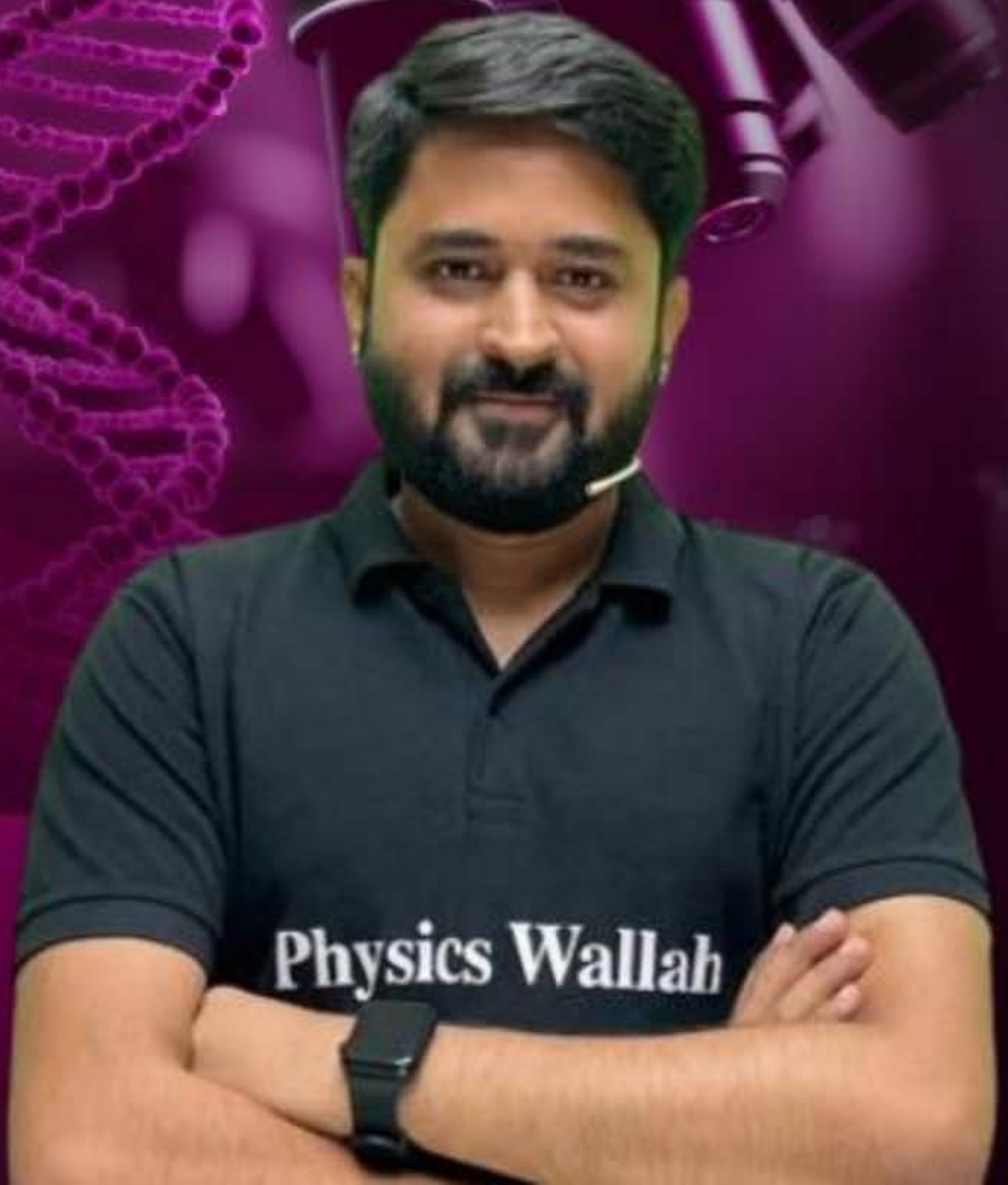
PRACHAND NEET

ONE SHOT

Inorganic Chemistry

CO-ORDINATION COUMPOUNDS

By – Hitesh Sopra Sir



Topics *to be covered*

1. CO-ORDINATION COMPOUNDS ONE SHOT

Coord Compds

Introduction (1Q)

- Intro./Types of Complex
- ☆ Ligands
- IUPAC Naming
- → Synergic Bonding
- → E.A.N. Rule

Theory of Bonding (1Q)

- → Werner
- → VBT
- → CFT

Isomerism & Application (1Q)

INTRODUCTION

2Q or 3Q

* Simple Salts → Acid + Base → Salt + Water

$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NaOH} \longrightarrow \overset{+}{Na}\overset{-}{Cl} + H_2O$

