

TOPICS TO BE COVERED



- 1.** Double Salt , Coordination Compounds and its Introduction
- 2.** IUPAC Nomenclature
- 3.** Werner's Theory , VBT & CFT
- 4.** Isomerism

D Block

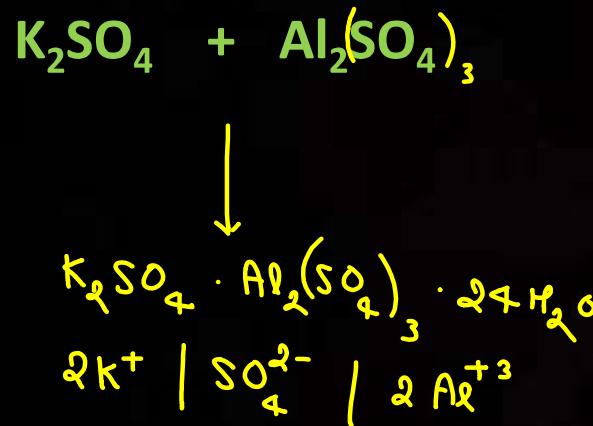
$3d$	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4d$	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
$5d$	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
$6d$	Ac	Rf								

$^{24}_{\text{Cr}} : [\text{Ar}] 4s^1 3d^5$

$^{29}_{\text{Cu}} : [\text{Ar}] 4s^1 3d^{10}$

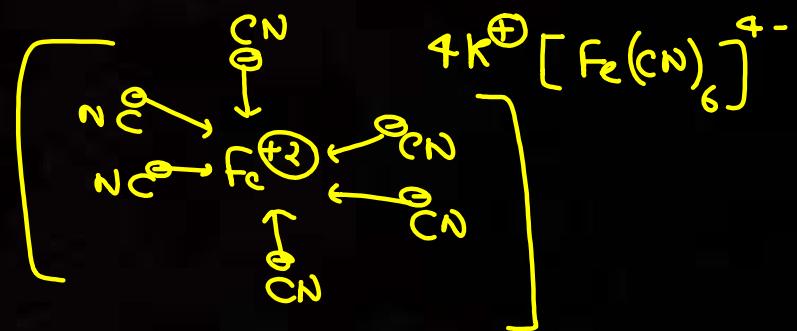
Addition compounds

The combination of two or more stable compounds



Double Salts

Ions in addition compound , don't lose their identity in aq. solution.



Coordination Compounds

Some ions in addition compound , lose their identity in aq. solution.

Co-ordination Entity

Co-ordination Sphere

Complex Ion

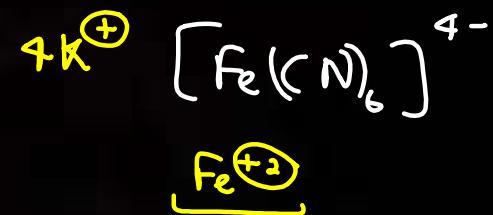
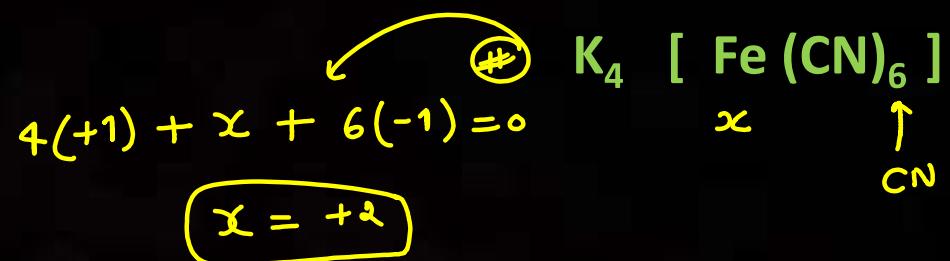
Central Metal

Ligands

Co-ordination Number

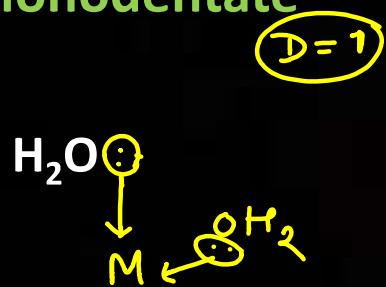
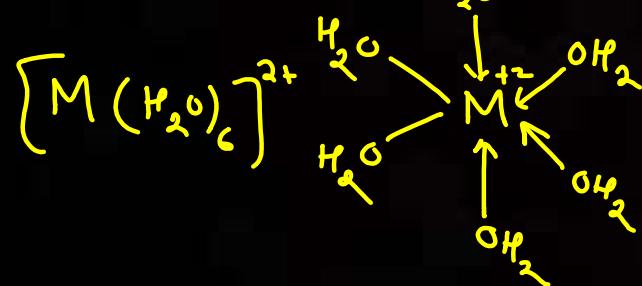
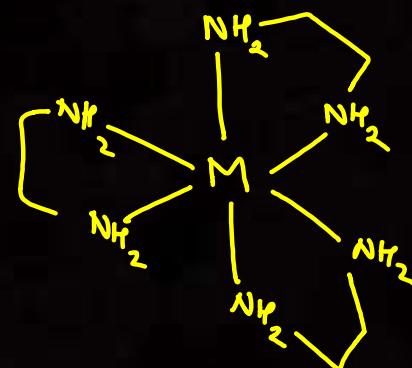
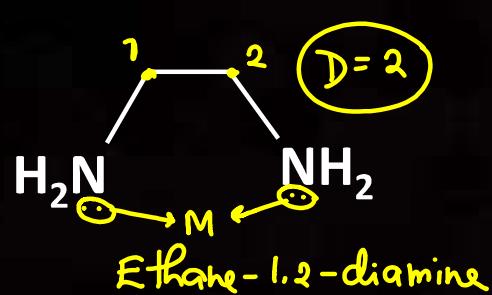
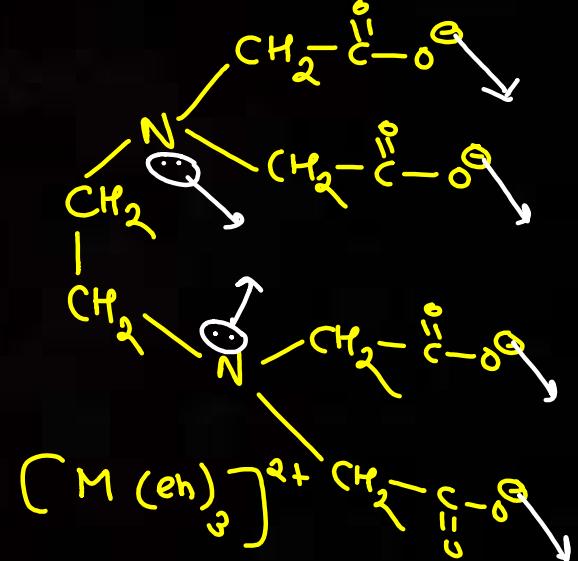
Counter Ion

Oxidation Number



Denticity

No. of coordinate bonds that a ligand can form with Metal

Monodentate **$\text{NH}_2 - \text{NH}_2$** **Bidentate****Polydentate ligand ($D > 2$)****EDTA** $D = 6$ **Chelation**

Chelates are generally more stable than non chelate complexes.



Nomenclature

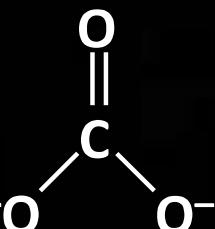


ite	ito	NO_2^-	Nitrite Nitrito	NH_2^-	Amido
ide	ido	OH^-	Hydroxo Hydroxo	$-\text{OH}$	Acetato
ate	ato	CO_3^{2-}	Carbamato Carbamato	H^-	Hydroxo
				CN^-	Cyano / cyanido
				O^{2-}	Oxo/oxido
				O_2^{2-}	Peroxido/peroxo
				O_2^-	Superoxo
				F^-	Fluorido
				Cl^-	Chlorido
				Br^-	Bromido

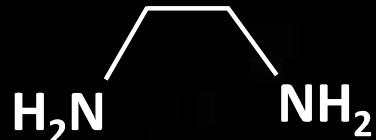
Ligands	Name		Ligands	Name
H ₂ O	Aquo		N ³⁻	Nitrido
CO	Carbonyl		N ₃ ⁻	Azido
NO	Nitrosyl		C ₂ O ₄ ²⁻	Oxalato
NH ₃	Ammine		SO ₄ ²⁻	Sulphato
C ₅ H ₅ N	Pyridine		S ₂ O ₃ ²⁻	thiosulphato
CH ₃ – NH ₂	Methylamine		SO ₃ ²⁻	Sulphito
PPh ₃	Triphenyl phosphene		S ²⁻	Sulphido
			NO ⁺	Nitrosonium
			N ₂ H ₅ ⁺	Hydrazinium



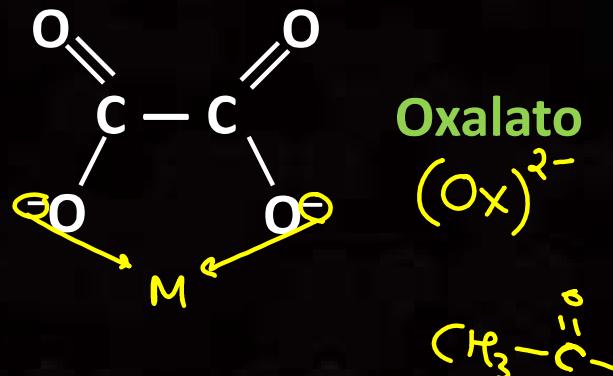
Bidentate Ligand



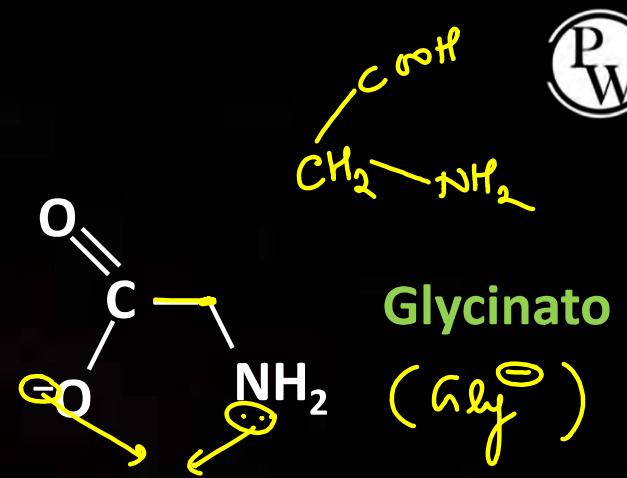
Carbonato



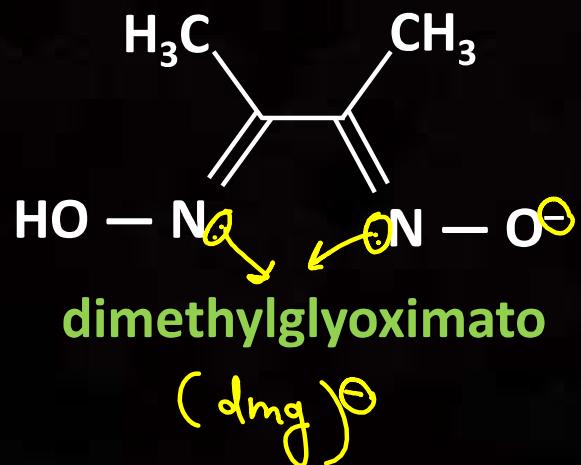
ethane -1, 2-diamine



Oxalato
 $(\text{Ox})^{2-}$

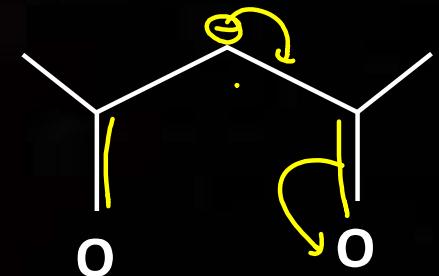


Glycinato
 (Gly^-)



dimethylglyoximato

$(\text{dmg})^-$



acetylacetonato
 (aca^-)

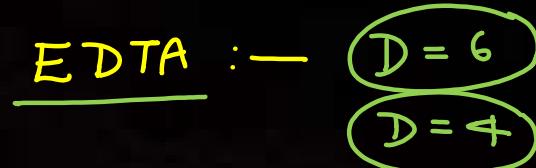




Flexidentate Ligand

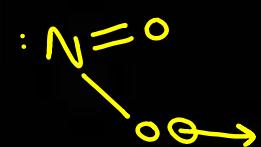
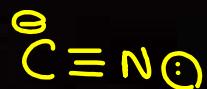
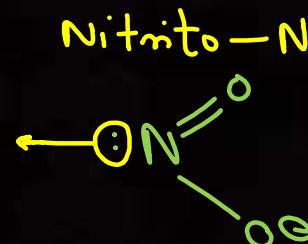


A polydentate ligand with different denticity
in different coordination compounds



Ambidentate Ligand

Ligands that have more than
one kind of donor sites



Homoleptic Complex

Metal is bound to only one kind of donor groups

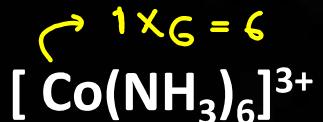


Heteroleptic Complex

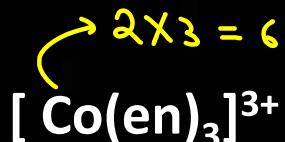
A metal is bound to more than one kind of donor groups



Co-ordination Number

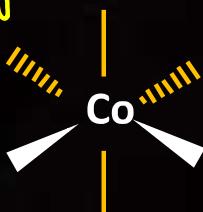


$$\text{NH}_3 \Rightarrow D = 1$$



$$\text{en} \Rightarrow D = 2$$

$$CN = n_{\text{lig}} \times D$$



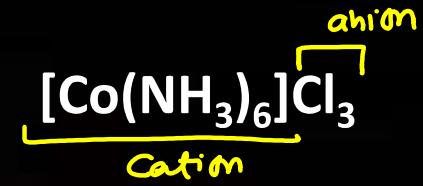


How to write a Coordination Compound ?



