) $-\frac{4}{5}\Delta_o + 2P$ (wrong a/c to logic but right a/c to examinar)

(c) $-\frac{9}{5}\Delta_o + 2P$

(d) $-\frac{9}{5}\Delta o + 2P$

The answer of this que. should be $-\frac{4}{5}\Delta o$ as there is no pairing energy in HS complexes.

Q⇒ A complex $[Cr L_6]^{2+}$ absorbs at 15000 cm^{-1}.

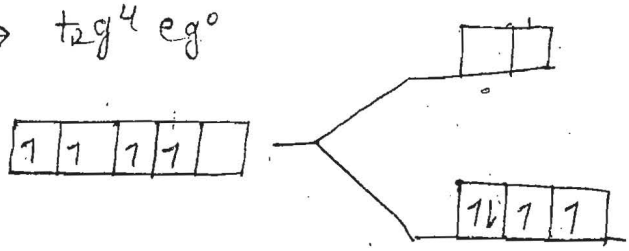
P = 12000 cm^{-1}. Calculate CFSE.

L = monodentate neutral ligand.

$Cr^{2+} \rightarrow {}_{24}Cr \rightarrow 3d^5 4s^1$

$\downarrow$

$3d^4 \rightarrow t_{2g}^4 e_g^0$



$\Delta_o > P \longrightarrow LS$

$\Delta_o < P \longrightarrow HS$

$\Delta_o = P$ HS and LS are in equilibrium

Here 15000 cm^{-1} (Δ_o) > 12000 cm^{-1} (P) = LS

$t_{2g}^4 e_g^0$

~~$-0.4 \times 4 + 1$~~

~~$-1.6 + P$~~

$= -0.4 \times 4 \times 15000 + 12000$

$= -12000\ cm^{-1}$

d^4 (LS) $\rightarrow t_2g^4\, eg^0$ CFSE $= -0.4\times4\,\Delta_o + P$

d^5 (LS) $\rightarrow t_2g^5\, eg^0$ CFSE $= -0.4\times5\,\Delta_o + 2P$

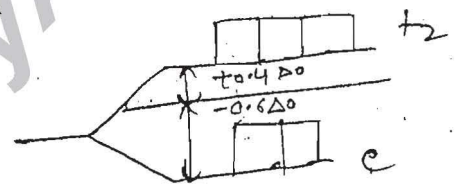
d^6 (LS) $\rightarrow t_2g^6\, eg^0$ CFSE $= -0.4\times6\,\Delta_o + 2P$

d^7 (LS) $\rightarrow t_2g^6\, eg^1$ CFSE $= [-0.4\times6 + 0.6\times1]\,\Delta_o + P$

HS ⟶ No pairing energy

CFSE in tetrahedral complexes ⇒

HS



$d^n \rightarrow e^p\ t_2^q$

CFSE $= [-0.6p + 0.4q]\,\Delta t$

$\Delta t = \frac{4}{9}\Delta o$

CFSE $= [-0.27p + 0.18q]\,\Delta t$

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Applications of CBSE ⇒

① Spinels ⇒

mixed oxides having formula AB_2O_4 or AB_2S_4 / AB_2Se_4

A ⟶ +2 oxidation state ⟶ Mg^{2+}, Ca^{2+}, Sn^{2+}, Ba^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}

B ⟶ +3 oxidation state ⟶ Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}

A and B either same or different atoms.

Examples ⇒ $NiFe_2O_4$ $\quad$ $NiO \cdot Fe_2O_3$

Mn_3O_4 $\quad$ $MnO \cdot Mn_2O_3$

Fe_3O_4 $\quad$ $FeO \cdot Fe_2O_3$

Classification :-

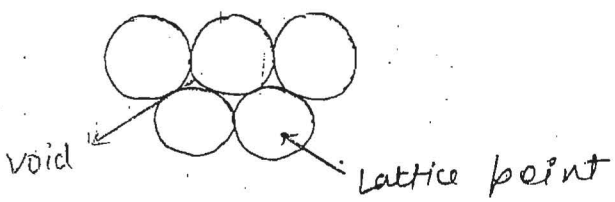
① Normal spinels ② Inverse spinels

O^{2-} ⟶ Lattice Points

metal ions ⟶ occupy Voids

Larger size ion (in general anion) → Constitute lattice point

Smaller size ion (In general cation) → occupy voids

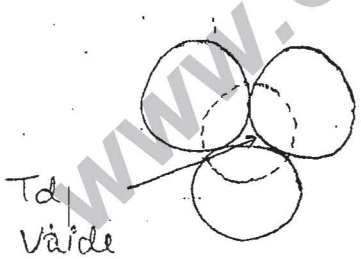


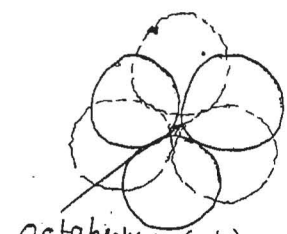
Voids or interstitial sites or interstices or hole → unoccupied space

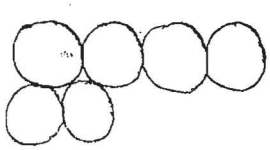
Two types voides

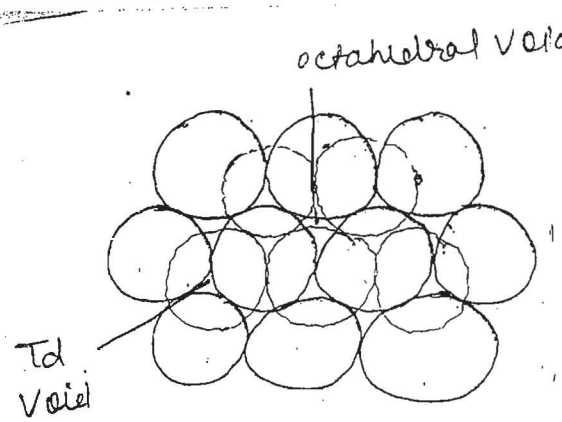
① Tetrahedral voides

② octahedral voides









No. of tetrahedral voids = 2 × No. of lattice points

No. of Oh voids = No. of lattice points

No. of Td voids = 2 × No. of Oh voids

= 2 × No. of lattice points

① Normal spinels ⇒

O^{2-} → constitute lattice points

A^{2+} → occupy $\frac{1}{8}^{th}$ of the tetrahedral voids

B^{3+} → occupy half of the octahedral voids

Lattice Points	Octahedral Voids	Tetrahedral Voids
4	4	8
$O^{2-} = 4$	B^{3+} $4 \times \frac{1}{2} = 2$	$8 \times \frac{1}{8} = 1$

A^{2+} B^{3+} O^{2-} | AB_2O_4
1 2 4

② Inverse spinels :-

O^{2-} → constitute lattice points

B^{3+} → occupy $\frac{1}{8}$th of the Td voids

B^{3+} → occupy $\frac{1}{4}$th of the Oh voids

A^{2+} → occupy $\frac{1}{4}$th of the Oh voids

	Lattice points	Oh voids	Td voids
	4	4	8
Normal	$O^{2-} = 4$	B^{3+} $4 \times \frac{1}{2} = 2$	$8 \times \frac{1}{8} = 1$
Inverse	$O^{2-} = 4$.	B^{3+} $4 \times \frac{1}{4} = 1$	$B^{3+} = 8 \times \frac{1}{8} = 1$
		A^{2+} $4 \times \frac{1}{4} = 1$	

$A_1 B_2 O_4$

Example ⇒

① Mn_3O_4

	Octahedral	Tetrahedral
$Mn^{2+} \rightarrow 3d^5$	$t_{2g}^3 e_g^2$	$d^5 \rightarrow e^2 t_2^3$
	$CFSE = (-0.4 \times 3 + 0.6 \times 2)\Delta_o$	$CFSE = [-0.27 \times 2 + 0.18 \times 3]\Delta_t$
	$= 0$	$= 0$
$Mn^{3+} \rightarrow 3d^4$	$t_{2g}^3 e_g^1$	$d^4 \rightarrow e^2 t_2^2$
	$CFSE = (-0.4 \times 3 + 0.6 \times 1)\Delta_o$	$CFSE = (-0.4 \times 2 + 0.6 \times 2)\Delta_t$
	$= -0.6\Delta_o$	$= -0.4\Delta_t$
		$= [-0.27 \times 2 + 0.18 \times 2]$
		$= -0.18\Delta_o$

$O^{2-} \rightarrow$ Lattice point

$Mn^{3+} \rightarrow$ Octahedral

$Mn^{2+} \rightarrow$ Tetrahedral

} Normal spinel

(2) Fe_3O_4

octahedral

$Fe^{2+} \rightarrow 3d^6$ $\quad t_{2g}^4 e_g^2$

$CFSE = (-0.4 \times 4 + 0.6 \times 2)\Delta_o$

$= -0.4\Delta_o$

Tetrahedral

$e^3 t_2^3$

$CFSE = [-0.27 \times 3 + 0.18 \times 3]\Delta_o$

$= (-0.81 + 0.54)\Delta_o$

$= -0.27\Delta_o$

$Fe^{3+} \rightarrow d^5$ $\quad t_{2g}^3 e_g^2$

$CFSE = 0$

d^5 $e^2 t_2^3$

$CFSE = 0$

Fe^{2+} → octahedral

Fe^{3+} → Tetrahedral } Inverse spinel

O^{2-} → Lattice Point

Spinels having Fe^{+3} ions — inverse spinels

(3) CO_3O_4

Octahedral	Tetrahedral
$Co^{2+} \rightarrow 3d^7$	$t_{2g}^5 e_g^2$
$CFSE = (-0.4\times5 + 0.6\times2)\Delta_o$	$= -0.800$
$Co^{3+} \rightarrow 3d^6$	$t_{2g}^4 e_g^2$
$CFSE = (-0.4\times6 + 0.6\times0)$	$CFSE = -2.4$

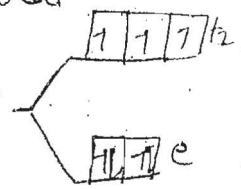
$Co^{2+} \rightarrow$ tetrahedral

$Co^{3+} \rightarrow$ octahedral

normal

Tetrahedral

$d^7 \rightarrow e^4 t_2^3$



$CFSE = (-0.27\times4 + 0.18\times3)\Delta_o$

$= (-1.08 + 0.54)\Delta_o$

$= -0.54\,\Delta_o$

$d^6 \rightarrow e^4 t_2^2$

$CFSE = (-0.27\times4 + 0.18\times2)$

$= (-1.08 + 0.36)$

$= -0.72\,\Delta_o$

$d^6 \rightarrow e^3 t_2^3$

$CFSE = (-0.27\times3 + 0.18\times3)$

$= (-0.81 + 0.54)$

$= -0.27\,\Delta_o$

(4) $NiFe_2O_4$

octahedral

Tetrahedral

$Ni^{+2} \rightarrow 3d^8$ $\quad t_{2g}^6 e_g^2$

$CFSE = (-0.4\times6 + 0.6\times2)\Delta_o$

$= (-2.4 + 1.2)\Delta_o$

$= -1.2\Delta_o$

$d^8 \rightarrow e^4 t_2^4$

$CFSE = (-0.27\times4 + 0.18\times4)\Delta t$

$= -1.08 + 0.72$

$= -0.36\Delta t$

$Fe^{+2} \rightarrow 3d^6$ $\quad t_{2g}^4 e_g^2$

$CFSE = (-0.4\times4 + 0.6\times2)\Delta_o$

$= -1.6 + 1.2$

$= -0.4\Delta_o$

$d^6 \rightarrow e^3 t_2^3$

$CFSE = (-0.27\times3 + 0.18\times3)\Delta t$

$= -0.81 + 0.54$

$= -0.27\Delta t$

$Fe^{+3} \rightarrow 3d^5$ $\quad t_{2g}^3 e_g^2$

$CFSE = (-0.4\times3 + 0.6\times2)\Delta_o$

$= 0$

$d^5 \rightarrow e^2 t_2^3$

$CFSE = (-0.27\times2 + 0.18\times3)$

$= -.54 + 0.54$

$= 0$

Ni^{+2} → octahedral

Fe^{+3} → tetrahedral

O^{2-} → Lattice point

} inverse

(5) $FeCr_2O_4$

Note ⇒ Spinals having Cr^{3+} ions → Normal spinels

	Oh	Td
$Fe^{+2} \rightarrow 3d^6$	$t_{2g}^4 e_g^2$ $CFSE = -0.4\Delta_o$	$e^3 t_2^3$ $CFSE = -0.27\Delta t$
$Cr^{+2} \rightarrow 3d^4$	$t_{2g}^3 e_g^1$ $CFSE = (-0.4\times3 + 0.6\times1)\Delta_o$ $= -1.2 + 0.6 = -0.6\Delta_o$	$e^2 t_2^2$ $CFSE = -0.27\times2 + 0.18\times2$ $= -0.54 + 0.36$ $= -0.18\Delta t$
$Cr^{+3} \rightarrow 3d^3$	$t_{2g}^3 e_g^0$ $CFSE = (-0.4\times3 + 0.6\times0)\Delta_o$ $= -1.2\Delta_o$	$e^2 t_2^1$ $CFSE = -0.27\times2 + 0.18\times1$ $= -0.54 + 0.18$ $= -0.36\Delta t$

Q ⇒ which of the following is a normal spinel ?

(i) $NiCrO_4$

(ii) $FeCrO_4$

(iii) $MnCo_3O_4$

(a) only (i) (b) only (i) and (ii) (c) only (ii) and (iii)

(d) (i), (ii), (iii)

$Ni^{2+} \rightarrow 3d^8 \rightarrow t_{2g}^6 e_g^2$

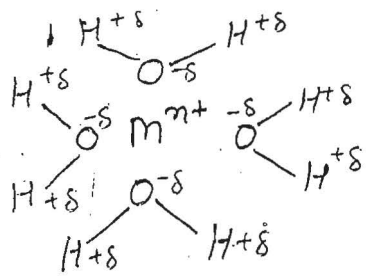
$CFSE = (-2.4 + 1.2)\Delta_o$

$= -1.2\Delta_o$

$Cr^{3+} \rightarrow 3d^3 \rightarrow CFSE = -1.2\Delta_o$

Hydration Energy ⇒

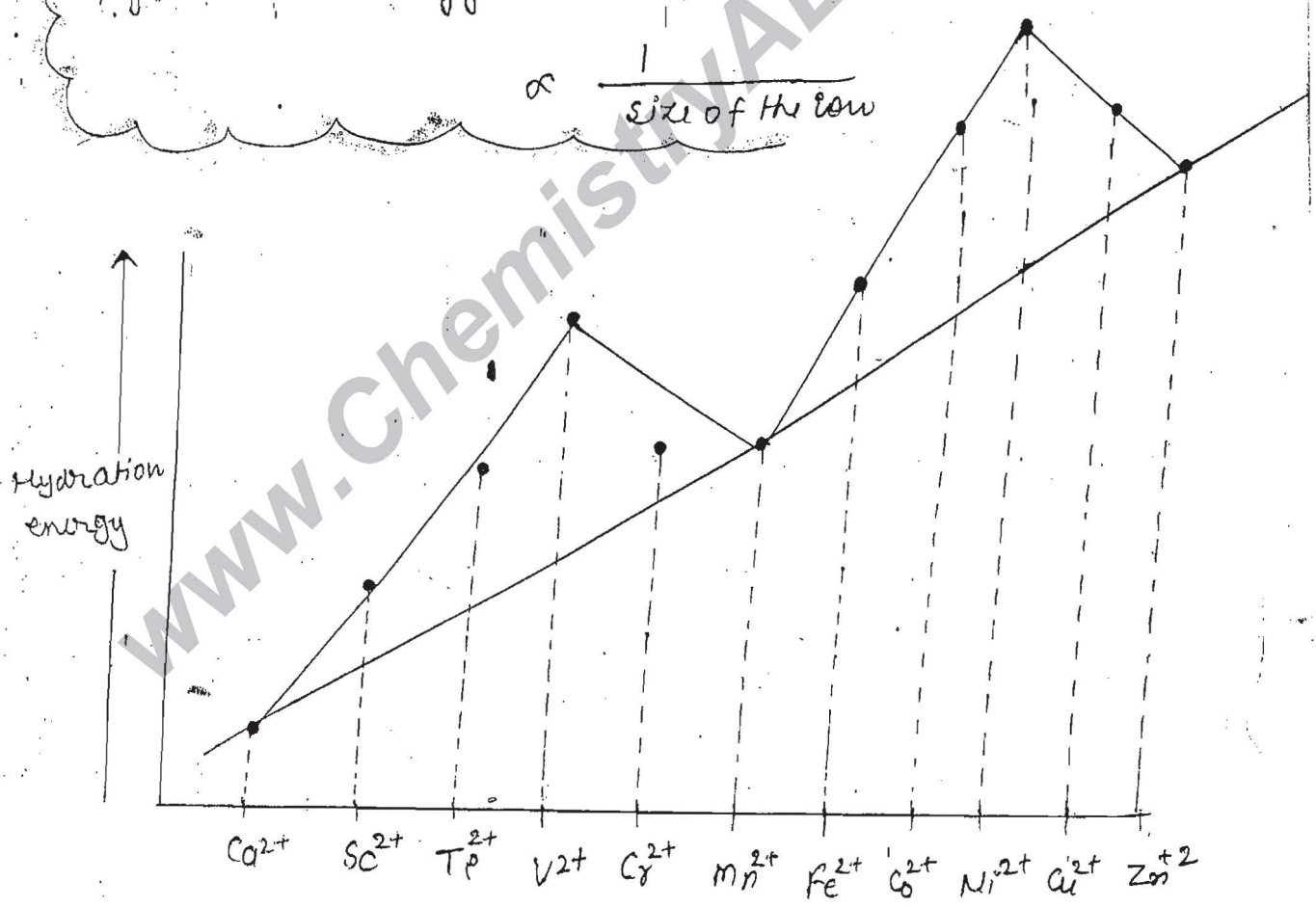
Hydration ⇒ Gathering of water molecules around cation or anion is k/a hydration. In this process some amount of energy is released which is known as hydration energy. This energy is used to break the ionic bond.



HYDRATION ENERGY

Hydration energy ∝ charge on the ion

$$\propto \frac{1}{\text{size of the ion}}$$



For dipositive metal ions of 3d series transition metal

$[Ca(H_2O)_6]^{2+} \rightarrow 3d^0 \longrightarrow t_{2g}^0\ e_g^0$

$CFSE = 0$

$[Sc(H_2O)_6]^{2+} \rightarrow 3d^1 \rightarrow t_{2g}^1\ e_g^0$

$CFSE = -0.4\Delta_o$

Experimental hydration energy = Theoretical or calculated hydration E + CFSE

$[Ti(H_2O)_6]^{2+} \longrightarrow 3d^2 \rightarrow t_{2g}^2\ e_g^0 \rightarrow CFSE = -0.8\ \Delta_o$

$[V(H_2O)_6]^{2+} \longrightarrow 3d^3 \rightarrow t_{2g}^3\ e_g^0 \rightarrow CFSE = -0.4\times3 = -1.2\ \Delta_o$

* $[Cr(H_2O)_6]^{2+} \longrightarrow 3d^4 \longrightarrow t_{2g}^3\ e_g^1 \rightarrow CFSE = -0.4\times3 + 0.6\times1 = -0.6\ \Delta_o$

* $[Mn(H_2O)_6]^{2+} \rightarrow 3d^5 \longrightarrow t_{2g}^3\ e_g^2 \rightarrow CFSE = -0.4\times3 + 0.6\times2 = -1.2 + 1.2 = 0$

$[Fe(H_2O)_6]^{2+} \longrightarrow 3d^6 \rightarrow t_{2g}^4\ e_g^2 \rightarrow CFSE = -0.4\Delta_o$

$[Co(H_2O)_6]^{2+} \rightarrow 3d^7 \longrightarrow t_{2g}^5 e_g^2 \rightarrow CFSE = -0.4\times5 + 0.6\times2 = -0.8\ \Delta_o$

$[Ni(H_2O)_6]^{2+} \rightarrow 3d^8 \rightarrow t_{2g}^6 e_g^2 \rightarrow CFSE = -0.4\times6 + 0.6\times2 = -1.2\Delta_o$

* $[Cu(H_2O)_6]^{2+} \rightarrow 3d^9 \rightarrow t_{2g}^6 e_g^3 \rightarrow CFSE = -0.4\times6 + 0.6\times3 = -0.6\ \Delta_o$

* $[Zn(H_2O)_6]^{2+} \rightarrow 3d^{10} \rightarrow t_{2g}^6 e_g^4 \rightarrow CFSE = -0.4\times6 + 0.6\times4 = 0$

Q7. The experimental hydration energy for Co^{2+} ion is $-540\ KJ\,mol^{-1}$ and $\Delta o = 12000\ cm^{-1}$, Calculate hydration energy without CFSE.

Given: $1\ KJ = 83.7\ cm^{-1}$ $\quad 1\ KKal = 4.18\ KJ$

$= 4.18 \times 83.7\ cm^{-1}$

$= 351\ cm^{-1}$

Soln. ⇒

Hydration energy without CFSE = Exp. hydration energy − CFSE

$Co^{2+} \rightarrow 3d^7 \rightarrow t_{2g}^5 e_g^2$

$CFSE = -0.8\Delta o$

$= -0.8 \times 12000$

$= -9600\ cm^{-1}$

$= \frac{-9600}{83.7}\ KJ$

$= -114.6\ KJ$

Hydration E = $-540 - (-114.6)$

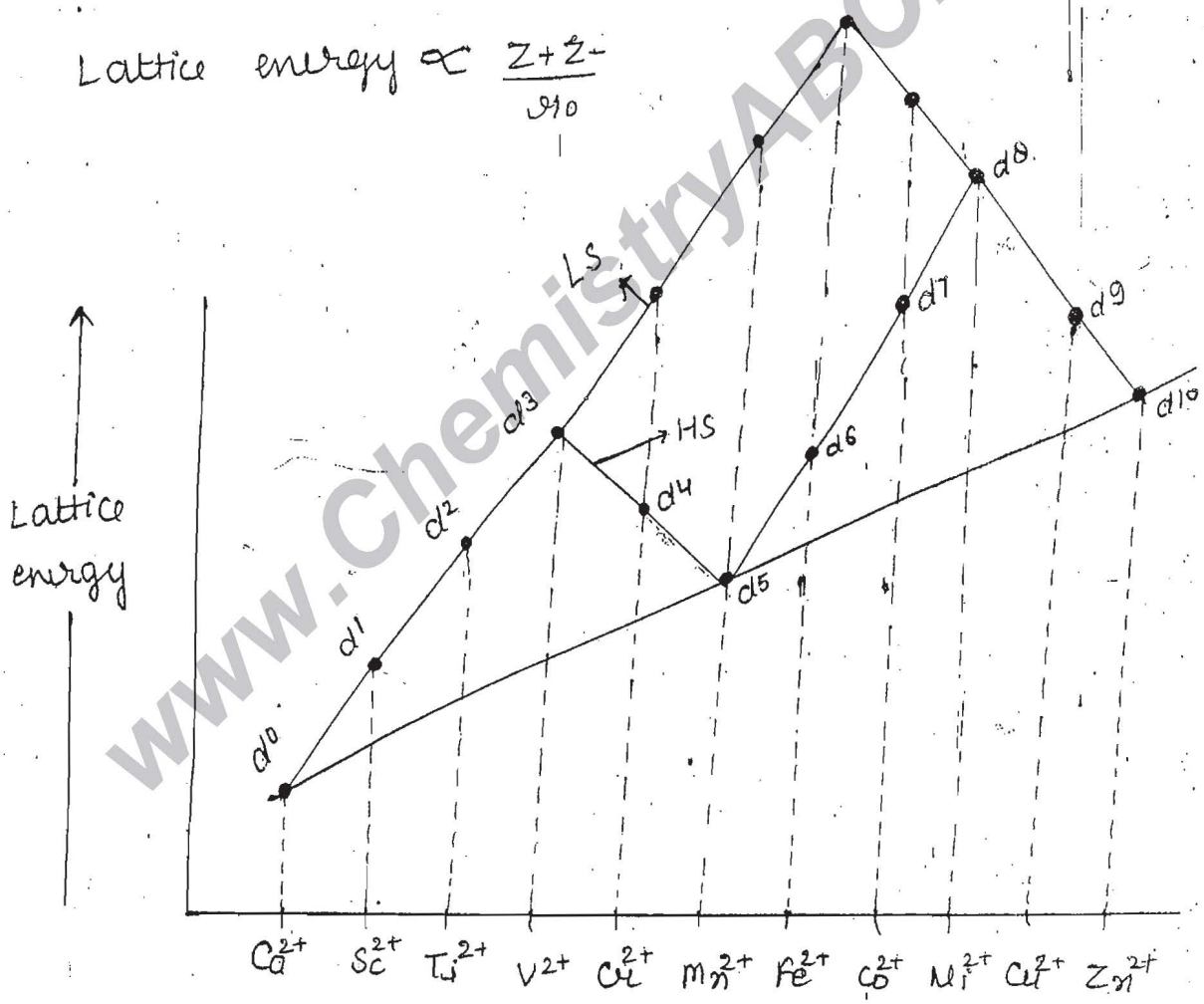
$= -425.4\ KJ\,mol^{-1}$

Lattice Energy ⇒ When one mole of an ionic crystal is formed from its constituent gaseous ions, some energy released → which is called lattice energy.

LATTICE ENERGY

$$\text{Lattice energy} = \frac{-NAZ^+Z^-}{r_0}\left(1-\frac{1}{n}\right)$$

$$\text{Lattice energy} \propto \frac{Z^+Z^-}{r_0}$$



Lattice energy of diposition transition metals of first transition series

$Ca^{+2}F_2^{-1}$

$Sc^{+2}F_2^{-1}$

$Ti^{+2}F_2^{-1}$

$V^{+2}F_2^{-1}$

$Cr^{+2}F_2^{-1}$

$Mn^{+2}F_2^{-1}$

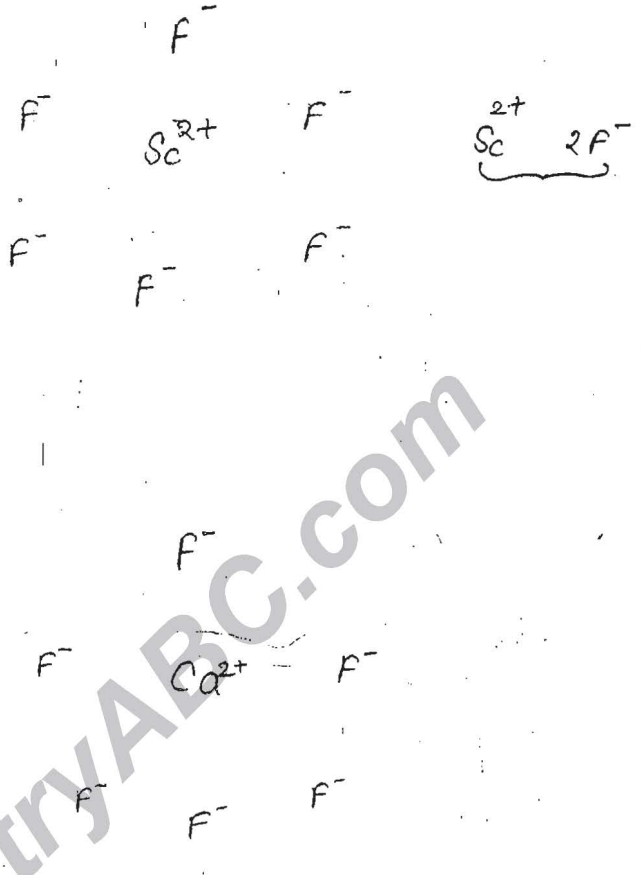
$Fe^{+2}F_2^{-1}$

$Co^{+2}F_2^{-1}$

$Ni^{+2}F_2^{-1}$

$Cu^{+2}F_2^{-1}$

$Zn^{+2}F_2^{-1}$



d^4 (LS) $\longrightarrow t_{2g}^4 e_g^0$ CFSE $= -1.6\Delta_o$

d^5 (LS) $\longrightarrow t_{2g}^5 e_g^0$ CFSE $= -2.0\Delta_o$

d^6 (LS) $\longrightarrow t_{2g}^6 e_g^0$ CFSE $= -2.4$

d^7 (LS) $\longrightarrow t_{2g}^6 e_g^1$ CFSE $= -1.8$

Lattice energy with CFSE or Experimental Lattice energy = Theoretical Lattice energy + CFSE

Q⇒ which of the following set of transition metal ions lie on the straight line of lattice energy curve of their fluorides?

(a) Mn^{2+}, Zn^{2+}, Ca^{2+}

(b) Mn^{2+}, Zn^{2+}, Fe^{2+}, Ca^{2+}

(c) Mn^{2+}, Zn^{2+}, Fe^{3+}

(d) Ca^{2+}, Mn^{2+}, Zn^{2+}, Fe^{3+}, Ga^{3+}

Ans. (c)

$_{30}Zn^{2+} \rightarrow 3d^{10}$

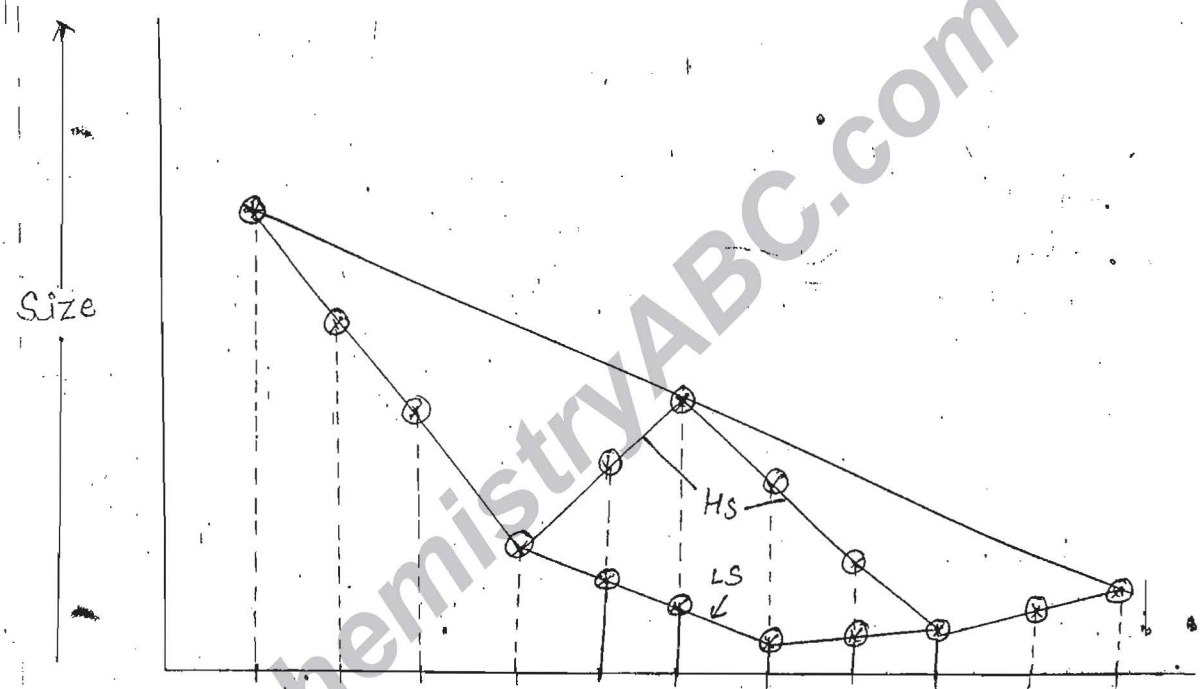
$_{31}Ga^{3+} \rightarrow 3d^{10}$

Q⇒ which of the above set of metal ions lie on the straight line of lattice energy curve of their fluorides?

Ans⇒ (d)

Size of complex ions

SIZE OF COMPLEX IONS



CFSE

$[Ca(H_2O)_6]^{2+}$ 0

$[Sc(H_2O)_6]^{2+}$ $-0.4\Delta_o$

$[Ti(H_2O)_6]^{2+}$ $-0.8\Delta_o$

-1.2

$-0.6\Delta_o$

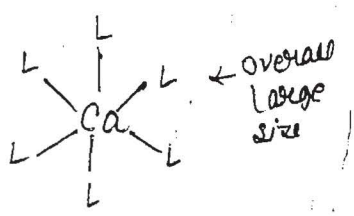
$[Zn(H_2O)_6]^{2+}$

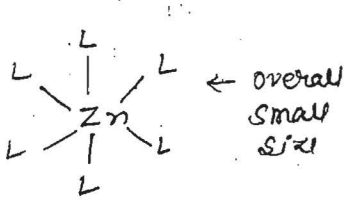
Ca^{2+}

Sc^{2+}

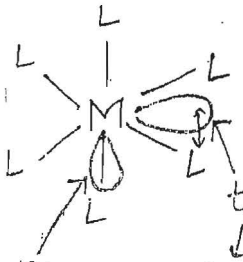
Size decreases

Zn^{2+}



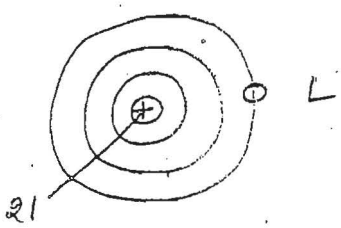


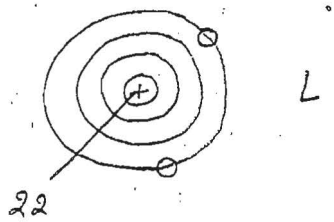
	HS Electronic configuration	CfSE	LS Electronic configuration	CfSE
d^0	$t_{2g}^0 e_g^0$	0	$t_{2g}^0 e_g^0$	0
d^1	$t_{2g}^1 e_g^0$	$-0.4\Delta_0$		
d^2	$t_{2g}^2 e_g^0$	$-0.8\Delta_0$		
d^3	$t_{2g}^3 e_g^0$	$-1.2\Delta_0$		
d^4	$t_{2g}^3 e_g^1$	$-0.6\Delta_0$	$t_{2g}^4 e_g^0$	$-1.6\Delta_0$
d^5	$t_{2g}^3 e_g^2$	0	$t_{2g}^5 e_g^0$	$+2.0\Delta_0$
d^6	$t_{2g}^4 e_g^2$	$-0.4\Delta_0$	$t_{2g}^6 e_g^0$	$-2.4\Delta_0$
d^7	$t_{2g}^5 e_g^2$	$-0.8\Delta_0$	$t_{2g}^6 e_g^1$	$-1.8\Delta_0$
d^8	$t_{2g}^6 e_g^2$	$-1.2\Delta_0$		
d^9	$t_{2g}^6 e_g^3$	$-0.6\Delta_0$		
d^{10}	$t_{2g}^6 e_g^4$	0		



eg
↓
on the axis
↓
more repulsion
↓
small CFSE

t_{2g}
↓
b/w the axis
↓
less repulsion
↓
large CFSE

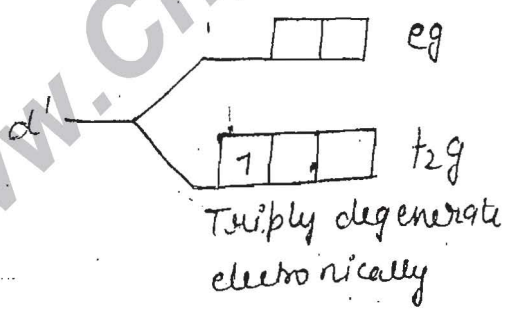




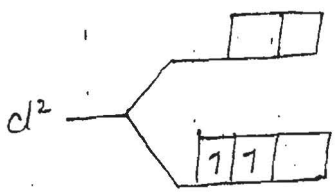
Tetragonal distortion, or John Teller distortion ⇒

John Teller Theorem ⇒ Any non linear molecule in its electronically degenerate state is unstable and undergoes some sort of distortion to remove its degeneracy, lowers energy and change in symmetry (lower in symmetry).