P
W

- ❖ Cation first followed by anion $K_4[Fe(CN)_6]$



- ❖ For the coordination sphere, central atom first then ligands in alphabetical order.

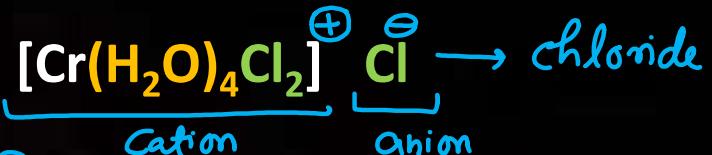


- Polyatomic ligands are enclosed in ()
- No space between metal atom/ion & ligands



IUPAC name of a complex

Cation is named first, followed by anion.



In naming of complex ion, the ligands are named first in the alphabetical order.

Use prefix di, tri, tetra for multiple ligands of same kind.



tetraqua



hexacyano



triammine

If ligand's name already contains any of these prefix, then we use bis, tris, tetrakis instead of di, tri & tetra and name of ligand is enclosed in parenthesis.

$(en)_2$ bis (ethylenediamine)
 ↳ Bis



If the complex ion is a cation, the metal is named same as the element.

$$x + 4 \times 0 + 2(-1) + (-1) = 0$$



If the complex is anion, name of metal ends with the suffix -ate.



Metal	Name in Cationic part	Name in Anionic part
Cr	chromium	Chromate
Pt	platinum	platinate
Co	cobalt	cobaltate
Ni	nickel	nickelate
Zn	zinc	zincate
Pd	palladium	palladate
Ti	titanium	titanate
Va	vanadium	vanadate

Metal	Name in Cationic part	Name in Anionic part
Mo	molybdenum	molybdate
Pb	lead	plumbate
Ag	silver	argentate
Au	gold	aurate
Sn	tin	stannate
Fe	iron	ferrate



$$3(+1) + x + 6(-1) = 0$$

$\curvearrowleft +3$



TetraCarbonyl nickel (0)

$x = +1$

$$x + 2(-1) = -1$$



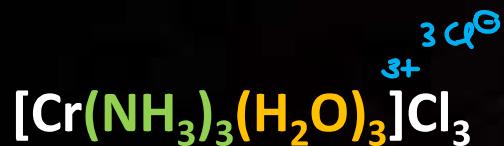
Diammine silver (I) dicyano argentate (I)



Diammine²⁻terachlorido platinum(IV)

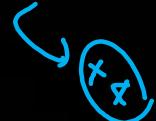


Dichlorido bis(triphenylphosphine) nickel (II)



Triammine triqua chromium(III) chloride

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



Pentaammine chlorido platinum(IV)bromide

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



ammonium diaquadi
~~oxalato~~nickelate(II)

(en)



Dichloridobis(ethylenediamine)platinum(IV)chloride

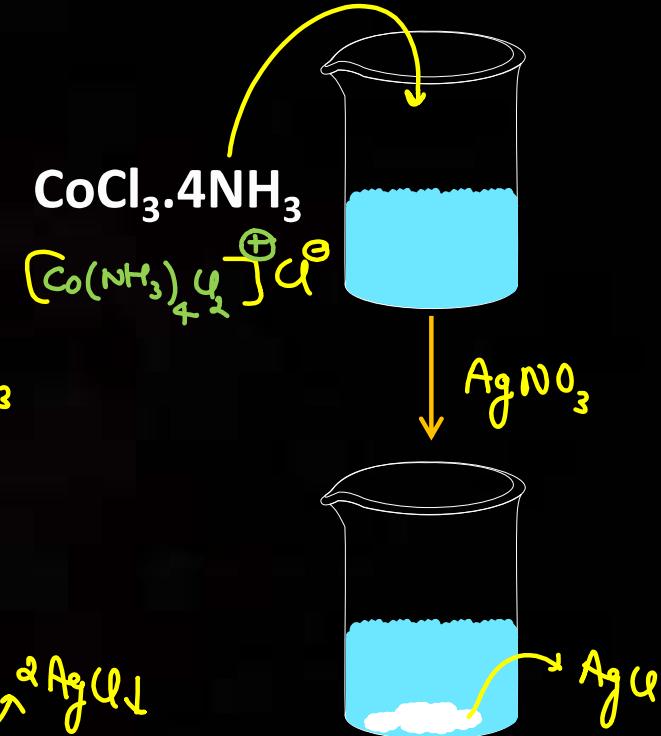
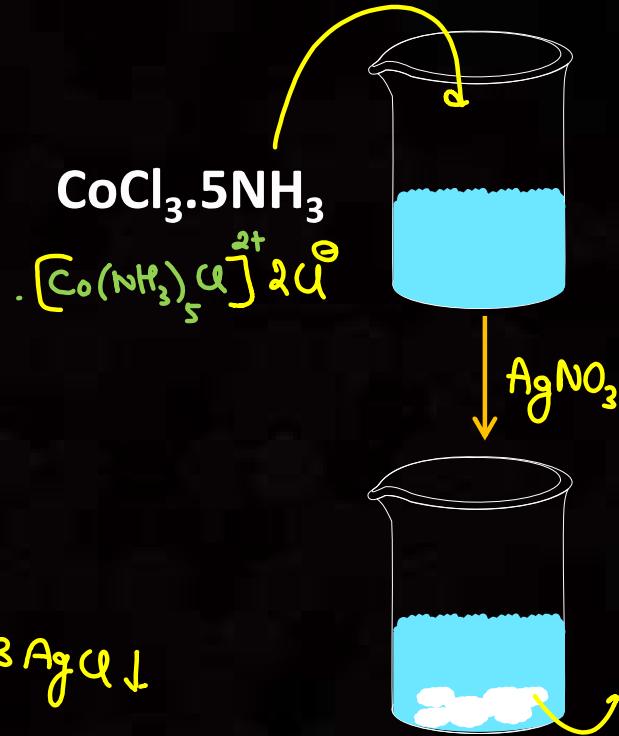
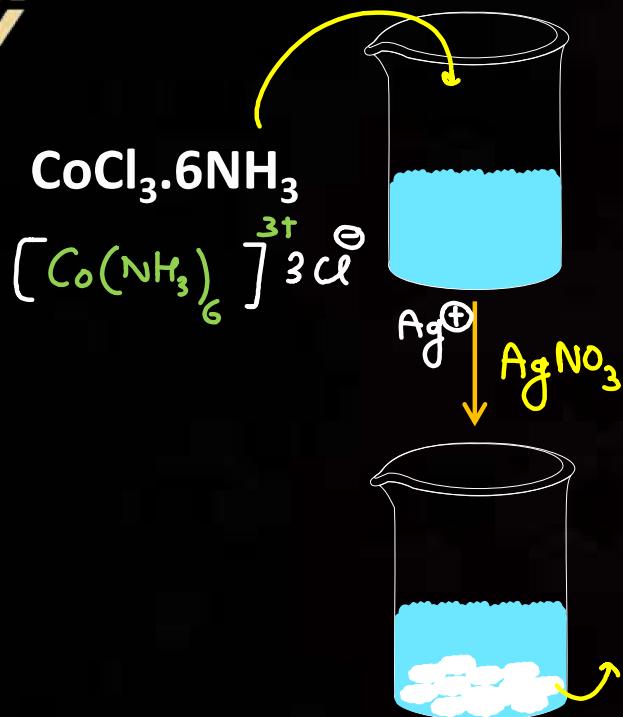


Pentacarbonyliron(0)



Werner's Theory

P
W



Conductivity

4 Ions

>

3 Ions

>

2 Ions



Valences of Metal



Ionic Interaction Primary Valency
 Ionisable Valency
 Non-directional

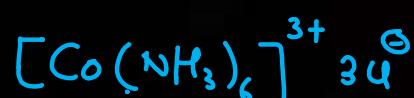
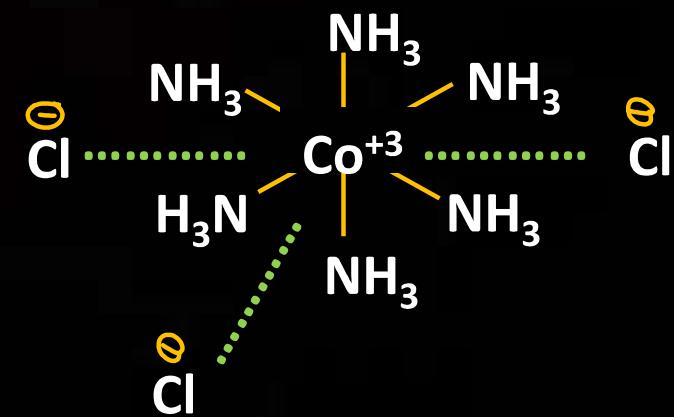
Modern : Oxidation state of metal

Representation : $[M \dots L]$



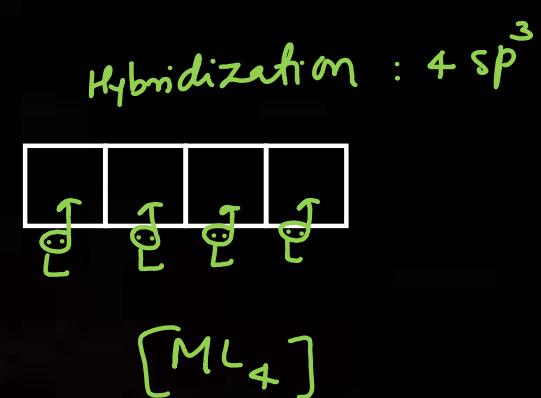
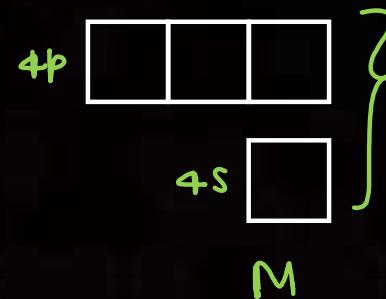
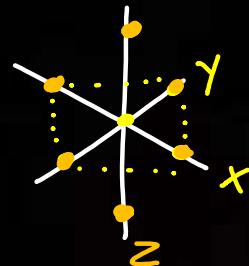
Secondary Valency
 Non-ionisable Valency

Directional
 Co-ordination no.