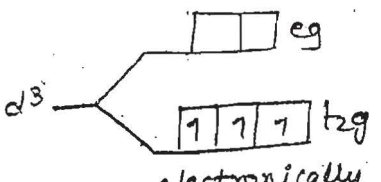
Ex:-



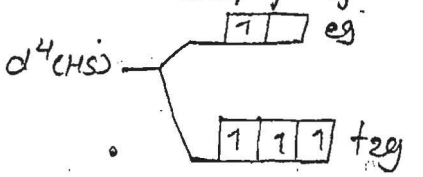
Triply degenerate electronically



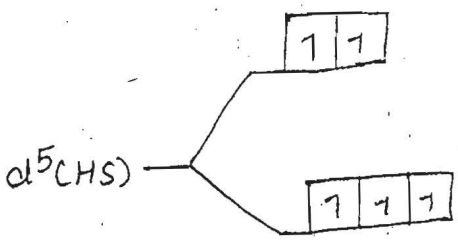
d_{xy} d_{yz}, d_{xy} d_{zx}, d_{yz} d_{zx} electronically triply degenerate



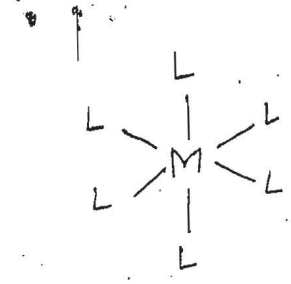
electronically non degenerate



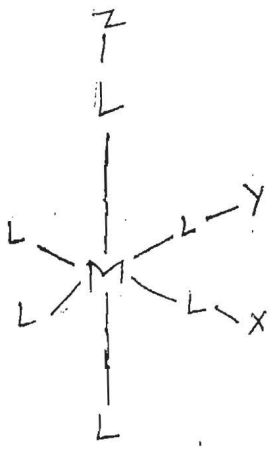
electronically doubly degenerate



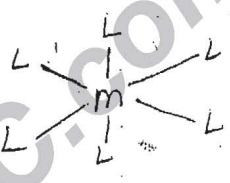
electronically non degenrate



Regular octahedron (All the M-L bond lengths same)



Tetragonal elongation OR Z out OR Tetragonal distortion (M-L bond lengths on Z axis large)



Tetragonal compression (OR Z-in) M-L bond length on Z-axis are shorter

10/09/13

Conditions for Jahn Teller distortion ⇒

① No distortion conditions ⇒

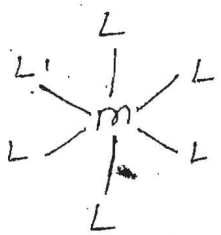
t_{2g} symmetrically filled

e_g symmetrically filled

e.g. → d^3 ($t_{2g}^3 e_g^0$), d^5 (HS) ⟶ ($t_{2g}^3 e_g^2$)

d^6 (LS) → ($t_{2g}^6 e_g^0$), d^8 ($t_{2g}^6 e_g^2$)

d^{10} ($t_{2g}^6 e_g^4$)



d^3 → d_{xy} d_{yz} d_{zx}

← no distortion ; regular octahedron

② conditions for slight distortion ⇒

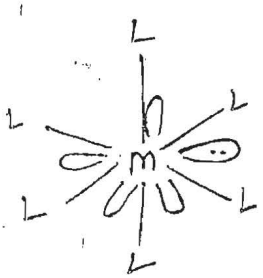
t_{2g} → unsymmetrically filled

e_g → symmetrically filled

e.g. → d^1 ($t_{2g}^1 e_g^0$), d^2 ($t_{2g}^2 e_g^0$)

d^4 (LS) → ($t_{2g}^4 e_g^0$), d^5 (LS) → ($t_{2g}^5 e_g^0$)

d^6 (HS) → ($t_{2g}^4 e_g^2$), d^7 (HS) → ($t_{2g}^5 e_g^2$)



Conditions for strong distortion ⇒

t_{2g} → symmetrically filled

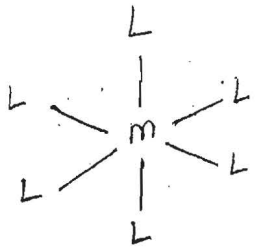
e_g → unsymmetrically filled

e.g. ⇒ d^4 (HS) → $t_{2g}^3 e_g^1$

d^7 (LS) → $t_{2g}^6 e_g^1$

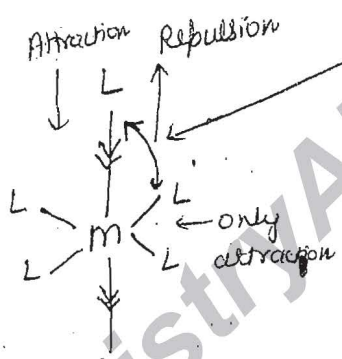
d^9 → $t_{2g}^6 e_g^3$

Tetragonal elongation ⇒



d^3 ($t_{2g}^3 e_g^0$)

d^4(HS) → $t_{2g}^3 e_g^1$

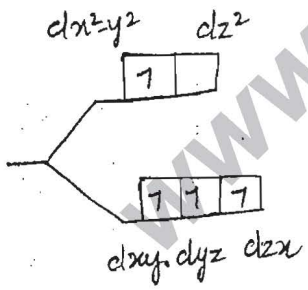


The distance b/w these two ligands increases, steric repulsion decreases → M-L bond decreases at x,y plane ligand fine d orbital is d^4 means nuclear area also ↑ so metal attracts ligand more as compared to in $t_{2g}^3 e_g^0$

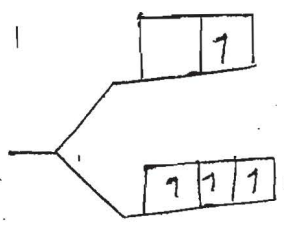
$t_{2g}^3 e_g^1$ $d_{z^2}^1$ $d_{x^2-y^2}^0$

(Tetragonal elongation → z-out distortion)

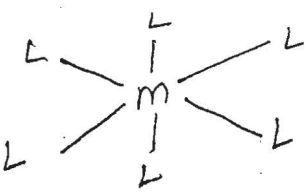
d^4 ⇒ d_{xy}^1 d_{yz}^1 d_{zx}^1 $d_{z^2}^0$ $d_{x^2-y^2}^0$ OR $d_{x^2-y^2}^1$ $d_{z^2}^0$

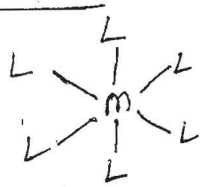


OR



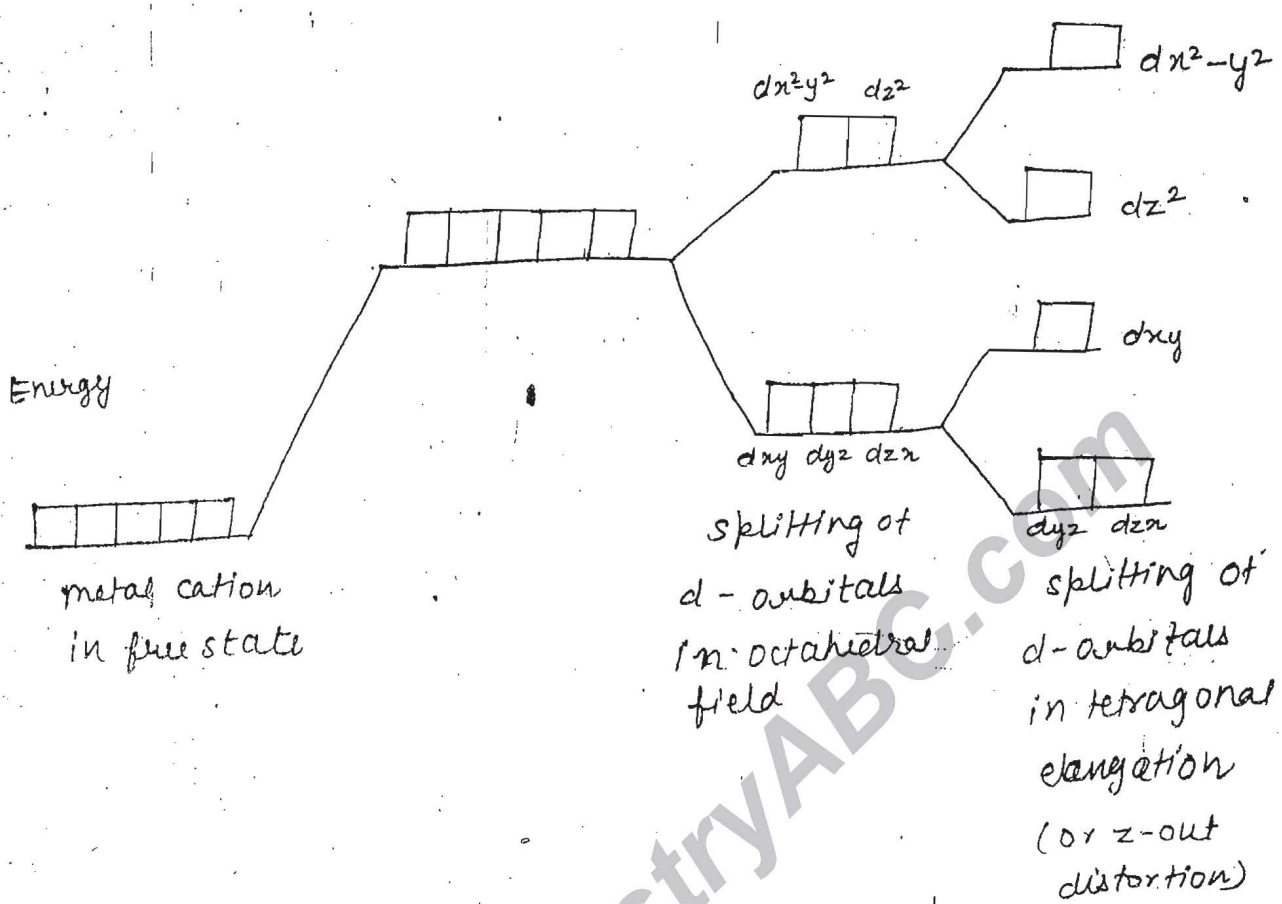
Tetragonal compression ⇒

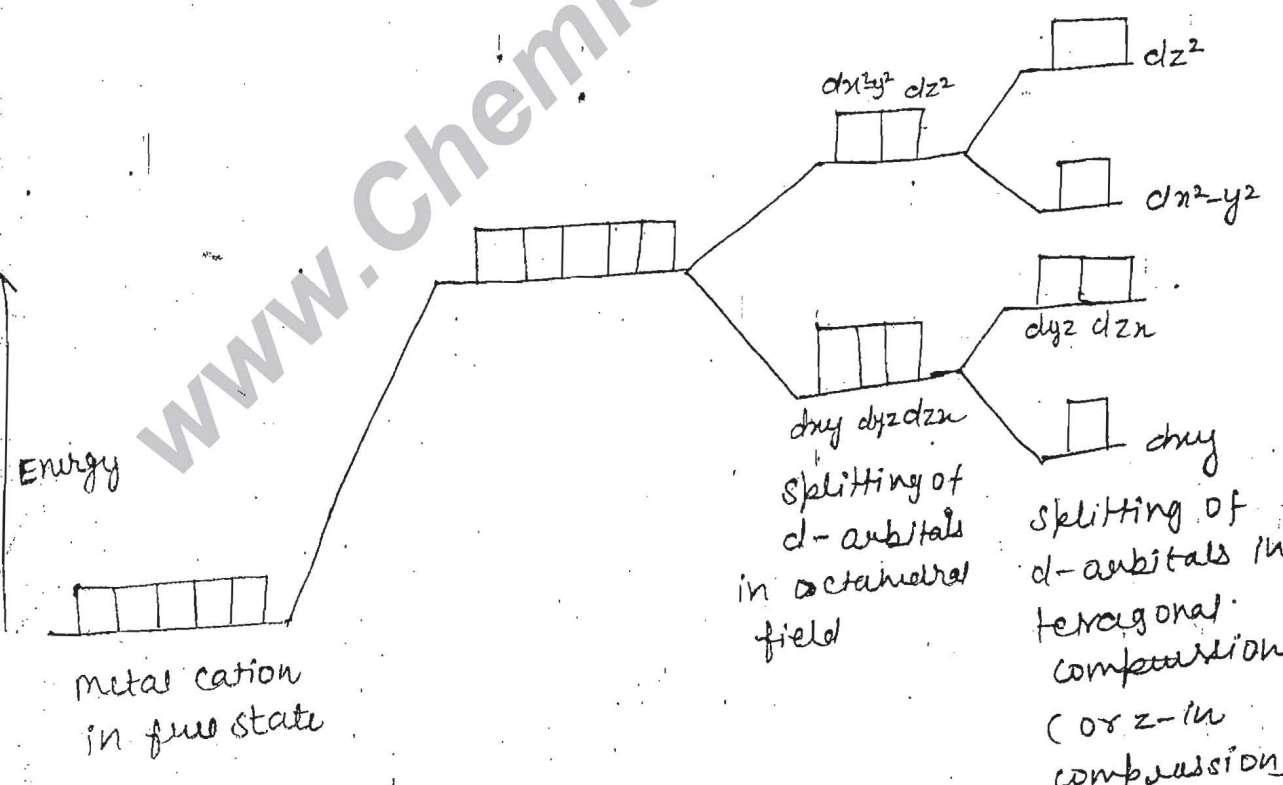


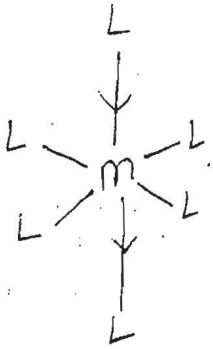


← Regular octahedron

(z-in distortion) d_{xy}^1 d_{yz}^1 d_{zx}^1 $d_{x^2-y^2}^1$ $d_{z^2}^0$

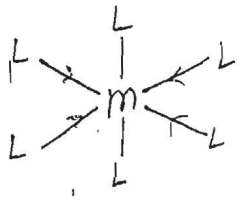






z-out

(repulsion by 2 ligands)
(more stable)

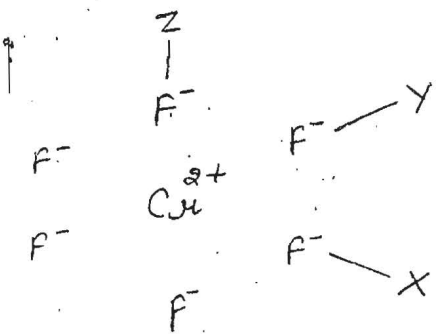


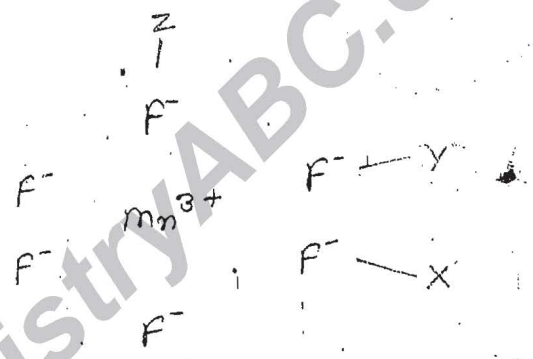
z-in

(repulsion by 4 ligands)
(less stable)

e.g.

CuF_2 , MnF_3





$Cu^{2+} \rightarrow 3d^9 \rightarrow t_{2g}^6 e_g^3$

(coz F is weak ligand)

z out

(e⁻ will enter in dz^2)

$Mn^{3+} \rightarrow 3d^4$

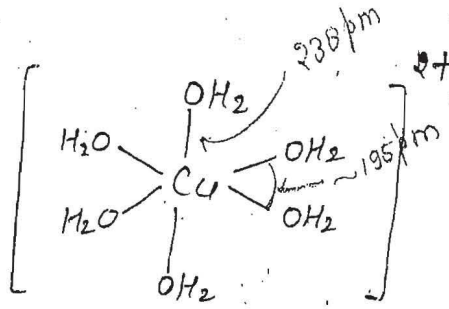
z out

(e⁻ will enter in dz^2)

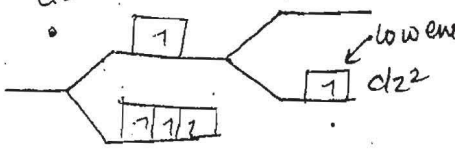
(Fluorine always makes ionic bond with metals.)

Consequences of John Teller Distortion →

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

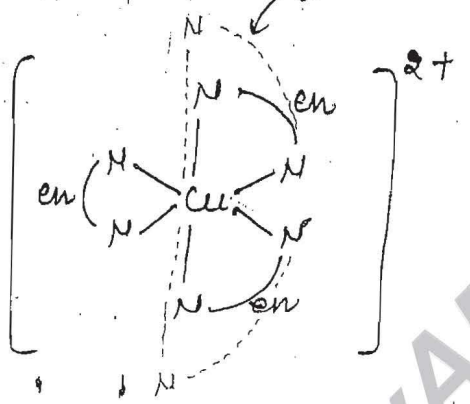


Stable due to stability of d_{z^2}



$[Cu(en)_3]^{2+}$

due to elongation of bond strain increases hence complex becomes unstable

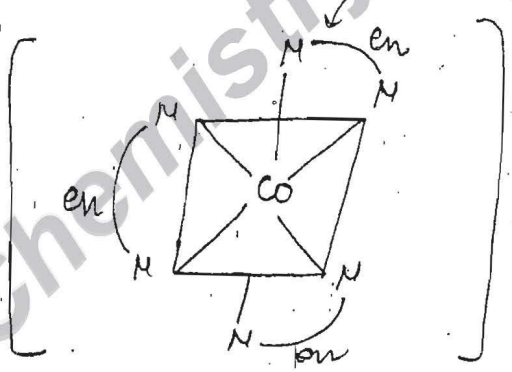


$_{29}Cu = 3d^{10}_{\uparrow\downarrow}\,4s^1$

$Cu^{+2} = 3d^9 \quad t_{2g}^6 e_g^3$

$[Co(en)_3]^{3+}$

Normal bond → no strain



$Co^{+3} = 3d^6 \qquad d^6 \rightarrow (t_{2g}^6\, e_g^0)$

$_{27}Co = 3d^7\,4s^2$

Assignment

Q⇒61 ⇒ The set of ions expected to show Jahn-Teller distortion is-

(a) Ti(III), Cu(II), Hs Fe(III)
$d^5 \rightarrow t_{2g}^3 e_g^2$; $d^{10} \rightarrow t_{2g}^6 e_g^4$; $d^8 \rightarrow t_{2g}$

(b) Cu(I), Ni(II), Hs Fe(III)
$d^9 \rightarrow t_{2g}^6 e_g^3$; $d^5 \rightarrow t_{2g}^5 e_g^0$; $d^9 \rightarrow t_{2g}^2 e_g^0$

✓(c) Cu(II), LS Fe(III), Ti(III)

(d) LS Fe(III), Mn(II), Cu(I)

Q⇒ The complex showing Jahn-Teller distortion is-

(a) $Co(NH_3)_6^{3+}$ (b) $Cr(H_2O)_6^{3+}$ ✓(c) $Cu(H_2O)_6^{2+}$ (d) $[Fe(CN)_6]^{4-}$

(a) $Co^{3+} \rightarrow 3d^6 \rightarrow t_{2g}^6 e_g^0$; $_{27}Co \rightarrow 3d^7 4s^2$

(b) $Cr^{3+} \rightarrow 3d^3 \rightarrow t_{2g}^3 e_g^0$; $_{24}Cr \rightarrow 3d^5 4s^1$

(c) $Cu^{+2} \rightarrow 3d^9 \rightarrow t_{2g}^6 e_g^3$; $_{29}Cu \rightarrow 3d^{10} 4s^1$

(d) $Fe^{+2} \rightarrow 3d^6 \rightarrow t_{2g}^6 e_g^0$; $_{26}Fe \rightarrow 3d^6 4s^2$

Q⇒ which one of the following complexes is Jahn-Teller distorted-

(a) $[Co(H_2O)_6]^{3+} \rightarrow d^6 \rightarrow t_{2g}^6 e_g^0$

✓(b) $[Co(NH_3)_6]^{2+} \rightarrow d^7 \rightarrow t_{2g}^5 e_g^2$

(c) $[Ni(NH_3)_6]^{2+} \rightarrow d^8 \rightarrow t_{2g}^6 e_g^2$

(d) $[Cr(CN)_6]^{3-} \rightarrow d^3 \rightarrow t_{2g}^3 e_g^0$

Crystal Field splitting in square planar complexes ⇒

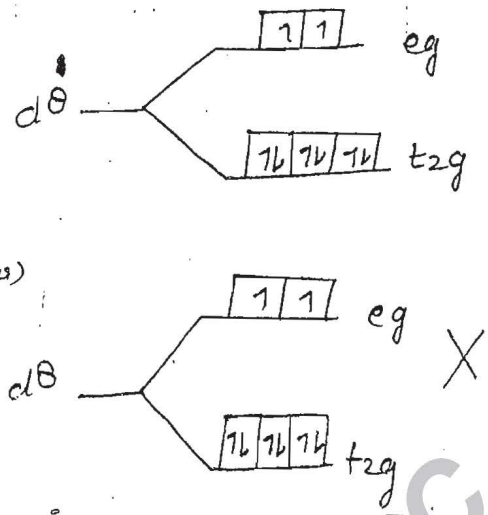
$[Ni(H_2O)_6]^{2+}$

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

(NH_3) → moderate ligand (not stronger nor weaker)

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

does not exist



$[Ni(CN)_4]^{2-}$

Ni forms only square planar complexes with strong ligands while octahedral (or Tetrahedral) complexes with weak ligands.

d^8

$[NiCl_4]^{2-}$ Td

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

$[Ni(NH_3)_6]^{2+}$ } octahedral

$[Ni(CN)_4]^{2-}$

$[PdCl_4]^{2-}$

$[PtCl_4]^{2-}$

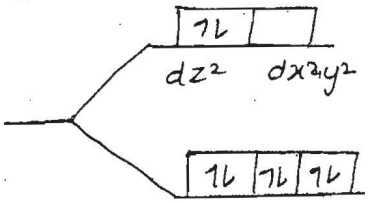
$[Pt(NH_3)_4]^{2+}$

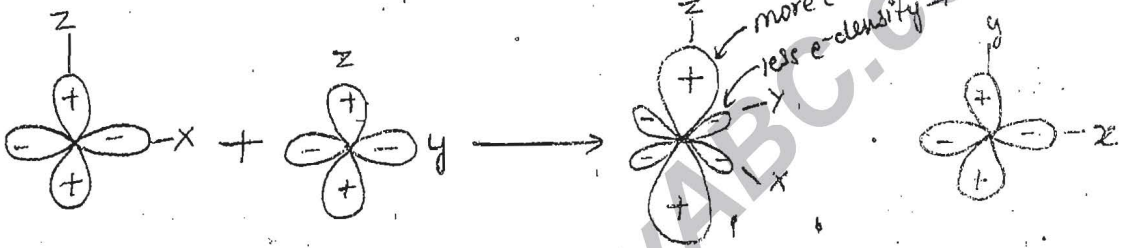
$[Pt(CN)_4]^{2-}$ } square planar

Pd^{2+}, Pt^{2+} form square planar complexes whether the ligand are strong or weak.

In square planar complexes of d^8 configuration :-

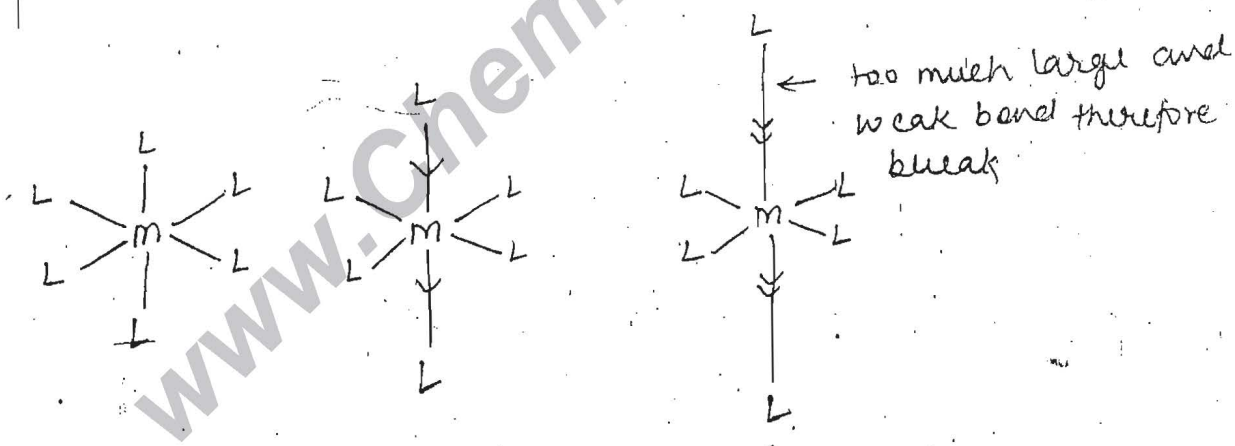
$[Ni(CN)_4]^{2-}$



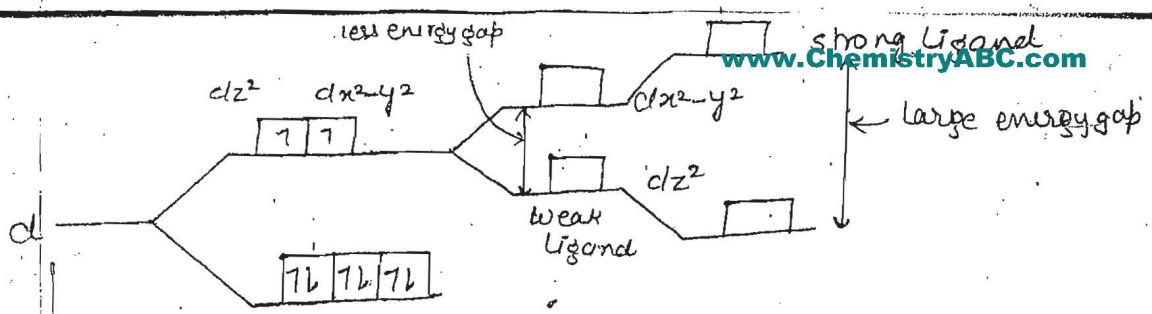


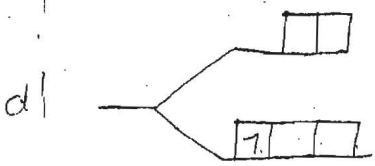
dz^2-x^2 dz^2-y^2 $dz^2-x^2-y^2$ dx^2-y^2

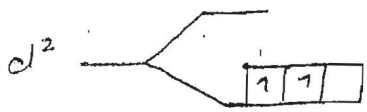
$\equiv dz^2$

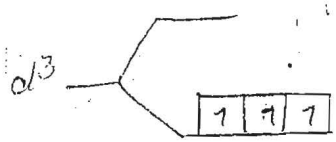


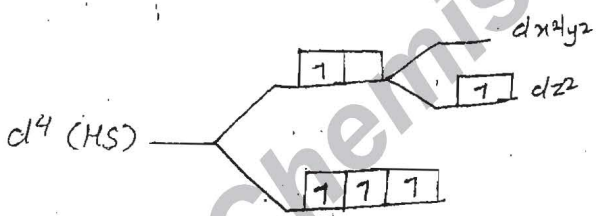
d^1z^2 dx^2y^2 dz^2 dx^2-y^2

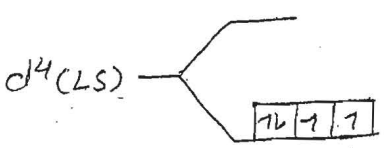


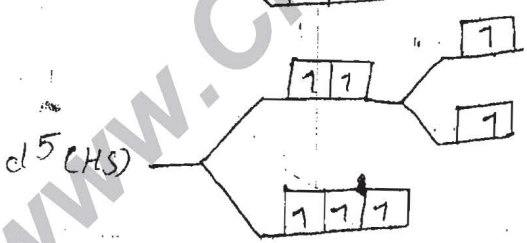


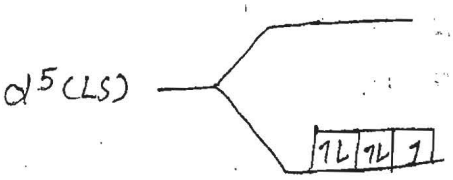


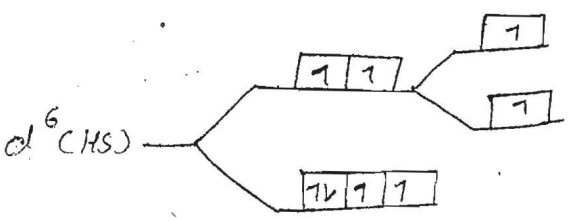


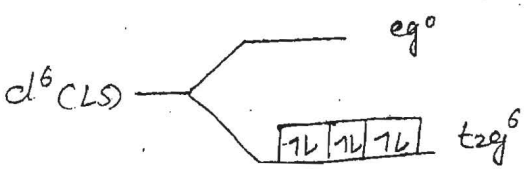


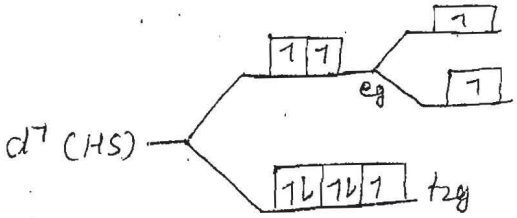


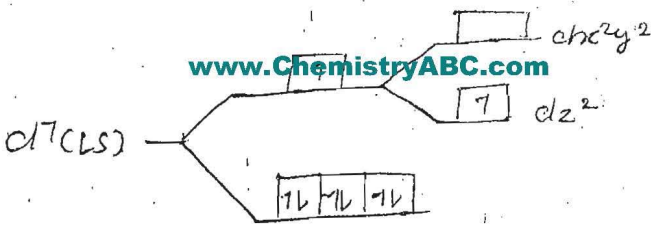


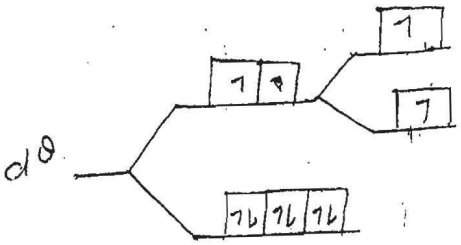




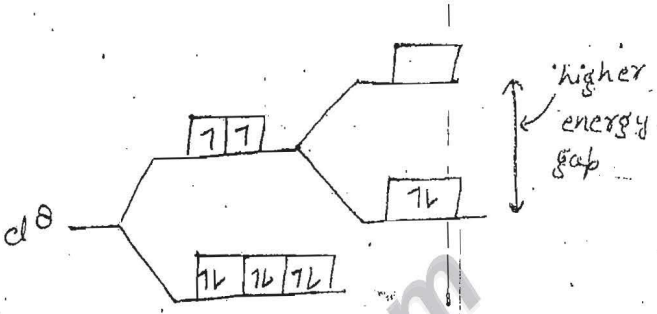




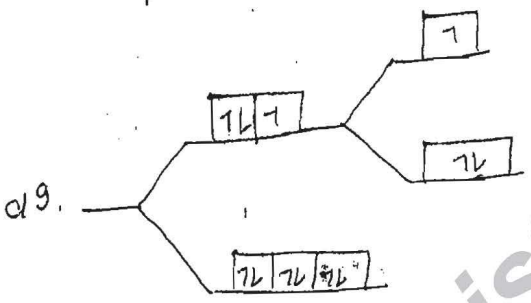




weak field complex



strong field complex

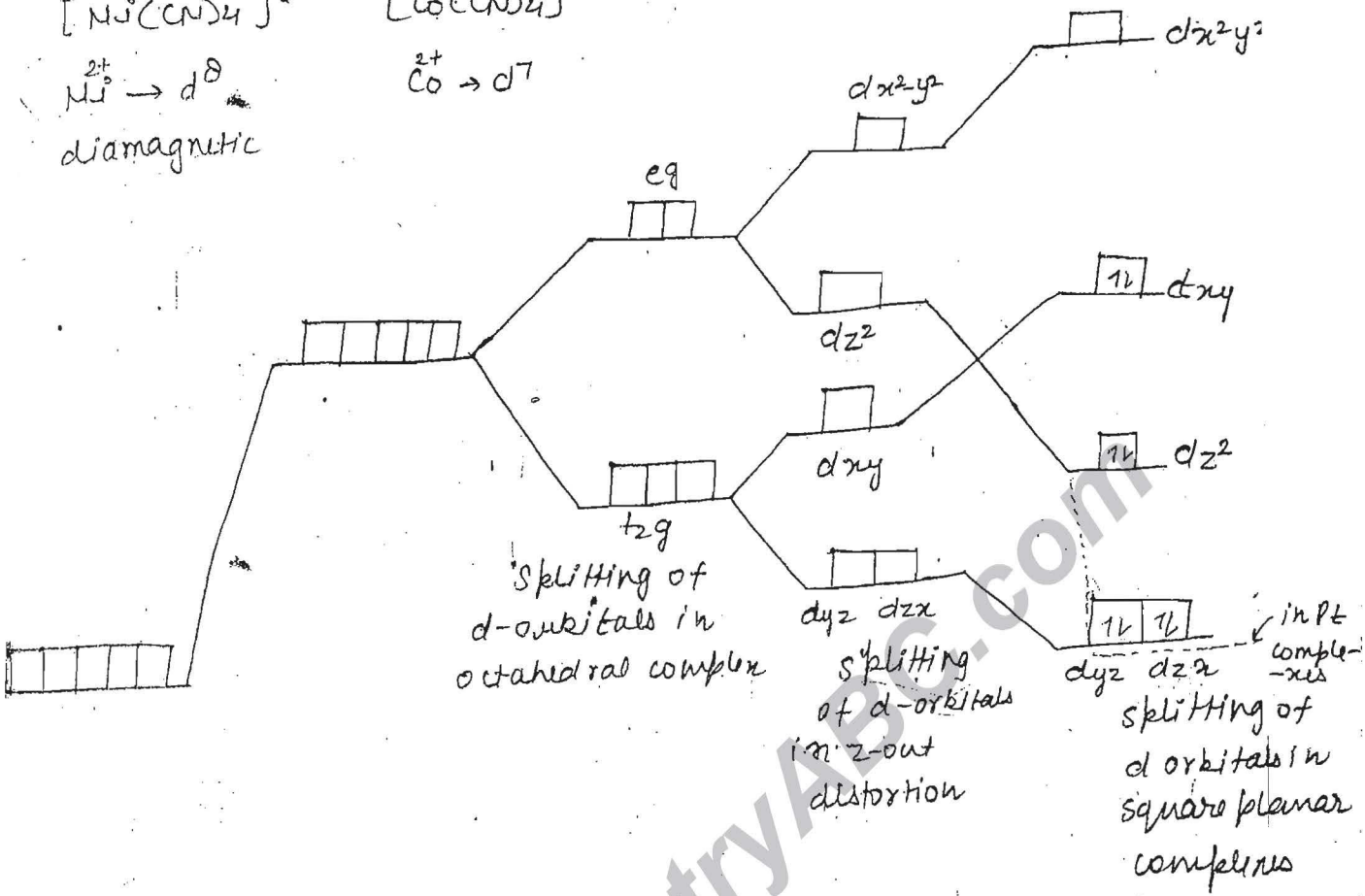


$[Ni(CN)_4]^{2-}$ $[Co(CN)_4]^{2-}$

$Ni^{2+} \rightarrow d^8$

diamagnetic

$Co^{2+} \rightarrow d^7$



Increasing order of energy of d-orbitals in square planar complexes

$$d_{yz} = d_{zx} < d_{z^2} < d_{xy} < d_{x^2-y^2}$$

23/09/13

Ligand Field Theory (LFT) or MOT

(Adjusted crystal field theory)

Limitations of CFT ⇒

CFT LIMITATION

① A/c to CFT the bonding b/w metal & ligand is purely ionic or electrostatic but in the given example the Ni and CO both are

$Ni(CO)_4$ Ni CO

neutral, hence there is no possibility of ionic bonding, only covalent bonding is possible.

② According to ESR, NQR spectroscopy, there is covalent character b/w metal and ligand. {ESR → Electron spin resonance. NQR → Nuclear quadrupole resonance}

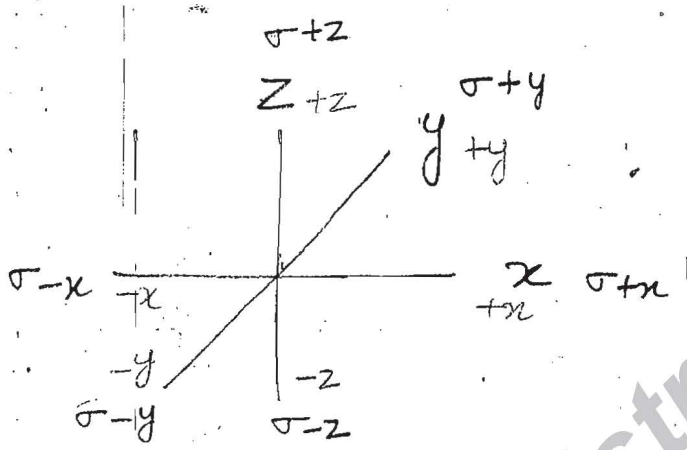
③ A/c to Nephelauxetic effect (delocalisation of d electrons of metals or ligands) there is covalent bonding b/w metal and ligand.

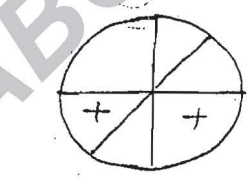
For σ-bonding in octahedral complexes ⇒

metal	s	a_{1g}
	px, py, pz	t_{1u}
	dxy, dyz, dzx	t_{2g}
	dx^2-y^2, dz^2	eg.

Ligand group orbitals (LGOs) ⇒

According to molecular orbitals calculations, the orbitals of all the ligands combine together and form new types of orbitals which have different symmetries and these orbitals are called ligand group orbitals (LGOs).





s- gerade
(a1g)

$$a_{1g} = \frac{1}{\sqrt{6}}(\sigma_{+x} + \sigma_{-x} + \sigma_{+y} + \sigma_{-y} + \sigma_{+z} + \sigma_{-z})$$

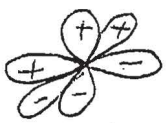
$$t_{1u} = \frac{1}{\sqrt{2}}(\sigma_{+x} - \sigma_{-x})\ \Sigma_x$$

$$\frac{1}{\sqrt{2}}(\sigma_{+y} - \sigma_{-y})\ \Sigma_y$$

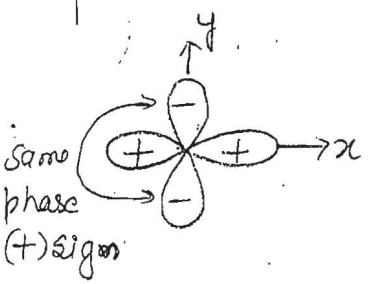
$$\frac{1}{\sqrt{2}}(\sigma_{+z} - \sigma_{-z})\ \Sigma_z$$

(p-orbital)

→ sign due to opposite phases

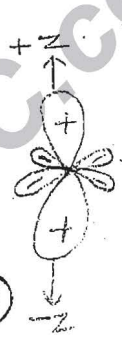


eg Σx^2-y^2 $\frac{1}{2}\{\sigma_{+x}+\sigma_{-x}-(\sigma_y+\sigma_{-y})\}$



$= \frac{1}{2}(\sigma_{+x}+\sigma_{-x}-\sigma_y-\sigma_{-y})\left\{\frac{1}{\sqrt{1^2+1^2+1^2+1^2}}\right.$

$\Sigma z^2 = 2\sigma_{+z}+2\sigma_{-z}$



$\Sigma z^2 = 2\sigma_{+z}+2\sigma_{-z}-(\sigma_{+x}+\sigma_{-x})-(\sigma_{+y}+\sigma_{-y})$

$dz^2 = d_{2z^2-x^2-y^2}$

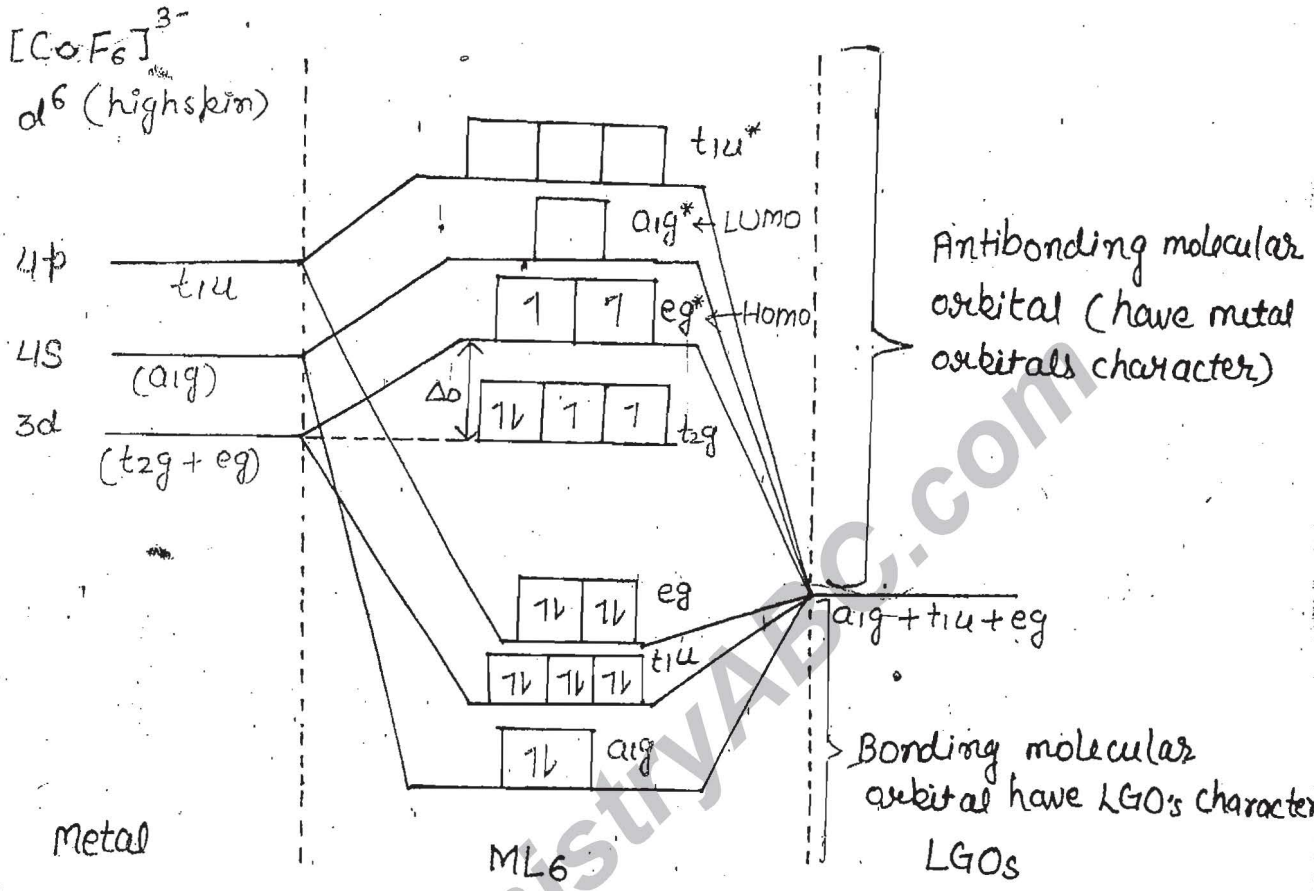
$= \frac{1}{\sqrt{12}}(2\sigma_{+z}+2\sigma_{-z}-\sigma_{+x}-\sigma_{-x}-\sigma_{+y}-\sigma_{-y})$

$= \frac{1}{2\sqrt{3}}(2\sigma_{+z}+2\sigma_{-z}-\sigma_{+x}-\sigma_{-x}-\sigma_{+y}-\sigma_{-y})$

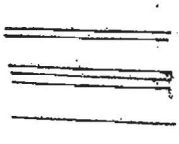
The LGOs having σ-symmetry = 6

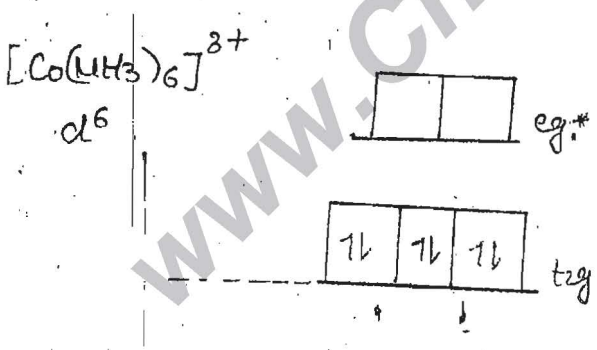
$\left\{\begin{matrix} 6 = & 1a_1g \\ & 3t_1u \\ & 2\,eg \end{matrix}\right\}$

Molecular orbital diagram for octahedral complexes (σ-bonding)



⇒ All 12 e⁻s in Bonding molecular orbital are of ligand because ligand donates its e⁻ to e⁻ deficient metal.