Valence Bond Theory



P
W

Coordination Number

Type of Hybridisation

Structure

4

sp^3

Tetrahedral

4

dsp^2 ($d_{x^2-y^2}$)

Sq. planar

6

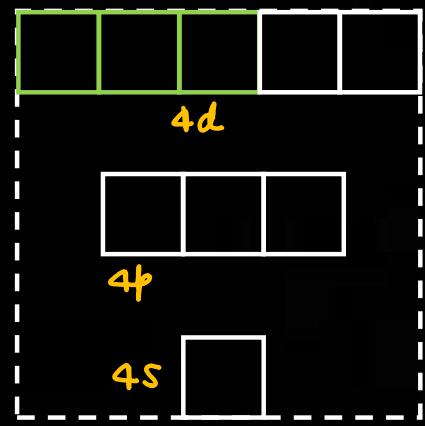
sp^3d^2 ($d_{z^2}/d_{x^2-y^2}$)

Octahedral

6

d^2sp^3

Octahedral



1	1	1	1	1
---	---	---	---	---

3d

$[ML_6]$: OOC

Fe^{3+} : 3d⁵ (5 Unpaired)

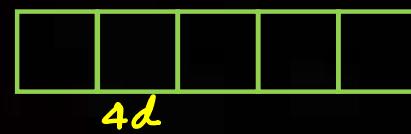
$[FeF_6]^{3-}$

Paramagnetic

OOC (sp^3d^2)

It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of VBT.

$$\text{Magnetic moment } \mu = \sqrt{n(n+2)}$$



1	1	1	1
---	---	---	---

4s

1l	1l	1l	1	1
----	----	----	---	---

3d

Co^{3+} : 3d⁶

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

d^2sp^3

$[ML_6]$: IOC

IOC

Diamagnetic





d-line for Hybridisation

Jwala : OP



$[ML_6]$



$[I_{OC}] d^2 sp^3$ (Always)

$Sc^{+3} : 3d^0$

$[Sc(H_2O)_6]^{3+} : d^2 sp^3$



$3d^{10}$

$[Sc(H_2O)_6]^{2+} : 3d^1$

$[Ti(H_2O)_6]^{2+} : 3d^2$

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

CFT
 $d^2 sp^3 / sp^3 d^2 : \text{Mag. Beh.}$

$[O_{OC}] sp^3 d^2$ (Always)



$4s$

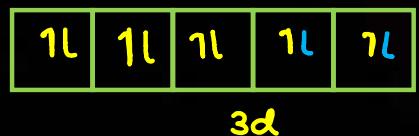
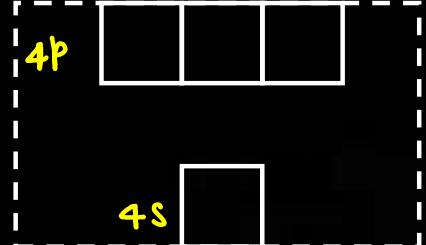


$4p$

$4d$

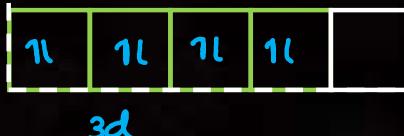
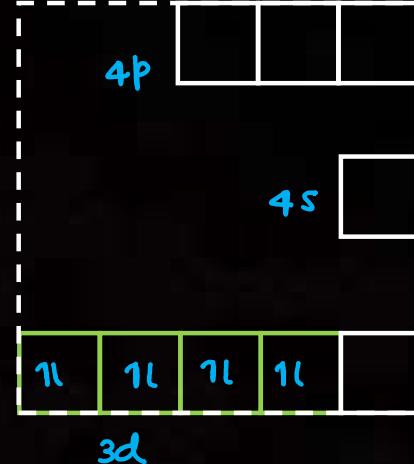
$[Zn(H_2O)_6]^{2+}$

$Zn^{+2} : 3d^{10}$



Diamagnetic

sp^3 : Tetrahedral



Diamagnetic

P
W

$d\ sp^2$: Sq. planar



Crystal Field Theory

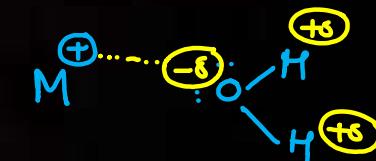
→ Most Imp.



Electrostatic model : which consider the metal – ligand bond to be ionic.

Ligands → Point charges in case of anions

Dipoles in case of neutral molecules



The diagram illustrates two 3D surfaces in a coordinate system defined by axes x , y , and z . The left surface, colored green, is a hyperboloid of two sheets, often denoted as $dx^2 - y^2$. The right surface, colored purple, is a hyperboloid of one sheet, often denoted as d_z^2 .

d-orbital

۷

d_{xz}

xy

1

$$1 \quad ax = y^2$$

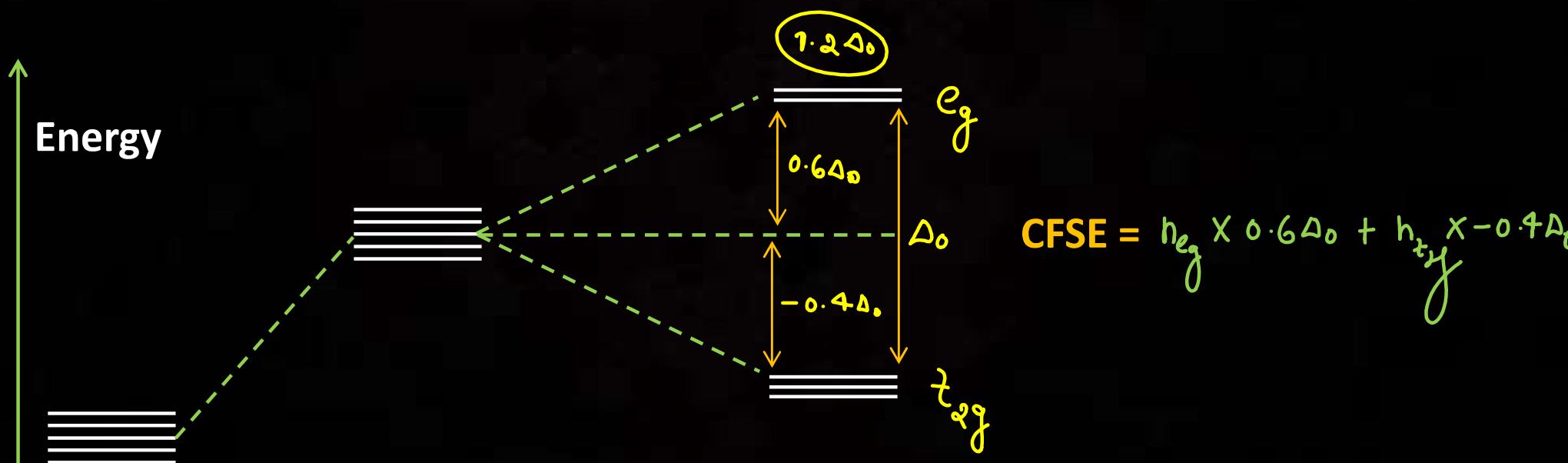
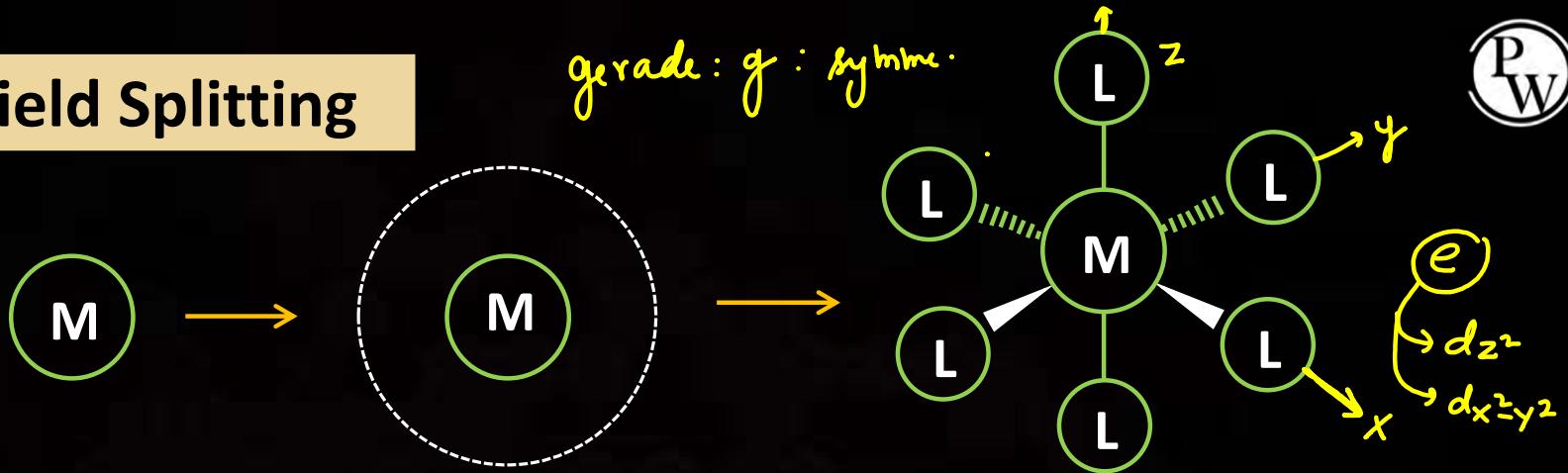
q72