⇒ Ligands have energy lower than metals because ligands are non metals while metals are electropositive.

π- bonding in octahedral complexes

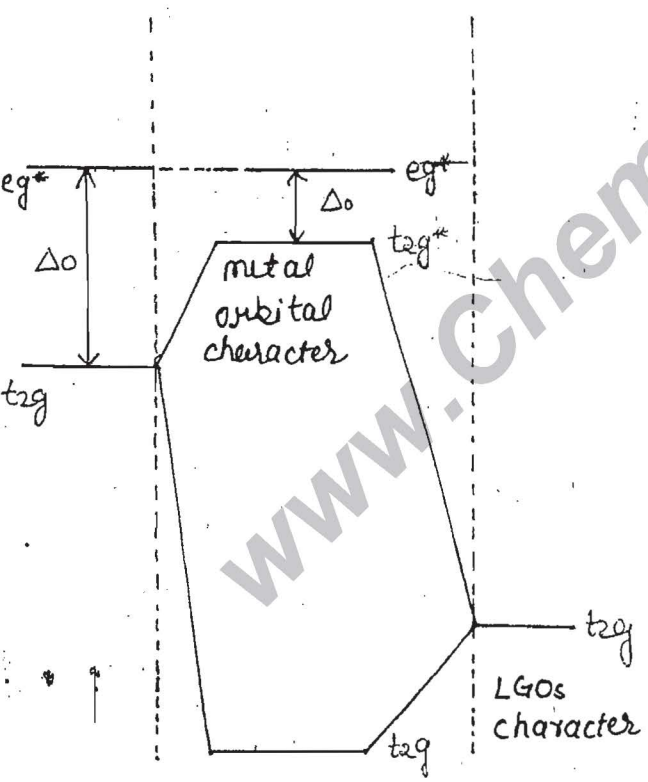
Acc to LFT, ligands may be-

Ligands → π-donors
Ligands → π-acceptors

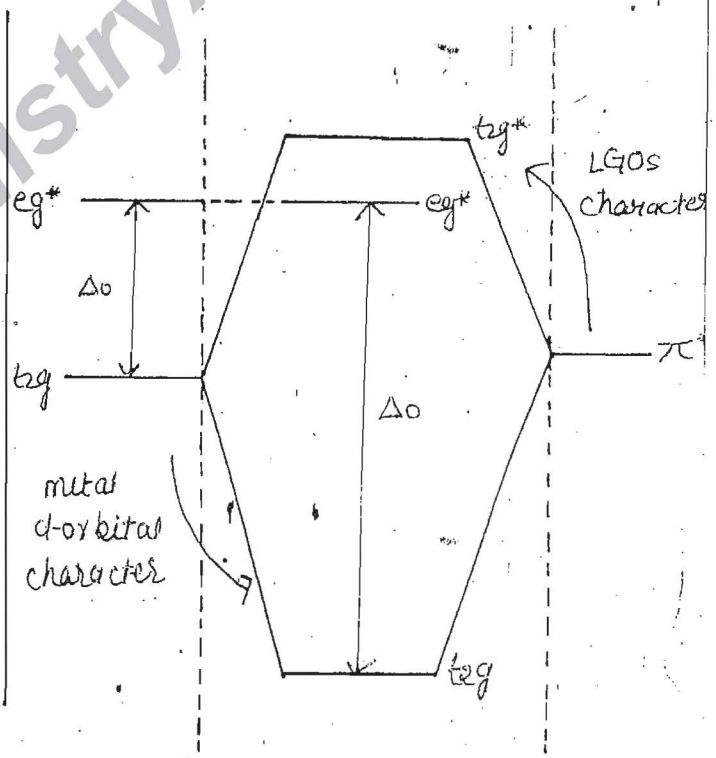
π- donors ⇒ F^-, Cl^-, Br^-, I^-, H_2O, OH^-, S^{2-} etc.

π- acceptors ⇒ have vacant π* Examples ⇒ CO, CN^-, NO, olefins, bpy, phen

π- donor

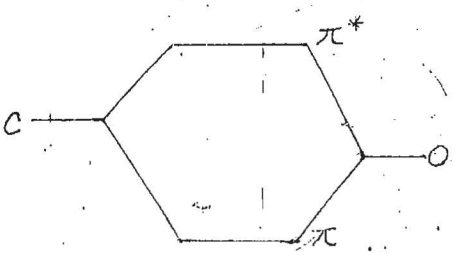


π- acceptor



⇒ The symmetry of t2g matches with π* not with π.

⇒ The energy of t2g is comparable with π*.



decreasing order π-donar tendency →

neither π-donor nor π-acceptor

$I^- < Br^- < S^{2-}, SCN^- < Cl^- < N_3^- < F^- < OH^- < H_2O < NH_3 < en, tpn < bpy, phen$

increasing order of π acceptor tendency

exceptions (strong σ donor)

$< NO_2^- < CH_3^- < C_6H_5^- < R_3P < CN^-, CO < NO$

Q⇒ CH_3^- and $C_6H_5^-$ are -

(a) only strong σ donor

(b) σ donor and π donor

(c) σ donor and π acceptor

(d) only π-acceptors

Types of π-bonds ⇒

① $d\pi - d\pi$

② $d\pi - p\pi$

③ $d\pi - \pi^*$

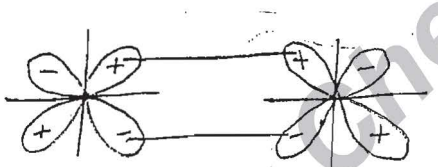
④ $d\pi - \sigma^*$

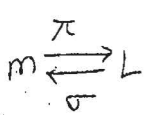
26/05/13

① $d\pi - d\pi$

Examples ⇒ R_3P, R_3As, R_3S etc.

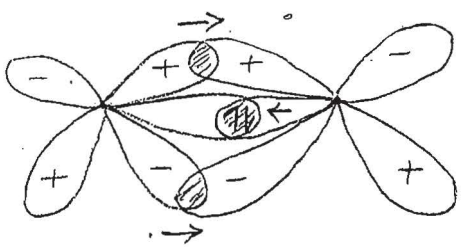
π electrons are donated from metal (t_{2g}) orbitals to vacant d-orbitals of the ligands.





metal — ligand

Low oxidation states (0, -1, +1 or some times +2)

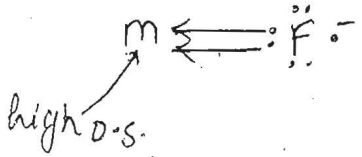


↙ electrone → donates e⁻

$Na[M(CO)_x]$ ← metal in -1 oxidation state.

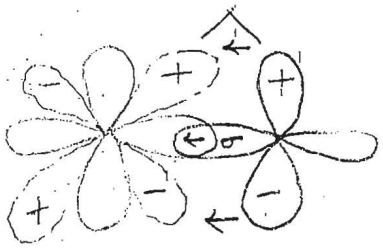
② $d\pi - p\pi$

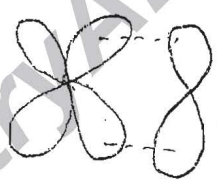
Examples ⇒ F^-, Cl^-, Br^-, I^-, H_2O, S^{2-}, OH^- etc



π-electron pair is donated from p-orbitals of the ligand to the d-orbitals of the metal.

less distance → π bond can be formed



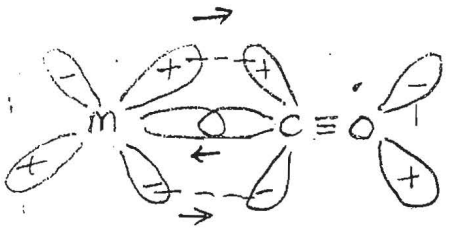


dxy px or py

③ $d\pi - \pi^*$

Examples ⇒ CO, $C\bar{N}$, NO, bpy, phen, olefins

π-acceptors



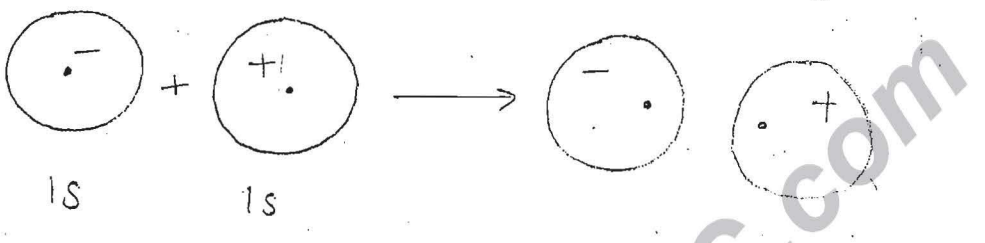
π-bond → metal to ligand

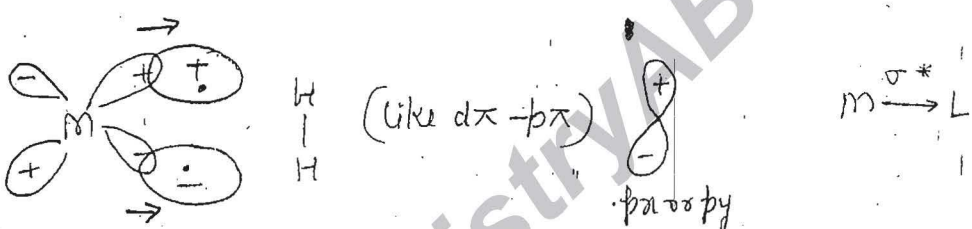
electron pair is donated from d-orbitals (t_{2g}) to vacant π^* of the ligands.

(4) $d\pi - \sigma^*$ (dominates over $d\pi - d\pi$)

Examples ⇒ R_3P, R_3As, R_2S, H_2 etc. (Having -C-H (σ bonding of alkylgp.)

$H_2 \rightarrow 2e^- \rightarrow \sigma 1s^2\ \sigma^*_{1s}{}^0$





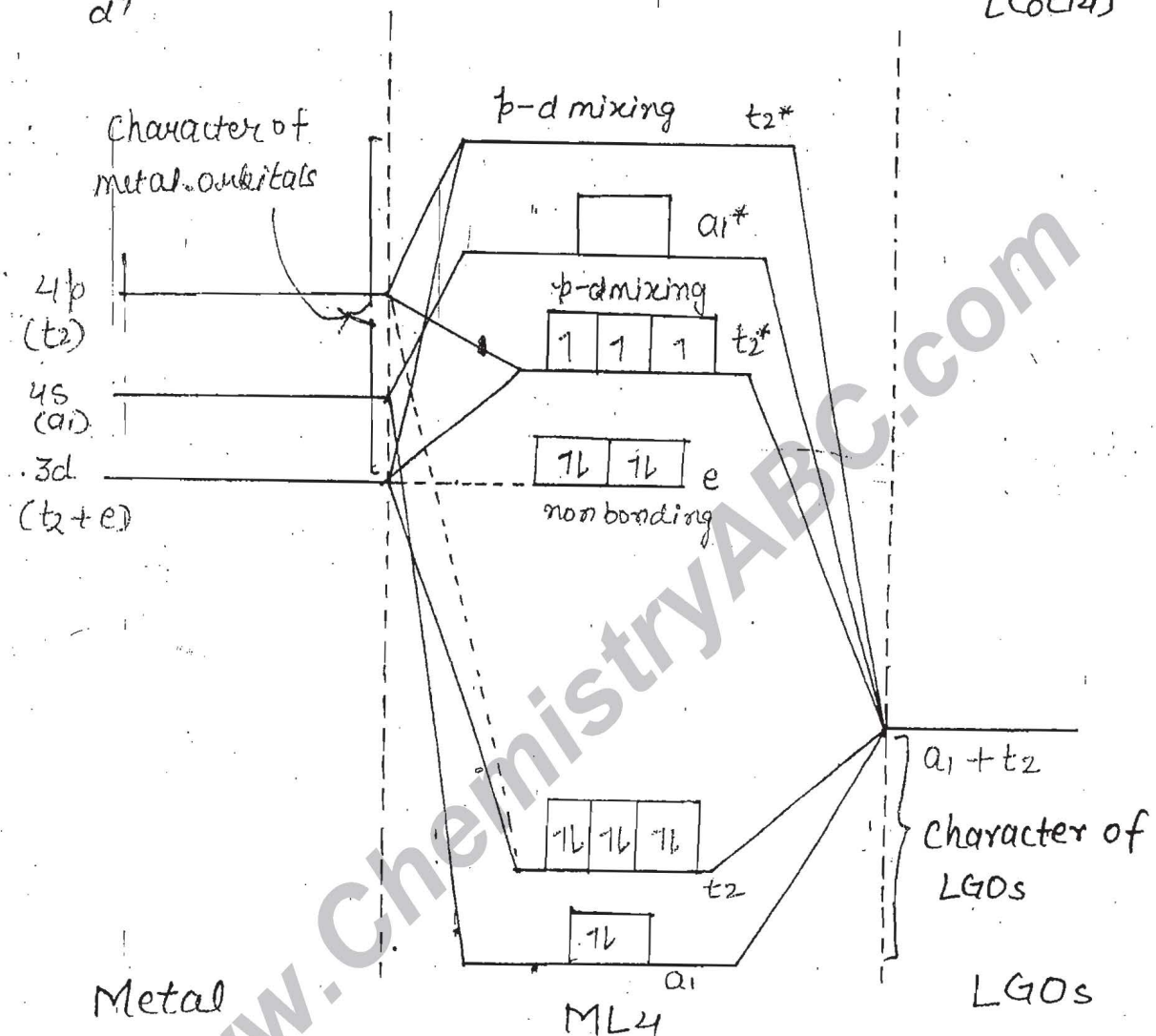
Molecular orbital diagram for σ-bonding in tetrahedral complexes ⇒

Example :-

$[CoCl_4]^{2-}$, $[NiCl_4]^{2}$

$[CoCl_4]^{2-}$

d^7



The symmetry of t_2 (4p) and t_2 (3d) are same, therefore both can bonded with Ligand's t_2 (p) but as the energy gap b/w t_2 (dxy, dyz, dzx) & and t_2 (Ligand) is less as compared to t_2 (px, py, pz) & metal, there will be more contribution from t_2 (dxy, dyz, dzx) and less contribution from t_2 (px, py, pz).

COLOUR & ELECTRONIC SPECTRA

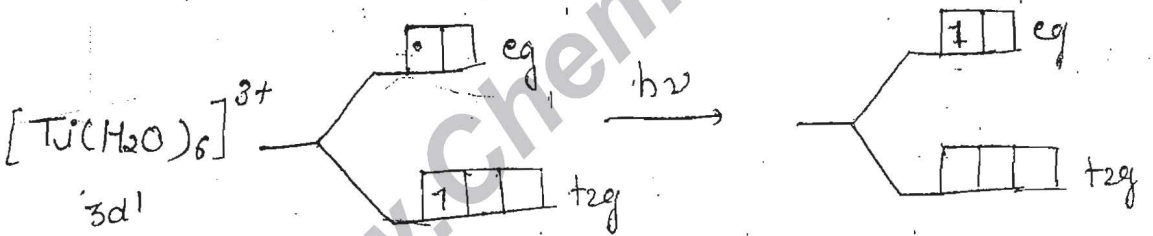
visible radiation

VIBGYOR

4000Å 7800Å

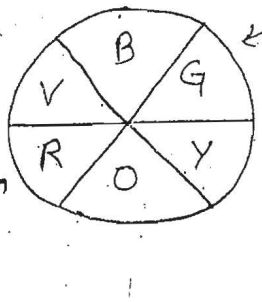
$$\Delta E = \frac{hc}{\lambda} = h\nu = hc\bar{\nu}$$

$\bar{\nu}$ = wave number = $\frac{1}{\lambda(cm)} = cm^{-1}$



→ Colour of absorbed radiation and that of reflected or transmitted radiations are complementary of one another.

Artist | Colour Wheel ⇒



Violet and Indigo colour are almost same and overlap each other so we can't different them.

A compound absorbs red → appears green

V + I + B + G + Y + O + R ⟶ Colourless

If red colour absorbed then

Reflected colour → V + I + B + G + Y + O (Green)

V + I + B + Y + O → Green

⇒ If all the radiations of visible lights are reflected → White or colourless

⇒ If all the radiations of visible lights are absorbed → Black

origin of colour ⇒

Excitation of an electron from lower energy state (grand state) to the higher energy state (excited state).

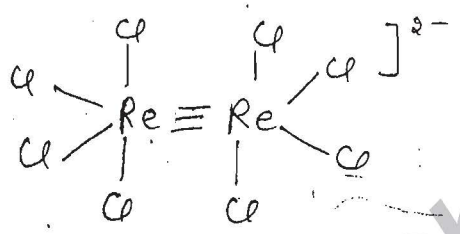
Types of transitions ⇒

① d-d transition
② charge transfer
} complexes

③ $\delta - \delta^*$ → cluster compounds containing m-m quadrupel bonds (m≡m)

Ex:- $Re_2Cl_8^{2-}$, $Mo_2Cl_8^{2-}$

Royal blue Intense yellow



④ In organic compounds

$\sigma - \sigma^*$ → always colourless

$\pi - \pi^*$ → may be coloured or colourless

$n - \pi^*$

$n - \sigma^*$

coloured: when conjugation is more → energy decreases → absorption occur in visible region

colourless: when no conjugation → energy high → absorption cant possib in visible region.

e.g. CH_3COCH_3 ↑ colourless

(5) Non metals → O_2, N_2, F_2, Cl_2, Br_2, I_2

↓

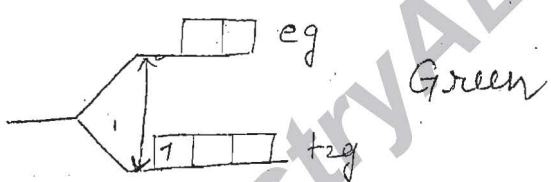
can be explained on the basis of MOT

(6) Non stoichiometric defects in solids (f-centre)

① Different colours of compounds ⇒

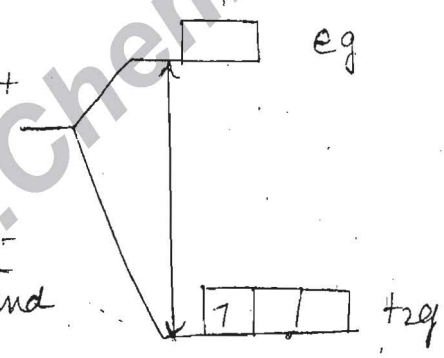
Depends upon energy difference b/w ground state and higher energy state.

$[TiCl_6]^{3-}$



Green

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



Violet

[water is comparatively strong ligand than Cl]

② Intensity of colours or Absorbance ⇒ Here we study about selection rules

P.T.O.

(i) Laporte Selection Rule →

$\Delta l = l_2 - l_1 = \pm 1$ Laporte allowed

Here,

l_1 and l_2 = azimuthal quantum number or orbital angular momentum quantum no.

$\Delta l = l_2 - l_1 = 0$ Laporte forbidden

OR

$g \leftrightarrow u$ → Laporte allowed

$g \leftrightarrow g$, $u \leftrightarrow u$ } Laporte forbidden

l_1	l_2	Δl
s ⟷ p		
0	1	1
p ⟷ d		
1	2	1
d ⟷ f		
2	3	1

OR

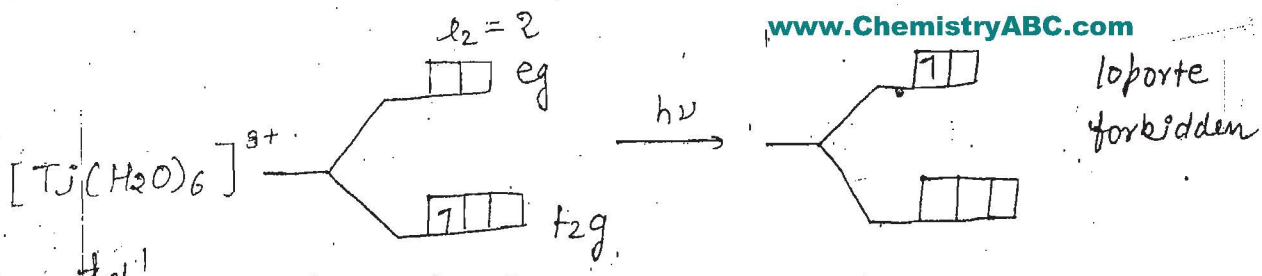
$s \rightarrow g$

$p \rightarrow u$

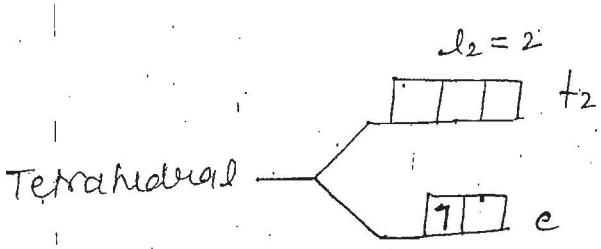
$d \rightarrow g$

$f \rightarrow u$

$g \rightarrow g$



$\Delta l = 0$

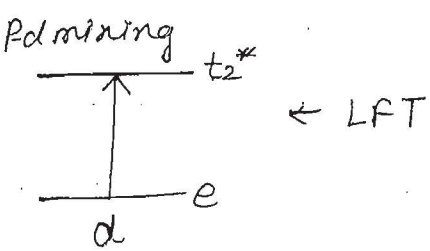


$\Delta l = 0$

CFT, a/c to ^should be Laporte forbidden
but it is partly allowed a/c to LFT

Relaxation in Laporte rule for d-d transition in tetrahedral complexes ⇒

In tetrahedral complexes
(no centre of symmetry)
↓
Some p-d mixing
↓
d-d transition is partly allowed



Relaxation in Laporte rule for d-d transition in octahedral complexes ⇒

Spin selection Rule ⇒

⇒ No change in spin direction during electronic transition

$$\boxed{\text{d-d transition} \rightarrow \text{spin allowed}}$$

O.R $\boxed{\Delta S = S_2 - S_1 = 0 \rightarrow \text{spin allowed}}$

where,

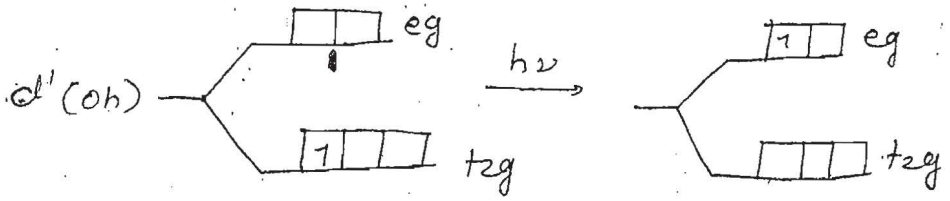
S_1 , S_2 → spin quantum numbers

⇒ If change in spin direction during electronic transition

$$\boxed{\text{d- d transition} \rightarrow \text{spin forbidden}}$$

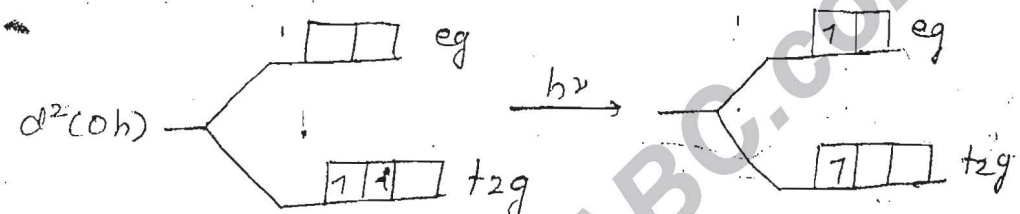
OR $\boxed{\Delta S \neq 0}$

Ex:-



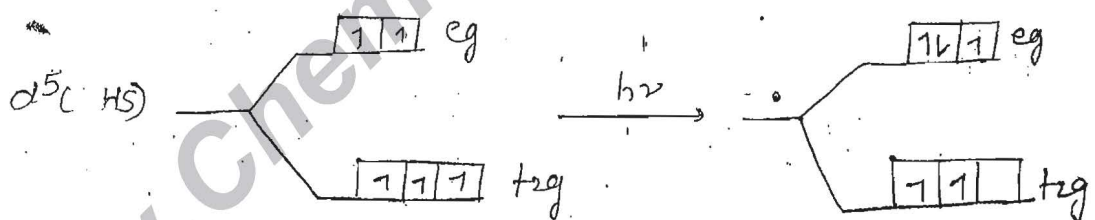
$S_1 = \frac{1}{2}$ $S_2 = \frac{1}{2}$

$\Delta S = \frac{1}{2} - \frac{1}{2} = 0 \rightarrow$ spin allowed



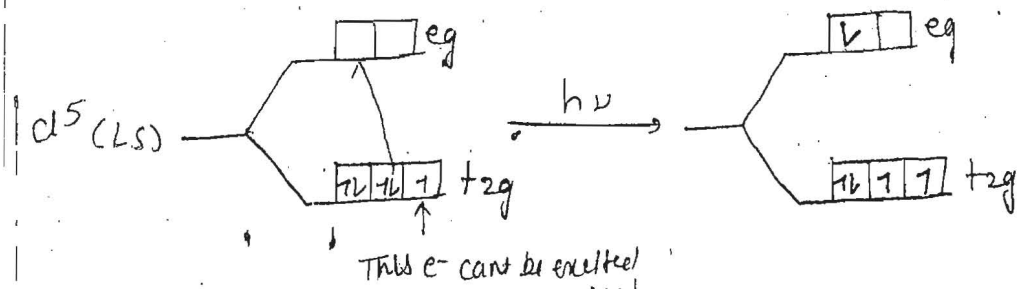
$S_1 = 1$ $S_2 = 1$

$\Delta S = 1 - 1 = 0$



$S_1 = \frac{5}{2}$ $S_2 = \frac{3}{2}$

$\Delta S = \left|\frac{3}{2} - \frac{5}{2}\right| = 1 \rightarrow$ spin forbidden



Pericyclic shortcut

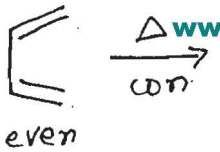
TEAC

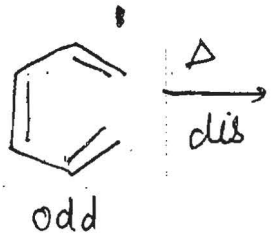
T → Thermal

E → even no. of π bonds

A → Antarafacial

C → conrotatory

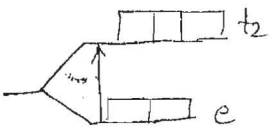




Peri-cyclic shortcut

Charge transfer ⇒ Transfer of an e⁻ from the orbitals of one species to the orbitals of another species is called charge transfer.

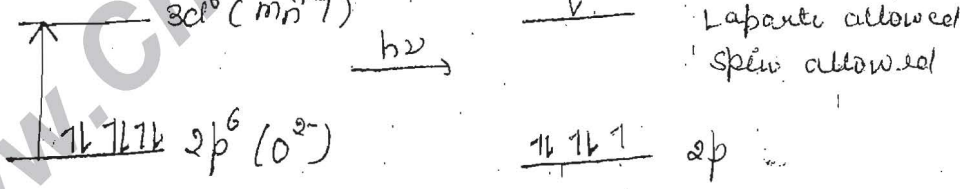
① MnO_4^- → Mn^{+7} → $3d^0 4s^0$ → no-d-d transition ✗



↓ no e⁻ in d-orbital

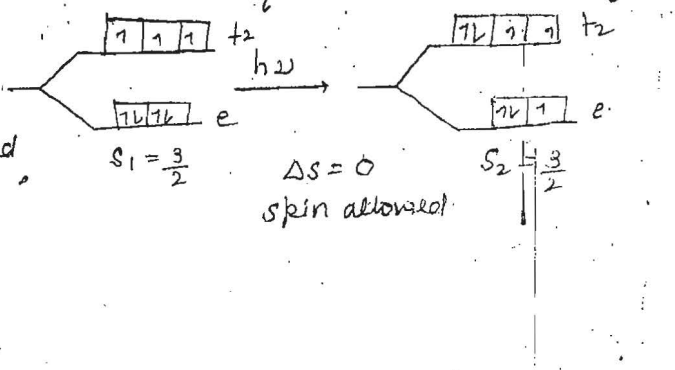
↓ Intense violet colour ($KMnO_4$)

In this case electrons are transferred from 2p of O^{2-} to 3d of Mn^{+7}



② d-d ⇒ $[CoCl_4]^{2-}$ → Co^{2+} → $3d^7$ →

{reference → S.M. Mukharjee}



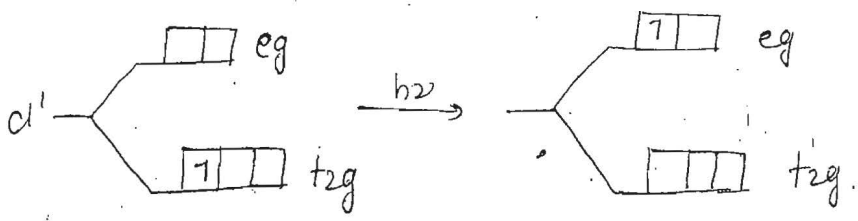
↓ Tetrahedral → Laporte partly allowed

Laporte selection Rule	Spin selection Rule	Type of spectra	Absorbance ($L mol^{-1} cm^{-1}$)	Examples
Allowed	Allowed	charge transfer	> 10,000	MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, CrO_3
Partly allowed	Allowed	d-d	800-1000	$[CoCl_4]^{2-}$, $[Co\,Br_4]^{2-}$
Forbidden	Allowed	d-d	~100	$[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, $[Ni(H_2O)_6]^{3+}$, $[Cu(H_2O)_6]^{3+}$
Partly allowed	forbidden	d-d	8-10	$[MnCl_4]^{2-}$, $[Mn\,Br_4]^{2-}$
5. Forbidden	forbidden	d-d	0.1-0.2	$[Mn(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$

Allowed + Allowed → intense colour — 1
Partly allowed + allowed → less intense — 2
Forbidden + allowed → very less intense — 3
Partly allowed + forbidden → very very less intense — 4
Forbidden + Forbidden → colourless — 5

↓ decreasing order of intensity

⇒ $[Ti(H_2O)_6]^{3+} \rightarrow 3d^1$ — (3)

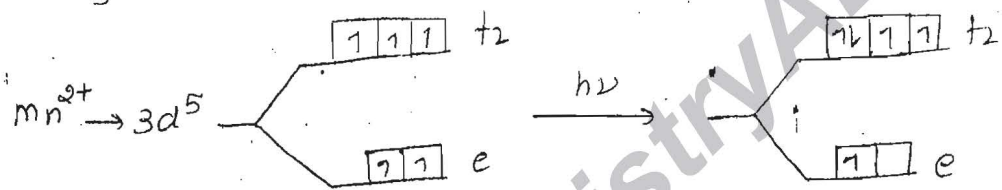


① octahedral → Laporte forbidden

② $S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$

$\Delta S = 0$ → spin allowed

⇒ $[MnCl_4]^{2-}$ — (4)

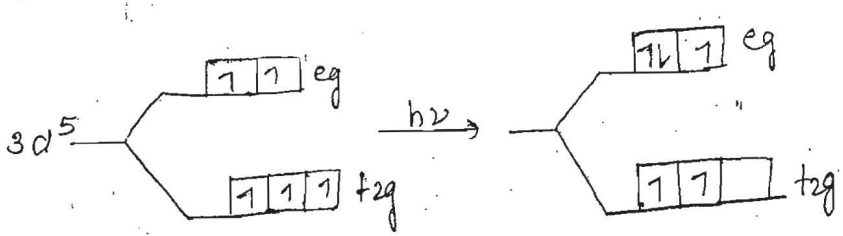


① Tetrahedral → Laporte partly allowed → p-d mixing

② $S_1 = \frac{5}{2}$, $S_2 = \frac{3}{2}$

$\Delta S = \left|\frac{3}{2} - \frac{5}{2}\right| = 1$ → spin forbidden

⇒ $[Mn(H_2O)_6]^{2+}$ — (5)



① octahedral → laporte forbidden

② $S_1 = \frac{5}{2}$, $S_2 = 3/2$, $\Delta S = 1$ → spin forbidden

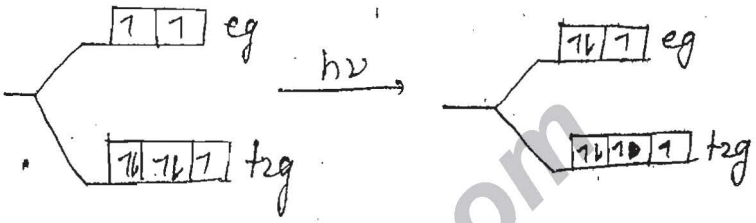
If upper levels in which excited e⁻ is going to accomodate is vacant spin of e⁻ will not be changed but if those are filled → spin will be chan

Q→ Arrange the following in the increasing order of their absorbance or intensity.

$[CoCH_2O)_6]^{2+}$, CrO_3 , $[VCl_4]^-$, $[TiCl_6]^{2-}$, $[Mn(NH_3)_6]^{2+}$

$[TiCl_6]^{2-} = CrO_3 > VCl_4^- > [Co(H_2O)_6]^{2+} = [Mn(NH_3)_6]^{2+}$

→ $[Co(H_2O)_6]^{2+}$ → Co^{2+} → $3d^7$



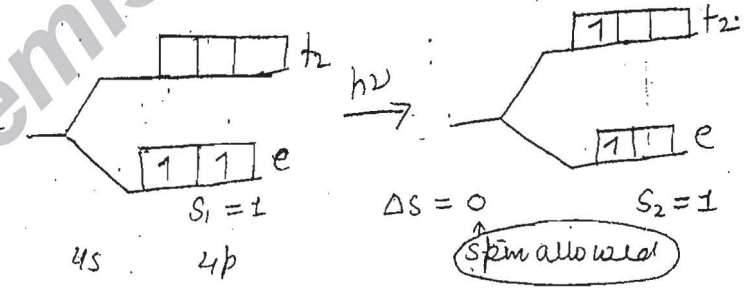
① octahedral → Laporte forbidden

② $S_1 = 3$, $S_2 = 3$

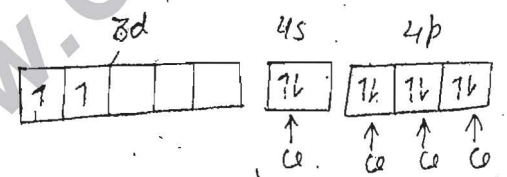
$\Delta S = 0$ Spin allowed

CrO_3

→ $[VCl_4]^-$ → V^{3+} → $3d^2$

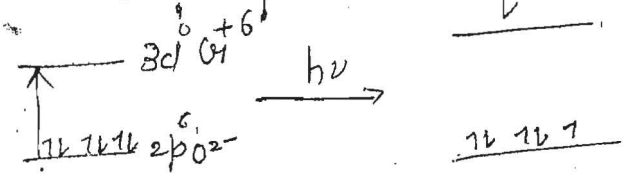


V^{3+} →



sp^3 → Tetrahedral → Laporte partly allowed

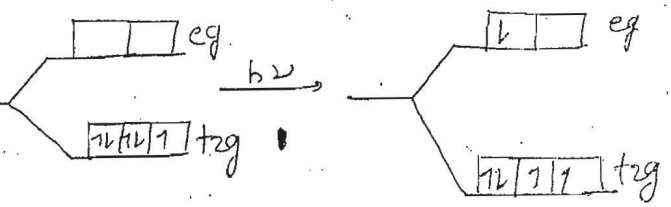
$CrO_3 \rightarrow Cr^{+6} \rightarrow 3d^0\ 4s^0$



Laporte allowed
Spin allowed

$TiCl_6^{2-} \rightarrow Ti^{+4} \rightarrow 3d^0 4s^0$

$[Mn(NH_3)_6]^{2+} \rightarrow Mn^{2+} \rightarrow d^5$



① octahedral → Laporte forbidden

② $S_1 = \frac{1}{2}$, $S_2 = \frac{1}{2}$ $\Delta S = 0$ → Spin allowed

Charge Transfer Spectra

27/09/13

Charge transfer ⇒ Electrons are transferred from one species to the orbitals of another species.

orbitals of

Classification ⇒

① Ligand to metal charge transfer (LMCT)

② metal to ligand charge transfer (MLCT)

③ Intervalence charge transfer

④ Intraligand charge transfer

① LMCT ⇒ electron transfer from ligand to metal

conditions ⇒ i) metal in high oxidation state

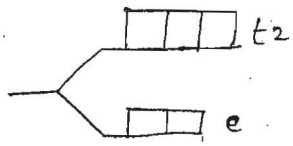
ii) ligand electron rich

iii) vacant d-orbitals on metal

Examples ⇒ MnO_4^- , CrO_4^{2-} , $Cr_2O_7^{2-}$, $[TiCl_6]^{2-}$, CrO_3 , CdS etc.

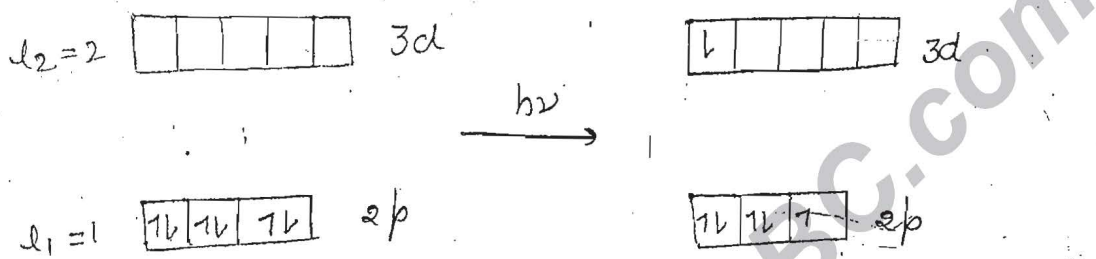
MnO_4^- ⇒ $Mn \rightarrow 3d^5 4s^2$

$Mn^{+7} \rightarrow 3d^0 4s^0$



No d-d transition

Electron transfer from $2p^6$ of O^{2-} to $3d^0$ of Mn^{+7}



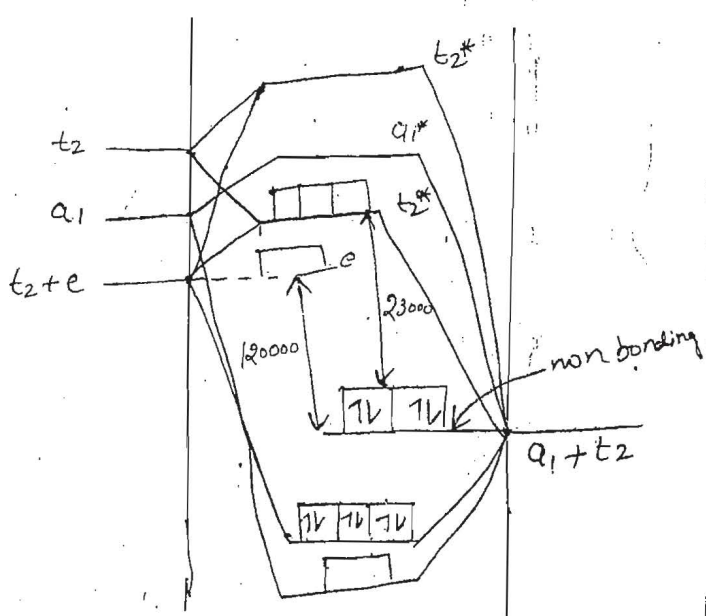
$\Delta l = 2 - 1 = 1 \rightarrow$ Laporte allowed

$\Delta S = 0 \rightarrow$ spin allowed

} Intense violet colour

Q⇒ MnO_4^- absorbs at 12000 cm^{-1} and 23000 cm^{-1} and show two peaks in its electronic spectrum. Calculate Δt.

At a time a ligand donates one lone pair to metal, hence there are some non bonding e^-s on that ligand which can be excited to higher energy levels depending on radiation.



$\Delta t = 11000 = (23000 - 12000)\ cm^{-1}$

Q⇒ $[TiCl_6]^{2-}$ absorbs at 20000 cm^{-1} and 30000 cm^{-1} and show two peaks in its electronic spectrum. Calculate Δ_o.