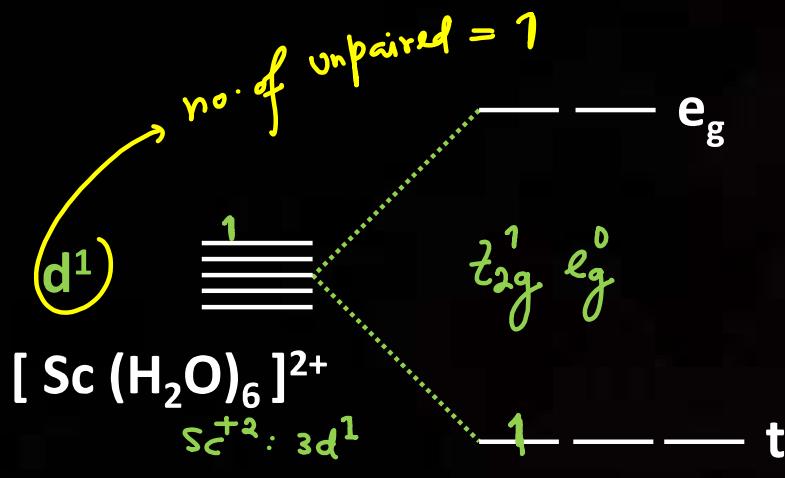
y
x



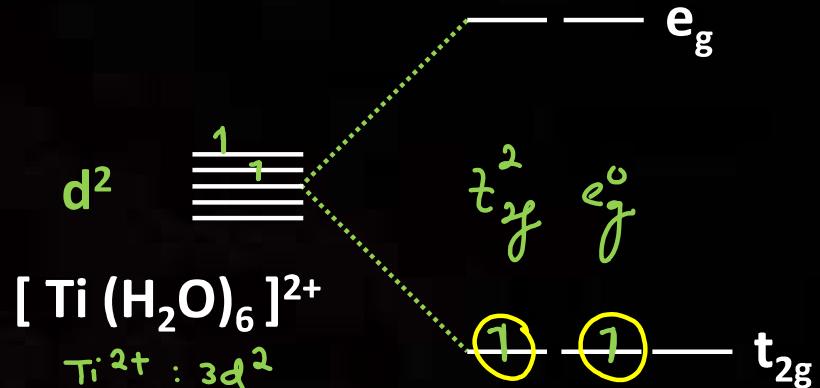
Crystal Field Splitting

P
W

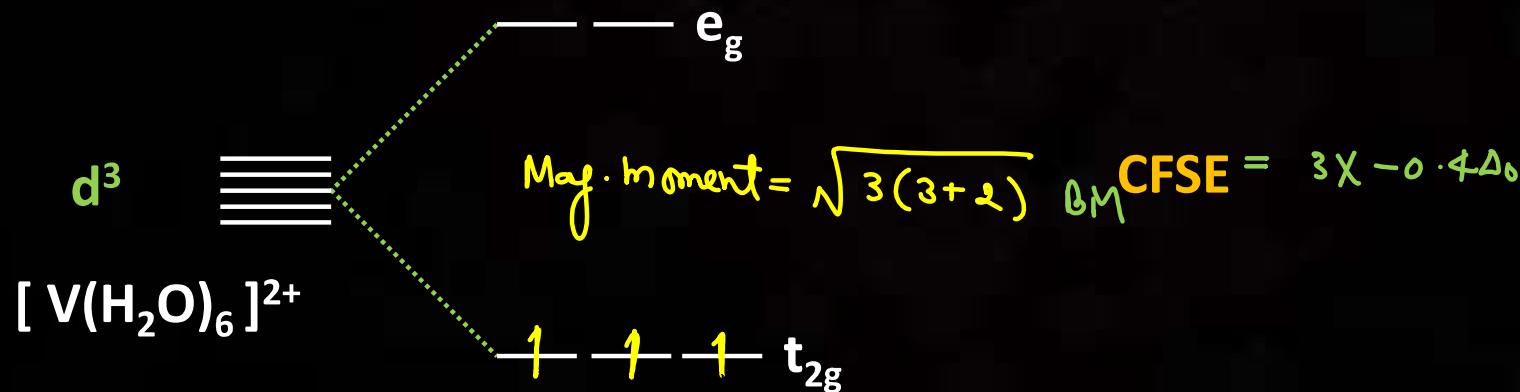


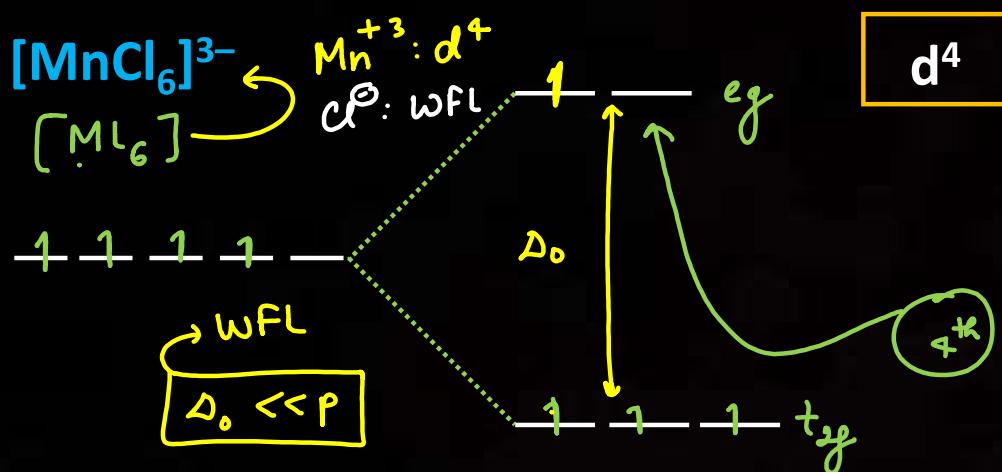


$$\begin{aligned} CFSE &= 1 \times (-0.4\Delta_0) + 0 \times 0.6\Delta_0 \\ &= -0.4\Delta_0 \end{aligned}$$



$$CFSE = 2 \times (-0.4\Delta_0) + 0 \times 0.6\Delta_0$$





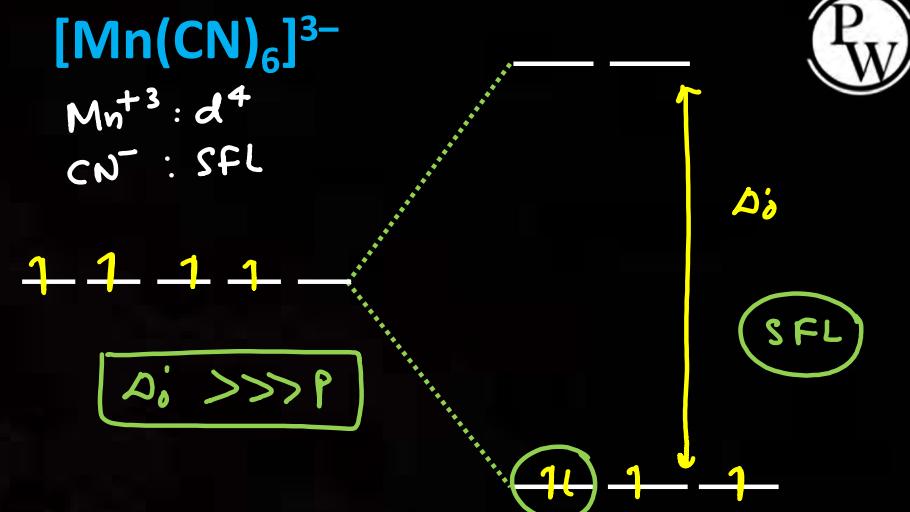
$$\Delta_0 < P$$

Ligands for which $\Delta_0 < P$ are known as weak field ligand.

$$\text{Configuration} = t_{2g}^3 e_g^1$$

$$\text{CFSE} = 3 \times (-0.4\Delta_0) + 1 \times 0.6\Delta_0$$

$$\text{Magnetic Moment} = \sqrt{4(4+2)} \text{ BM}$$



$$\Delta_0 > P$$

Ligands for which $\Delta_0 > P$ are known as strong field ligand.

$$\text{Configuration} = t_{2g}^1 e_g^1$$

$$\text{CFSE} = 4 \times (-0.4\Delta_0) + \text{pairing energy}$$

$$\text{Magnetic Moment} = \sqrt{2(2+2)} \text{ BM}$$



Spectrochemical Series



Δ_o : Halogen donors < Oxygen donors < Nitrogen donors < Carbon donors



3d Series

Metal (+2) : I⁻ to en : WFL

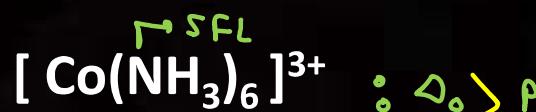
Metal (+3) : I⁻ to H₂O : WFL

Metal (+4) : All ligands are SFL.



\curvearrowright O/N/C : SFL

WFL



4d / 5d Series

Metal (+2)

Metal (+3)

Metal (+4)

WFL

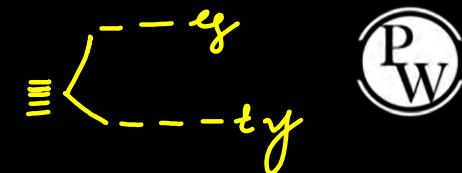
SFL

Δ_0 depends on

Charge ↑ : $\Delta_0 \uparrow$

Series : $3d < 4d < 5d$

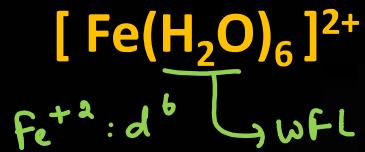
Ligands → SFL : $\Delta_0 T$
WFL : $\Delta_0 J$



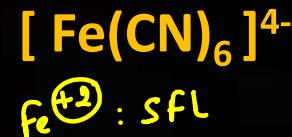
Complex	kJ mol^{-1}
$[\text{Co}(\text{NH}_3)_6]^{3+}$	296
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	406
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	490

Δ_0

d⁶



1l 1 1 1 1 1



1l 1 1 1 1

1l 1l 1l

Configuration : t_{2g}⁴ e_g²

CFSE : 4 (-0.4Δ₀) + 2(0.6Δ₀)

CFSE = 6x(-0.4Δ₀) + 2p

No. of unpaired
electrons

Magnetic Moment

P
W

Hybridisation and CFT

P
W



$\text{Mn}^{+3} : d^4$
 $\text{CN}^- : \text{SFL}$

$\text{Mn}^{+3} :$



3d

$d^2sp^3 : \text{IOC}$



4s

4p

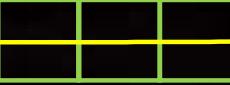


$\text{Cl}^- : \text{WFL}$

$\text{Mn}^{+3} :$



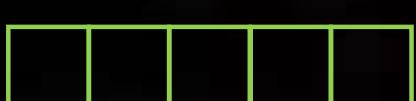
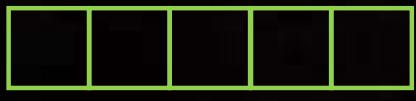
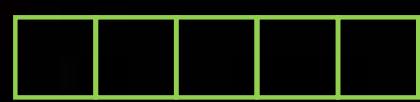
3d



4s



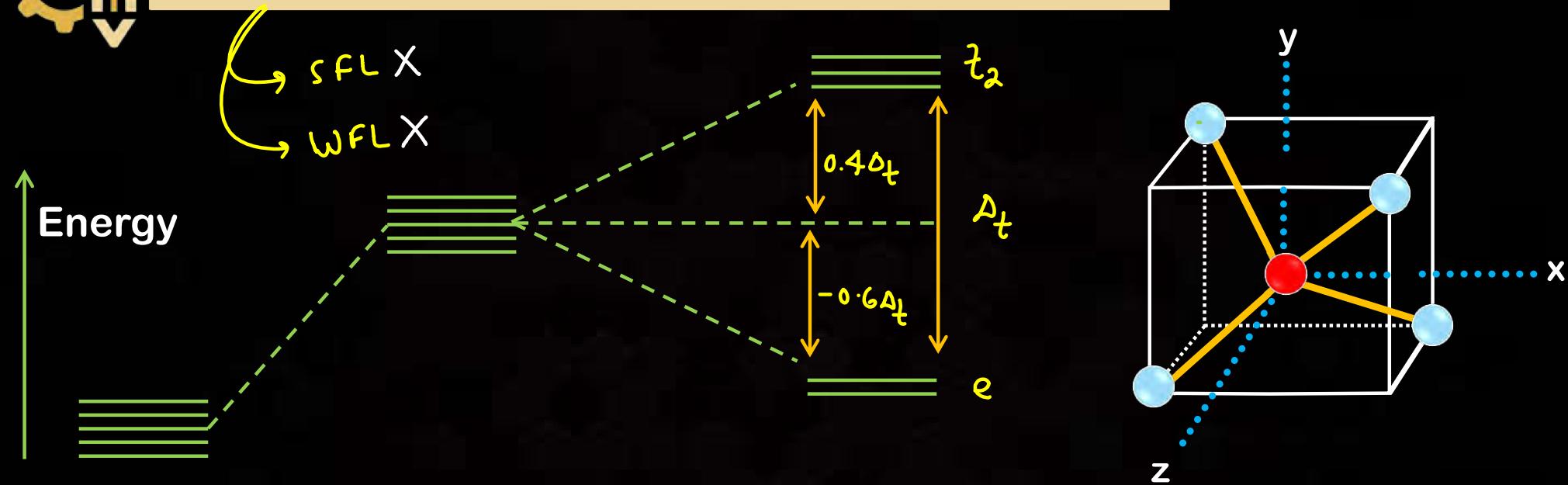
4d



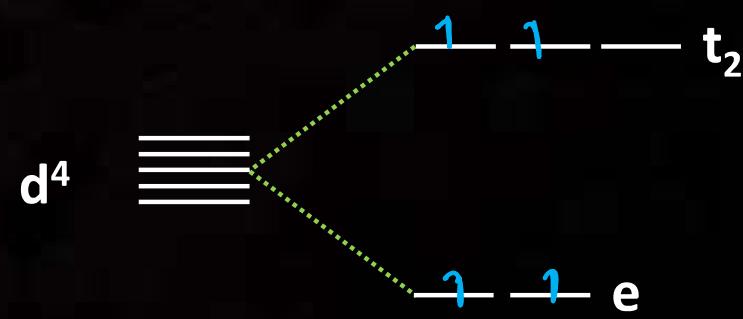
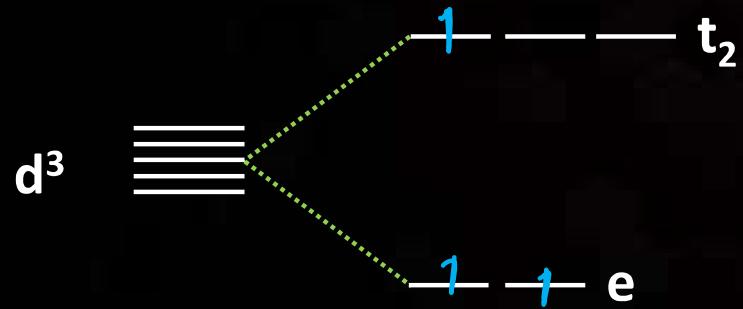
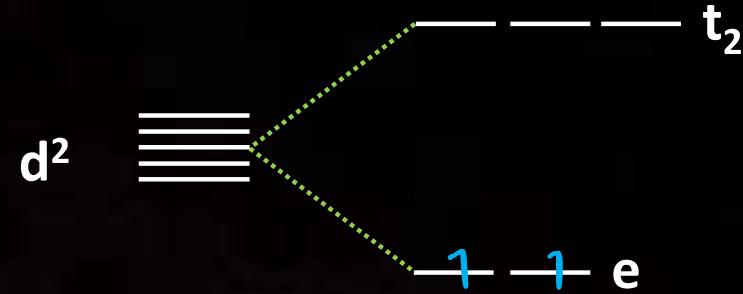
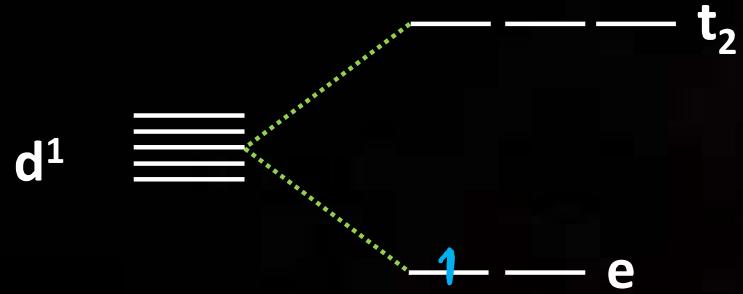