$\Delta_o = 10,000$

Energies of LMCT

Energies of LMCT ⇒

coloured absorbed in Vis. region	MnO_4^-	$3d^0$	$2p \rightarrow 3d$
	TcO_4^-	$4d^0$	$2p \rightarrow 4d$
colourless absorbed in UV due to high energy gap	ReO_4^-	$5d^0$	$2p \rightarrow 5d$

increasing order of LMCT energy ↓

decreasing order of oxidising power ↓

14 Oct ⇒ The correct order of LMCT energies is-

(a) $MnO_4^- < CrO_4^{2-} < VO_4^{3-}$

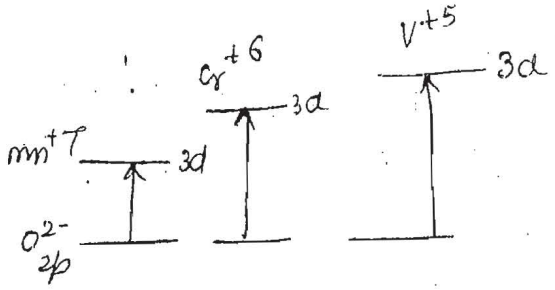
(b) $MnO_4^- > CrO_4^{2-} > VO_4^{3-}$

(c) $MnO_4^- > CrO_4^{2-} < VO_4^{3-}$

(d) $MnO_4^- < CrO_4^{2-} > VO_4^{3-}$

$\overset{+7}{Mn}O_4^- < \overset{+6}{Cr}O_4^{2-} < \overset{+5}{V}O_4^{3-}$

$_{25}Mn$ $3d^0$ $\quad$ $_{24}Cr$ $3d^0$ $\quad$ $_{23}V$ $3d^0$



V^{+5} $\quad$ Cr^{+6} $\quad$ Mn^{+7} → decreasing order of size

→ decreasing order of energy

Q 7.

decreasing order of M-L bond length

CrO_4^{2-} (+6) $\quad MnO_4^{2-}$ (+6) $\quad FeO_4^{2-}$ (+6) $\quad CoO_4^{2-}$ (+6)

→

Increasing order of oxidising power

decreasing order of stability

MnO_4^{-} (+7) $\quad CrO_4^{2-}$ (+6) $\quad VO_4^{3-}$ (+5)

→

decreasing order of oxidising power

$ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$

order of strong oxidising power

② metal to ligand charge transfer ⇒ Electron transfer from metal d-orbitals to empty π^* of the ligand

Conditions ⇒ (i) metal low oxidation state (0, -1, +1, +2)

(ii) ligand → vacant orbitals

Examples ⇒ CO, CN^-, NO, phen, bpy etc.

→ π-acceptors

$[Fe(phen)_3]^{2+}$; Hemoglobin (Fe^{+2} (HS)) → blue $(t_{2g}^4 e_g^2)$ e- transfers from eg ; oxy hemoglobin (Fe^{+2} (LS)) → red $(t_{2g}^6 e_g^0)$ e- transfers from t_{2g}

③ Intervalence charge transfer ⇒

metal to metal electron transfer

↑ Low oxidation state ↑ high oxidation state

Ex:- Prussian blue

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

Turnbull blue

$Fe_4^{+3}[Fe^{+2}(CN)_6]_3$

⇒ A/c to modern ESR, Prussian blue & turnbull blue are identical not different.

Electron transfers from Fe^{2+} to Fe^{3+}.

Ex:- $[(H_3N)_5Ru^{+2}-N\langle\rangle N-Ru^{+3}(NH_3)_5]^{+5}$ ← shows intense colour

Ex:- Pb_3O_4 $\quad 2PbO \cdot PbO_2$

red colour $\quad Pb^{2+} \rightarrow Pb^{4+}$

Q⇒ $Fe^{+2} + K_3[Cr(CN)_6] \longrightarrow$ complex (red) $\xrightarrow{100^\circ C}$ complex (green)

ionisation Isomers

$KFe[Cr(CN)_6]$ ← red

↓ 100°C

$KCr[Fe(CN)_6]$ ← green

Q⇒ Cu(II) form pink complex with o-phenanthroline $[Cu(Phen)_3]$ when this complex is reduced, the colour of the complex disappears. The colour of the complex is due to:

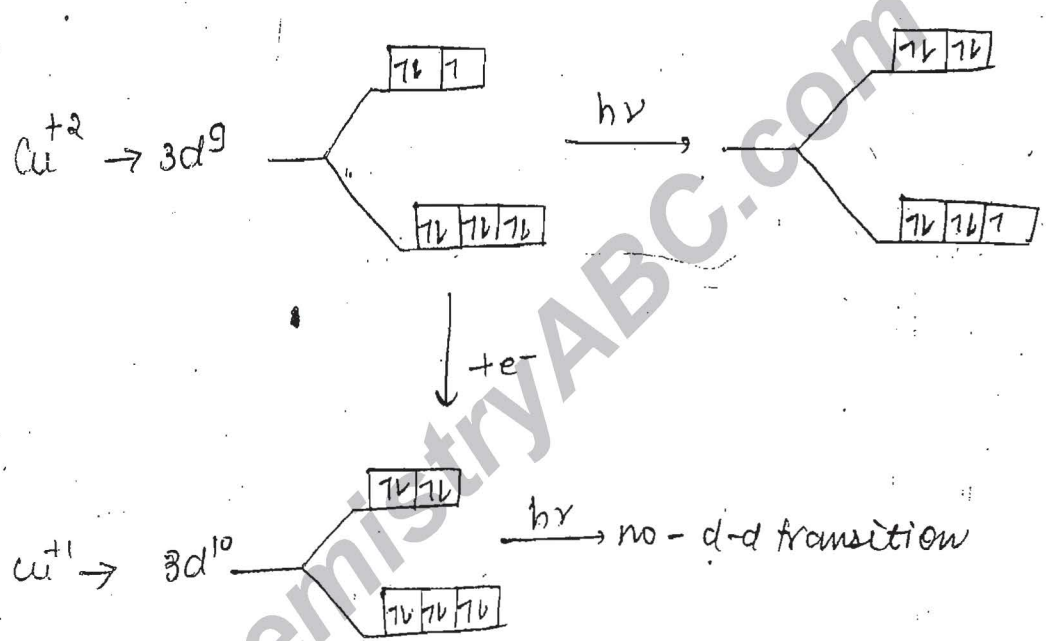
(a) LMCT

(b) MLCT

(c) Intraligand CT

✓ (d) d-d transition

Sol⇒



④ Intraligand charge transfer ⇒

Chromophores ⇒ Coloured

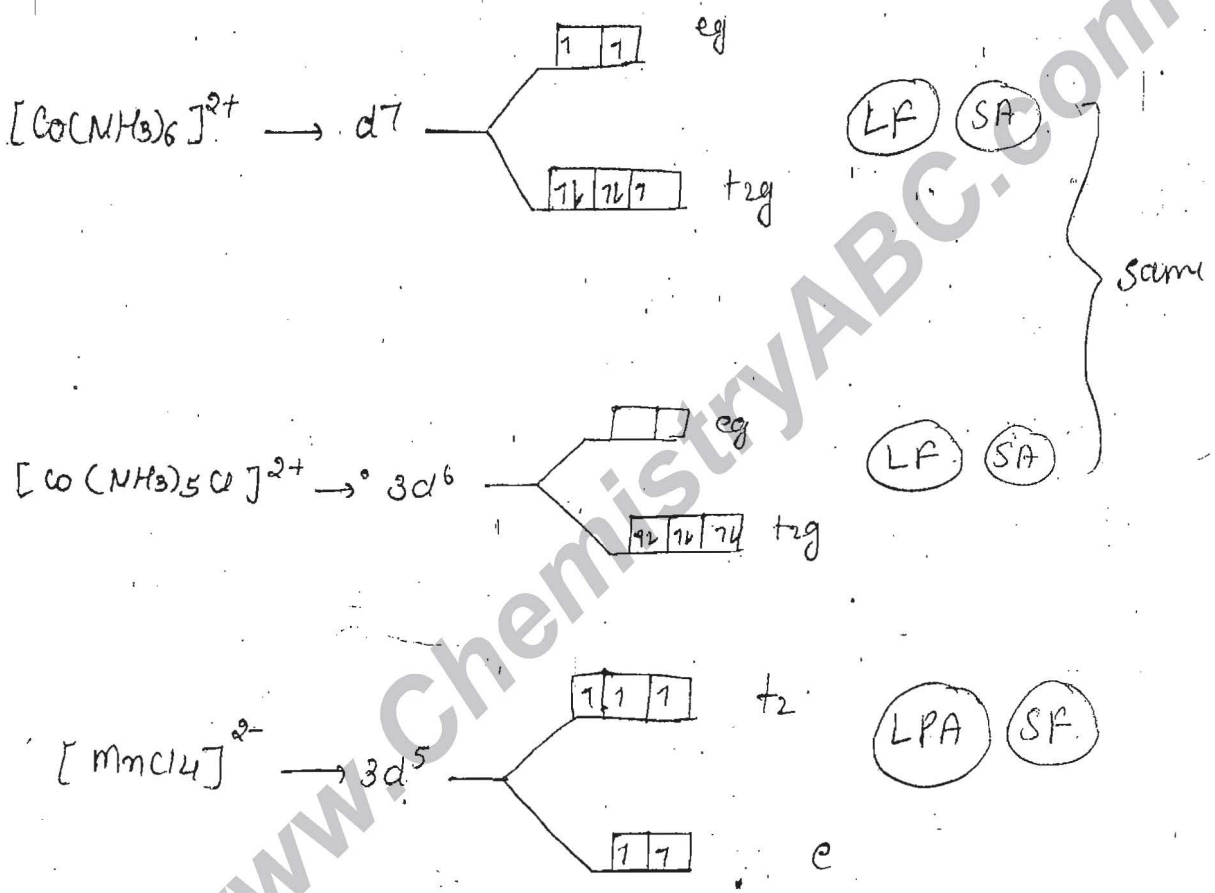
44 Q ⇒ The absorption of $Co(NH_3)_6^{2+}$ is —

(a) Stronger than that of $[Co(NH_3)_5Cl]^{2+}$

(b) Stronger than that of $[MnCl_4]^{2-}$

(c) Weaker than that of $[MnCl_4]^{2-}$ but stronger than that of $[Co(NH_3)_5Cl]^{2+}$

(d) Weaker than those of both $[MnCl_4]^{2-}$ and $[Co(NH_3)_5Cl]^{2+}$



ELECTRONIC SPECTRA

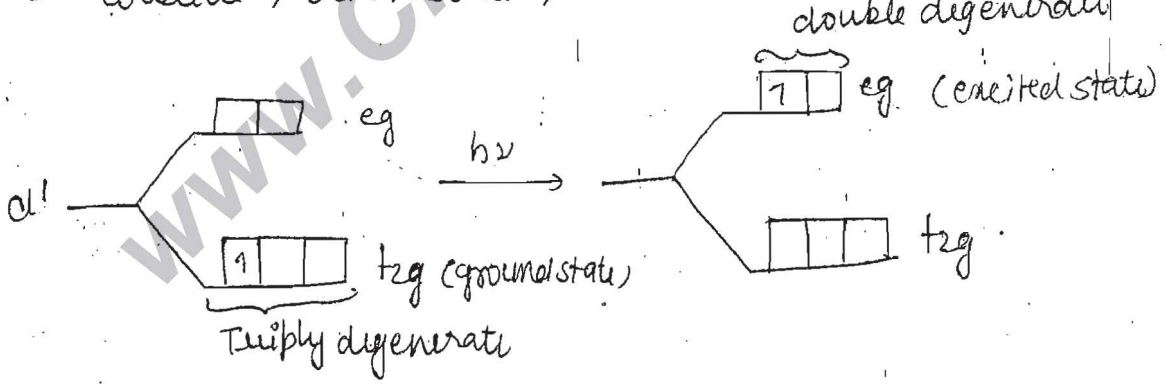
System	Ground state term symbol	First excited state with same spin multiplicity
d^1, d^9	^2D	—
d^2, d^8	^3F	^3P
d^3, d^7	^4F	^4P
d^4, d^6	^5D	—
d^5	^6S	—

Mulliken Term Symbols: MULIKEN

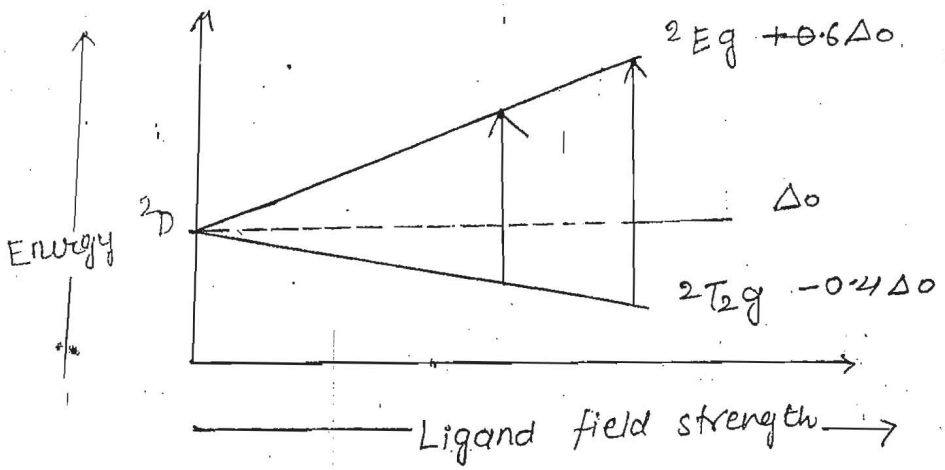
Atomic spectroscopic term symbol	Mulliken term symbols	
	octahedral	Tetrahedral
S	A_1g	A_1
P	T_1g	T_1
D	$T_2g + Eg$	$T_2 + E$
F	$T_1g + T_2g + A_2g$	$T_1 + T_2 + A_2$

Orgel diagram and electronic spectra ⇒

① d^1 – orbital ⇒ octahedral ⇒



Ground state term → $^2D \longrightarrow {}^2T_{2g} + {}^2Eg$

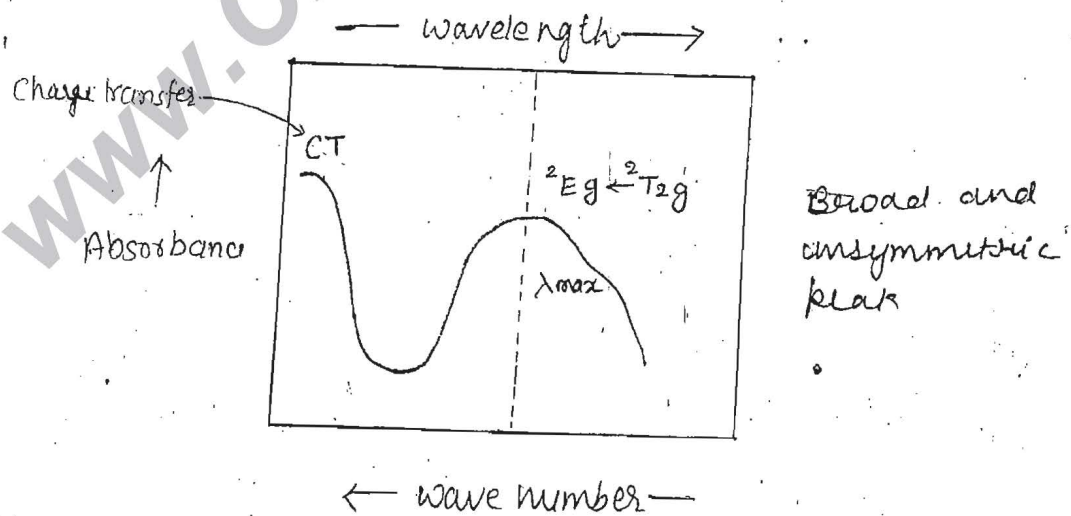


$[Ti(H_2O)_6]^{3+}$ $[Ti(CN)6]^{3-}$ $[TiF_6]^{3-}$

20300 cm^{-1} 22300 cm^{-1} 18900 cm^{-1}

One electronic transition and one peak

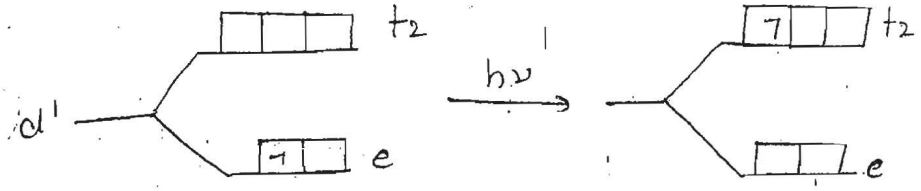
$^2Eg \leftarrow {}^2T_2g$



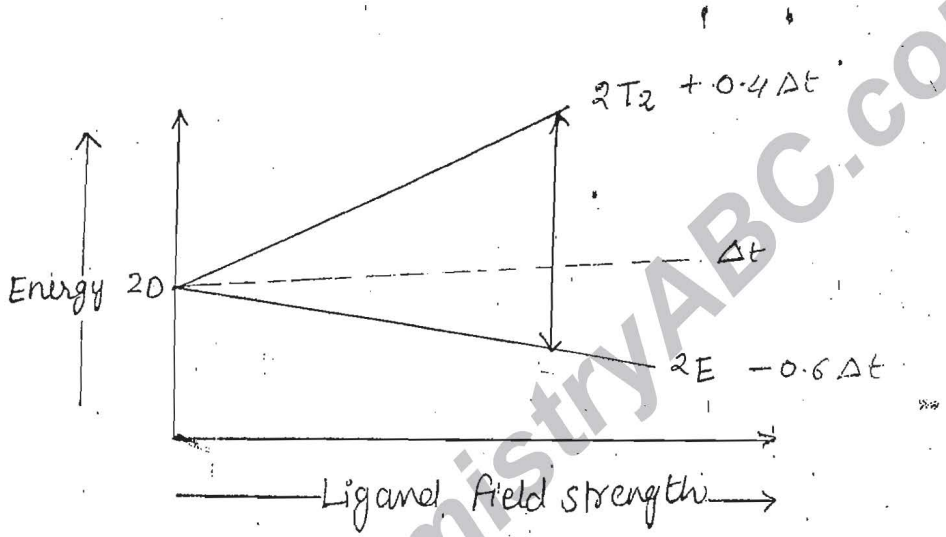
Broad and unsymmetric peak

λmax ⇒ At this wave length absorption is maximum

② d^1 tetrahedral ⇒

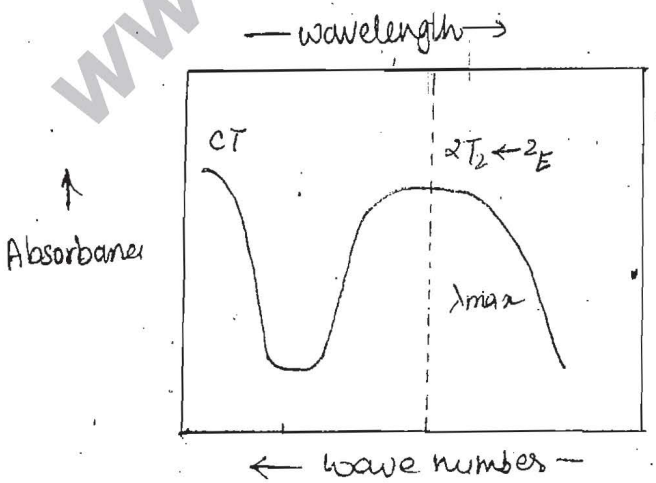


Ground state term $^2D \longrightarrow {}^2T_2 + {}^2E$

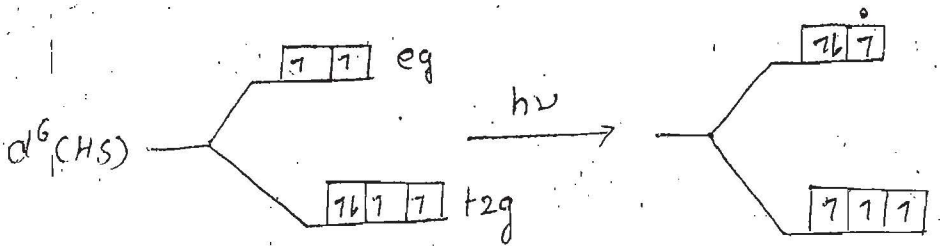


one transition one peak

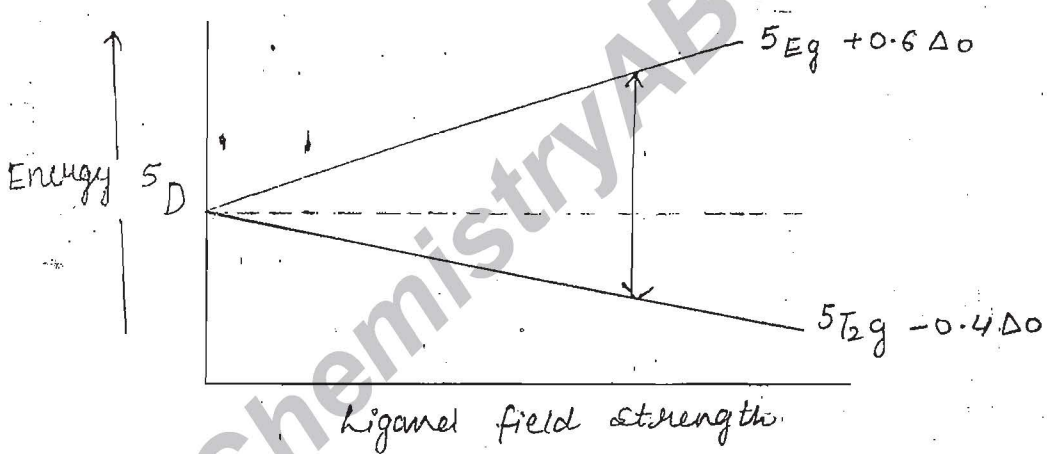
$^2T_2 \longleftarrow {}^2E$



d^6 (HS) octahedral ⇒



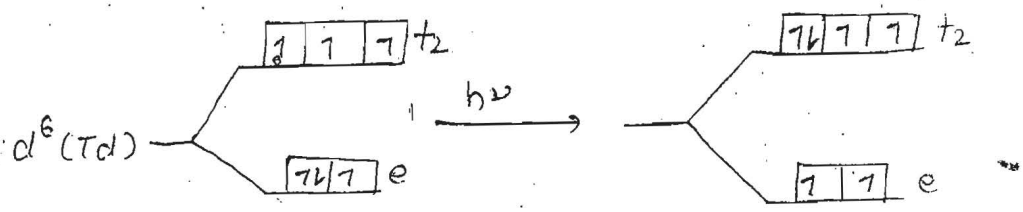
Ground state term → ^5D → $^5t_{2g} + {}^5E_g$



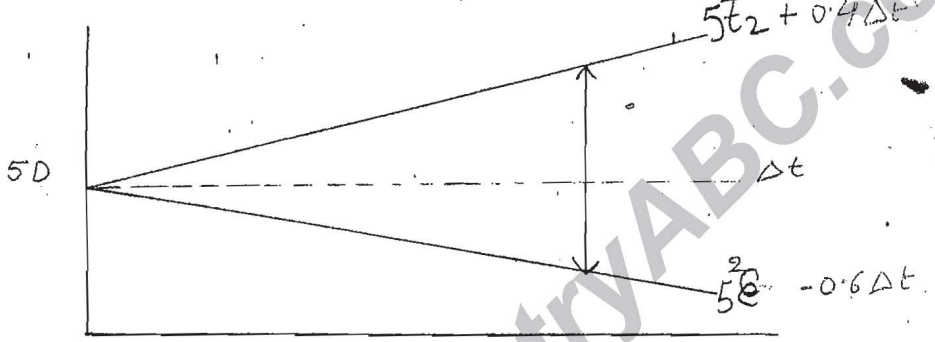
only one electronic transition → only one peak

$^5E_g \leftarrow {}^5T_{2g}$

d^6 tetrahedral ⇒



Grounel state term → $^5D \longrightarrow {}^5T_2 + {}^5E$

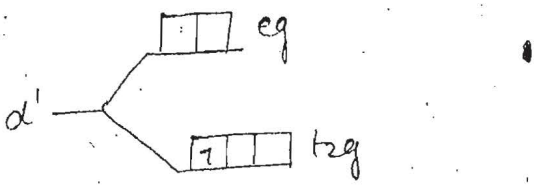


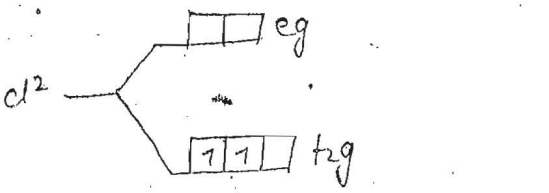
Only one transition → only one peak

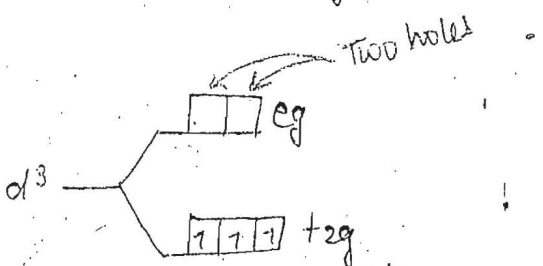
$^5T_2 \leftarrow {}^5E$.

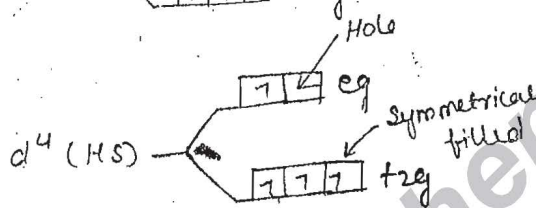
Hole Formulation ⇒

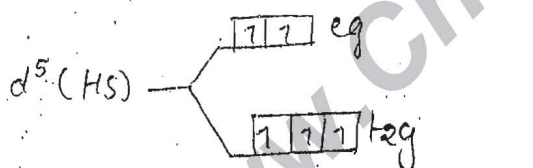
octahedral complexes ⇒

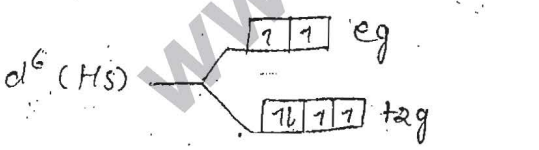


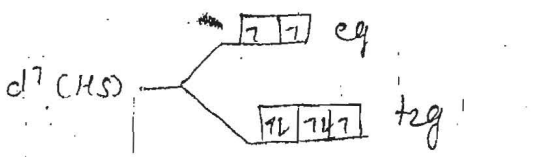


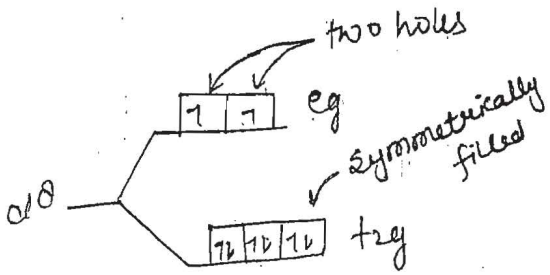


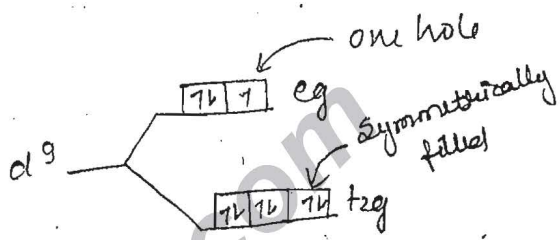


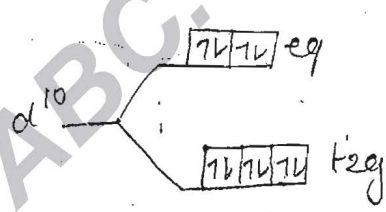








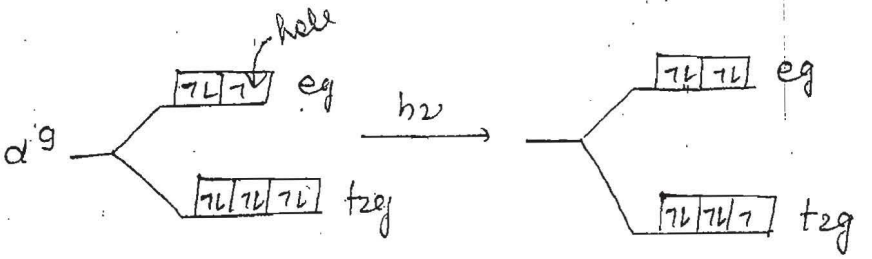




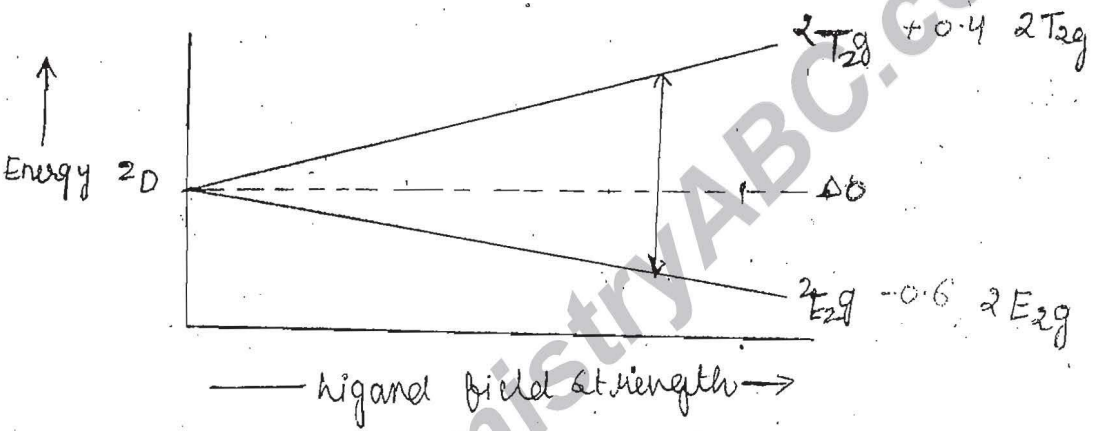
⇒ lower most energy levels must be symmetrically filled for hole formulation.

⇒ If in oh complexes hole is formed then hole will also be formed in Td complexes.

d^9 octahedral ⇒



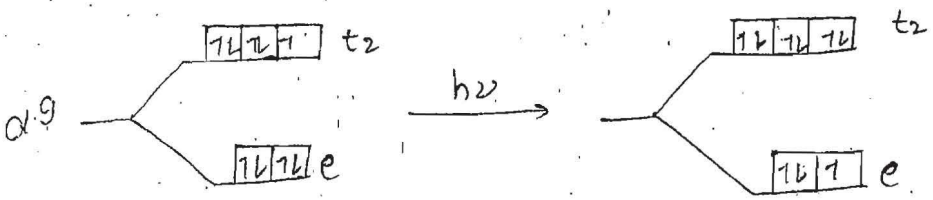
Ground state term → $^2D \longrightarrow {}^2T_{2g} + {}^2E_{eg}$



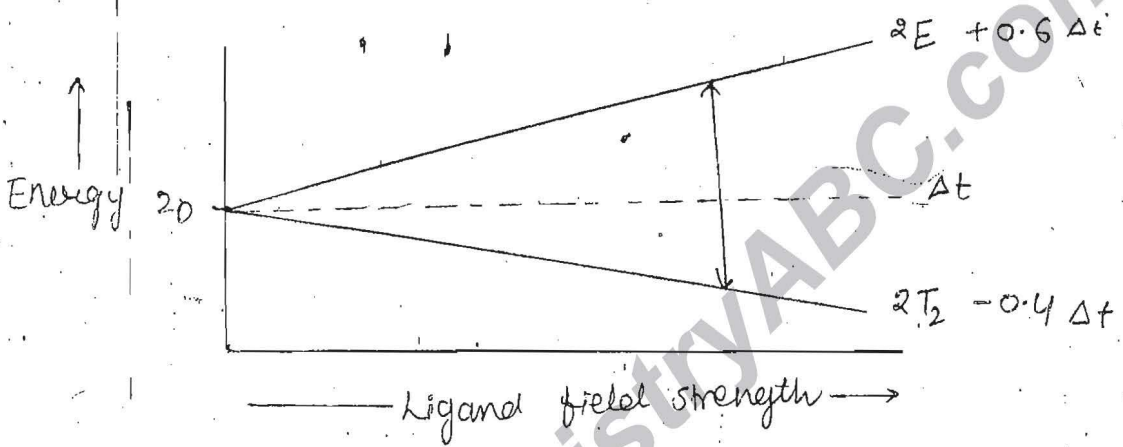
1 Hole transition → only one peak

$^2T_{2g} \leftarrow {}^2Eg$

d^9 tetrahedral ⇒



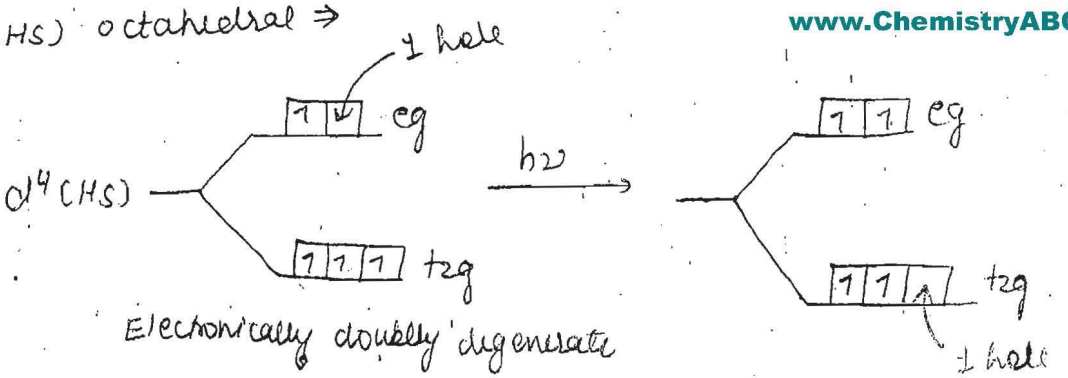
Ground state term → $^2D \rightarrow {}^2T_2 + {}^2E$



1 hole transition → only one peak

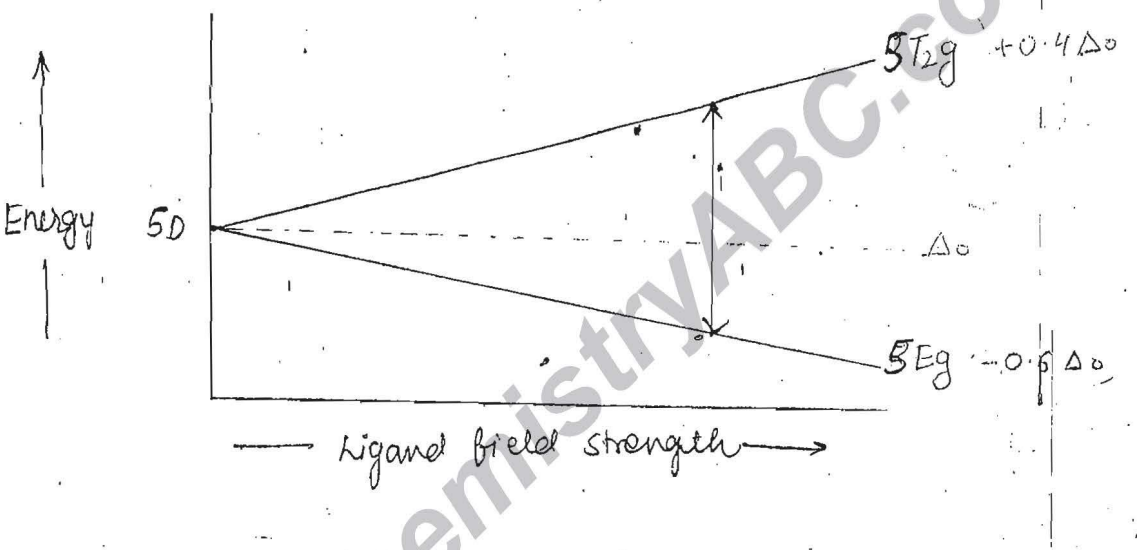
$^2E \leftarrow {}^2T_2$

d^4 (HS) octahedral ⇒



Electronically doubly degenerate

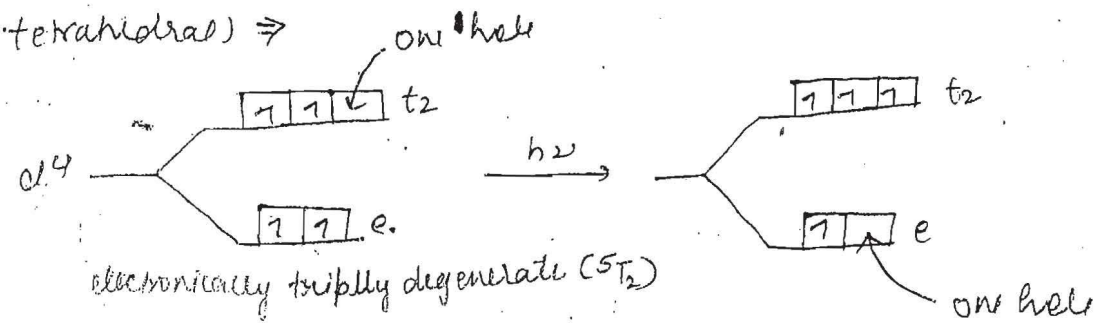
Ground state term → $^5D \rightarrow {}^5T_{2g} + {}^5E_g$



1 Hole transition → only one peak

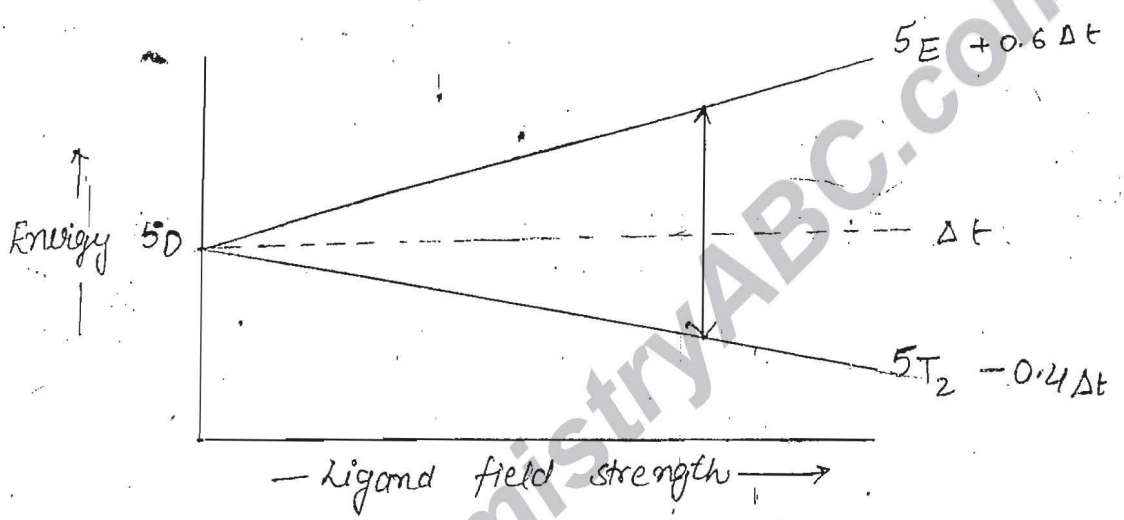
$^5T_{2g} \leftarrow {}^5E_g$

d^4 (tetrahedral) ⇒



electronically triplly degenerate ($^5T_2$)

Ground state term → $^5D \rightarrow {}^5T_2 + {}^5E$



1 Hole transition → only one peak

$^5E \leftarrow {}^5T_2$

In case of d^1, d^6, d^4 and d^9 → complexes

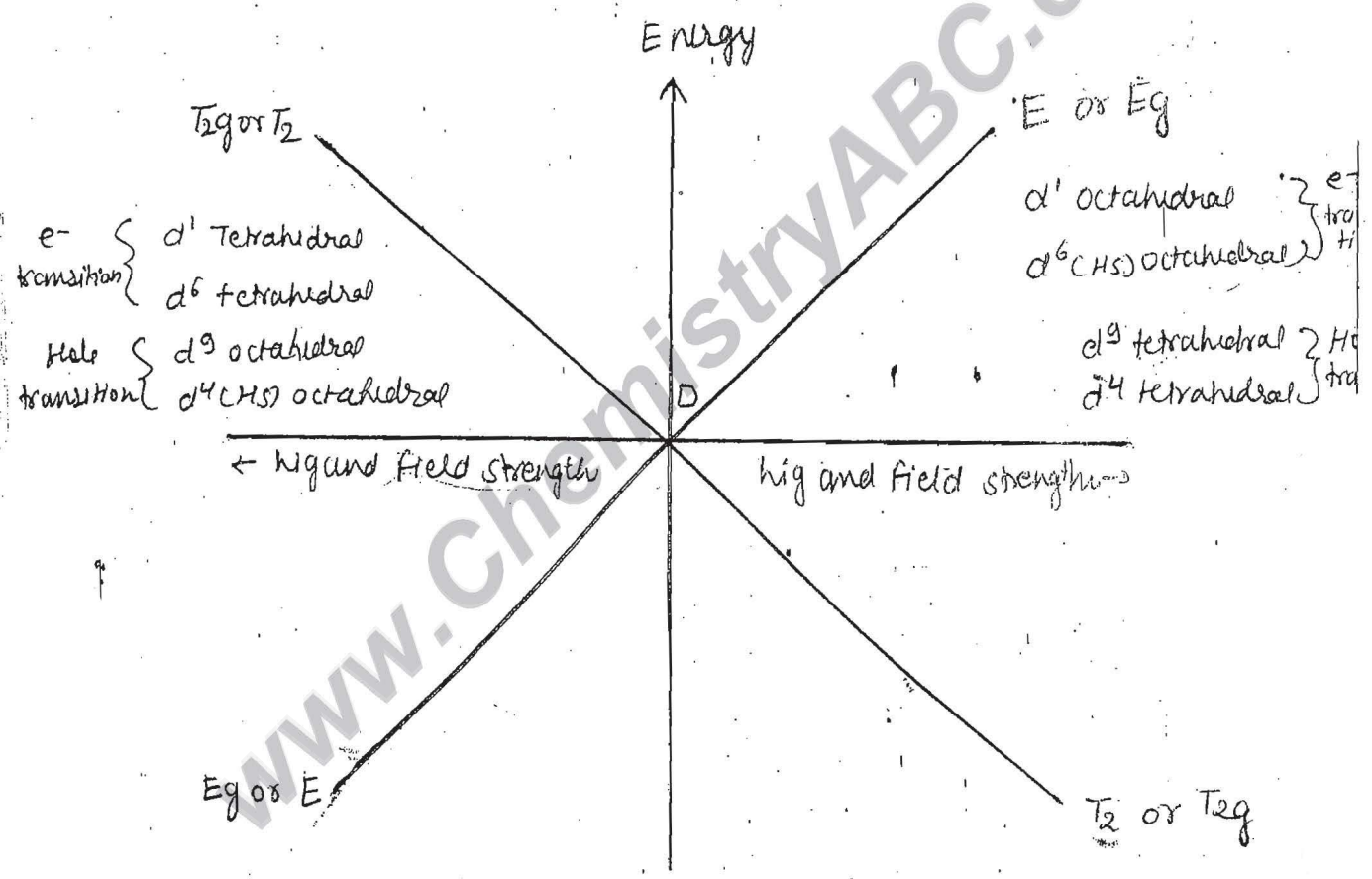
↓

only one electronic transition

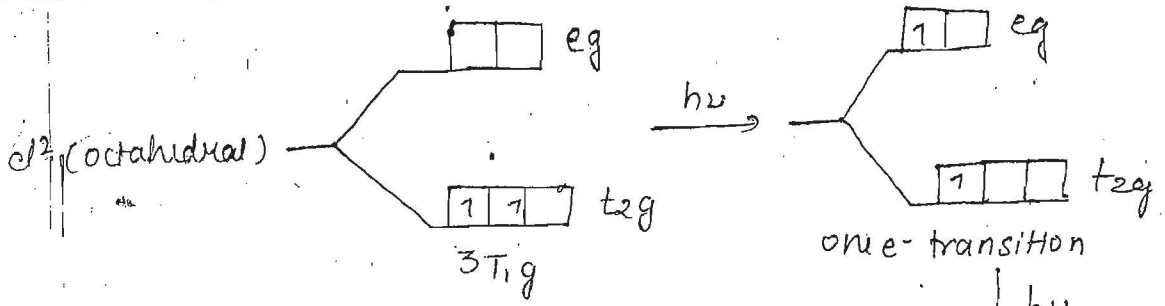
↓

This transition will give the value of Δ.