Crystal field splitting in tetrahedral complex

P
W

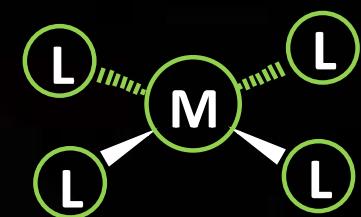
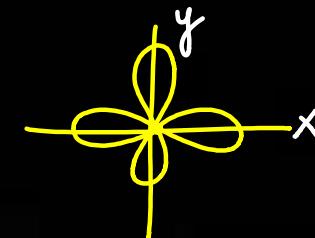
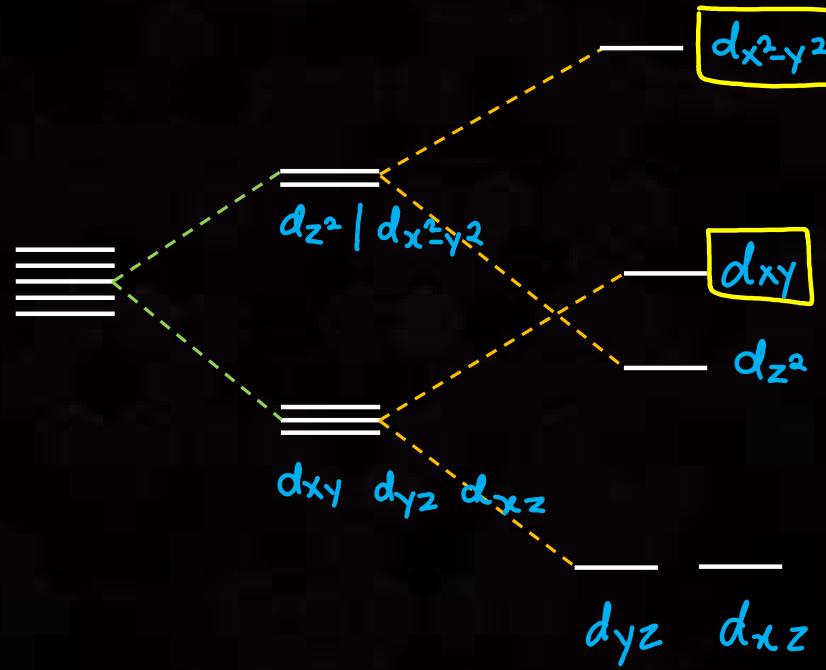
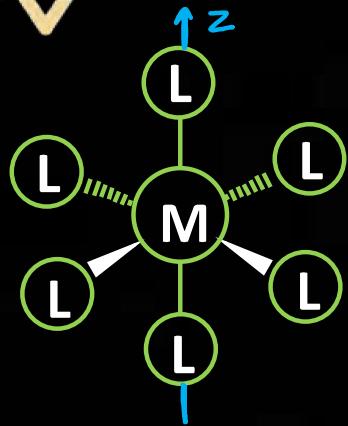


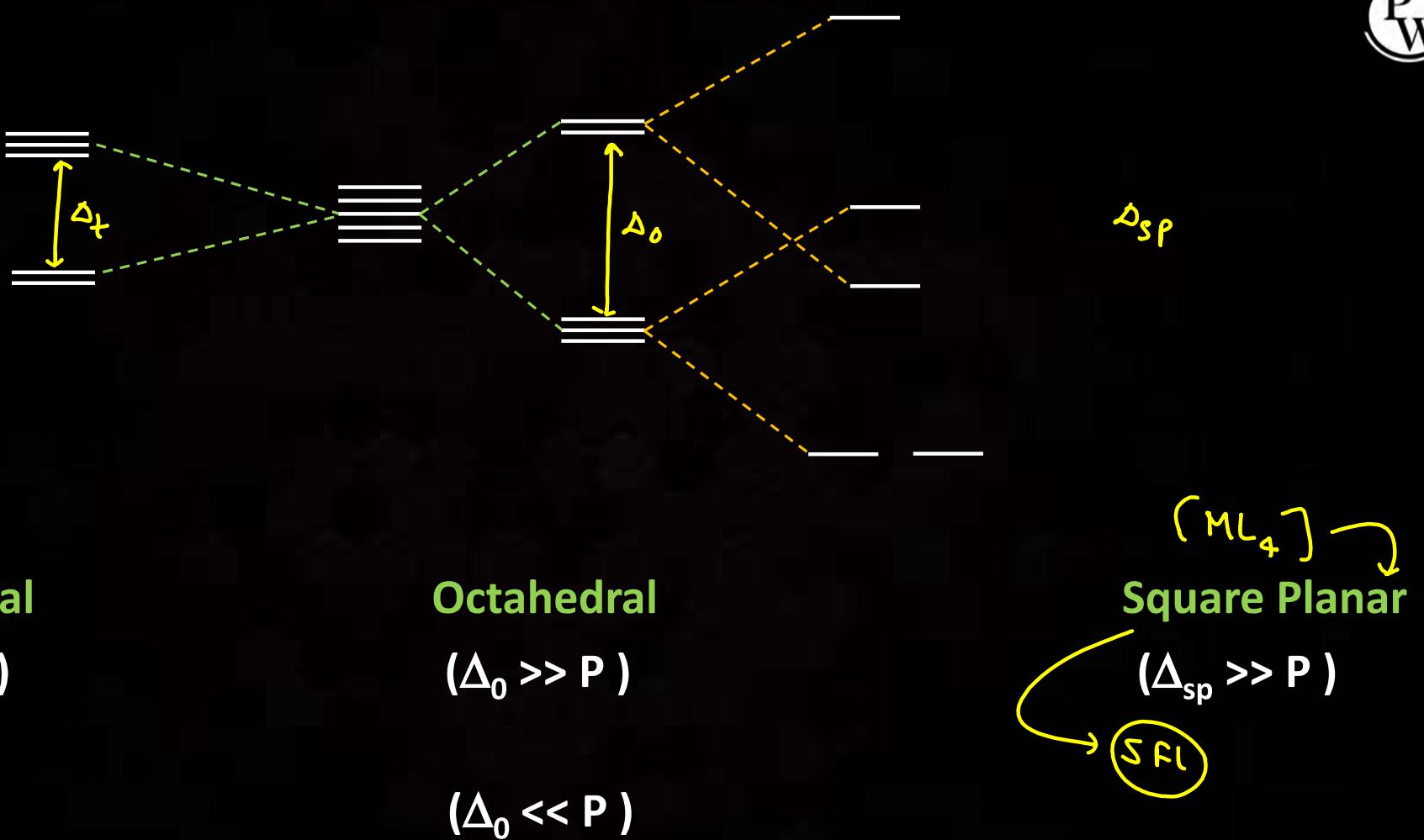
$$\text{CFSE} = n_e (-0.6\Delta_t) + n_{t_1} (0.4\Delta_t)$$





Crystal Field splitting in square complex

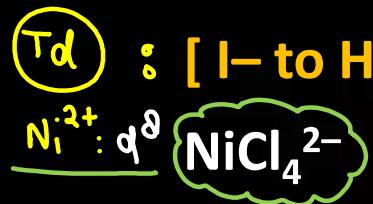




Tetrahedral & Square Planar



3d series (+2 Metal)



All Ligands of

3d series (+3 / +4)

4d / 5d series (+2/+3/+4)

Jwala : OP

d^8 d^9

C.N. = 4

d^8 d^9

PtCl_4^{2-}

Td / SP

$[\text{ML}_4]$

ZnCl_4^{2-}

W

d^{10}

$\text{Ni}(\text{CO})_4$

Tetrahedral

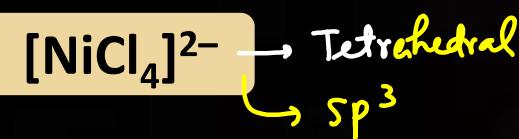
$\text{Ni} : 4s^2 3d^8$
 $: 3d^{10} 4s^0$

[NH₃ to CO] : sp

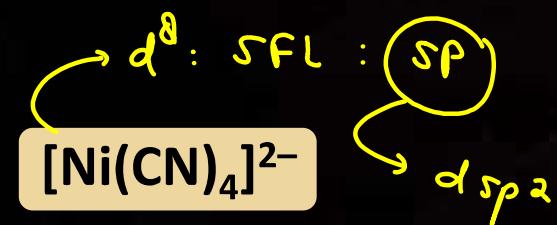
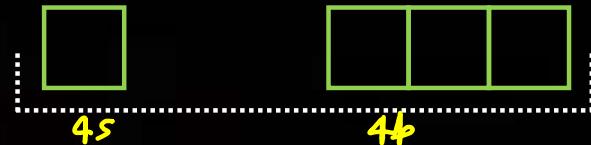
$[\text{Cu}(\text{NH}_3)_4]^{2+}$

$\text{Ni}(\text{CN})_4^{2-}$

Hybridisation and CFT



1L	1L	1L	1	1
----	----	----	---	---



1L	1L	1L	1	1
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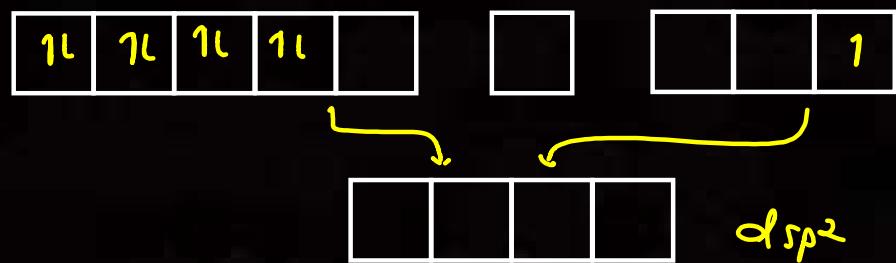
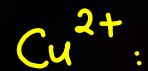


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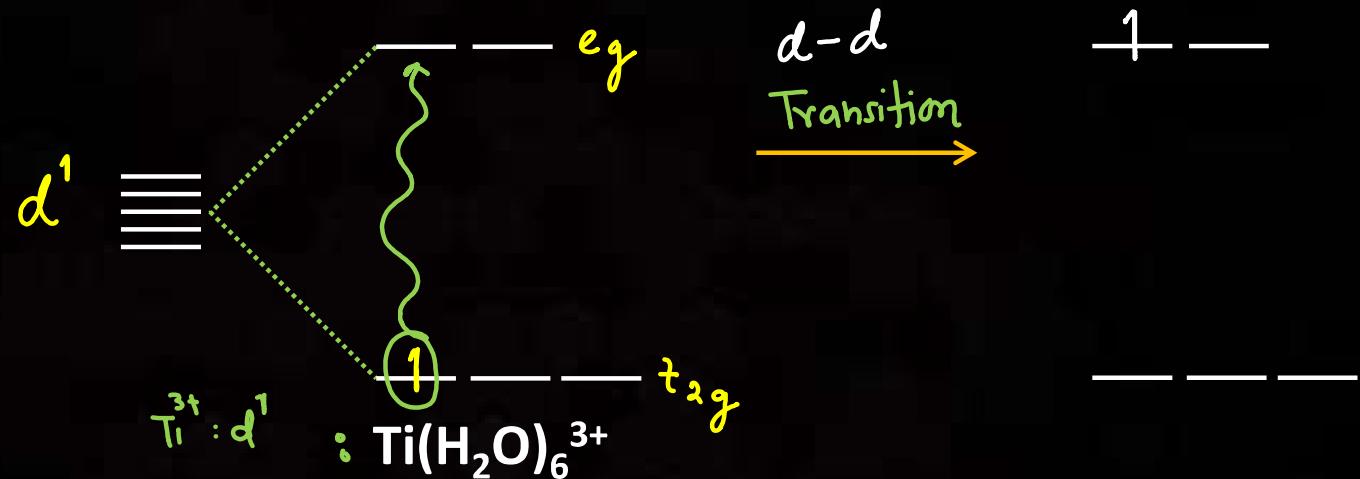
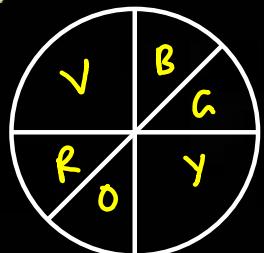
The complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is a sq. planar and has dsp^2 hybridisation.