Combined orgel diagram for d^1, d^4, d^6 and d^9 - complex

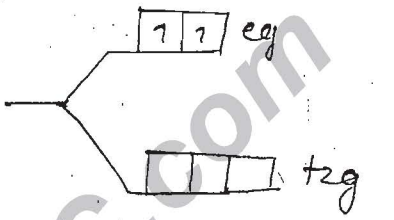


d^2 octahedral complexes ⇒

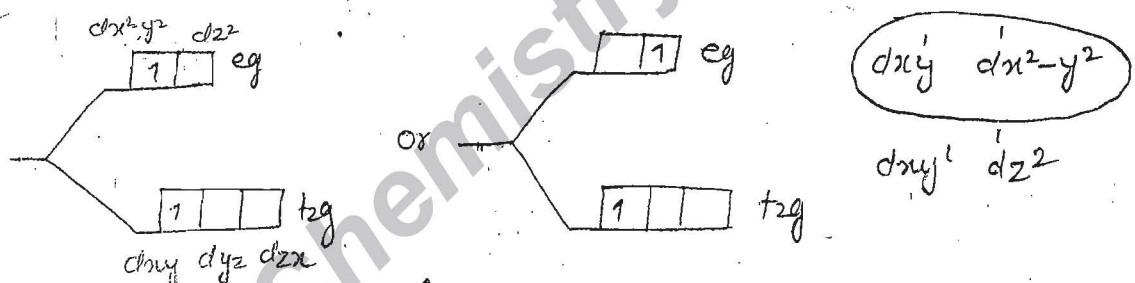


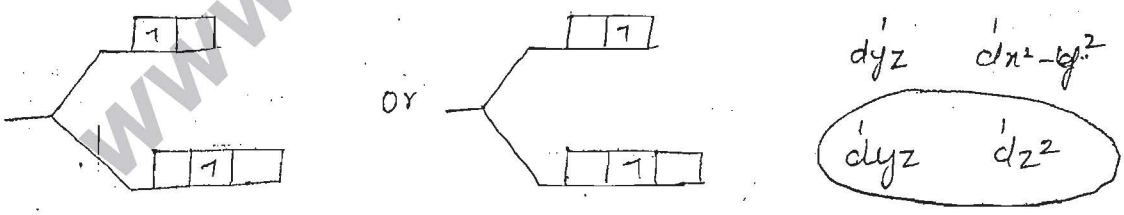
Ground state term → $^3F \rightarrow {}^3T_1g + {}^3T_2g + {}^3A_2g$

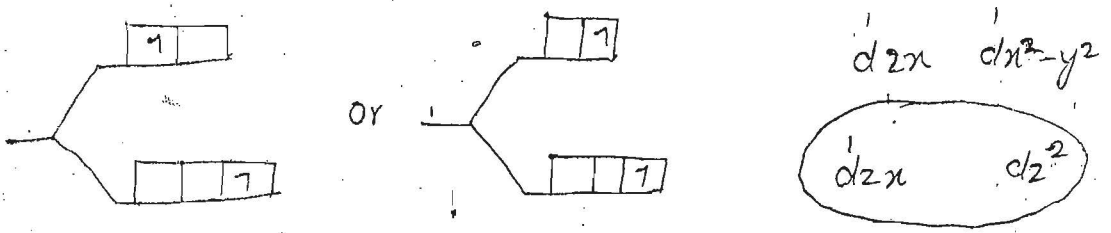
First excited state → $^3P \rightarrow {}^3T_1g(P)$



(when there are two holes – T_1g)





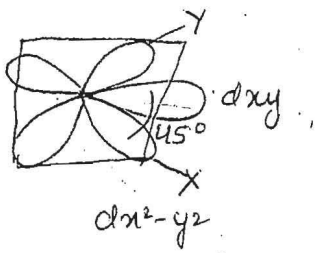


orbitals having two axis only –

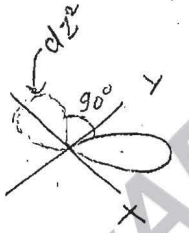
d_{xy} $d_{x^2-y^2}$, d_{yz} d_{z^2} , d_{zx} d_{z^2} (T_{1g})

orbitals having three axis –

d_{xy} d_{z^2} , d_{yz} $d_{x^2-y^2}$, d_{zx} $d_{x^2-y^2}$ (T_{2g})



small angle – more repulsion

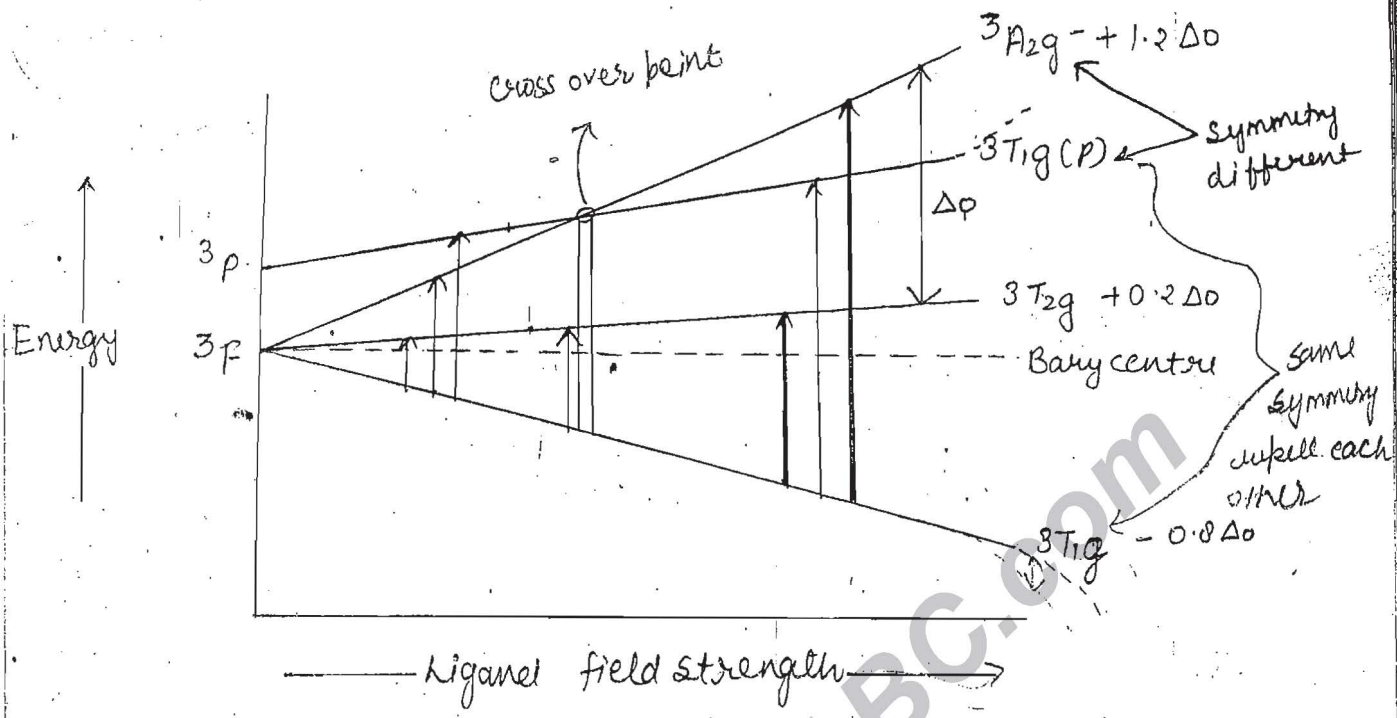


large angle → less repulsion

degeneracy is of both two sets i.e. of t_{2g} and e_g or t_2 & e both.

Higher energy → T_{1g} (P)

Low energy → T_{2g}



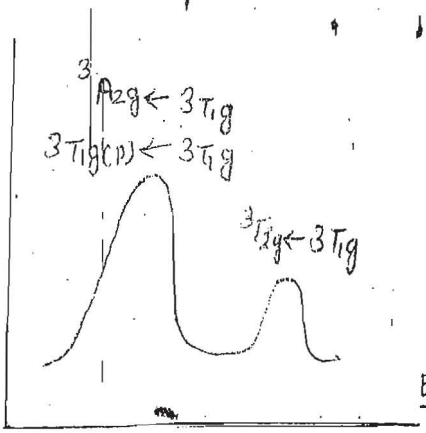
Three transitions → Three peaks

$^3T_2g \leftarrow {}^3T_1g$

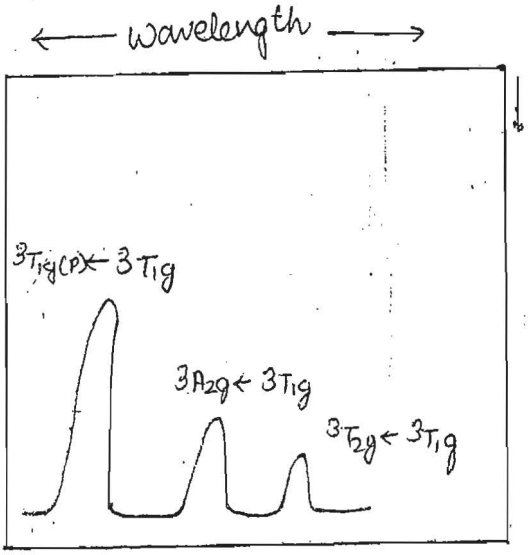
$^3A_2g \leftarrow {}^3T_1g$

$^3T_1g(P) \leftarrow {}^3T_1g$

At or near the cross over point → Three transitions → two peaks



Absorbance
$Lmol^{-1}\,cm^{-1}$

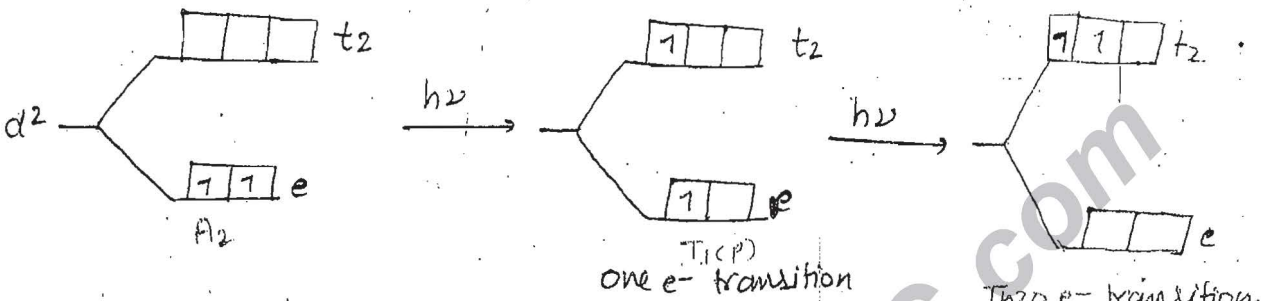


Examples ⇒ $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, $[V(ox)_3]^{3-}$ etc.

Energy difference b/w A_{2g} and $T_{2g} \longrightarrow \Delta_o$

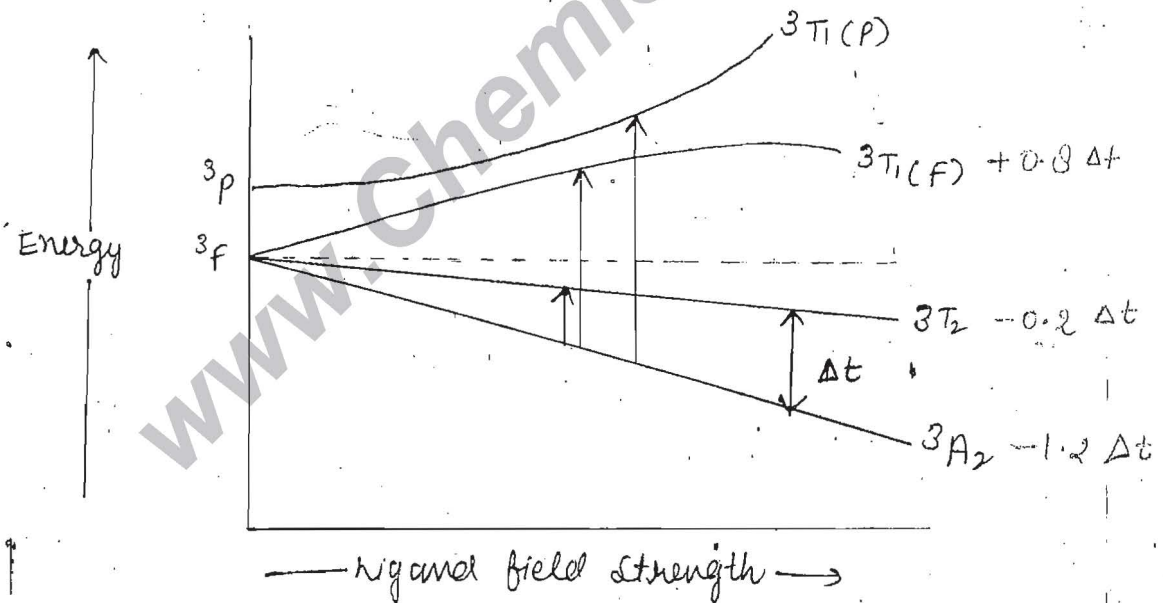
$$\Delta_o = ({}^3A_{2g} \leftarrow {}^3T_{1g}) - ({}^3T_{2g} \leftarrow {}^3T_{1g})$$

d^2 tetrahedral ⇒

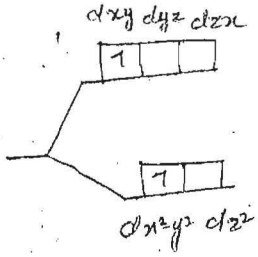


Ground state term → ${}^3F \longrightarrow {}^3T_1 + {}^3T_2 + {}^3A_2$

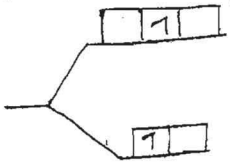
First excited state → $3p \longrightarrow {}^3T_1(P)$



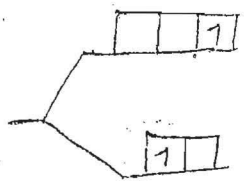
Hole may be equal to e⁻ but never more than e⁻.



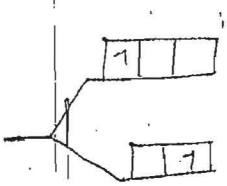
$d_{x^2-y^2}$ d_{xy}



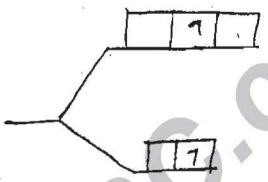
$d_{x^2-y^2}$ d_{yz}



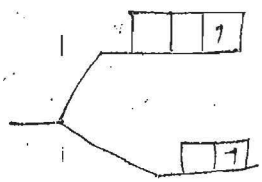
$d_{x^2-y^2}$ d_{zx}



d_{z^2} d_{xy}



d_{z^2} d_{yz}

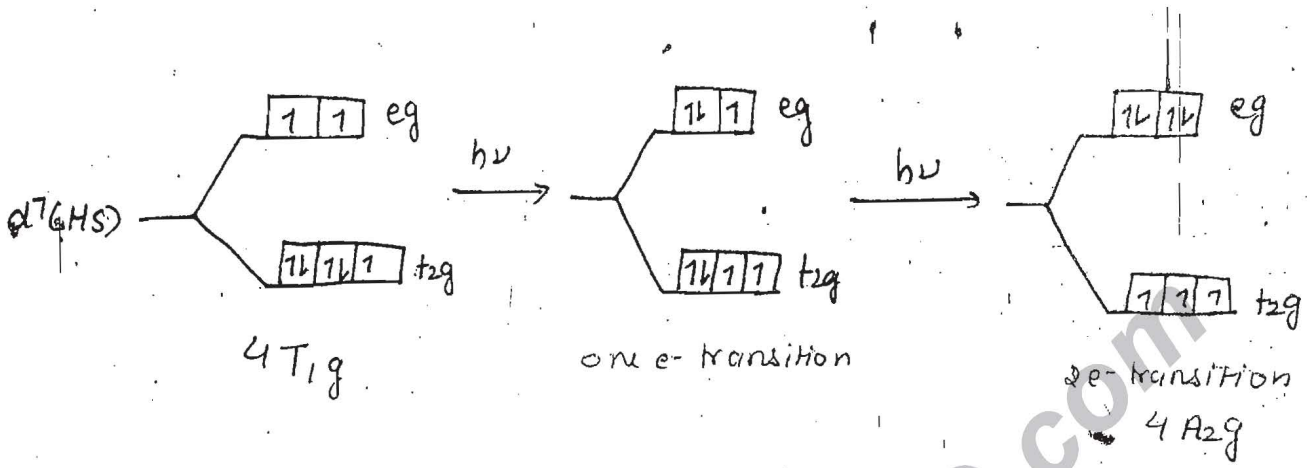


d_{z^2} d_{zx}

orbitals having two axis – $d_{x^2-y^2}$ d_{xy} , d_{z^2} – d_{yz} , d_{z^2} d_{zx} (T_1)

orbital having three axis – $d_{x^2-y^2}$ d_{yz} , $d_{x^2-y^2}$ d_{zx} , d_{z^2} . d_{xy} (T_2)

d^7(HS) octahedral ⇒



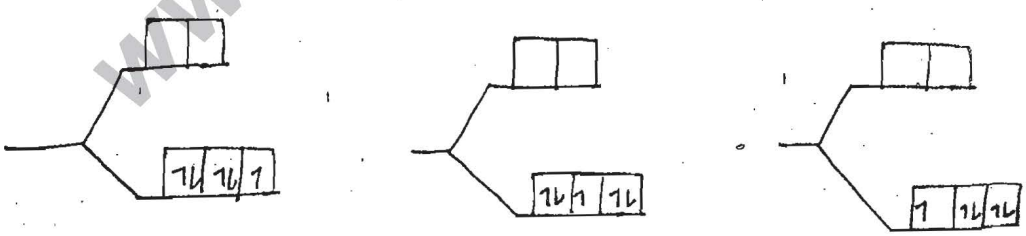
Ground state term – $^4F \rightarrow {}^4T_1g + {}^4T_2g + {}^4Ag$

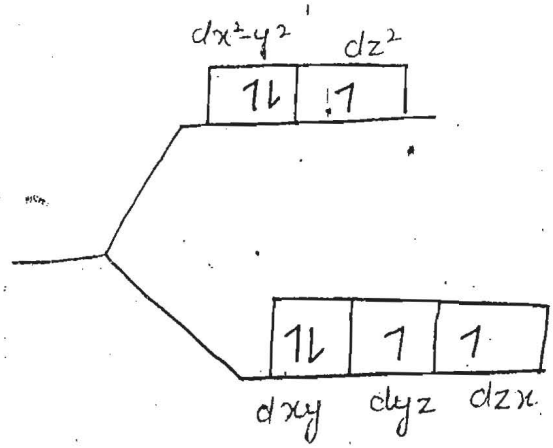
first excited state- $^4P \rightarrow {}^4T_1g$ (P)

t_2g → unsymmetrically filled → Electronically trikly degenerate

eg → unsymmetrically filled → Electronically doubly degenerate

t_2g & eg both symmetrically → Electronically non degenerate filled





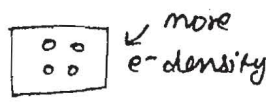
d_{xy} $d_{x^2-y^2}$ d_{yz} d_{z^2}

d_{x^2y} d_{z^2} d_{y^2z} $d_{x^2-y^2}$

d_{z^2x} d_{z^2} d_{z^2x} $d_{x^2-y^2}$

d_{xy} $d_{x^2-y^2}$, d_{yz} d_{z^2} , d_{zx} d_{z^2} $^4T_1g(P)$

d_{y^2z} $d_{x^2-y^2}$, d_{xy} d_{z^2} , d_{z^2x} $d_{x^2-y^2}$ ^4T_2g

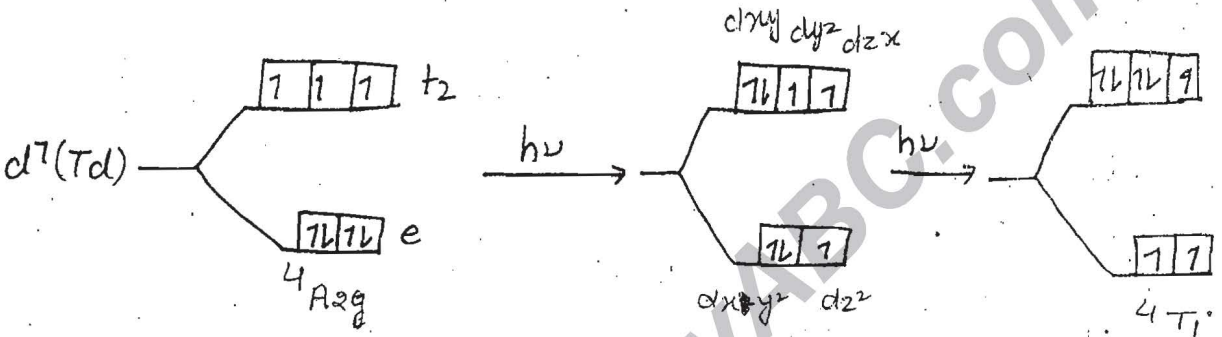


Energy difference between t_{2g} and $A_{2g} = \Delta_o$

(Energy of $^4A_{2g} \leftarrow {}^4T_{1g}$ transfer) - (Energy of $^4T_{2g} \leftarrow {}^4T_{1g}$ transition)

$= \Delta_o$

d^7 Tetrahedral ⇒



Ground state term → $^4F \rightarrow {}^4T_1 + {}^4T_2 + {}^4A_2$

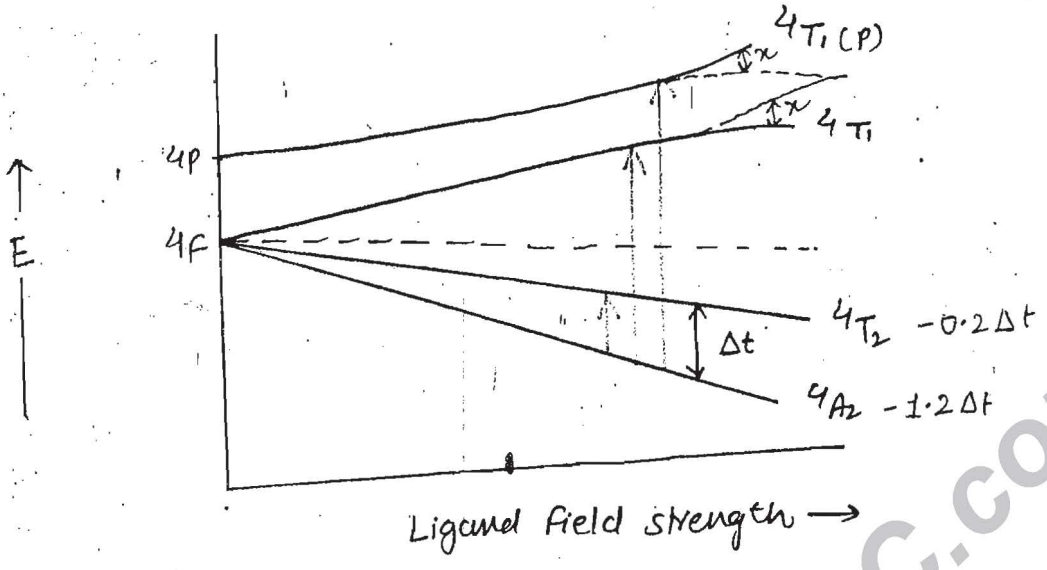
First excited state → $^4P \rightarrow {}^4T_1(P)$

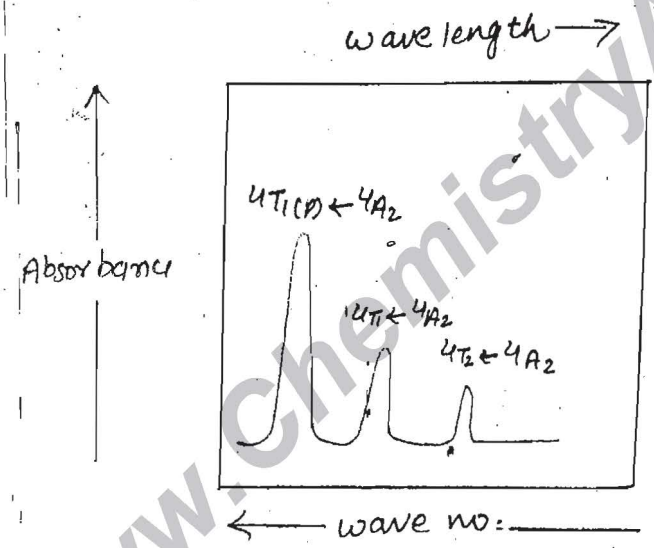
$d^2_{x^2-y^2}\ d^2_{xy}$, $d^2_{x^2-y^2}\ d^2_{yz}$, $d^2_{x^2-y^2}\ d^2_{zx}$

$d^2_z\ d^2_{xy}$, $d^2_z\ d^2_{yz}$, $d^2_z\ d^2_{zx}$

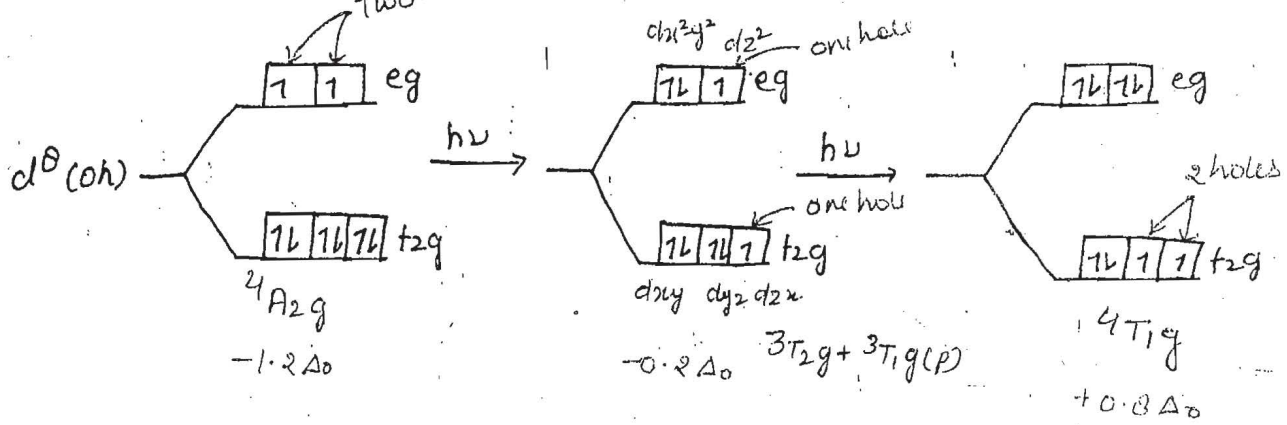
$d^2_{x^2-y^2}\ d^2_{xy}$, $d^2_z\ d^2_{yz}$, $d^2_z\ d^2_{zx} \rightarrow {}^4T_1(P)$

$d^2_{x^2-y^2}\ d^2_{yz}$, $d^2_{x^2-y^2}\ d^2_{zx}$, $d^2_z\ d^2_{xy} \rightarrow {}^4T_2$





d^8 octahedral ⇒



Ground state term ⇒ $^3F \rightarrow {}^3T_1g + {}^3T_2g + {}^3A_2g$

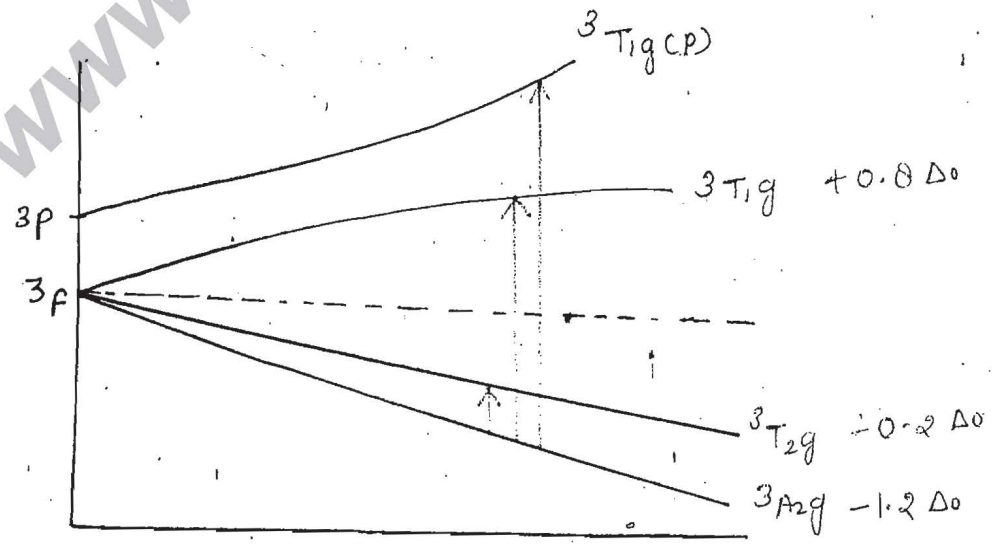
First excited state ⇒ $^3P \rightarrow {}^3T_1g(P)$

d^2_{xy} $d^2_{x^2-y^2}$, d^2_{yz} $d^2_{x^2-y^2}$, d^2_{zx} $d^2_{x^2-y^2}$ ✗

d^2_{xy} d^2_{z} , d^2_{yz} d^2_{z} , d^2_{zx} d^2_{z}

d^2_{xy} $d^2_{x^2-y^2}$, d^2_{yz} $d^2_{z^2}$, d^2_{zx} $d^2_{z^2}$ $^4T_1g(P)$

d^2_{yz} $d^2_{x^2-y^2}$, d^2_{zx} $d^2_{x^2-y^2}$, d^2_{xy} $d^2_{z^2}$ $^4T_2$



hole

$d_{zx}\ d_{z^2}$, $d_{zx}\ d_{x^2-y^2}$

$d_{yz}\ d_{z^2}$, $d_{yz}\ d_{x^2-y^2}$

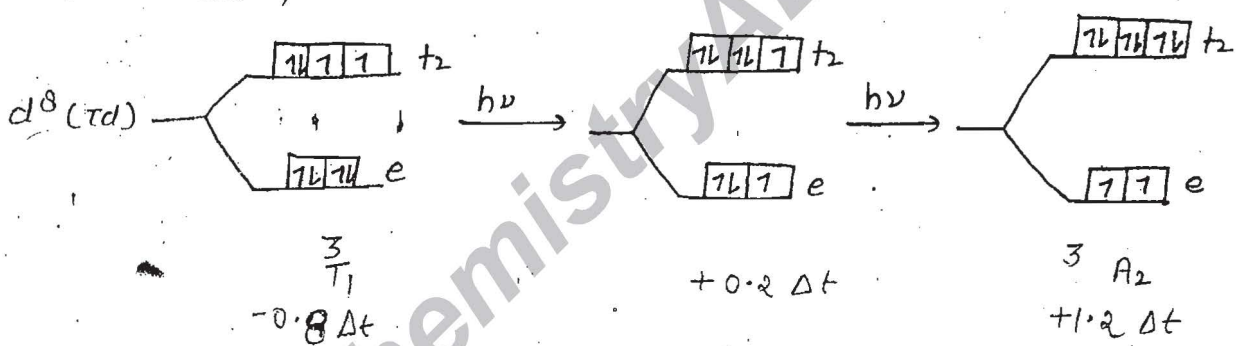
$d_{zx}\ d_{z^2}$, $d_{zx}\ d_{x^2-y^2}$

← Hole formulation

$d_{zx}\ d_{z^2}$, $d_{yz}\ d_{z^2}$, $d_{zx}\ d_{z^2} \longrightarrow {}^3T_1(g)\ P$

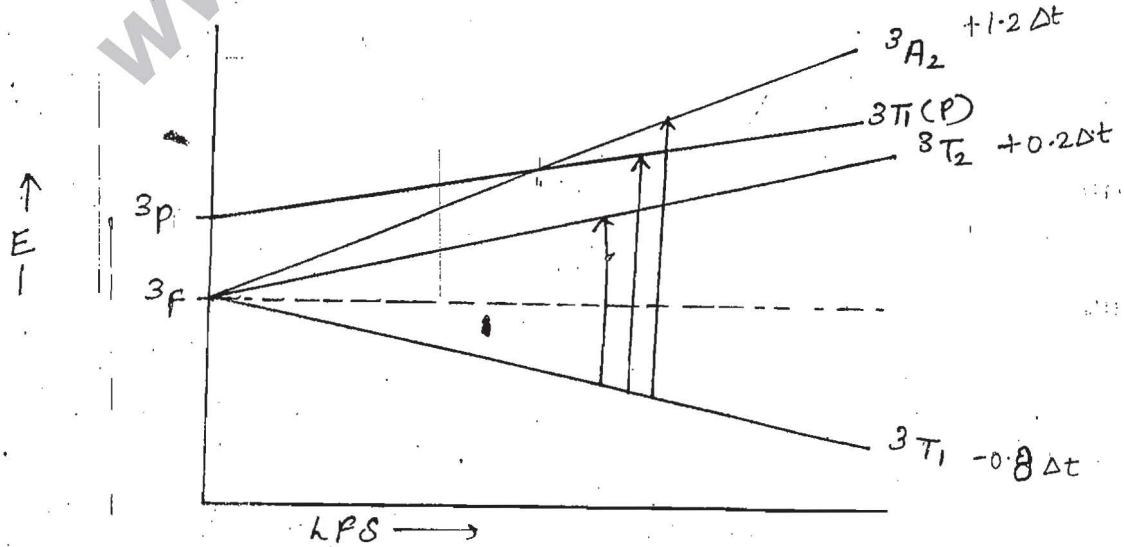
$d_{zx}\ d_{x^2-y^2}$, $d_{yz}\ d_{x^2-y^2}$, $d_{zx}\ d_{x^2-y^2} \longrightarrow {}^3T_2 g$

d^8 Tetrahedral ⇒



ground state term ⇒ ${}^3F \rightarrow {}^3T_1 + {}^3T_2 + {}^3A_2$

First excited state ⇒ ${}^3P \rightarrow {}^3T_1(P)$



d_{z^2} d_{zx} ; d_{z^2} d_{yz} , d_{z^2} d_{xy} $^3T_1(P)$

$d_{x^2-y^2}$ d_{zx} , $d_{x^2-y^2}$ d_{yz} , $d_{x^2-y^2}$ d_{xy} $^3T_2$

Hole transitions –

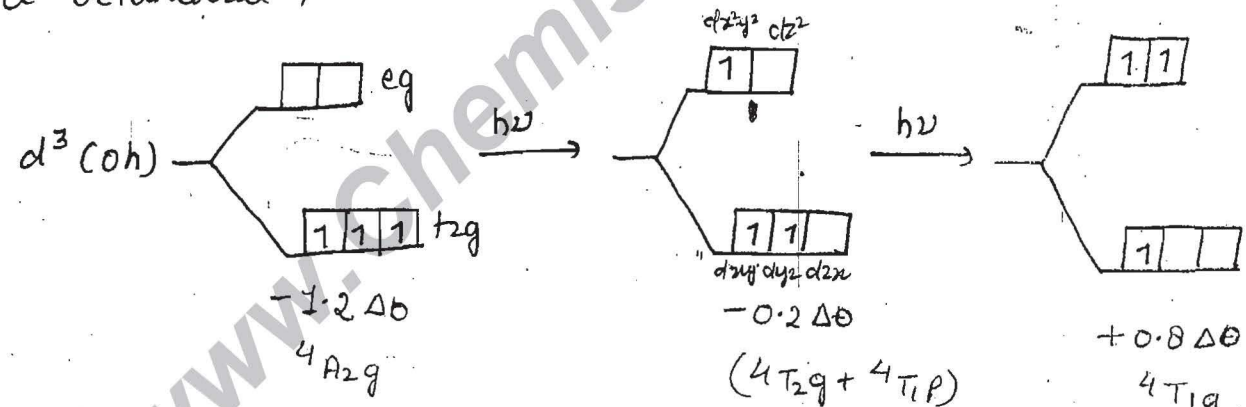
$^3T_2 \leftarrow {}^3T_1$

$^3A_2 \leftarrow {}^3T_1$

$^3T_1(P) \leftarrow {}^3T_1$

$[CoF_6]^{4-}$ gives only one peak in UV-visible region as 2 peaks are observed in IR region.

d^3 octahedral ⇒

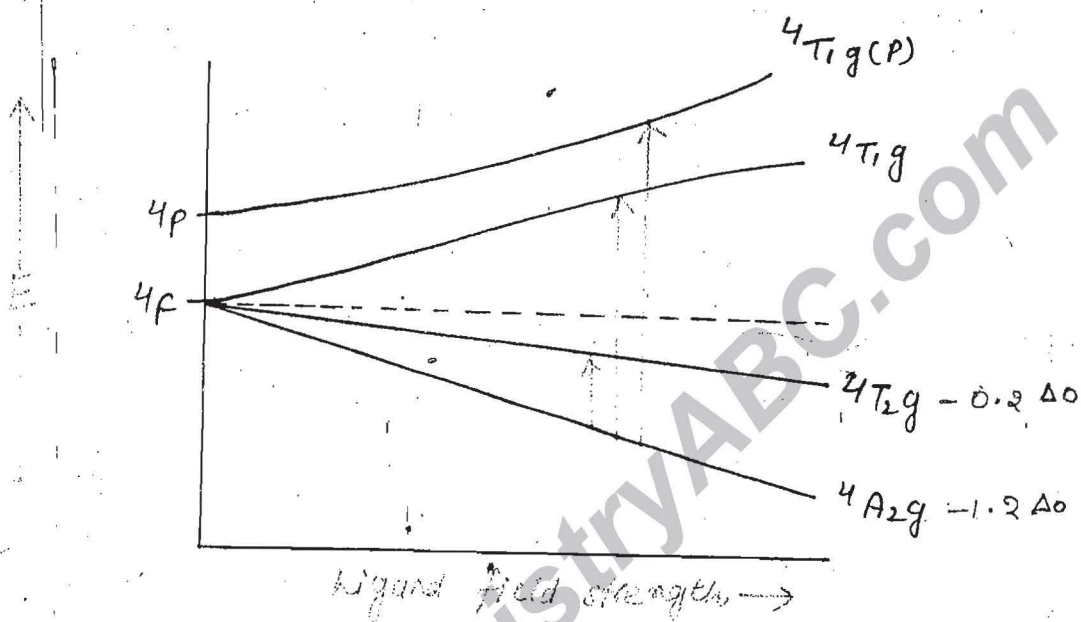


Ground state term ⇒ ^4F ⇒ $^4T_1g + {}^4T_2g + {}^4A_2g$.