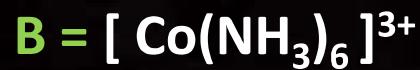
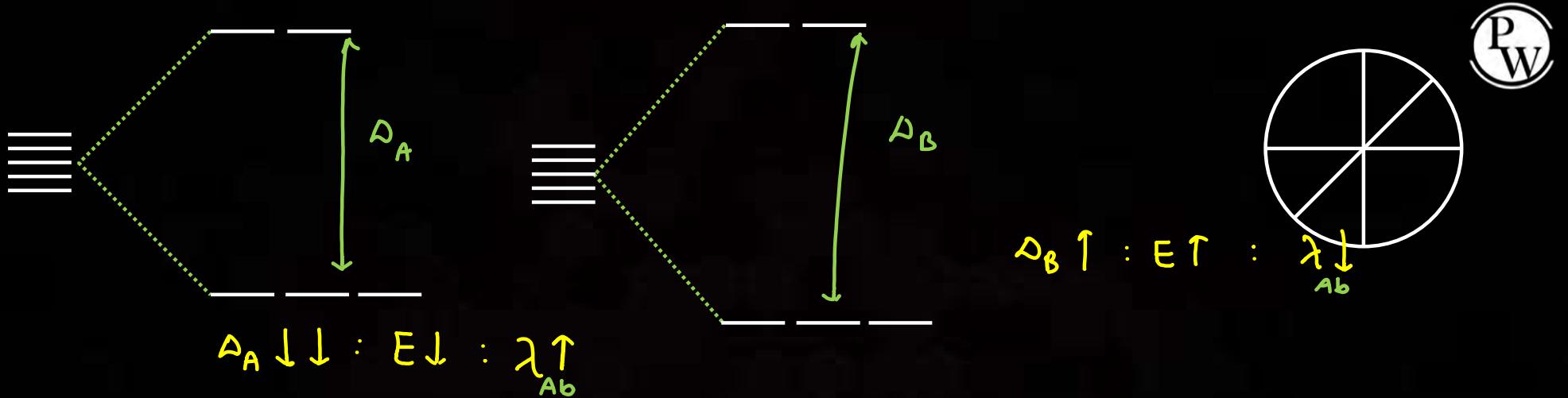
Colour in Co-ordination compounds

P
W



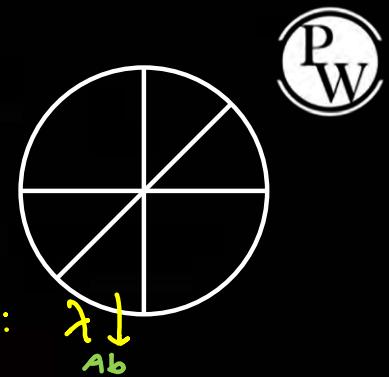
When light of certain frequency falls on the complex, it absorbs light from visible range for transition of electrons from lower d-energy level to higher d energy level. This transition is called **d-d transition of electron**.

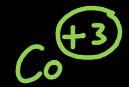
Colour of the compound is the complementary colour of absorbed light.



$\lambda_{\text{Absorbed}}$: A > B

$\lambda_{\text{Absorbed}}$: A < B



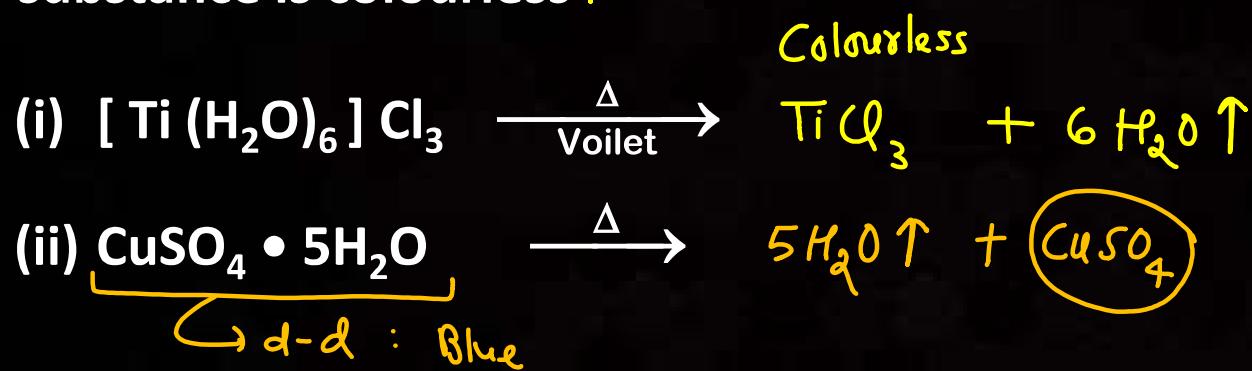


Coordination Comp.	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	535	Yellow	Violet
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$	500	Blue Green	Red
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow Orange
$[\text{Co}(\text{CN})_6]^{3-} : \Delta_g \uparrow\uparrow$	310	Ultraviolet	Pale Yellow
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+} : \Delta_g \downarrow\downarrow$	600	Red	Blue
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	498	Blue Green	Violet



Colour in Co-ordination compounds

In absence of ligand crystal field splitting does not occur and hence the substance is colourless.





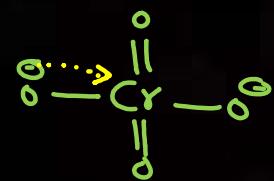
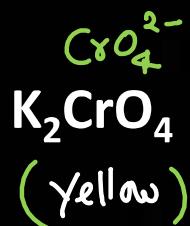
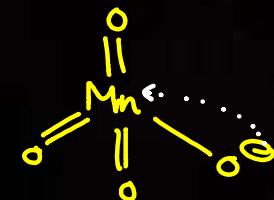
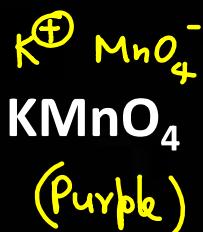
Charge transfer spectra

CTS

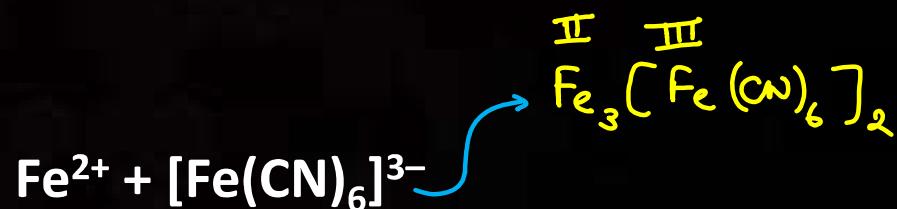
P
W

Ligand to Metal

Mn^{+7} : d^0 : No d-d transition



Metal to Metal



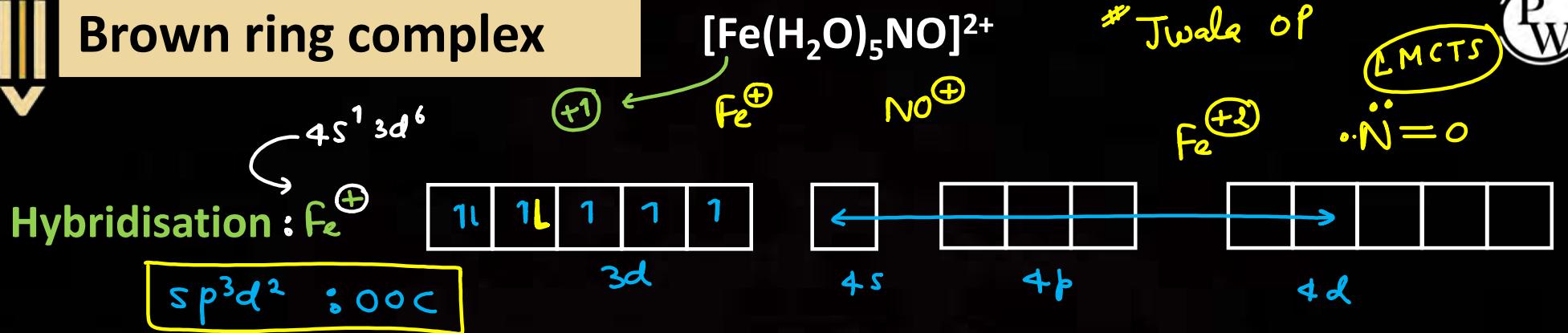
Turn bulls blue



Prussian blue



Brown ring complex



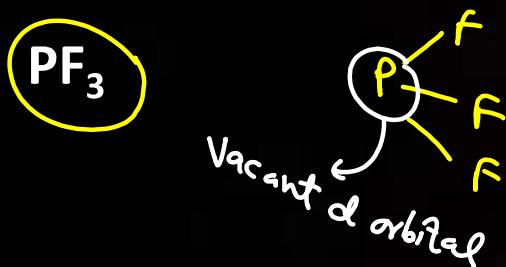
No of unpaired electrons = 3

Magnetic Moment = $\sqrt{3(3+2)} \text{ BM}$



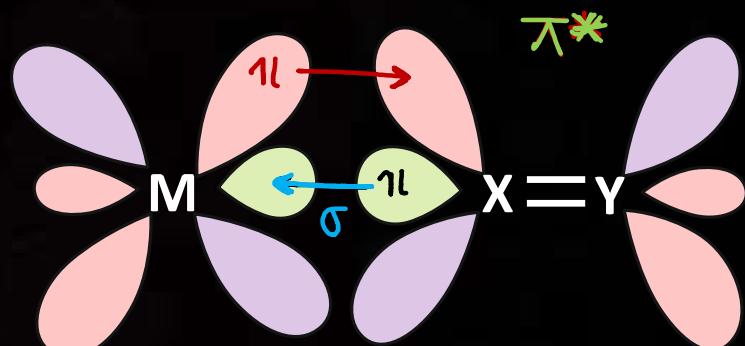
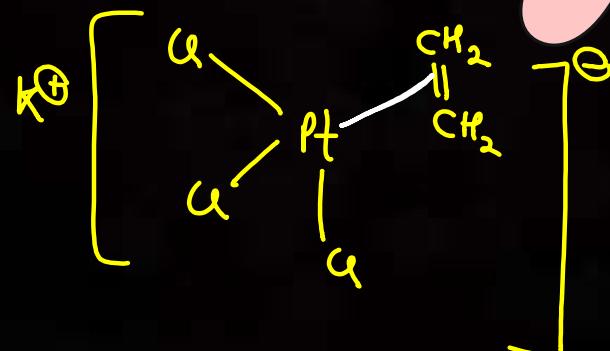
Non Classical / π - acceptor / π -acid ligands

CO, CN⁻, NO⁺, C₂H₄ : $\pi^* MO$



Zeise's Salt

K [PtCl₃ (η^2 - C₂H₄)]

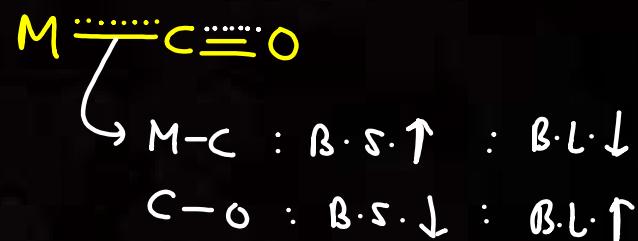
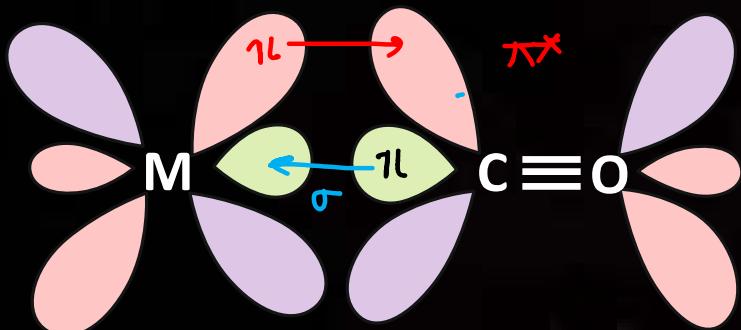




Bonding in Metal Carbonyls

P
W

The metal-carbon bond in metal carbonyls possess both σ and π character.