First excited state term ⇒ ^4P ⇒ $^4T_1(P)$

d_{zx} d_{z^2} , d_{yz} d_{z^2} , d_{xz} d_{z^2} $^4T_{1g}(P)$

d_{zx} $d_{x^2-y^2}$, d_{yz} $d_{x^2-y^2}$, d_{xz} $d_{x^2-y^2}$ $^4T_{2g}$

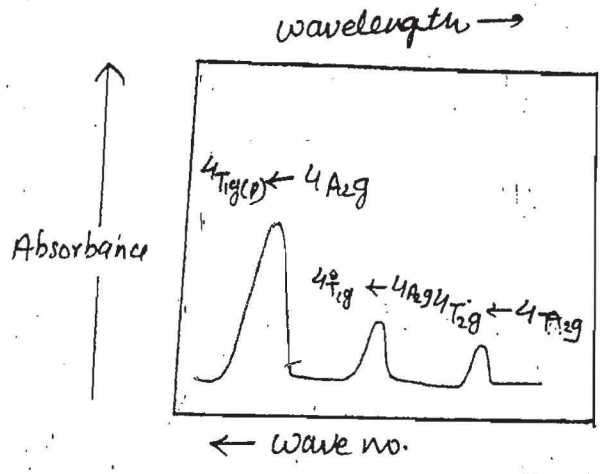


3 hole transitions –

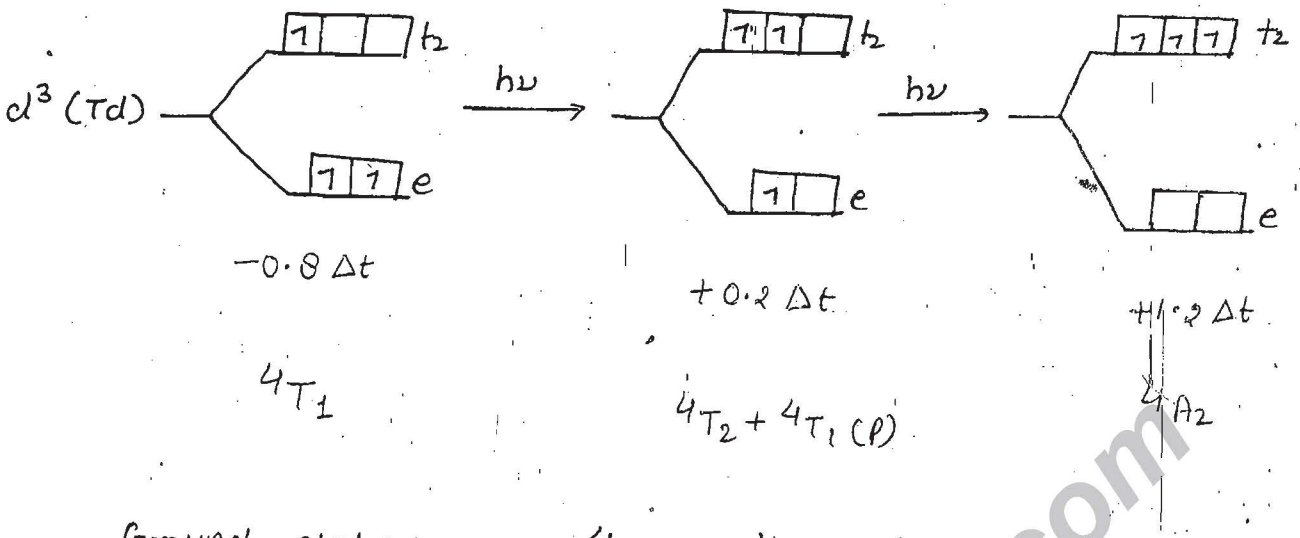
$^4T_{2g} \leftarrow {}^4A_{2g}$

$^4T_1g \leftarrow {}^4A_{2g}$

$^4T_1g(P) \leftarrow {}^4A_{2g}$



d^3 tetrahidral ⇒

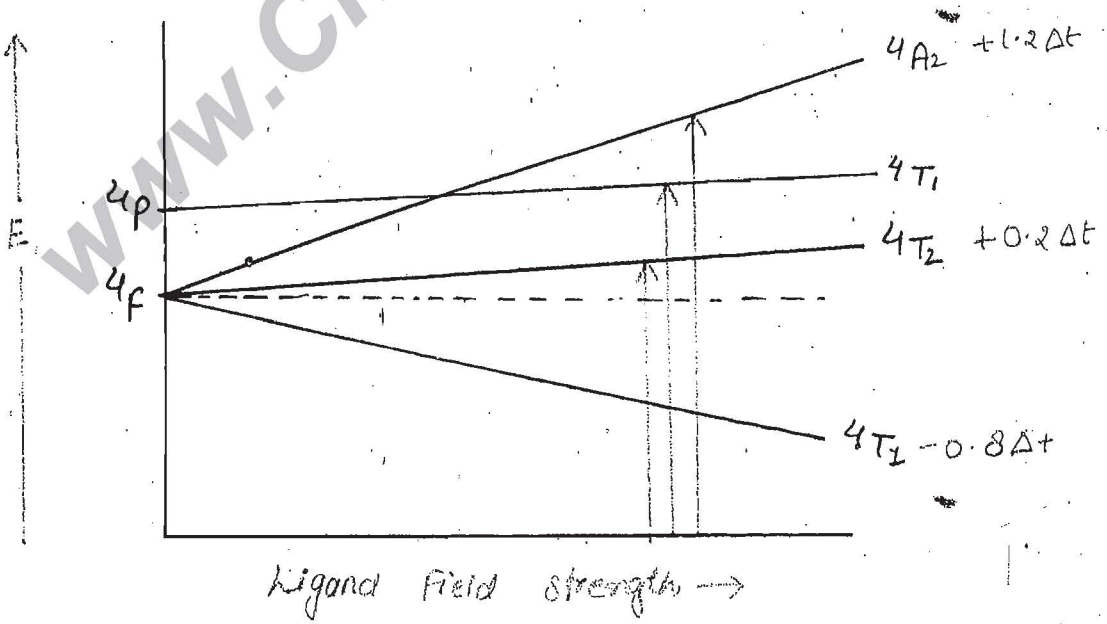


Ground state term → $^4F \rightarrow {}^4T_1 + {}^4T_2 + {}^4A_2$

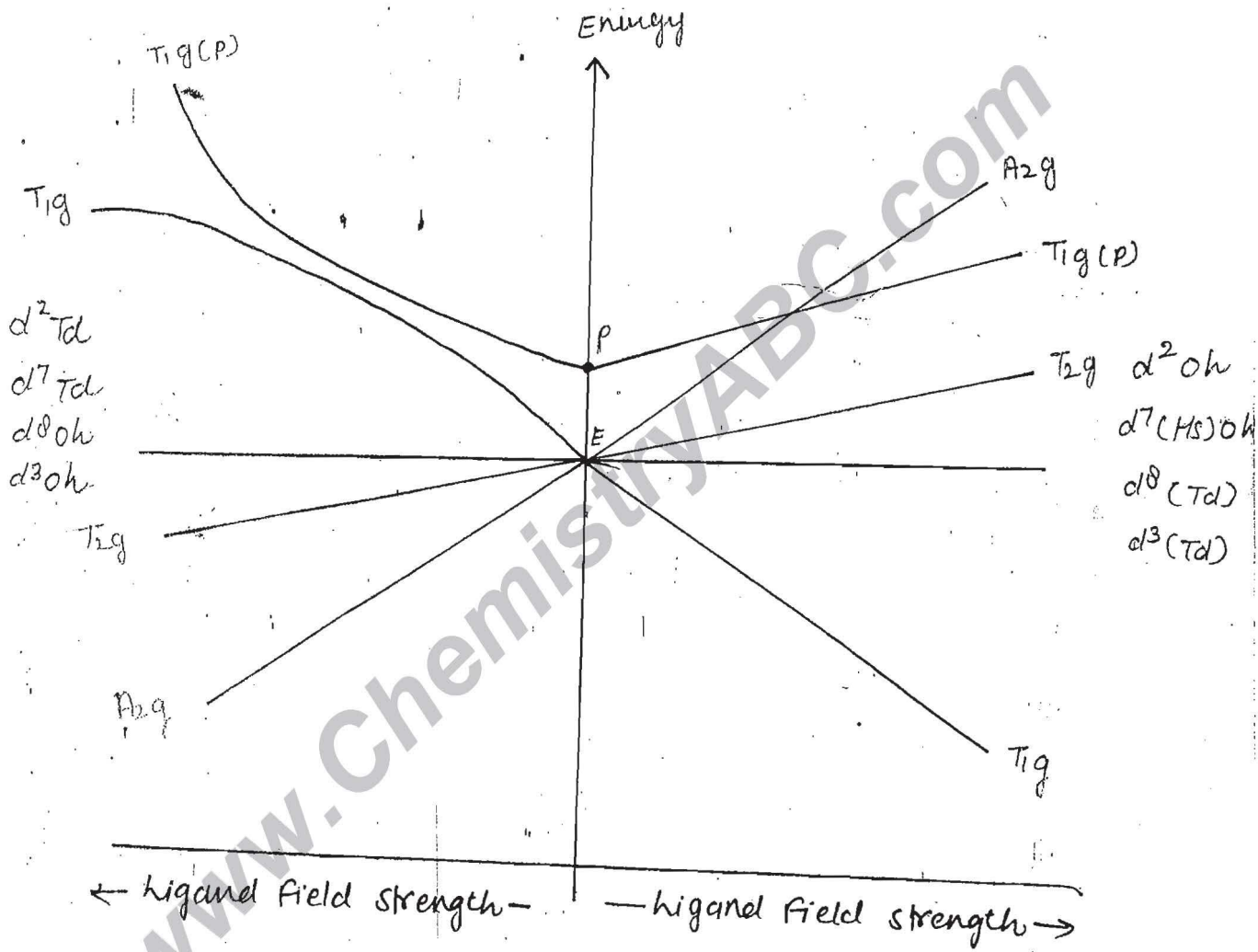
First excited state term → $^4P \rightarrow {}^4T_1(P)$

$d_{z^2}\ d_{zx}$, $d_{z^2}\ d_{yz}$, $d_{z^2}\ d_{xz} \rightarrow {}^4T_1(P)$

$d_{x^2-y^2}\ d_{zx}$, $d_{x^2-y^2}\ d_{yz}$, $d_{x^2-y^2}\ d_{xz} \rightarrow {}^4T_2$



Combined orgel diagram for d^2, d^7, d^8 and d^3 complexes ⇒



Racah Parameter and Nephelauxetic effect ⇒

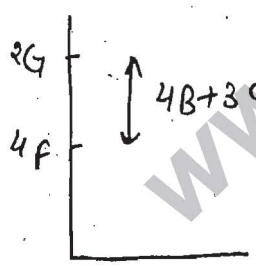
Energy difference b/w spectroscopic states of atoms is measured in terms of positive integers called as Racah parameter (B and C).

RACAH PARAMETER

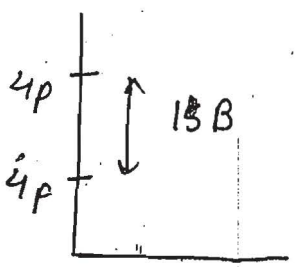
If spin multiplicity of two spectroscopic states is same, Energy difference b/w these state is measured in terms of B only.

If spin multiplicities of two spectroscopic states are different, energy difference b/w these states is measured in terms of both B and C. C is approx 4 times of B.

4 times of B.



Cr^{3+}



$B = 700 - 1000\ cm^{-1}$

In complexes, value of B and C are lower than those of free metal ions.

$$B_{\text{metal ion}} > B'_{\text{complex}}$$

Decrease in the value of B in complexes is due to delocalisation of metal d-e^- on ligands. (in molecular orbitals).

Delocalisation of de^- on ligands is called nephilauxetic effect.

Due to delocalisation of de^- on metal to ligand, the repulsion b/w e^- decreases resulting in lowering the energy and increase in stability.

NEPHELAUXETIC PARAMETER

$$\text{Nephelauxetic parameter } (\beta) = \frac{B'_{\text{complex}}}{B_{\text{metal ion}}} < 1$$

Value of B' decreases with increases in delocalisation of metal d-electrons $\longrightarrow$ β decreases.

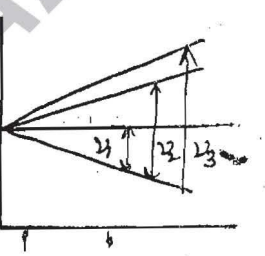
Nephelauxetic series ⇒

$$F^- > H_2O > NH_3 > en > NCS > Cl^- > CN^- > Br^-$$

If three electronic transitions are observed then B' can be calculated from the equation.

$$15\,B' = \nu_3 + \nu_2 - 3\nu_1$$

$\nu_1 < \nu_2 < \nu_3$



d^5 (HS) octahedral and Tetrahedral complexes ⇒

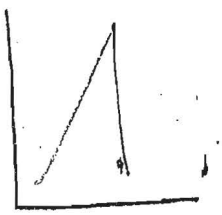
Electronic transitions in these complexes are spin forbidden

→ No orgel diagram.

→ No sharp peak is observed.

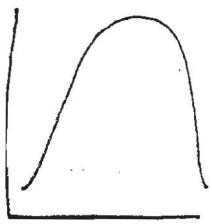
Reference – cox

Broad, and unsymmetric peaks in complexes of transition metals ⇒



Sharp peak

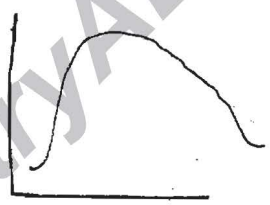
Lanthanide complexes



Broad peak

Transition metal complexes

Symmetric peak

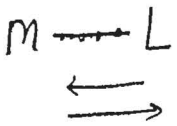


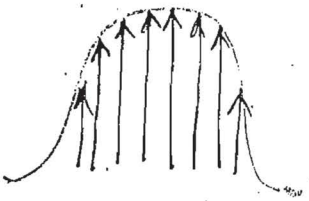
Unsymmetric peak

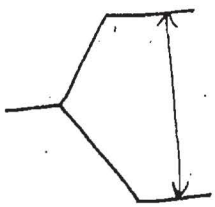
The reasons of peak broadening are–

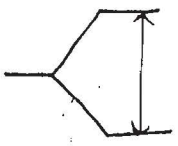
1. Vibronic coupling
2. John-Teller coupling
3. L-S coupling

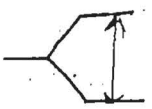
1. **Vibronic coupling ⇒** Simultaneous electronic transitions and vibrations







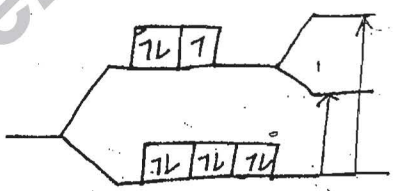


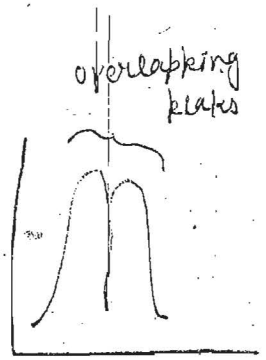


There are millions of transitions in between one vibration. As ligand approaches metal repulsion between metal e⁻ and ligand e⁻ takes place resulting in more splitting. The ligand approaches metal gradually i.e there are different vibrational levels points in one complete vibrations resulting in broadening of signals.

② John-Teller distortion ⇒

$[Cu(H_2O)_6]^{2+} \longrightarrow 3d^9$





Here in this complexes only one peak should be obtained but due to John-Teller distortion eg splits in to two with lower energy difference b/w these two levels, hence transition takes place to those two regions and two overlapping peaks are observed.

these peaks can be seen only by resolution.

JOHN TELLER

Angular Momentum Coupling

L-S coupling ⇒

$d^1 \rightarrow t_{2g}^1 \; eg^0$

Ground state term → ^2D

$S = \frac{1}{2}$ $\qquad 2S+1 = 2\times\frac{1}{2}+1 = 2$

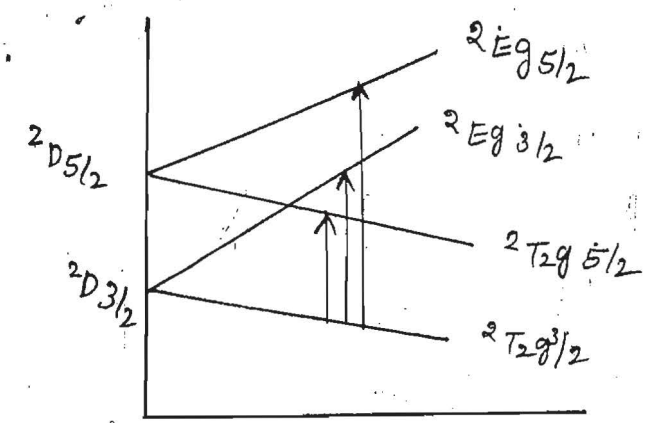
$L = 2$

$J = |L+S| \ldots\ldots |L-S| = \left|2+\frac{1}{2}\right| \ldots\ldots \left|2-\frac{1}{2}\right|$

$= \frac{5}{2}, \frac{3}{2}$

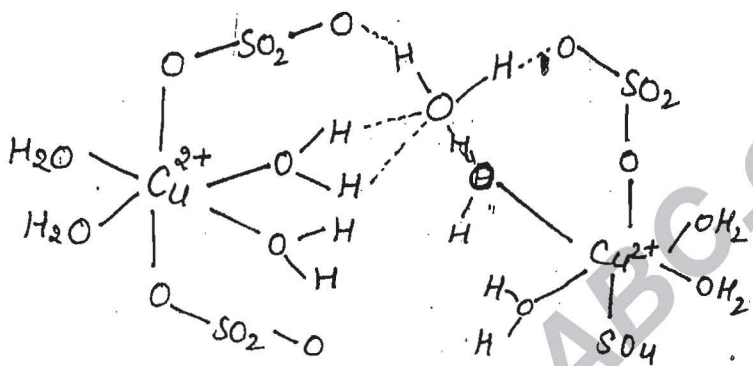
$^2D_{3/2}$, $^2D_{5/2}$ $\qquad D \rightarrow {}^2T_{2g} + {}^2Eg$

lower energy $\qquad$ Higher energy



$CuSO_4 \cdot 5H_2O$

light blue colour.



$$CuSO_4 \cdot 5H_2O \xrightarrow[-2H_2O]{warm} CuSO_4 \cdot 3H_2O \xrightarrow[-2H_2O]{warm} CuSO_4 \cdot H_2O \xrightarrow[-H_2O]{350^\circ C} CuSO_4 \text{ colourless}$$

$$CuSO_4 \xrightarrow{700^\circ C} CuO + SO_3$$

Colour due to –

Transition $^2T_{2g} \leftarrow {}^2Eg$
electronic transition $^2Eg \leftarrow {}^2T_{2g}$

MAGNETIC PROPERTIES

Diamagnetic, Paramagnetic, ferromagnetic, ferrimagnetic and Antiferromagnetic substances ⇒

Charge particle ⟶ In motion ⟶ generates a magnetic field.

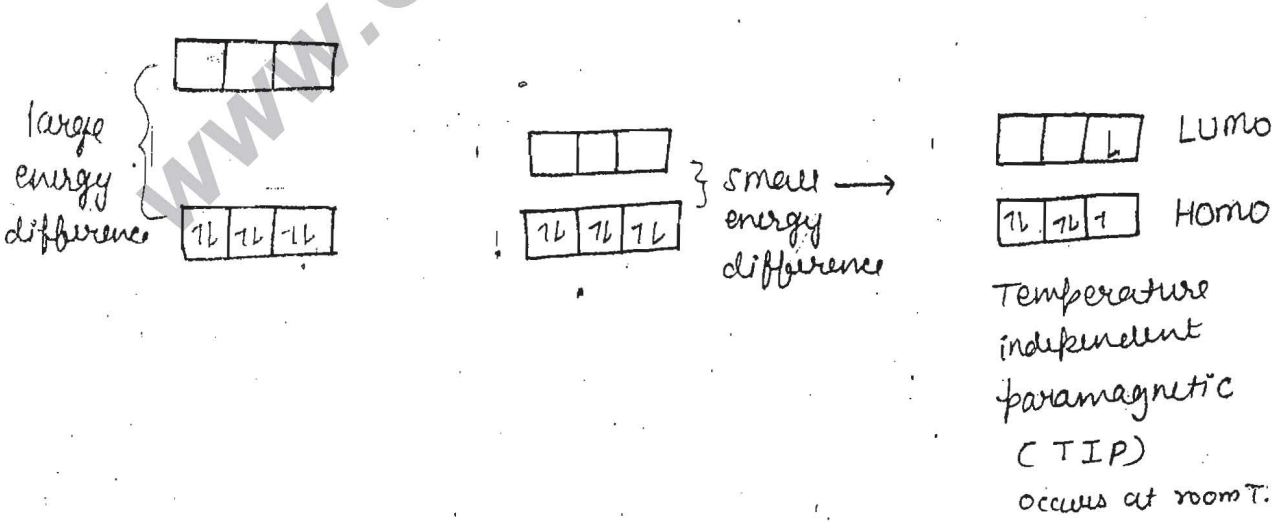
Diamagnetic substances ⇒

⇒ Magnetic moment, $\mu = 0$

⇒ All e^-s paired.

Applied magnetic field ⟶

⟵ induced magnetic field



Temperature independent paramagnetic (TIP) occurs at room T.

A complex may has—

① All paired electrons. d^6 (LS) → eg ← diamagnetic; t2g

② unpaired electrons with paired e's. —— d^7 (HS) → eg; t2g; paramagnetic

③ All unpaired electrons only —— d^5 (HS) → eg; t2g; paramagnetic

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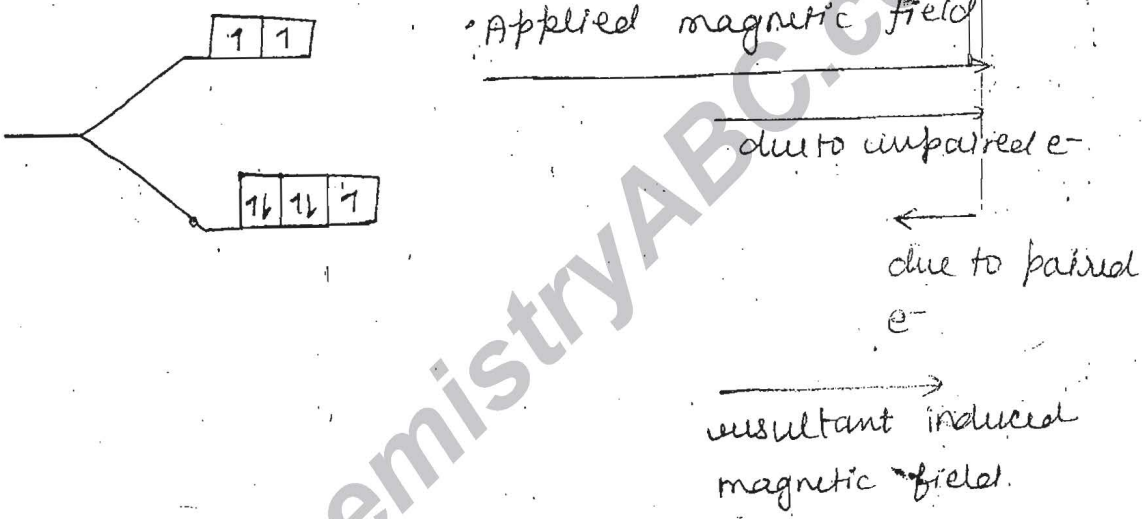


In case of magnetically dilute substances.

↓

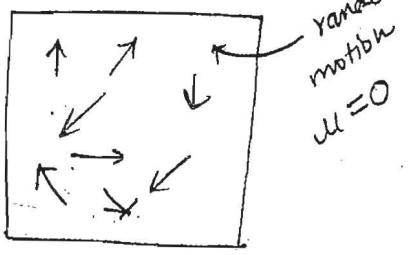
No interaction among the magnetic moments of individual atoms, ions or molecules of a substance.

↓

Substances are always paramagnetic whether the temp^r is low or high.

magnetic moment of paramagnetic substances ($\mu = 0$)

$$\text{paramagnetism} \propto \frac{1}{\text{Temperature}}$$



magnetic moment is of a particular ion or atom not of whole substance.

At low temp^{r} randomisation decreases, therefore there will be some value of μ while at high T due to more randomisation μ becomes zero.

The substances which are not magnetically dilute

↓

Interaction among the magnetic moments of individual particle.

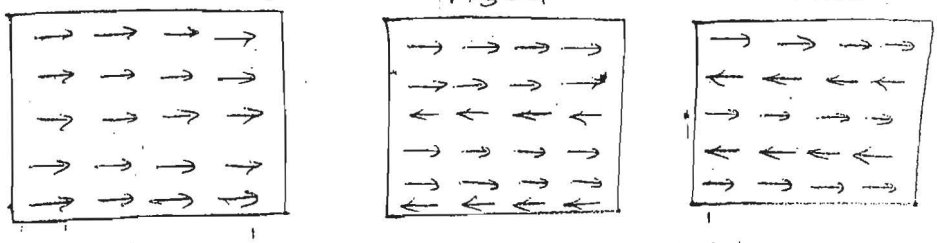
↓

Paramagnetic substances may converted into ferromagnetic, ferrimagnetic or antiferromagnetic substances

↓

Occurs below critical temp^{r}

Ex:- Fe, CO, Ni, CrO_2 | Fe_3O_4 | MnO



Ferromagnetic | Ferrimagnetic | Antiferromagnetic

Ferromagnetic & Ferrimagnetic → below critical Temp^r called as curie's Temp^r (T_c)

Antiferromagnetic → below critical temp^r called Neel's temp^r

magnetic moment-

ferromagnetic > ferrimagnetic > Antiferromagnetic

Iron once converted into ferromagnetic will be remain ferro. whether the temp^r is increased or not. i.e it becomes permanent magnet.

[redacted] → Na thiosulfate used in photography to make photos from -ve

Magnetic susceptibility ⇒

H = Applied magnetic field

B = induced magnetic field in the sample

$$\Delta H = B - H \quad \text{—(1)}$$

for diamagnetic substances $B < H$

" paramagnetic " $B > H$

ΔH = -ve for diamagnetic substances

ΔH = +ve for paramagnetic "

difference between B and H is measured in terms of intensity magnetisation (I).

$$4\pi I = B - H \quad \text{—(2)}$$

or

$$4\pi \frac{I}{H} = \frac{B}{H} - 1 \quad \text{—(3)}$$

$\frac{B}{H}$ = magnetic permeability

$\frac{I}{H}$ = magnetic susceptibility per unit volume (K) (Kappa)

$$K = \frac{I}{H} \quad -(4)$$

Magnetic susceptibility ⇒ Tendency of a substance to be magnetised

if volume → m.s. per unit volume

if moles – " " " moles

$$\chi = \frac{K \,/\, (V)}{d\,(V)\,/\,\text{mass}} = \frac{K}{d\ \text{mass}} \quad -(5)$$

Specific magnetic susceptibility i.e. magnetic susceptibility per unit mass.

$$\chi_m = \chi \cdot M \quad -(6)$$

χ_m ↑ molar magnetic susceptibility

M ↑ molar mass

↑ magnetic susceptibility per mole → degree to which one mole of a substance interacts with extend magnetic field

From classical theory-

$$\chi_m = \frac{N^2 \mu^2}{3RT} \quad -(7)$$

N → Avogadro no.

μ → magnetic moment (B.M.)

R – gas const.

$$\mu = \left(\frac{\chi_m \cdot 3RT}{N^2}\right)^{1/2} \quad -(8)$$

χ_m^P ← paramagnetic susceptibility

χ_m^d ← diamagnetic susceptibility

$$\chi_m^P \text{ corrected} = (\chi_m^P - \chi_m^d)$$

↑ very small

↑ can be neglected

$$\mu = 2.84 (\chi_m \cdot T)^{1/2} \quad \text{—⑨}$$

from eqn ① :-

$$\chi_m = \frac{C}{T}$$

C = Curie's constant

$$= \frac{N^2 \mu^2}{3R}$$

$$\text{Paramagnetic susceptibility} \propto \frac{1}{T}$$

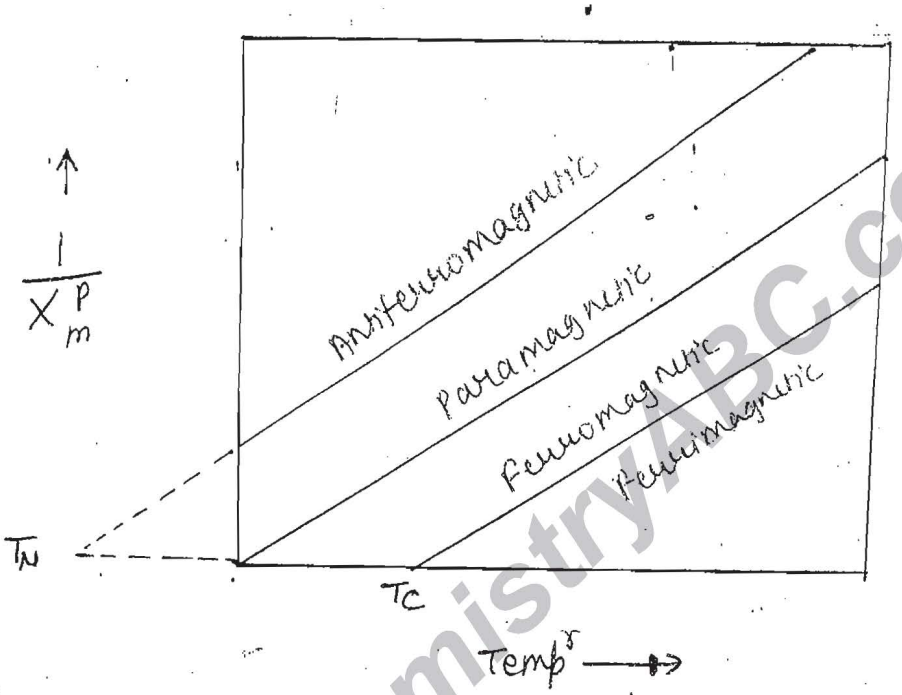
For ferromagnetic, ferrimagnetic or antiferromagnetic substances :-

$$\chi_m = \frac{C}{(T-\theta)}$$

θ = an empirical constant and has the unit of temp

θ = +ve → Ferromagnetic or Ferrimagnetic

θ = -ve → Antiferromagnetic



V.V.I.

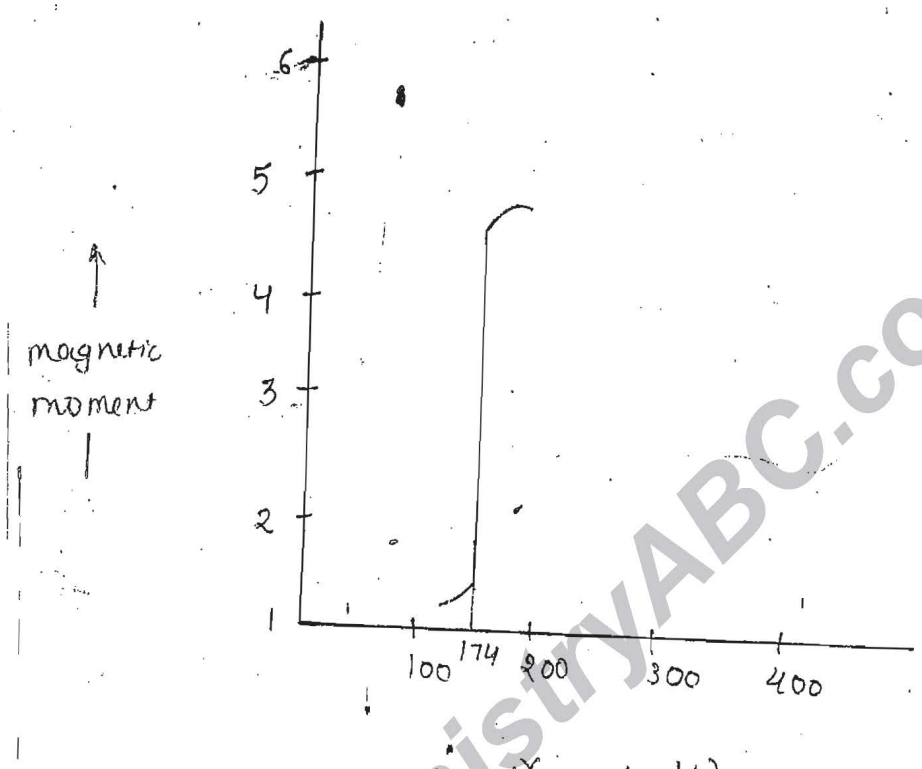
High spin and low spin equilibrium ⇒

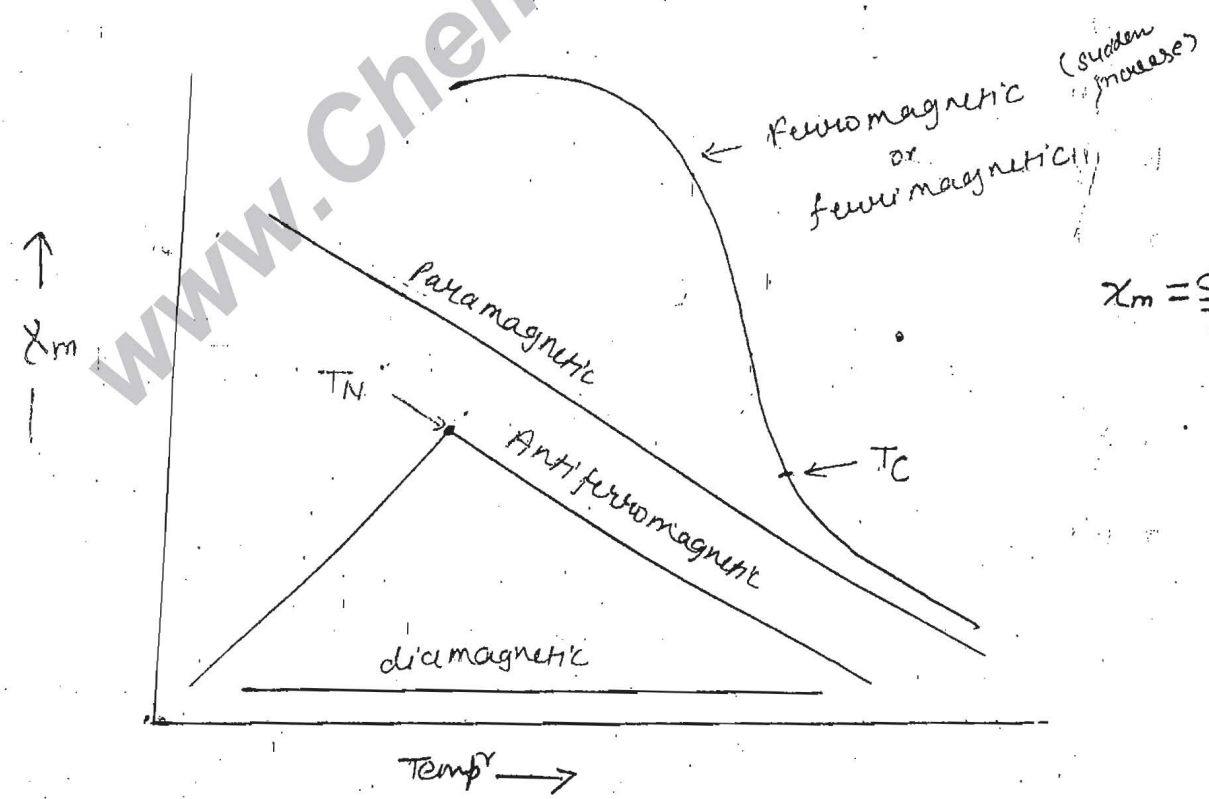
d^4, d^5, d^6 and d^7 — HS → weak ligand
LS → strong ligand

$[Fe(Phen)_2(NCS)_2]$ ← exist both as HS & LS equilibrium at 174K

$Fe^{2+} \rightarrow d^6$

only known compound which exist both in HS & LS





$\chi_m = \frac{C}{T}$

Magnetic Moment ⇒

due to orbital motion and spin motion

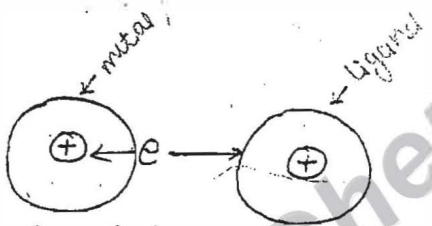
$$\mu_{L+S} = \mu_J = g\sqrt{J(J+1)} \quad B.M.$$

used for heavier elements like lanthanides

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

$J = L+S$ (for more than half filled)

$J = L-S$ (for less than half filled)



due to +nce of ligand the orbital motion is cancelled in case of d block elements hence only spin motion is remained. It is called quenching of orbital motion.

In case of Lanthanides there is no interaction with ligand hence no quenching of orbital motion occur hence both spin and orbital motion are counted.