The metal to ligand bonding creates a **synergic effect** which strengthens the bond between CO and the metal





Effective Atomic Number

[ML₆]

Stability of Co-ordination Compound

P
W

EAN = No. of e⁻ present on the metal atom/ion + no. of e⁻'s donated by ligands

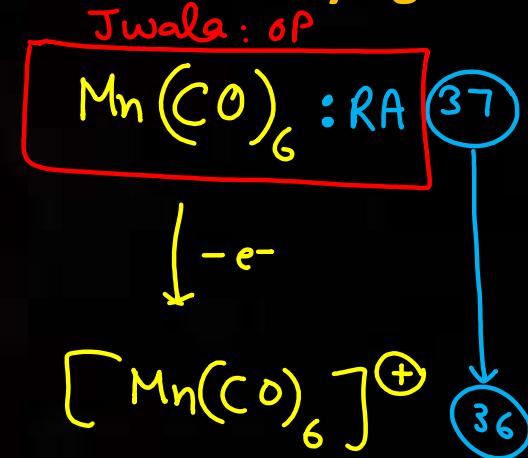
$$\text{Co}^{+3} : 27 - 3 = 24$$



$$\text{Fe}^{2+} : 26 - 2 = 24$$



$$\text{Mn} : 25$$



[\text{Mn}(\text{CO})_6] can act as a reducing agent because the metal carbonyl is stable when EAN is equal to the nearest noble gas configuration by losing one electron.



Isomerism in Coordination Compound

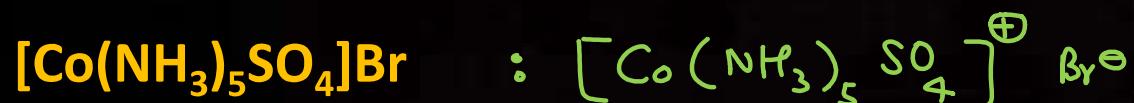
Isomer
M.F. : Same

Structural Isomerism
Different

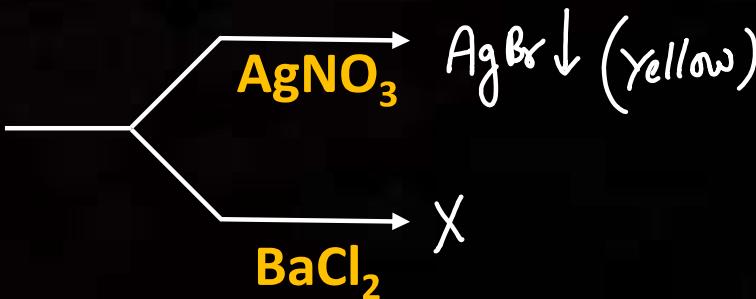
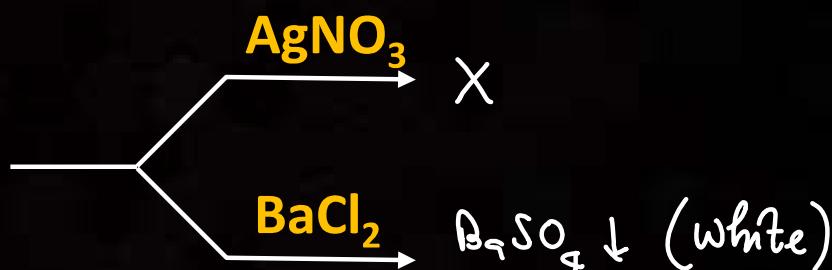


Ionization Isomerism

same molecular formula but give different ions in solution on ionization.



Experimental Proof

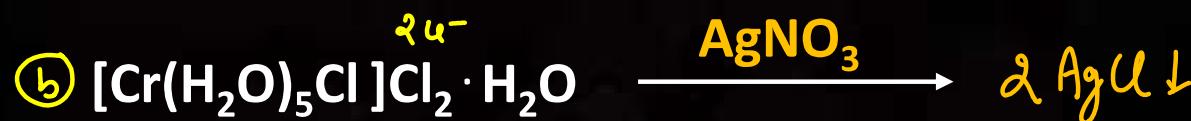


$$\text{DA} : \frac{\text{Com. } \text{H}_2\text{SO}_4}{\text{P}_2\text{O}_5}$$



Hydration Isomerism

same molecular formula, but differ in the number of water molecules outside the coordination sphere.



Order of Conductivity : (a) > (b) > (c)

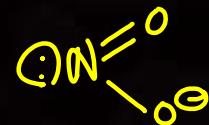
Order of Weight Loss by using Dehydrating agent: (a) < (b) < (c)



Linkage Isomerism

P
W

Ligands with two different donor atoms : Ambidentate ligands



.





Coordination Isomerism

Polynuclear Complexes : Partial or complete exchange of ligands between complex ions.



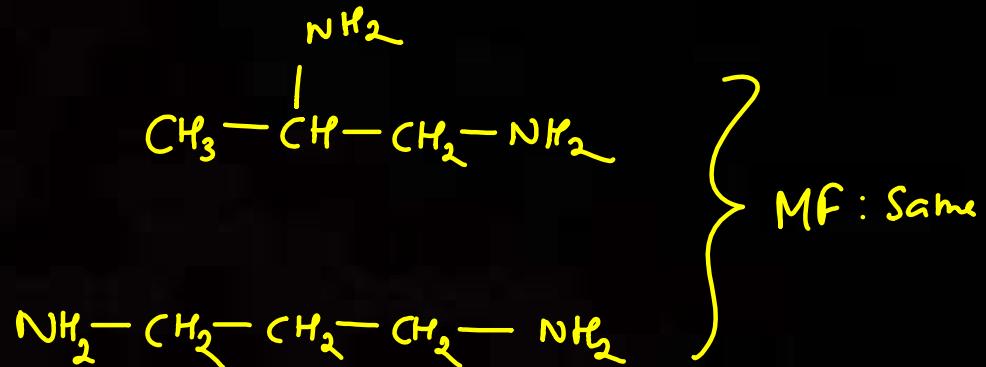
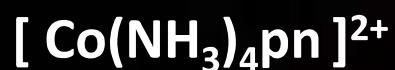


Ligand Isomerism

P
W

pn : propylenediamine

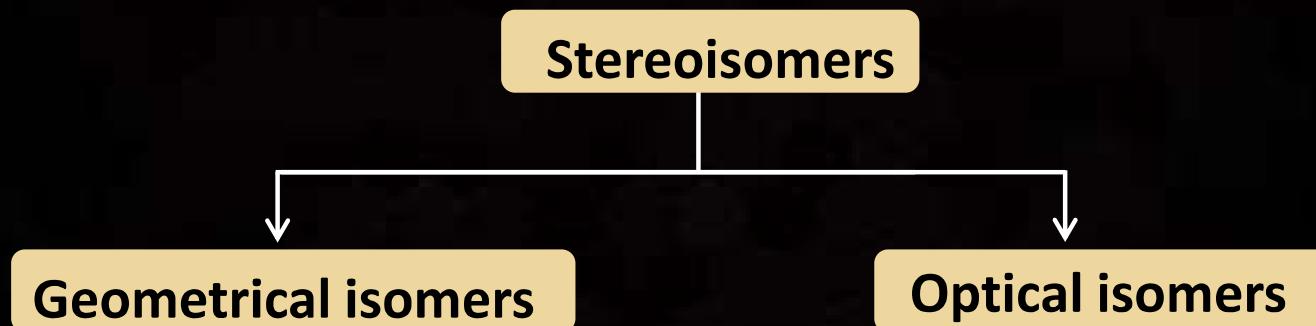
tn : trimethylenediamine





Stereoisomers

Same connections among atoms = Same Structure
Different arrangement of the atoms in space

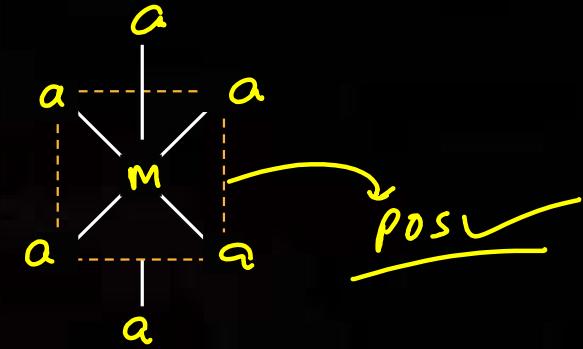
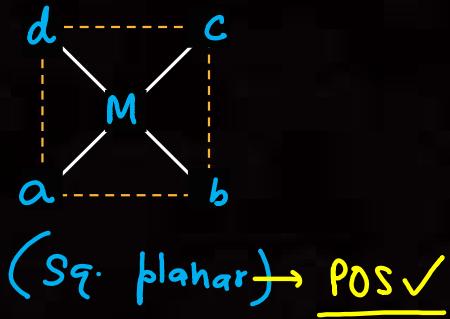




Element of Symmetry

P
W

Plane of symmetry



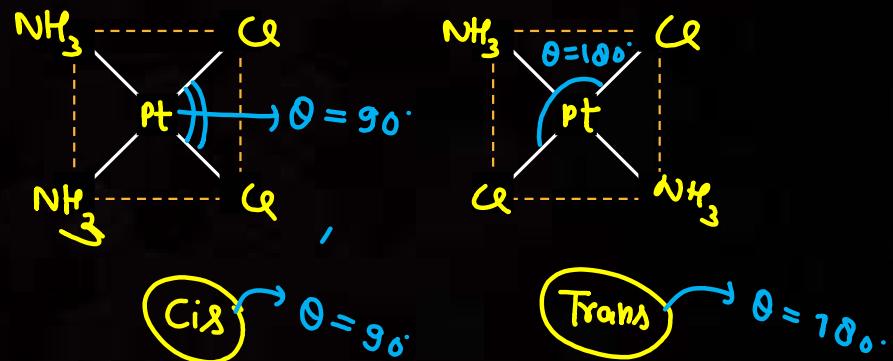
~~Centre of symmetry~~

Geometrical isomers

Distance between two ligands must be different



Cisplatin



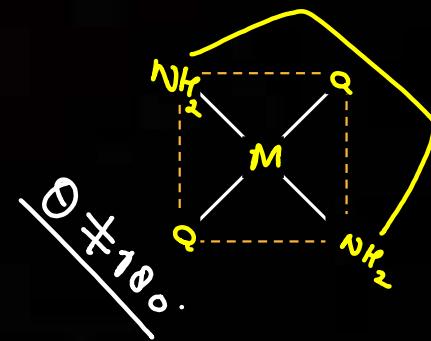
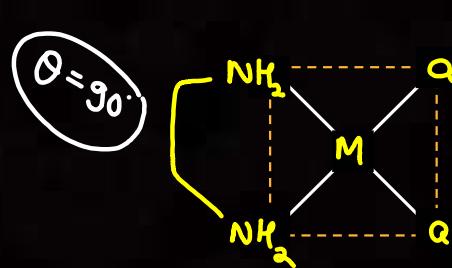
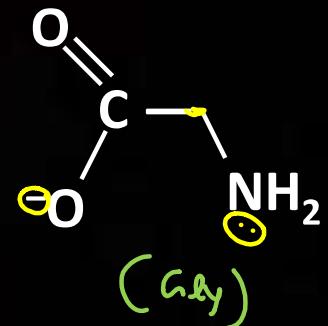
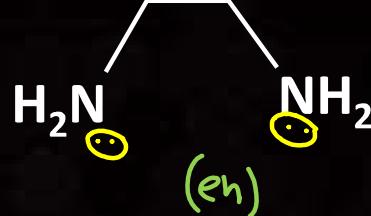
Representation Metal (M)

PYQ'S : App : Up load.

P
W

Monodentate ligand (a, b, c, d, ...)