For | skin motion –

$L = 0$

$J = S$

$g = \frac{3}{2} + \frac{1}{2} = 2$

$\mu_S = 2\sqrt{S(S+1)} = \sqrt{4S(S+1)}$

for orbital motion –

$S = 0$

$J = L$

$g = \frac{3}{2} - \frac{1}{2} = 1$

$\mu_L = 1\sqrt{L(L+1)}$

$$\mu_{L+S} = \sqrt{4S(S+1)} + \sqrt{L(L+1)}$$

B.M. mathematically right

$$\mu_{L+S} = \sqrt{4S(S+1) + L(L+1)}$$

B.M. ac to books

In complexes of transition metal there is quenching of orbital motion i.e.

$$L = 0$$

$$\mu_{spin\ only} = \sqrt{4S(S+1)} \quad B.M.$$

For one unpaired e^- –

$$S = \frac{1}{2}$$

for n unpaired e^- –

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

$$\therefore \mu_S = \sqrt{4 \times \frac{n}{2}\left(\frac{n}{2}+1\right)}$$

$$\mu_{spin\ only} = \sqrt{n(n+2)} \quad B.M.$$

Orbital contribution ⇒

For orbital contribution –

t_{2g} or t_2 → unsymmetrically filled → orbital contribution

In octahedral complexes –

$d^1 \rightarrow t_{2g}^1 e_g^0$ ← Orbital contribution

$d^2 \rightarrow t_{2g}^2 e_g^0$ ← "

$d^3 \rightarrow t_{2g}^3 e_g^0$

d^4 (HS) $\rightarrow t_{2g}^3 e_g^1$

d^4 (LS) $\rightarrow t_{2g}^4 e_g^0$ ← orbital contribution

d^5 (HS) $\rightarrow t_{2g}^3 e_g^2$

d^5 (LS) $\rightarrow t_{2g}^5 e_g^0$ ← orbital contribution

d^6 (HS) $\rightarrow t_{2g}^4 e_g^2$ ← "

d^6 (LS) $\rightarrow t_{2g}^6 e_g^0$

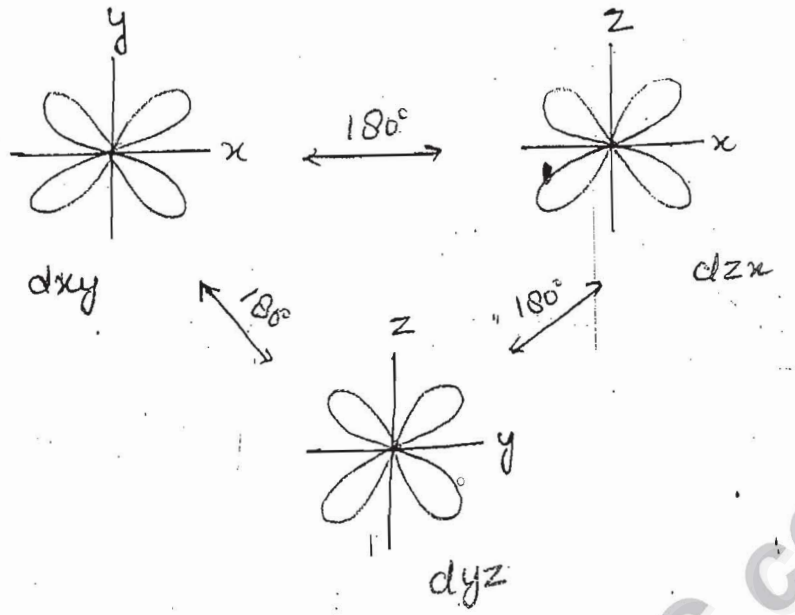
d^7 (HS) $\rightarrow t_{2g}^4 e_g^3$ ← orbital contribution

d^7 (LS) $\rightarrow t_{2g}^6 e_g^1$

d^8 (HS) $\rightarrow t_{2g}^6 e_g^2$

$d^9 \rightarrow t_{2g}^6 e_g^3$

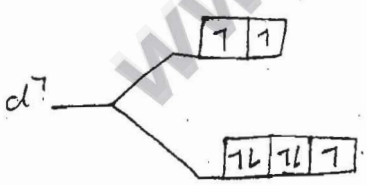
$d^{10} \rightarrow t_{2g}^6 e_g^4$



The dxy, dyz and dzx orbitals can be converted into one another due to same symmetry. Hence one e⁻ may be present any one of these. In case of dx^2-y^2 and dz^2 orbitals which are not of same symmetry. the conversion is not possible

d^7 (HS) octahedral complex ⇒

* Calculated and experimental magnetic moment.



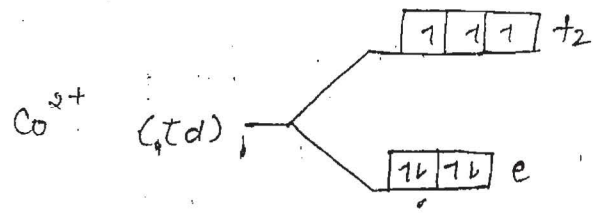
$n = 3$

$\mu_S = 3.87$ B.M. ← calculated

$\mu_S = 5.2$ B.M. ← experimental → due to orbital contribution

In case of tetrahedral complexes of d⁷

$\mu_s = 3.87$ $\quad \mu_{exp} = 4.32$ BM ← no orbital contribution as t_2 is symmetrically filled.



The experimental value is more in this case is due to skin orbital coupling.

$$\mu_{eff} = \mu_{s.o.}\left(1 - \frac{\alpha \cdot \lambda}{\Delta}\right)$$

λ = skin orbital coupling constant

α = constant

for $d^1, d^2, d^3, d^4 \rightarrow +ve$

$d^6, d^7, d^8, d^9 \rightarrow -ve$

for

^2D and $^5D \Rightarrow \alpha = 2$

^3F and $^4F \rightarrow \alpha = 4$

for $^6S \rightarrow \alpha = 0$

Q⇒ which of the following complexes has highest value of magnetic moment ?

(a) $[CoF_4]^{2-}$

(b) $[CoCl_4]^{2-}$

(c) $[CoBr_4]^{2-}$

(d) $[CoI_4]^{2-}$

F is strong ligand, hence the value of Δ will be large.

Hence μ_{eff} is greater for $[CoF_4]^{2-}$.

Here Co is +nt in +2 oxidation state means as d^7 in all complexes. hence it cant be determined by n value.

The Atomic term symbol is ^4F for all, so it also cant be determined by α value.

Stability of complexes and Reaction mechanism.

CH_3-CH_3 — Kinetically stable → as σ bond breaks hardly
Thermodynamically least stable

$CH_2=CH_2$

$CH\equiv CH$ — Kinetically least stable → as π bond breaks easily
Thermodynamically stable

Stability → Ability of a compound to be exist in nature

- (1) Thermodynamic stability
  - measured in terms of → equilibrium or formation or stability constant
  - → Standard reduction potential
  - → Gibb's free energy change
  - → Acid-base nature of medium (i.e. pH value)
- (2) Kinetic stability

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$M + L \rightleftharpoons ML$

$K_f = \frac{[ML]}{[M][L]}$ OR $[M(H_2O)_n]^{n+} + xL \rightleftharpoons [ML_x]^{n+} + xH_2O$

K_f ↑ formation constant

L = neutral monodentate ligand

$$K = \frac{[mL_x]^{n+}[H_2O]^x}{[m(H_2O)_x]^{n+}[L]^x}$$

$$K = \frac{K}{[H_2O]^x} = \frac{[mL_x]^{n+} \times 1}{[m(H_2O)_x]^{n+}[L]^x}$$

↑ equilibrium const (depends only on temp^r)
or
formation const
or
stability const

$$\log \frac{K_2}{K_1} = \frac{\Delta G^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \leftarrow \text{Vont Hoff Isotherm}$$

K_1 and K_2 → equilibrium const at T_1 and T_2 respectively

In exothermic rxn, on increasing T equilibrium const decreases

In endothermic rxn:

ΔG° = −ve

$T_2 > T_1$

$$\log K_2 - \log K_1 = \frac{\Delta G^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

ΔG°: −ve; $\left[\frac{T_2 - T_1}{T_1 T_2}\right]$: +ve; $2.303R$: +ve

$\log K_2 - \log K_1 > 0$

$\log K_2 > \log K_1$

In endothermic rxn, on increasing T equilibrium constant increases.

$$\Delta G^\circ = +ve$$

$$\log K_2 > \log K_1$$

Stoichiometric coefficient

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$$

$$K_2 = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$$

$$\boxed{K_1 = K_2^2}$$

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

$$K_2' = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

$$\boxed{K_1 = \frac{1}{K_2'}}$$

$$\text{Active mass} = \frac{\text{No. of moles}}{\text{Volume}} = \frac{\text{mass}}{\text{molar mass} \times \text{Volume}}$$

↓ conc.

K doesn't depend on conc.

$$= \frac{d \leftarrow \text{const.}}{M \leftarrow \text{const.}} = \text{const.}$$

Higher the value of equilibrium constant, more will be the stability of the product. Reactant will be less stable.

$$\boxed{\Delta G^\circ = -RT \ln K}$$ not ΔG X

Reaction quotient ⇒ The extent to which rxn is completed.
(How much a/m of product is formed or a/m of reactant decomposed)

$$Q = \frac{[mL]}{[m][L]}$$

Higher the -ve value of ΔG°, more will be the stability of the product.

$$\Delta G^\circ = -NfE^\circ = -RT \ln K$$

Stepwise formation of complex and stepwise formation constant ⇒

$$M + L \overset{K_1}{\rightleftharpoons} ML \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \overset{K_2}{\rightleftharpoons} ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \overset{K_3}{\rightleftharpoons} ML_3 \qquad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

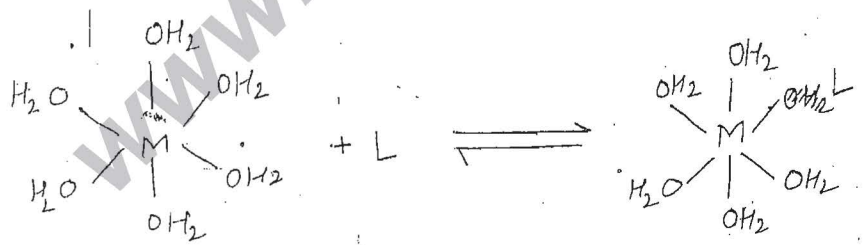
$$\vdots \qquad\qquad \vdots \qquad\qquad \vdots$$

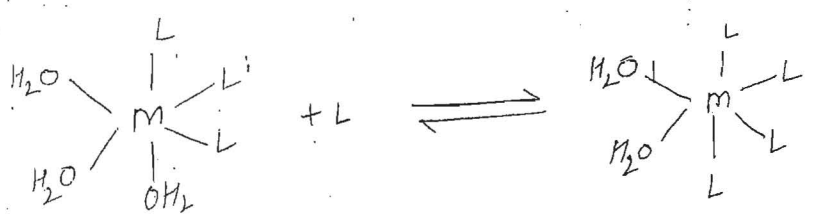
$$ML_{n-1} + L \qquad ML_n \qquad K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

$K_1, K_2, K_3, \cdots\cdots, K_n$ are the stepwise formation constants or Stability constants or equilibrium constants.

In general it is observed that

$$K_1 > K_2 > K_3 > \cdots\cdots, K_{n-1} > K_n$$





Assig Q63 Coordinated water molecules of a Cd(II) complex can be successively replaced by Br^- finally to result in $[CdBr_4]^{2-}$. In this process, the fourth equilibrium constant is observed to be higher than the third one, because

(a) equilibrium constant for the last step is always the highest

(b) three molecules of H_2O are released during the fourth step.

(c) The aquo-Cd(II) species is octahedral.

(d) an anion (Br^-) replaces a neutral (H_2O) molecule from the coordination sphere.

Soln ⇒

$$[Cd(H_2O)_6]^{2+} + Br^- \overset{K_1}{\rightleftharpoons} [Cd(H_2O)_5Br]^+ + H_2O$$

$$[Cd(H_2O)_5Br]^+ + Br^- \overset{K_2}{\rightleftharpoons} [Cd(H_2O)_4Br_2] + H_2O$$

$$[Cd(H_2O)Br_2] + Br^- \overset{K_3}{\rightleftharpoons} [Cd(H_2O)_3Br_3]^- + H_2O$$

$$[Cd(H_2O)_3Br_3]^- + Br^- \overset{K_4}{\rightleftharpoons} [CdBr_4]^{2-} + 3H_2O$$

K_4 is the combination of 3 equi constant as 3 water molecules are removed simultaneously and hence K_4 is the combination of K_4, K_5 & K_6 hence K_4 will be greater than K_3.

Here also str. of complex changes from oh to square planar and entropy also changes, hence K_4 will be > K_3.

If there is any change in complex (in str., entropy etc) it will increase the stability of complex.

Q ⇒

$$Fe^{2+} + phen \overset{K_1}{\rightleftharpoons} [Fe(phen)]^{2+}$$

$$[Fe(phen)]^{2+} + phen \overset{K_2}{\rightleftharpoons} [Fe(phen)_2]^{2+}$$

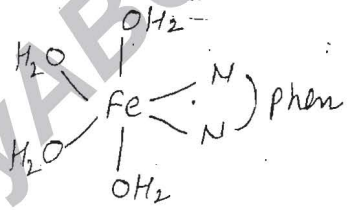
$$[Fe(phen)_2]^{2+} + phen \overset{K_3}{\rightleftharpoons} [Fe(phen)_3]^{2+}$$

$K_1 > K_2 < K_3$ .. ?

Soln ⇒

$$[Fe(H_2O)_6]^{2+} + phen \rightleftharpoons$$

HS



$[Fe(H_2O)_4(phen)]^{2+}$

HS

$$[Fe(H_2O)_4(Phen)]^{2+} + phen \rightleftharpoons [Fe(H_2O)_2(phen)_2]^{2+} + 2H_2O$$

(weak ligand; strong ligand)

HS

$$[Fe(H_2O)_2(phen)_2]^{2+} + phen \rightleftharpoons [Fe(phen)_3]^{2+} + 2H_2O$$

HS — LS

less CFSE will change/release — more CFSE will change/release

Here change in electronic str. takes place and electronic change stabilize the complex

d^6 (HS) $\longrightarrow t_{2g}^4 e_g^2$ $\qquad$ d^6 (LS) $\longrightarrow t_{2g}^6 e_g^0$

Overall formation of complex and overall formation constant ⇒

$$M + L \overset{\beta_1}{\rightleftharpoons} ML \qquad \beta_1 = \frac{[ML]}{[M][L]}$$

$$M + 2L \overset{\beta_2}{\rightleftharpoons} ML_2 \qquad \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$M + 3L \overset{\beta_3}{\rightleftharpoons} ML_3 \qquad \beta_3 = \frac{[ML_3]}{[M][L]^3}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$M + nL \overset{\beta_n}{\rightleftharpoons} ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

$\beta_1, \beta_2, \beta_3, \ldots \beta_n$ → overall formation or stability constant.

Relationship b/w $K_1, K_2, K_3, \ldots K_n$ and β_n ⇒

$$M + 3L \rightleftharpoons ML_3$$

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

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

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

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

$\beta_3 = K_1 \cdot K_2 \cdot K_3$

or $\boxed{\beta_n = K_1 \cdot K_2 \cdot K_3 \cdots K_n}$

$$\boxed{\log \beta_n = \log K_1 + \log K_2 + \log K_3 + \cdots + \log K_n}$$

Ex:- $Cd^{2+} + NH_3 \rightleftharpoons [Cd(NH_3)]^{2+}$ $K_1 = 10^{2.65}$

$[Cd(NH_3)]^{2+} + NH_3 \rightleftharpoons [Cd(NH_3)_2]^{2+}$ $K_2 = 10^{2.10}$

$[Cd(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cd(NH_3)_3]^{2+}$ $K_3 = 10^{1.44}$

$[Cd(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$ $K_4 = 10^{0.93}$

rxn can be done either in aq. soln. or gaseous phase.

The above rxn carried out in gaseous phase as value of equili. const. decreased.

$\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4$

$= 10^{2.65} \times 10^{2.10} \times 10^{1.44} \times 10^{0.93}$

$\beta_4 = 10^{7.12}$

If rxn would be carried out in aq. phase

$K_4 > K_3$

Factors affecting stability of complexes ⇒

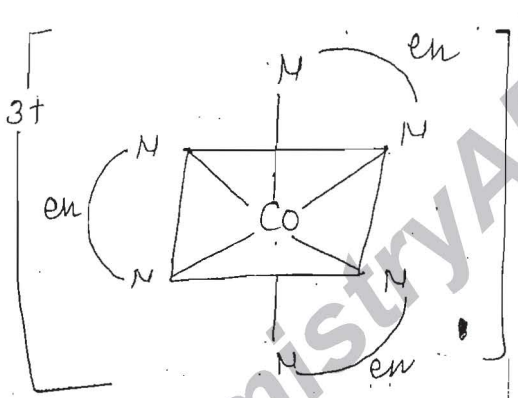
① Chelate effect ⇒ ligands which form cyclic complexes are called chelating ligands.

Chelating ligands → polydentate ligands (bidentate, tridentate ---- Hexadentate).

⇒ The complex containing cyclic or ring structures are called chelates.

Ex:-

① $[Co(en)_3]^{3+}$



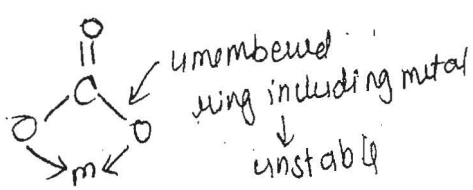
② $[Ca(edta)]^{2-}$

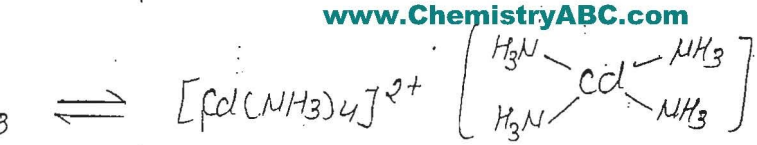
⇒ Chelates are more stable than the non chelated complex, this is called chelate effect.

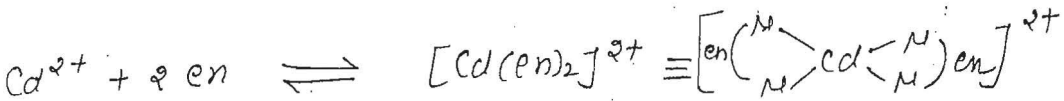
$$[Co(en)_3]^{3+} > [Co(NH_3)_6]^{3+}$$

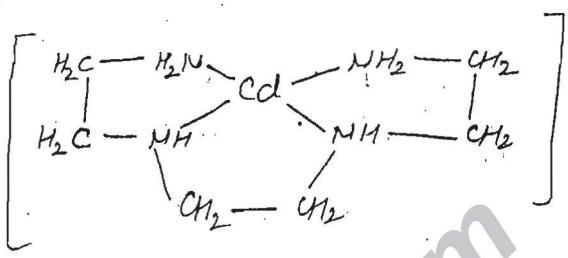
⇒ Stability of chelates increases with increase in no. of rings per ligands.

⇒ Stability of chelates increases with increase in size of rings- (upto 6 membered rings after than decreases) due to steric hindrance as more atom at one metal



$Cd^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$ 

$Cd^{2+} + 2\,en \rightleftharpoons [Cd(en)_2]^{2+} \equiv$ 

$Cd^{2+} + trien \rightleftharpoons$ 

$n_1 = 5$ $\qquad$ $n_2 = 5$ $\qquad$ $\Delta n = 0$

$[Cd(H_2O)_4]^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+} + 4H_2O \qquad \Delta S_1 = 0$

$n_1 = 3$ $\qquad$ $n_2 = 5$ $\qquad$ $\Delta n = 2$

$[Cd(H_2O)_4]^{2+} + 2\,en \rightleftharpoons [Cd(en)_2]^{2+} + 4H_2O \qquad \Delta S_2 = +ve$

$n_1 = 2$ $\qquad$ $n_2 = 5$ $\qquad$ $\Delta n = 3$

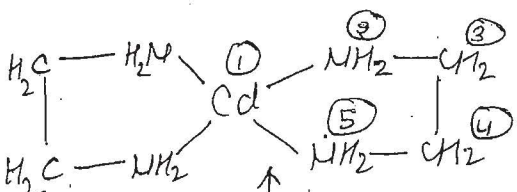
$[Cd(H_2O)_4]^{2+} + trien \rightleftharpoons [Cd(trien)]^{2+} + 4H_2O \qquad \Delta S_3 = +ve$

$\Delta S_3 > \Delta S_2 > \Delta S_1$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Enthalpy of formation is -ve in general which is nessary for complex formation.

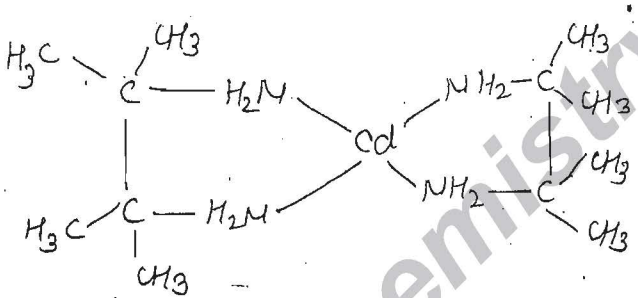
$\Delta H = (-ve)$ same for all complexes as same no. of bonds are formed with Nitrogen.

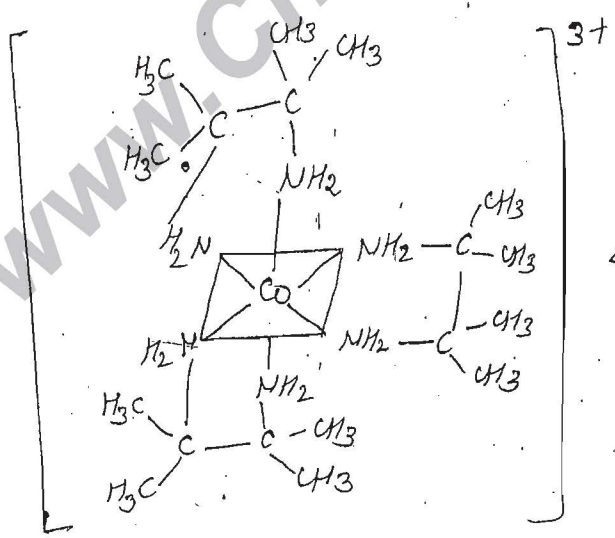


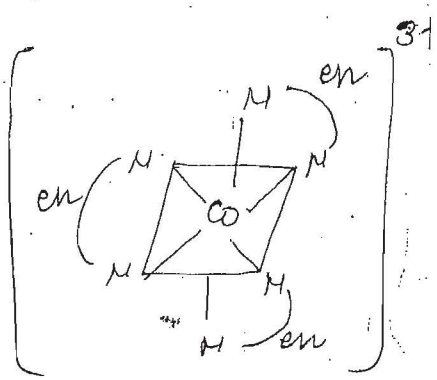
5 membered ring including metal

⇒ 3 and 4 membered rings including metal are less stable.

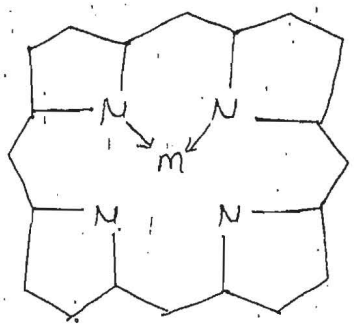
⇒ If bulky groups are attached to donor atoms or adjacent to donor atoms, stability of chelate decreases.







Macrocyclic effect ⇒



Macrocyclic complex like Hb, Mb (chlorophyll) are more stable than that of chelating complex. This effect is called macrocyclic effect. Macrocyclic complex are stable because metal is +nt in cavity and surrounded by ligands.

Nature of Metal Cation ⇒

① charge on metal ion ⇒ Higher the charge (on the metal ion) more will be the stability of complexes

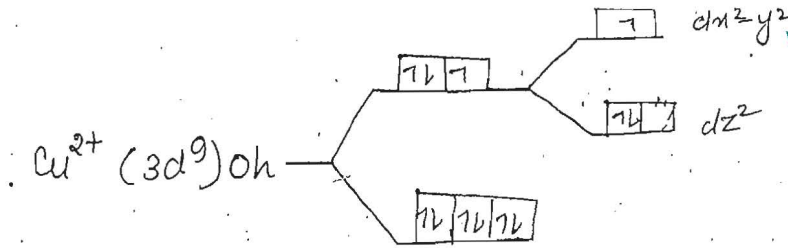
② Size of metal ion ⇒

Imp
Irving-William series —

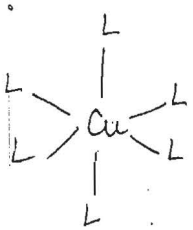
$$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

↑ large size than Cu → less stable.

stability increases ⟶

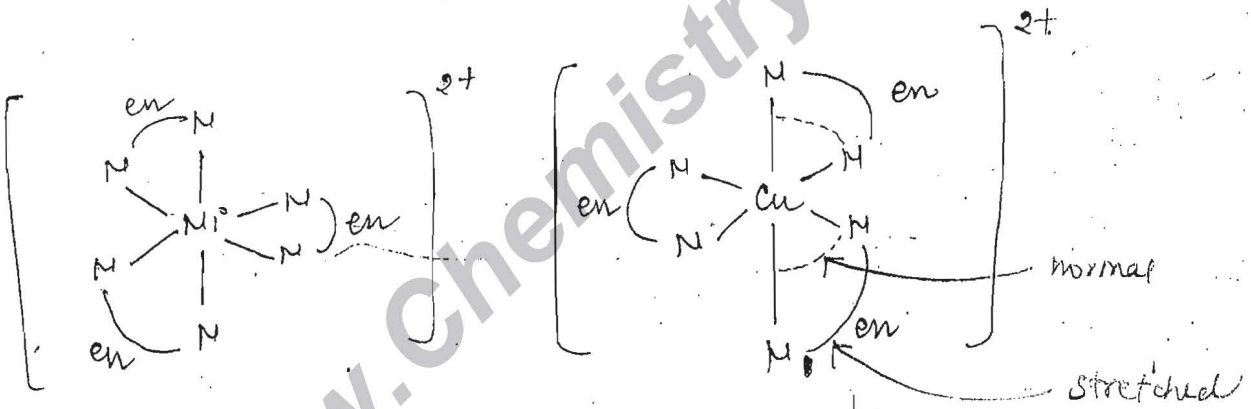


due to John-Teller distortion the energy of 2e- decreases and 1e- increases but overall energy ↓ hence Cu^{2+} is stable



$[Ni(en)_3]^{2+} > [Cu(en)_3]^{2+}$

$[Cu(H_2O)_6]^{2+} > [Ni(H_2O)_6]^{2+}$



due to largening of bonds strain occur → less stable complex due to John Teller distortion

$[Cu(H_2O)_6]^{2+} > [Cu(en)_3]^{2+}$

Here John-T dist decreases energy → more stable

John Teller distortion will cause ring strain in this complex → less stable

metal form more stable complex with -ve ligands in high oxidation state and with π-acceptor ligand in low oxidation state as back π bonding will occur which strengthen metal-ligand bond.

Class 'a' and class 'b' metals ⇒ metals classified as-

(a) Class 'a' metals

(b) class 'b' metals

(c) Borderline metals

28[oct]3

(a) Class 'a' metals ⇒

and acids $\left\{\begin{array}{l} Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Sc^{3+}, \\ Ti^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ir^{4+}, Ln^{3+}, Ce^{3+}, Ce^{4+}, Gd^{3+}, \\ Zr^{4+} \end{array}\right.$

These form stable complexes in the order of

$F^- > Cl^- > Br^- > I^-$

$N > P > As > Sb$

$O >> S > Se > Te$

Class 'b' metals ⇒ Sof Acids

Cu^+, Ag^+, Au^+, Te^+, Cd^{2+}, Hg_2^{2+}, Hg^{2+}, Pd^{2+}, Pt^{2+}, Te^{3+} (Thallium)

order of stability of complexes –

$I^- > Br^- > Cl^- > F^-$

$Sb > As > P > N$

$Te > Se > S > O$

© Border Line metals ⇒

Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}

order of stability –

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

(Irving – william series)

Nature of ligands ⇒

Covalent character ⇒ Higher the covalent character, more will be the stability.

$AgF_2^- < AgCl_2^- < AgBr_2^- < AgI_2^-$

order of covalent character
order of stability

Kinetic Stability ⇒ refers to the rate of rxn.

depends on rate const. & Activation energy.

$$k = A e^{-Ea/RT}$$ (Arrhenius eqn)

k = rate const.

A = Pre-exponential factor
or
Arrhinius constant
or
frequency factor

Ea = energy of activation

R = gas constant

T = Absolute Temp^{r}.

Absolute temperature ⇒ Temperature measured in Kelvin.

$$\log \frac{K_2}{K_1} = \frac{Ea}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Frequency factor is applicable only for 1st order as Arrhenius eqn is only for unimolecular rxn.

VVI

Kinetic stability.

Lability

Inertness

Labile complex → rate of rxn fast

$t_{1/2} < 1$ minute

Inert complexes → unreactive or less reactive.

$t_{1/2} > 1$ minute

In case of complexes-

substitution rxn → slow → Inert complexes

→ fast → labile complexes

- Lability and inertness on the basis of VBT ⇒

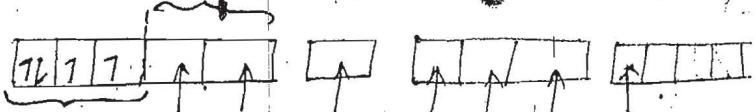
low lying (below hybrid orbitals) empty d-orbitals

→ complex will be labile

If no low lying vacant d-orbital → Inert

e.g. $[Cr(CN)_6]^{4-}$ $Cr^{2+} \rightarrow 3d^4$

hybrid orbitals (more energy)



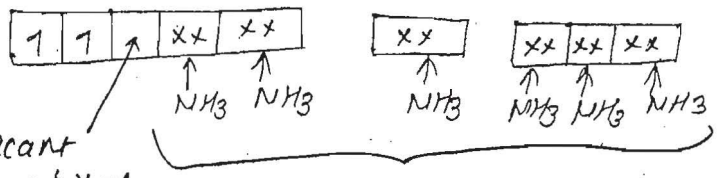
novacant (less energy)

low lying d-orbital → Inert

d^2sp^3 inner orbital complex

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

$3d^2$



vacant d-orbital

d^2sp^3 hybrid.

Active site for incoming ligand

↓

low energy

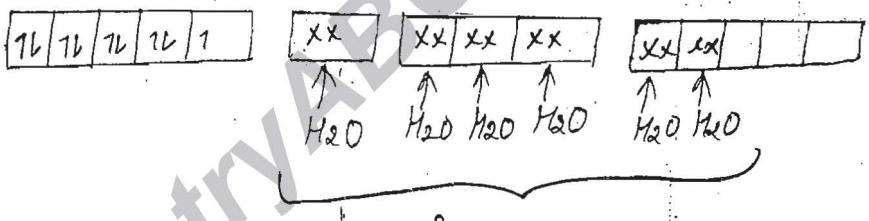
↓

forms stable complex with ligand

↓

new m–l bond is stronger than pre existing

$[Cu(H_2O)_6]^{2+} \rightarrow 3d^9$



sp^3d^2

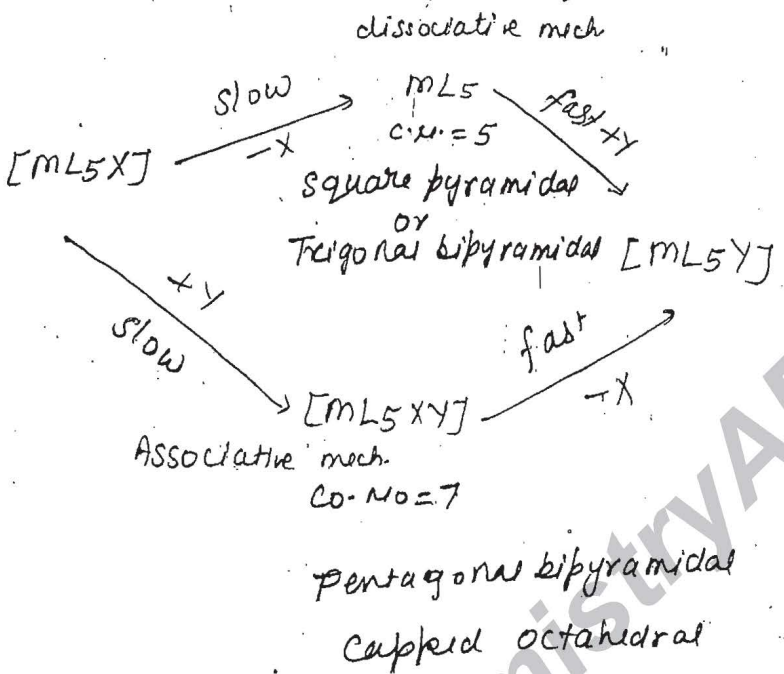
This complex should be inert but it is most labile complex. Hence this is exception of this theory.

As we move down in 4d and 5d series all transition metals make inert complex whether vacant d orbitals are present or not.

A/c to this theory formation of m-L complex follow associative mech. which is not correct.

$[ML_5X] + Y \longrightarrow [ML_5Y] + X$

Nucleophilic substitution



Most of the substitution rxn in octahedral complexes proceed through dissociative mechanisms.

Loss in CFSE (change in CFSE on going from Oh to intermediate is negative) complex → Inert

No loss or gain in CFSE → complex is labile

Basolo and Pearson ⇒ experimentally found the value of change in CFSE.

Change in CFSE

System	high spin	Low spin
d^0	0	0
d^1	+0.57	+0.57
d^2	+1.14	+1.14
d^3	−2.00	−2.00
d^4	+3.14	−1.43
d^5	0	−0.86
d^6	+0.57	−4.00 (most inert)
d^7	+1.14	+1.14
d^8	−2.00	−2.00
d^9	+3.14	+3.14
d^{10}	0	0

Q70 Assign) Designate the following complexes X, Y, and Z as labile-

- X = $[Al(C_2O_4)_3]^{3-}$ → $3d^0$ → 0 labile
- Y = $[V(H_2O)_6]^{2+}$ → $3d^3$ → −2.00 → Inert
- Z = $[Cr(C_2O_4)_3]^{3-}$ → $3d^3$ → −2.00 → Inert

(d) X is labile, Y and Z are inert

All the complexes of coordination no. 4 (square planar or Tetrahedral are always labile because less sterically hinderance or negligible steric hinderance).

complexes of 4d & 5d series transition metals (Octahedral complexes) are always inert).

Lability of coordination no. 4 complexes decreases down the group.

Ni
Pd
Pt
↓ decreasing order of lability.

Q⇒ Arrange the following complexes in the increasing order of inertness.

(Co forms L.S. comp. in +3 except halides)

$[Co(NH_3)_6]^{3+}$	$[Cr(H_2O)_6]^{3+}$	$[Co(H_2O)_6]^{3+}$	$[M(H_2O)_6]^{2+}$
P	Q	R	S
d^7 L.S.	d^4 H.S.	d^6 L.S.	d^8 H.S.
+1.14	+3.14	+4.00	−2.00

Q < P < S < R

for non transition metals ⇒

① oxidation state of metals ⇒ Higher the oxidation state, more will be the inertness.

Ex:- $[AlF_6]^{3-}$ ($+3$) < $[SiF_6]^{2-}$ ($+4$) < $[PF_6]^{-}$ ($+5$) < $[SF_6]$ ($+6$)

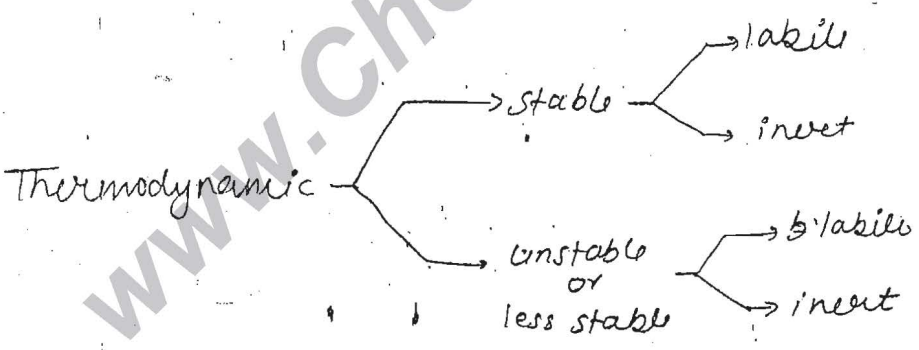
order of inertness

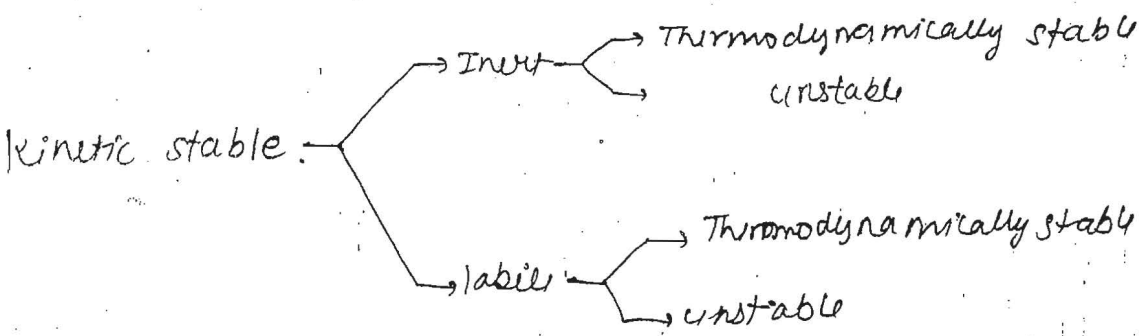
② Size of metal ions ⇒ Inertness increases with decrease in size of metal ion.

Ex:- $[Cs(H_2O)_6]^{+}$ < $[Rb(H_2O)_6]^{+}$ < $[K(H_2O)_6]^{+}$ < $[Na(H_2O)_6]^{+}$

order of inertness

Relationship b/w Thermodynamic and kinetic stability ⇒





Examples ⇒

$[Ni(CN)_4]^{2-} + 4\,{}^{13}CN^- \longrightarrow [Ni(^{13}CN)_4] + 4\,CN^-$

labile $t_{1/2}$ = 30 sec

$[Mn(CN)_6]^{3-} + 6\,{}^{13}CN^- \longrightarrow [Mn(^{13}CN)_6]^{3-} + 6\,CN^-$

moderate inert $t_{1/2}$ = 1 hr

$[Cr(CN)_6]^{3-} + 6\,{}^{13}CN^- \longrightarrow [Cr(^{13}CN)_6]^{3-} + 6\,CN^-$

inert $t_{1/2}$ = 24 days

Thermodynamically stable

$[Co(NH_3)_6]^{2+} + 6H_3O^+ \longrightarrow [Co(H_2O)_6]^{2+} + 6\,NH_4^+$

Thermodynamically unstable

d^7 → kinetically labile

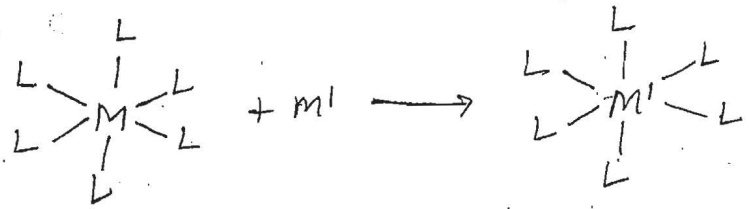
Substitution reactions in octahedral complexes ⇒

① Electrophilic substitution reactions

② Nucleophilic substitution reactions

① Electrophilic substitution reactions ⇒

$ML_6 + M' \longrightarrow M'L_6 + M$



not possible because high energy is consumed in breaking 6 M–L bonds.

(2) Nucleophilic substitution reactions ⇒

$$[ML_5X]^{n\pm} + Y \longrightarrow [ML_5Y]^{n\pm} + X$$

Mechanism ⇒

1. Dissociative (D)
2. Associative (A)
3. Interchange (I)

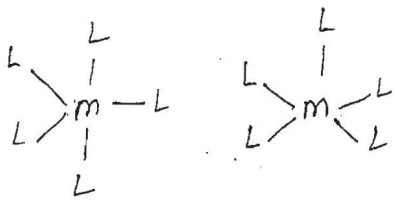
(1) Dissociative ⇒ Mechanism ⇒

$$[ML_5X]^{n\pm} \xrightarrow[-X]{\text{Slow}} [ML_5] \longrightarrow [ML_5Y]^{n\pm}$$

[Rate determining step]

Coordination No. = 5

may be square pyramidal (SP) or Trigonal bipy. (TBP)



TBP SP

$$\text{Rate} \propto [ML_5X]$$

$$\text{Rate} = k[ML_5X]$$

② Associative mechanism ⇒ (S_N2 mechanism)

$$[ML_5X]^{n\pm} \xrightarrow[\text{slow}]{+Y} [ML_5XY]^{n+} \xrightarrow[-X]{\text{fast}} [ML_5Y]$$

pentagonal bipyramidal
or
capped octahedral

Rate $\propto [ML_5X][Y]$

Rate $= k[ML_5X][Y]$ 2nd order rxn

③ Interchange mechanism ⇒

Simultaneous bond formation and breaking.

$$Y + [ML_5X]^{n\pm} \xrightarrow{\text{slow}} [Y\text{----}ML_5\text{----}X] \xrightarrow{\text{fast}} [ML_5Y] + X$$

Transition state
or
Activated complex

① Dissociative Interchange (Id)

② Associative interchange (Ia)

① dissociative interchange (Id) ⇒

Bond formation begins before the complete breaking of bond

Bond breaking is the dominating factor.

$$Y\text{----}ML_5\text{---}X$$

(2) Associative interchange (Ia) ⇒

Bond breaking begins before the complete formation of new bond.