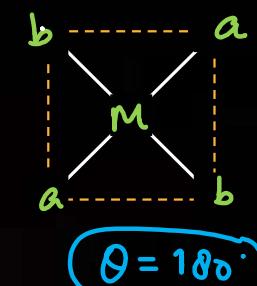
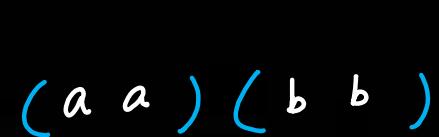
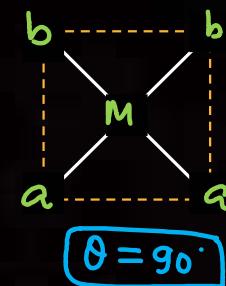
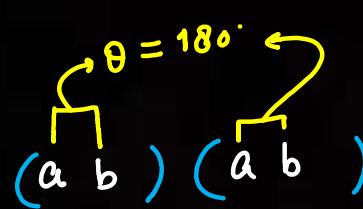
Bidentate ligand (AA) or (AB)



Trans pairs

Ma_2b_2

$$\begin{array}{l} (\alpha \alpha) (\beta \beta) \\ (\alpha \beta) (\alpha \beta) \end{array} \xrightarrow{\quad} \overline{6 \cdot I \cdot = 2}$$

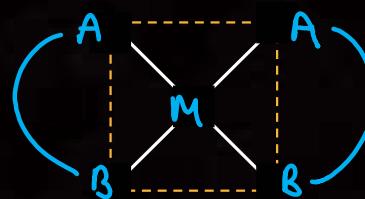


P
W

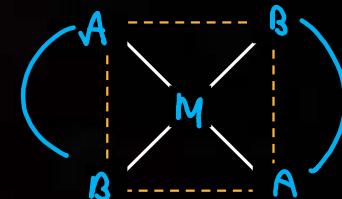
M(AB)_2

$$(\text{A A}) (\text{B B}) \Rightarrow 1$$

$$(\text{A B}) (\text{B A}) \Rightarrow 2$$



②



①



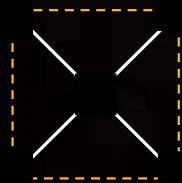
G.I. in Square planar complex



$$a = \alpha^-/\text{f}\theta/\text{CN}^-$$

Ma_4

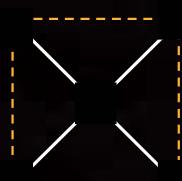
$(aa)(aa)$



Ma_3b

$(aa)(ab)$

No, C.I.

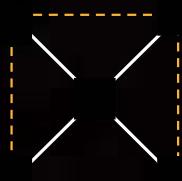


Ma_2b_2

$(aa)(bb)$
 $(ab)(ab)$

C.I.

T_{form}

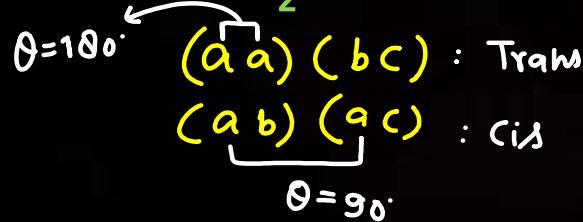




G.I. in Square planar complex

$$G \cdot I =$$

Ma₂bc



$$G \cdot I = 3$$

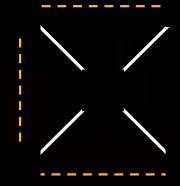
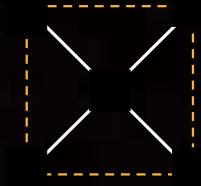
Mabcd

[Pt NH₃ Br Cl Py]

$$G \cdot I = 3$$

$$O \cdot I = 0$$

$$\underline{\text{Total} = 3}$$



Optical Isomerism in SP

PW

POS ✓

Optically
Inactive



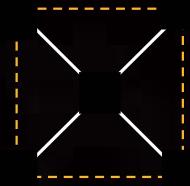


G.I. in Square planar complex



M(AA)a₂

(A α) (A α)

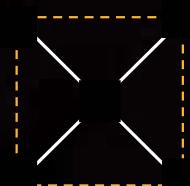


$$G \cdot I = 2$$

M(AB)ab

(A α) (B δ)

(A b) (B α)



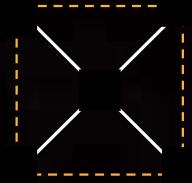


G.I. in Square planar complex



$M(AA)_2$

$(A\ A)$ $(A\ A)$



$M(AB)_2$

$(A\ A)$ $(B\ B)$
 $(A\ B)$ $(B\ A)$



$M(AA)(BB)$

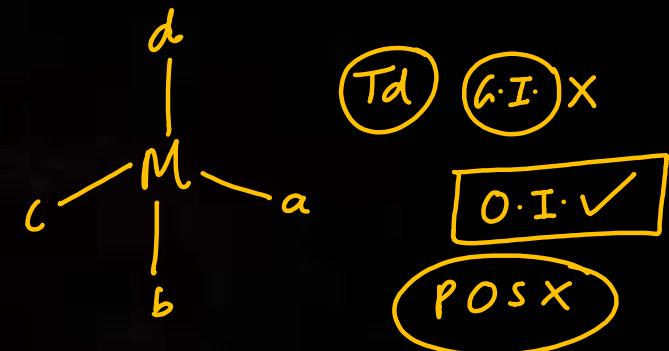
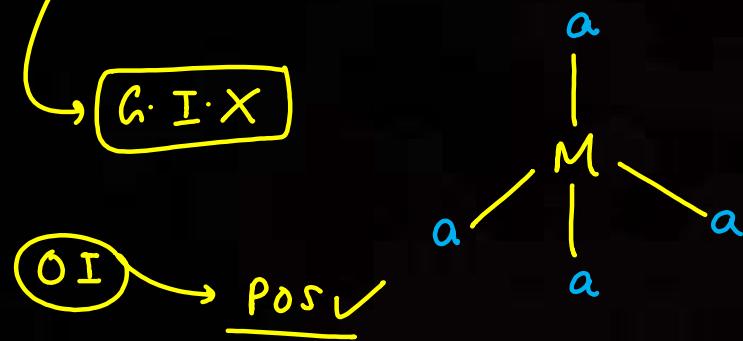
(A^B) (A^B)





G.I. in Tetrahedral complex

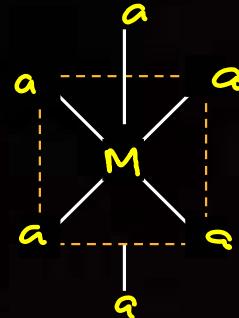
P
W



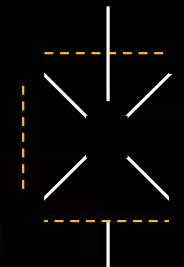


Geometrical & Optical isomerism in Octahedral

Ma_6
 $(aa)(aa)(aa)$



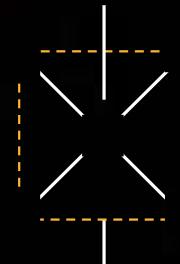
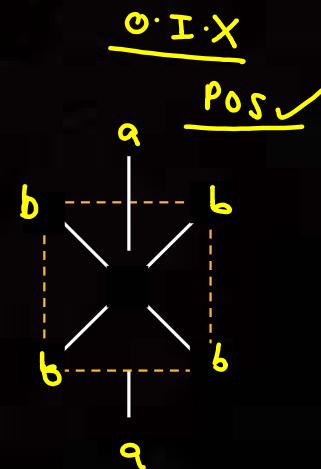
Ma_5b
 $(aa)(aa)(ab)$



$$C \cdot I = 2$$

Ma_2b_4

$(aa)(bb)(bb)$
 $(ab)(ab)(bb)$



Ma_4bc

$(aa)(aa)(bc)$

$(aa)(ab)(ac)$

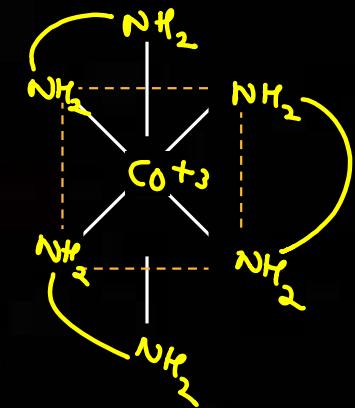
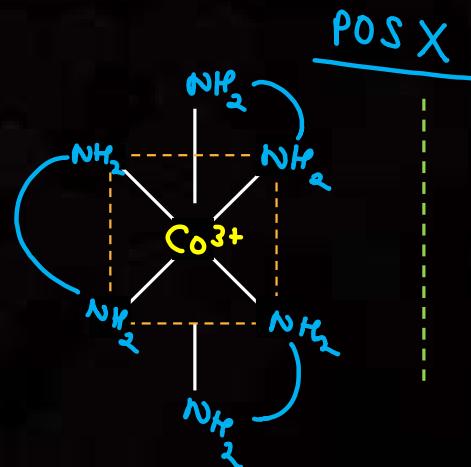
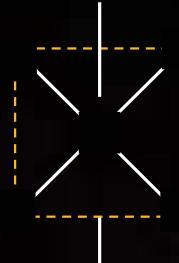
JWala : OP

$M(AA)_3$

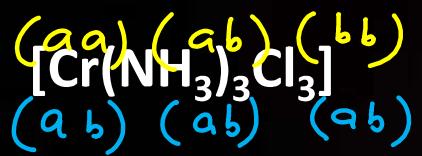
$[Co(en)_3]^{3+}$

Optically active

$$\begin{aligned} O \cdot I \cdot &= 2 \\ C \cdot I \cdot &= 0 \\ \text{Total} &= 2 \end{aligned}$$



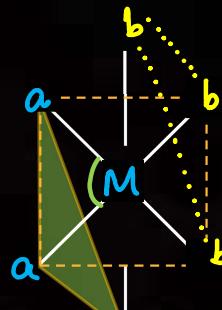
$$C \cdot I = 2$$



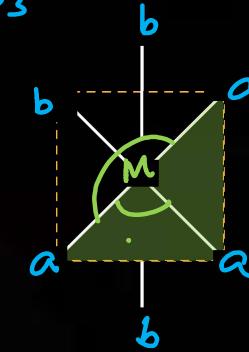
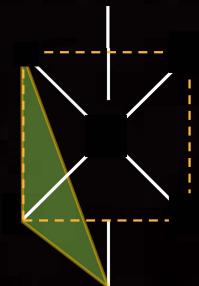
fac-

mer-

facial



$$3 \quad \theta = 90^\circ$$

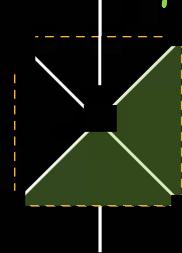
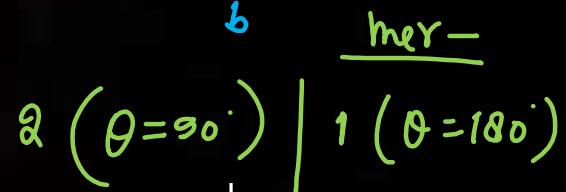


P
W

mer

W

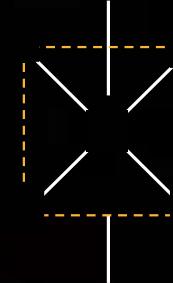
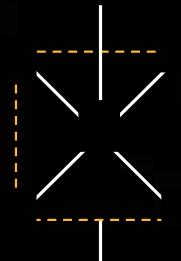
$$\theta = 180^\circ$$



Mabcdef

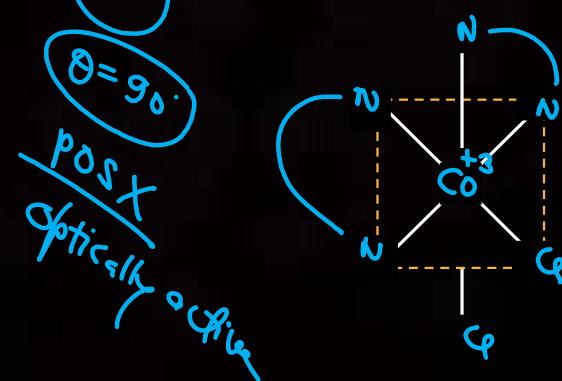
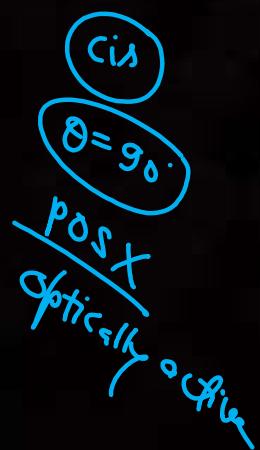


M(AA)a₄



M(AA)₂a₂

Total isomers = $2 + 1$



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

Jwala
 σ_p

$\theta = 180^\circ$

Trans.
 pos ✓
 optically
 inactive