Y- — — ML5 - - - - X

Experimentally it is observed that most of the nucleophilic substitution reactions proceed through dissociate mechanism. (SN1 mechanism)

Imp Evidence in favour of dissociative mechanism ⇒

(1) water exchange ⇒

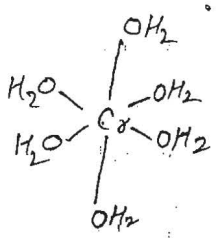
(a) Class (1) ⇒ The rate of water exchange is very fast.

$$k = 10^{8}\ s^{-1} \leftarrow \text{unit of first order}$$

Ex:- alkali metals, alkaline earth metals (except Be^{2+}, Mg^{2+}), Group 12 elements (except Zn^{2+}), Cr^{2+} and Cu^{2+} from 3d series. Cr^{2+} and Cu^{2+} make most stable complexes hence most labile.

$$[Cr(H_2O)_6]^{2+} + 6H_2O^{*} \rightleftharpoons [Cr(H_2O^{*})_6] + 6H_2O$$

Due to John-Teller distortion R.O.R. is fast.



(b) Class (2) ⇒ The rate of water exchange is also high.

$$k = 10^{4} - 10^{8}\ sec^{-1}$$

Examples ⇒ dipositive metal ions of 3d series (except V^{2+}, Cr^{2+} & Cu^{2+}), Mg^{2+}, Ti^{3+} and tri lanthanides.

(c) Class (3) ⇒ Rate constant

$$k = 1 - 10^{4}\ sec^{-1}$$

Examples ⇒ most of the positive tri transition metal ions from 3d-series, Be^{2+}, V^{2+}, Al^{3+}, Ga^{3+}

(d) Class (4) ⇒ Rate constant

$$k = 10^{-6} \text{ to } 10^{-2}\ sec^{-1}$$

Examples ⇒ Co^{3+}, Cr^{3+}, Rh^{3+}, Ru^{3+}, Ir^{3+}

Order of water exchange -

di+ve → (learn) $V^{2+} < Mn^{2+} < Fe^{2+} < Mn^{2+} < Zn^{2+} < Cr^{2+} < Cu^{2+}$

tri+ve → $Cu^{3+} < V^{3+} < Fe^{3+} < Ti^{3+}$

Anation Reaction ⇒

In these complexes an anion replaces H_2O molecule from its complex.

$$[M(H_2O)_6]^{n+} + X^{\ominus} \longrightarrow [M(H_2O)_5X]^{(n-1)+} + H_2O$$

Ex:-

$$[Ni(H_2O)_6]^{2+} + X^{\ominus} \longrightarrow [Ni(H_2O)_5X]^{+} + H_2O$$

$X^{\ominus}$ =	$F^{\ominus}$	$SCN^{\ominus}$	$CH_3COO^{\ominus}$
$k(s^{-1})$	8×10^{3}	6×10^{3}	30×10^{3}

$$[Ni(H_2O)_6]^{2+} + NH_3 \longrightarrow [Ni(H_2O)_5NH_3]^{2+} + H_2O$$

$k = 4\times10^{3}\ s^{-1}$ not anation rxn

(V.V.I)

Aquation rxns or hydrolysis reactions ⇒

In acidic medium ⇒

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

$X^{-} = F^{-}, Cl^{-}, Br^{-}, I^{-}, SCN^{-}, NO_3^{-}$

		(may be exist or not)	
$FeCl_3$ → exist	$SnCl_4$	TlI_3 X	$Tl^{+} > Tl^{3+}$
$FeBr_3$ → exist (less stable)	$SnBr_4$	TlI .	
FeI_3 → X	SnI_4 X		

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \quad \times 2$$

$$2I^- \longrightarrow I_2 + 2e^-$$

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

$$KI + I_2 \longrightarrow KI_3$$

Iodine is a strong reducing agent and reduces Fe^{3+} into Fe^{2+}. Therefore FeI_2 forms.

In alkaline medium—

$$[Co(NH_3)_5X]^{2+} \xrightarrow{+OH^-} [Co(NH_3)_5OH]^{2+} + X^-$$

(OH^- from water)

Fast Acid hydrolysis ⇒

$$[Co(NH_3)_5X]^{2+} + H_2O \xrightarrow{H^+} [Co(NH_3)_5(H_2O)]^{3+} + X^-$$

rate $= k_a [Co(NH_3)_5X]^{2+}$

(k_a = rate const. for acid hydrolysis)

here H^+ binds with $X^\ominus$ and tightly bound it by which $X^\ominus$ can't further take part in rxn.

Factors affecting rate of acid hydrolysis ⇒

① Nature of leaving group ⇒

$$Co-F < Co-Cl < Co-Br < Co-I$$

It is dissociative mechanism.

② Charge effect ⇒

$$[\overset{+3}{Co}(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + Cl^-$$

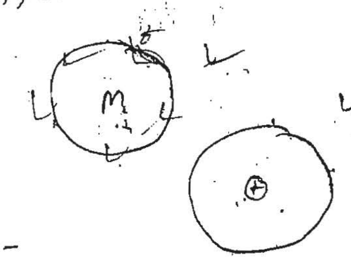
$$k_a = 6.7 \times 10^{-6}\ sec^{-1}$$

$$[\overset{+3}{Co}(NH_3)_4Cl_2]^{+} + H_2O \longrightarrow [Co(NH_3)_4Cl\,H_2O]^{2+} + Cl^-$$

$$k_a = 1.8 \times 10^{-3}\ s^{-1}$$

Rate of acid hydrolysis increases with decrease in charge on the complex ion, this is called charge effect.

③ Effect of chelation ⇒



(I) $$[Co(NH_3)_5Cl]^{2+} \xrightarrow{slow} [Co(NH_3)_5]^{3+} + Cl^-$$

Small size intermediate ← will attract ligand more

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

(II) $$[Co(en)_2(NH_3)Cl]^{2+} \xrightarrow{slow} [Co(en)_2(NH_3)]^{3+} + Cl^-$$

Large size intermediate

$$[Co(en)_2(NH_3)]^{3+} + H_2O \xrightarrow{fast} [Co(en)_2(NH_3)(H_2O)]^{3+}$$

Reaction (I) is faster than reaction (II).

Base hydrolysis ⇒

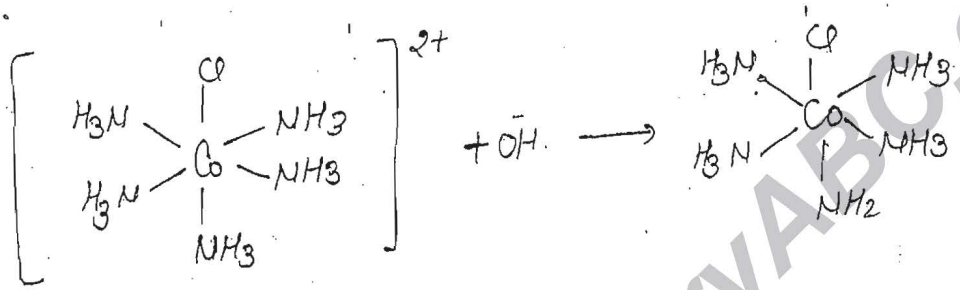
$NH_3 \rightleftharpoons NH_2^{\ominus}$ (conjugate base of NH_3)
$-H^+$

(i) $[Co(NH_3)_5Cl]^{2+} + OH^- \underset{}{\overset{Fast}{\rightleftharpoons}} [Co(NH_3)_4(NH_2)Cl]^{+} + H_2O$

CB ← conjugate base

(ii) $[Co(NH_3)_4(NH_2)Cl]^{+} \xrightarrow[k_b]{Slow} [Co(NH_3)_4NH_2]^{2+} + Cl^-$

(iii) $[Co(NH_3)_4(NH_2)]^{2+} + H_2O \xrightarrow{fast} [Co(NH_3)_5(OH)]^{2+}$



$K_b > K_a$ because –

① charge effect

② NH_2 stabilizes intermediate by forming π bond

③

Rate of rxn depends only on the conc. of base.

It is called S_N1 conjugate base mechanism.

From rxn (i)

$$K = \frac{[CB][H_2O]}{[Co(NH_3)_5Cl]^{2+}[OH^-]} \quad \text{or} \quad [CB] = \frac{K[Co(NH_3)_5Cl]^{2+}[OH^-]}{[H_2O]}$$

$$\text{Rate} = K_b [CB]$$

$$= \frac{K K_b}{H_2O} [Co(NH_3)_5Cl]^{2+} [\bar{O}H]$$

$$= k' [Co(NH_3)_5Cl]^{2+} [\bar{O}H] \quad \text{— ①}$$

A/c to eqn ① –

Reaction is 1st order w.r.t. $\bar{O}H$ and 1st order w.r.t. $[Co(NH_3)_5Cl]^{2+}$. So, this rxn is consistent with 2nd order. But as conc of $[Co(NH_3)_5Cl]^{2+}$ is in excess as compared to $\bar{O}H$. Hence it may be considered as constant like in pseudounimolecular rxn. Hence the rate is totally depend on $\bar{O}H$.

$$[Co(Py)_5Cl]^{2+} + \bar{O}H \xrightarrow[\text{rxn}]{\text{very slow}}$$

It has no H

This rxn is independent of $\bar{O}H$ conc.

Substitution reactions without breaking of M–L bond ⇒

$$[(H_3N)_5Co-OCO_2]^{+} + 2H_3O^{+} \longrightarrow [(H_3N)_5Co(H_2O)]^{3+} + 2H_2O + CO_2$$

(with ^{18}O labelling)

mechanism ⇒

$$[(H_3N)_5Co-O-C(=O)-O]^{+} + H^{+} \rightleftharpoons [(H_3N)_5Co-O-C(OH)-O]^{2+}$$

$$\longleftrightarrow [(H_3N)_5Co-O(H)\cdots C(=O)-O]^{2+} \longrightarrow [(H_3N)_5Co(OH)]^{2+} + CO_2$$

decarboxylation

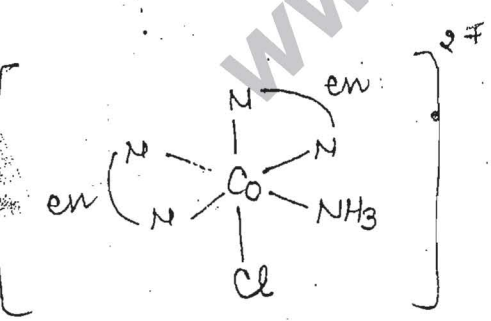
$$\downarrow H^{+}$$

$$[(H_3N)_5Co(H_2O)]^{3+}$$

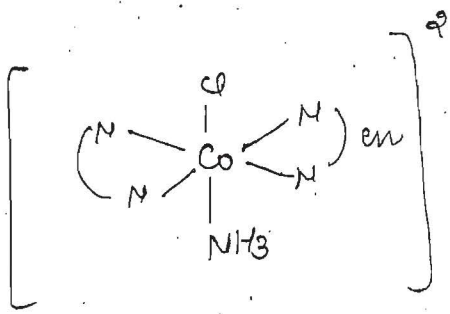
imp

Stereochemistry of acid hydrolysis ⇒

$[Co(en)_2AX]^{2+}$ $[Co(en)_2(NH_3)Cl]^{2+}$

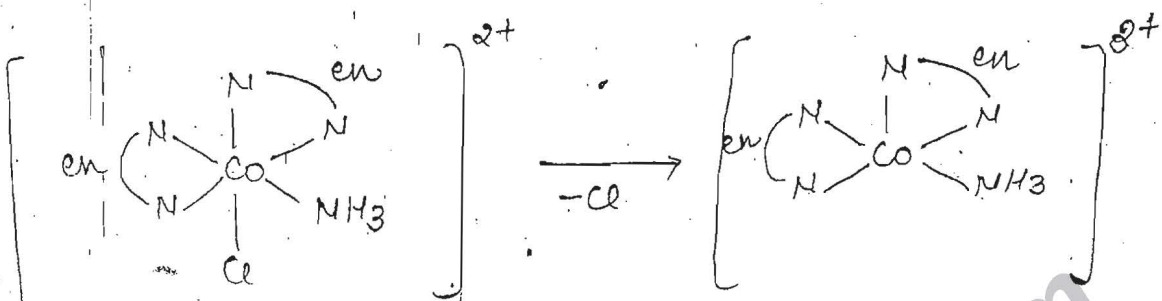


cis



trans

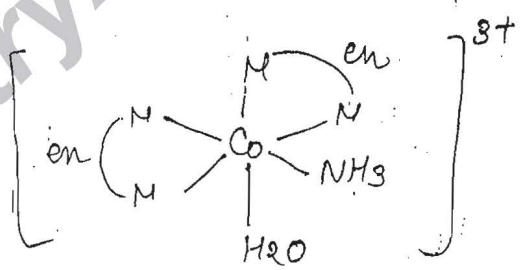
In case of acid hydrolysis intermediate is always square pyramidal.



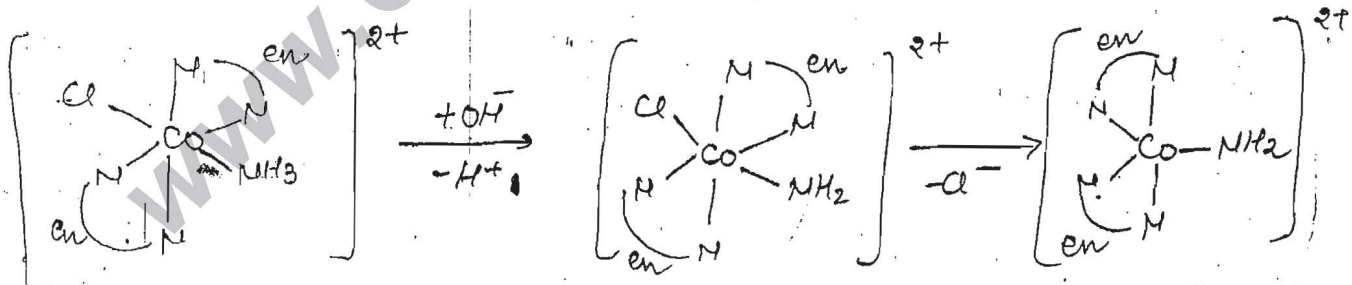
cis

SP (square pyramidal)

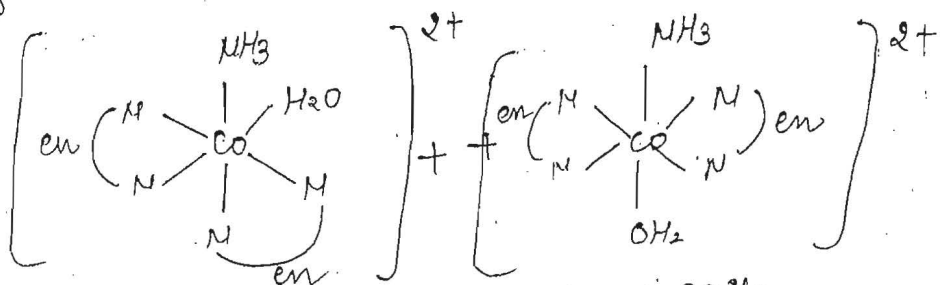
[If π donor ligand is +nt in Intermediate then TBT interme. will also form]



cis – 100%



Trans



cis- 70%

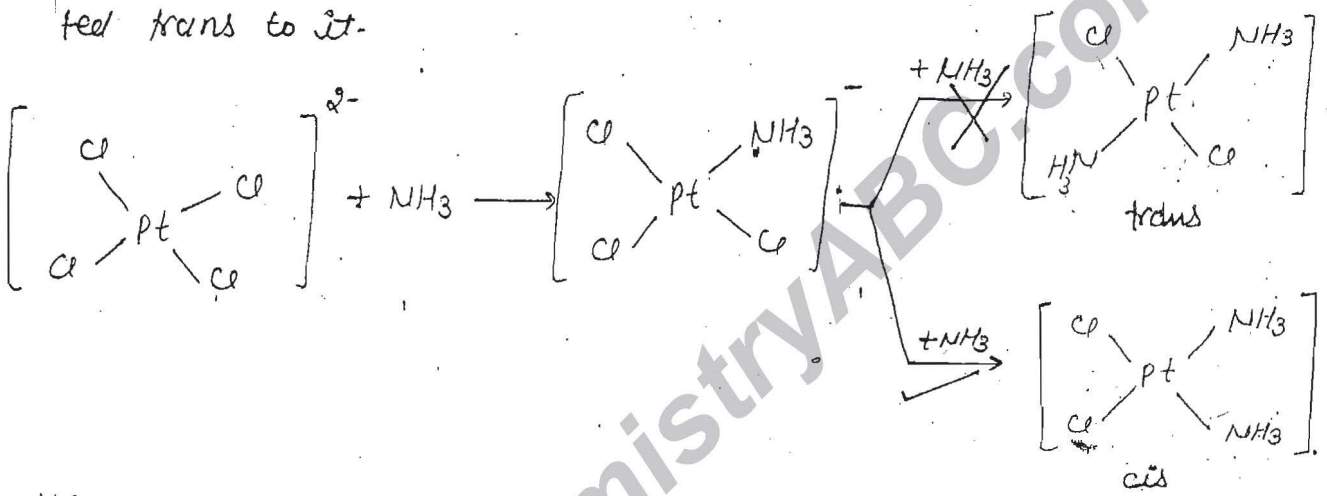
trans -30%

31/oct/13 Substitution reactions in square planar complexes ⇒

Trans effect ⇒ Trans effect of a group or ligand (spectator ligand) co-ordinated to the metal cation is the tendency of that group to direct an incoming ligand to occupy the position trans to that group.

OR

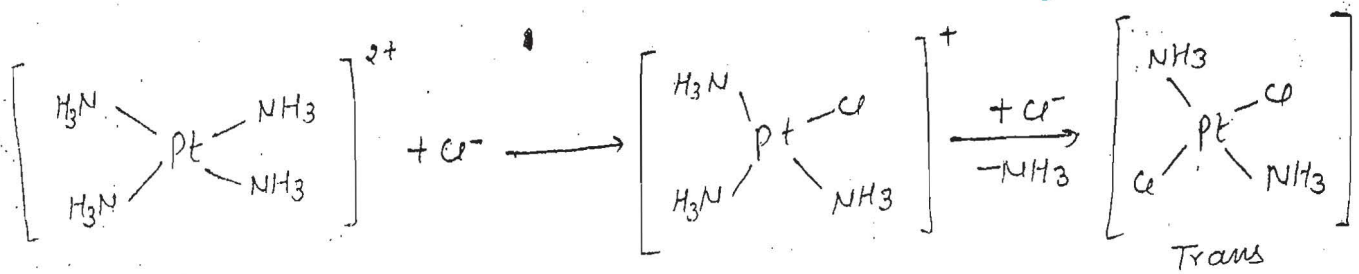
Spectator ligand increases the lability of the group coordinated trans to it.

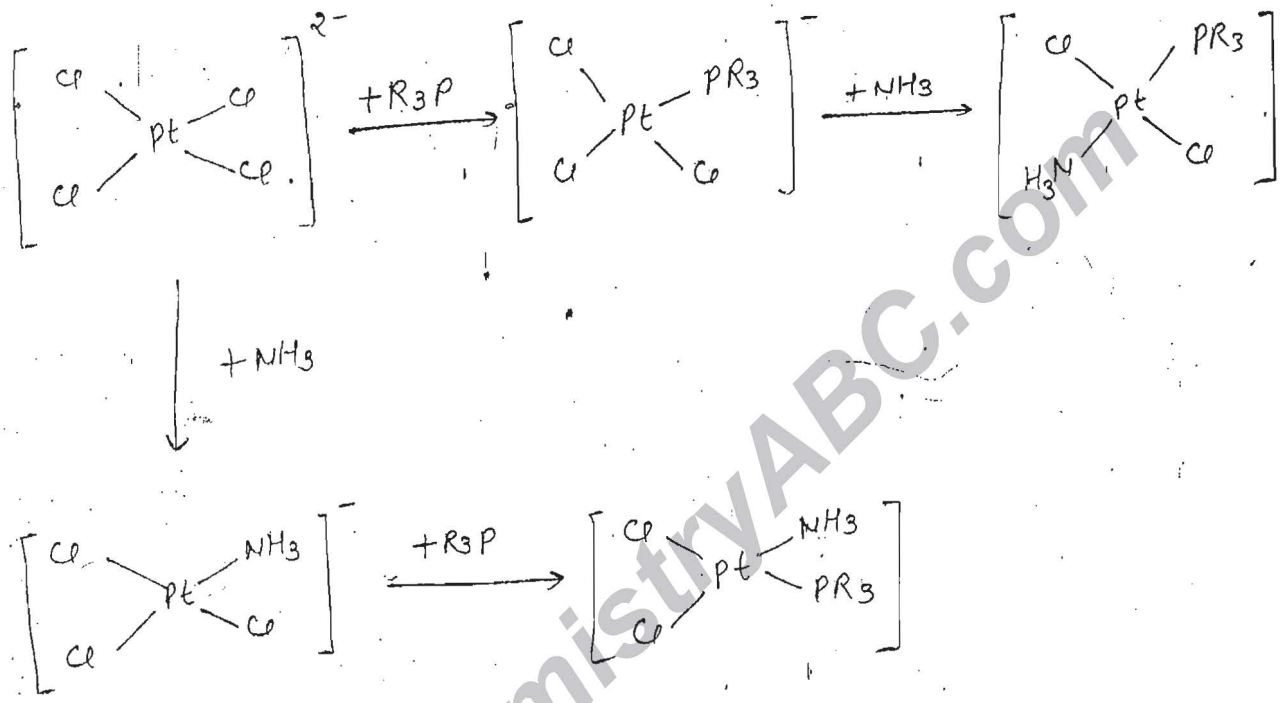


Here, Cl^- have greater trans effect than NH_3. So the final product will be cis-product.

Trans effect series ⇒ (Trans directing series) ⇒

$CN^-, CO, NO, C_2H_4 > PR_3, AsR_3, H^- > CH_3^-, SC(NH_2)_2 > C_6H_5^-, NO_2^-, SCN^- > Br^- > Cl^- > py > RNH_2, NH_3 > F^-, > OH^- > H_2O$





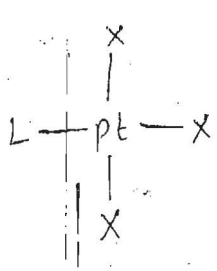
Theories of trans effect ⇒

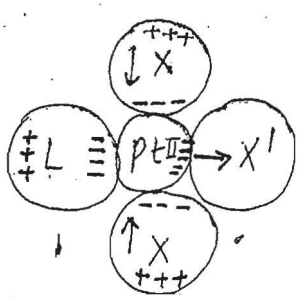
① Polarisation theory

② π - bonding theory

① Polarisation theory ⇒ Only for ligands having less trans effect.

e.g. $F^{\ominus}$, Cl^-, Br^-, I^-



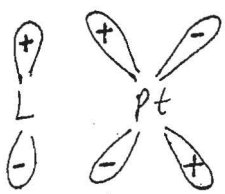


Here Pt^{2+} polarised the large sized ligand and the charge density increases on Pt & it repell the X ligand. Hence weaker will be the (Pt-X') bond

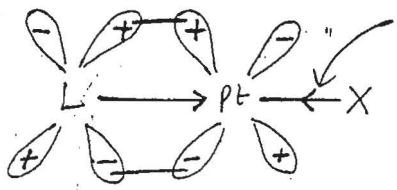
$I^- > Br^- > Cl^- > F^-$ (Polarization effect)

② π-bonding theory ⇒ for strong trans directing ligands.

π-acceptors → CO, CN^-, NO, C_2H_4, R_3P etc.



pπ-dπ

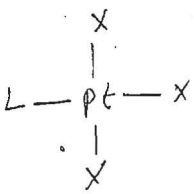


polar bond = (weak bond)

dπ-dπ (R_3P)

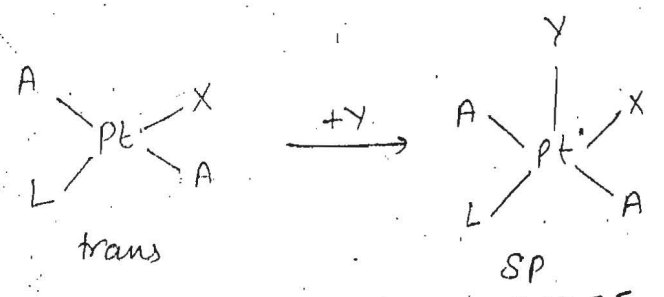
OR

dπ-π* (CO, NO, C_2H_4)



Here, if both ligand & spectator ligand are polar then the metal donates its e⁻ to the spectator ligand, due to this e⁻ density on the metal decreases then the bond b/w ligand and metal will become weaker due to attraction of e⁻ from ligand to metal.

Mechanism :- (of substitution rxn in square planar complexes → associative mechanism)



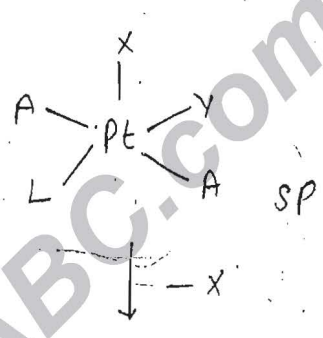
X, Y, L at equatorial position

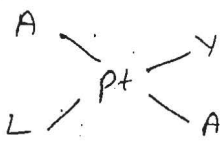
A → at axial position

cis forms cis product

and trans forms trans product

Reactions are stereospecific.

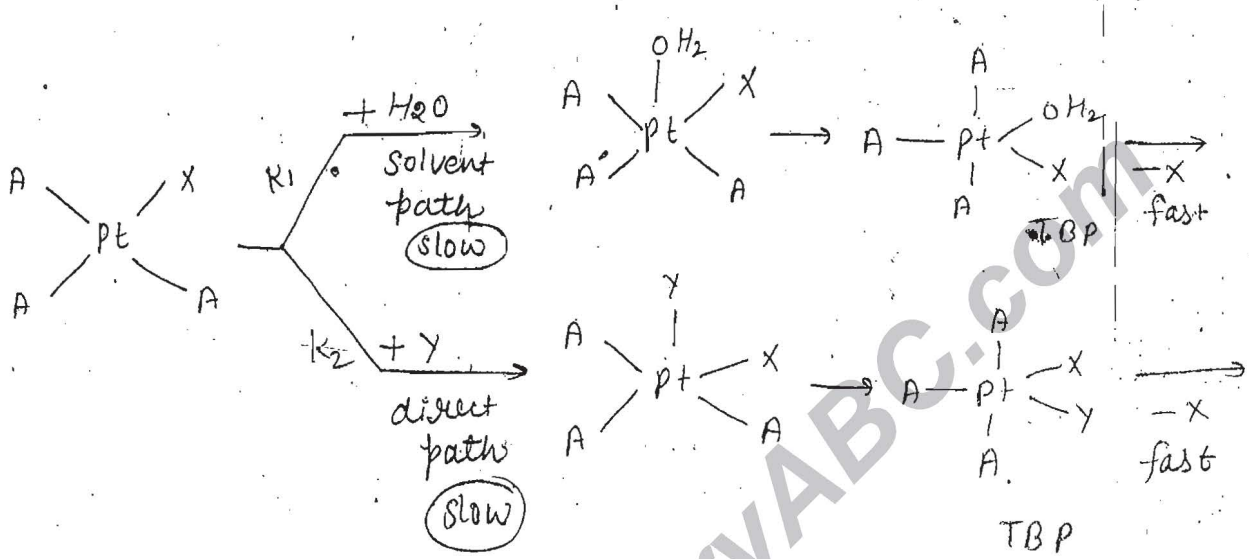




$$[PtA_3X] + Y \xrightarrow{H_2O} [PtA_3Y] + X$$

$$\text{Rate} = k_1[PtA_3X] + k_2[PtA_3X][Y]$$

$$= \{k_1 + k_2[Y]\}[PtA_3X]$$



If Y is in excess → [Y] constant

$$k_{observed} = k_1 + k_2[Y] \Rightarrow k_{ob} = k_s + k_Y[Y]$$

(k_s ← solvent)

$$\text{Rate} = k_{observed}[PtA_3X]$$

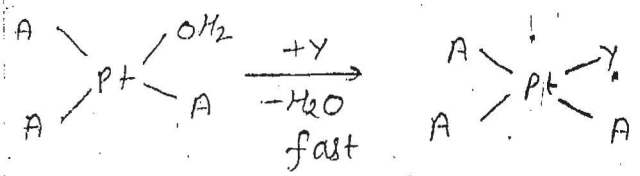
NET Prob :- order of reacⁿ :-

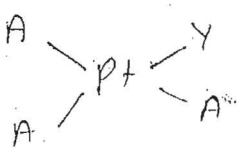
$$\text{Rate} = \frac{k_1 k_2}{k_1 + k_2[A]}[A]^2[B]$$

(a) 2 = (c) 1

(b) 3 (d) cant be determined

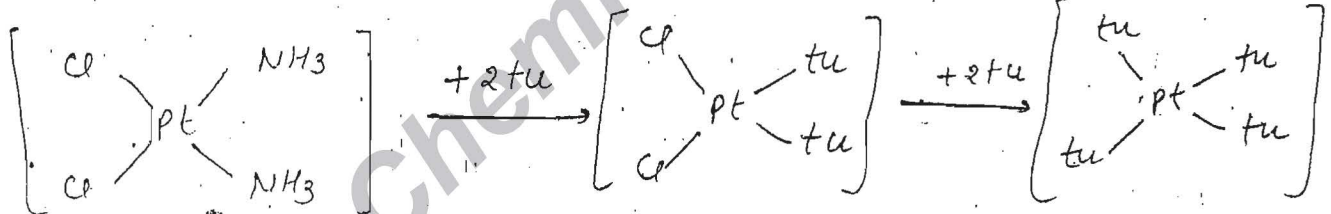
Reason ⇒ If $k_1 \times k_2[A]$ then we can find order of rxn and if $k_1 + k_2[A]$ then we cant find order of rxn.

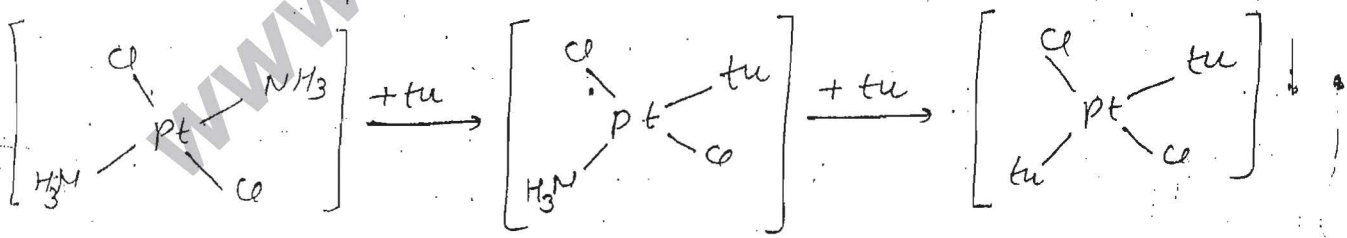




To distinguish cis & trans isomers:- [By William L. Jolly]

This is K/a Kurnakov test. Here trans effect works.



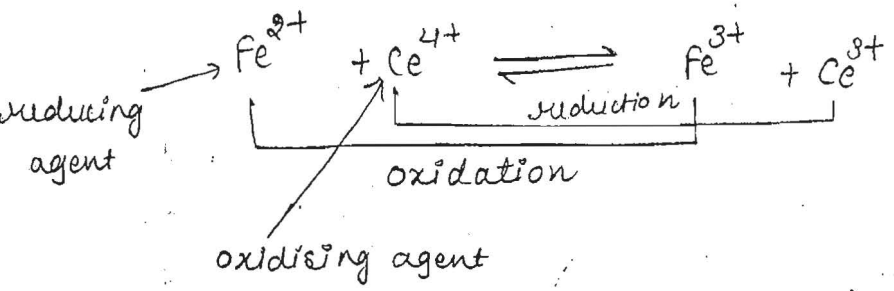


Imp

Electron transfer reactions (or Redox reactions)

reversible rxn

- with chemical change
- without chemical change



① Inner sphere e⁻ transfer rxns ⇒

② Outer sphere e⁻ transfer rxns ⇒

① Inner sphere e⁻ transfer rxns ⇒

→ one complex inert and other labile

→ Inert complex must have atleast one bridging ligand.

→ e⁻ transfer from reductant to oxidant through bridging ligand.

→ e⁻ from e orbital (σ^*) of reductant to e orbital (σ^*) of the oxidant

→ Rate of e⁻ transfer increases with increase in polarisability of bridging ligand.

$$I^- > Br^- > Cl^- > F^-$$

order of rate of e⁻ transfer

→ conjugation in the bridging ligand enhances the rate of e⁻ transfer.

Example ⇒

$$[Co^{+3}(NH_3)_5Cl]^{2+} + [Cr^{+2}(H_2O)_6]^{2+} + 5H_3O^+ \longrightarrow [Co^{+2}(H_2O)_6]^{2+} + [Cr^{+3}(H_2O)_5Cl]^{2+} + 5NH_4^+$$

Mechanism :-

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \xrightarrow{-H_2O} [(H_3N)_5Co^{+3}-Cl-Cr^{+2}(H_2O)_5]^{4+}$$

LS — HS

$d^6 \rightarrow t_{2g}^6 e_g^0$ — $d^4 \rightarrow t_{2g}^3 e_g^1$

inert — labile

$$[(H_3N)_5Co^{2+}]^{+} + [Cl-Cr^{+3}(H_2O)_5]^{4+}$$

labile — inert

$$\downarrow +H_2O$$

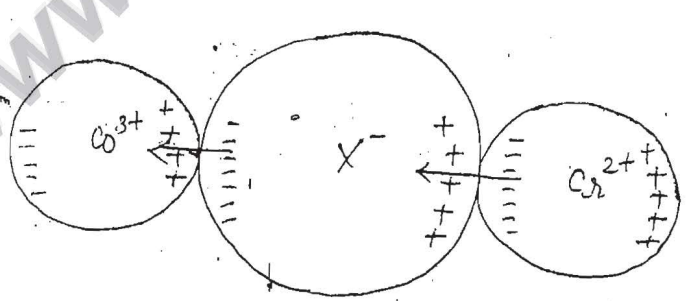
$$[Cr(H_2O)_5Cl]^{2+} + [(H_3N)_5Co(H_2O)]^{2+}$$

P

$$\downarrow +5H_3O^+$$

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

P



Ex:-

$$[IrCl_6]^{2-} + [Cr(H_2O)_6]^{2+} \longrightarrow [Cl_5Ir-Cl-Cr(H_2O)_5]^{0}$$

inert labile

$$\rightleftharpoons [Cl_5Ir-O-Cr(H_2O)_5]$$

more Inert less Inert

$$\downarrow +H_2O$$

$$[IrCl_6]^{3-} + [Cr(H_2O)_6]^{2+}$$

No chemical change

Adjacent and Remote attack ⇒

$$[(H_3N)_5Co(SCN)]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow ?$$

$$[(H_3N)_5Co(SCN)]^{2+} + [Cr(H_2O)_6]^{2+} \xrightarrow[-H_2O]{} [(H_3N)_5Co-S-C\equiv N-Cr(H_2O)_6]^{4+}$$

Adjacent attacks

$$\rightleftharpoons [(H_3N)_5Co-S-C\equiv N-Cr(H_2O)_5]^{4+}$$

labile inert

$$\downarrow +H_2O$$
$$+5H_3O^{+}$$

$$[Co(H_2O)_6]^{2+} + [Cr(H_2O)_5(SCN)]^{2+}$$
$$+ 5NH_4^{+}$$

$$[(H_3N)_5Co(SCN)]^{2+} + [Cr(H_2O)_6]^{3+} \xrightarrow[-H_2O]{} [(H_3N)_5Co{-}SCN{-}Cr(H_2O)_5]^{4+}$$

$$\Downarrow$$

$$[\underbrace{(H_3N)_5Co^{+2}}_{\text{labile}}-SCN-\underbrace{Cr^{+3}(H_2O)_5}_{\text{inert}}]^{4+}$$

$$\downarrow +H_2O,\ +H_3O^+$$

$$[Co(H_2O)_6]^{3+} + [Cr(H_2O)_5(NCS)]^{2+} + 5NH_4^+$$

(2) outer sphere mechanism ⇒

→ Both complexes may be labile or inert or one complex is inert and other is labile.

→ Electron transfer from filled t_{2g} (or π^* ← no π antibonding) HOMO of the reductant to the vacant t_{2g} (or π^*) of the oxidant. LUMO

→ No appreciable change in bond length.

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

LS LS

$d^6 \rightarrow t_{2g}^6 e_g^0$ $d^5 \rightarrow t_{2g}^5 e_g^0$

OR $(\pi^*)^6(\sigma^*)^0$ $(\pi^*)^5(\sigma^*)^0$

195 pm 192 pm

e⁻ transfer from $(\pi^*)^6$ of reductant to the $(\pi^*)^5$ of the oxidant

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

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

both the complexes comes as close to each other as possible.

Tunneling effect ⇒ e^- transfer through tunnel

$[Ru(NH_3)_6]^{2+} + [Ru^*(NH_3)_6]^{3+} \rightleftharpoons [Ru(NH_3)_6]^{3+} + [Ru^*(NH_3)_6]^{2+}$

$4d^6 \rightarrow t_{2g}^6 e_g^0$ $\quad 4d^5 \rightarrow t_{2g}^5 e_g^0$

($\pi^* \rightarrow \pi^*$ e^- transfer)

Ex:-

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

d^7 – HS $\quad d^6$ – LS

$(t_{2g}^5 e_g^2)$ $\quad (t_{2g}^6 e_g^0)$

inner sphere fast

slow

$Co^{2+}\ (\pi^*)^5 (\sigma^*)^2 \rightleftharpoons (\pi^*)^6 (\sigma^*)^1$ electron transfer $(\pi^*)^5 (\sigma^*)^1$ $(\pi^*)^6 (\sigma^*)^1$

$Co^{3+}\ (\pi^*)^6 (\sigma^*)^0$ $\quad (\pi^*)^5 (\sigma^*)^1$ $(\pi^* - \pi^*)$

Ground state (Reactants) $\quad$ excited state $\quad$ excited state

$(\pi^*)^6 (\sigma^*)^0$ Co^{3+}

$(\pi^*)^5 (\sigma^*)^2$ Co^{2+}

Ground state (Products)

$$[Co(H_2O)_6]^{2+} + [{}^{*}Co(H_2O)_6]^{3+} \rightleftharpoons [Co(H_2O)_6]^{3+} + [{}^{*}Co(H_2O)_6]^{2+}$$

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

HS HS

$(t_{2g}^4 e_g^2)$ $(t_{2g}^3 e_g^2)$

Acceleration of rate of e⁻ transfer on going from outer sphere to inner sphere electron transfer ⇒

HOMO	LOMO	Example	Acceleration of rate of e⁻ transfer on going from outer sphere to inner sphere e⁻ transfer
← σ*	σ*	Cr^{2+} / Co^{3+}	10^{10}
→ σ*	π*	Cr^{2+} / Ru^{3+}	10^2
π*	σ*	V^{2+} / Co^{3+}	10^4
π* ↑ fast	π*	V^{2+} / Ru^{3+}	No acceleration

$Cr^{2+} \rightarrow t_{2g}^3 e_g^1$ $Co^{3+} \rightarrow t_{2g}^6 e_g^0$ $(\sigma^* \rightarrow \sigma^*)$

$Cr^{2+} \rightarrow t_{2g}^3 e_g^1$ $Ru^{3+} \rightarrow t_{2g}^5 e_g^0$ $(\sigma^* \rightarrow \pi^*)$

$V^{2+} \rightarrow t_{2g}^3 e_g^0$ $Co^{3+} \rightarrow t_{2g}^6 e_g^0$ $(\pi^* \rightarrow \sigma^*)$

$V^{2+} \rightarrow t_{2g}^3 e_g^0$ $Ru^{3+} \rightarrow t_{2g}^5 e_g^0$ $(\pi^* \rightarrow \pi^*)$