Na^+ → Simple Cation

Cl^- → Simple Anion

TYPES OF SALTS

$KCl\ MgCl_2 \cdot 6H_2O$

K^+ Mg^{+2}

Cl^- $2Cl^-$

① simple Salts

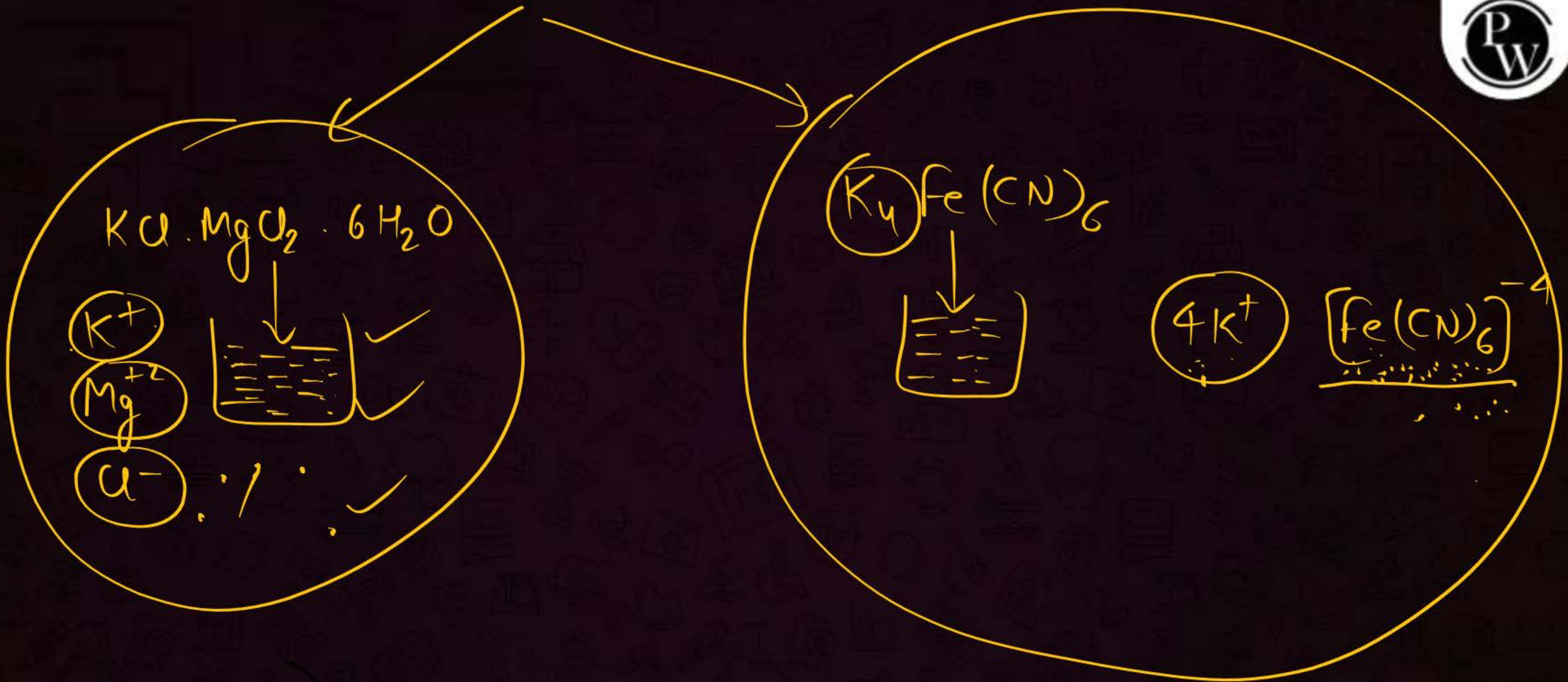
② **Addition Compounds** :

$KCl \cdot MgCl_2 \cdot 6H_2O \Rightarrow$ Carnallite

$K_4Fe(CN)_6$ $\quad 4K^+ + [Fe(CN)_6]^{-4}$

Pot. Ferrocyanide

DOUBLE SALT	COMPLEX SALT
① Addition Compds which dissociate completely in aq soln	① Addition Compds. which doesn't dissociate completely in aq. soln
② All constituent ions show their identity in aqueous solution	② All constituent ions do not show their identity in aqueous solution
Ex: Carnallite → $KCl \cdot MgCl_2 \cdot 6H_2O$ Potash Alum → $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ Mohr's Salt → $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$	Ex: $K_4Fe(CN)_6$ $Ni(CO)_4$ $[Co(NH_3)_6]Cl_3$


$KCl \cdot MgCl_2 \cdot 6H_2O$
K^+
Mg^{+2}
Cl^-
$K_4Fe(CN)_6$
$4K^+$
$[Fe(CN)_6]^{-4}$

QUESTION (2022)

Select the correct formula of carnallite :

(A) $KCl.MgCl_{2.}6H_2O$

(B) $KCl.MgCl_{2.}4H_2O$

(C) $K_4Fe(CN)_6$

(D) $k_2SO_4.Al_2SO_4.24H_2O$

QUESTION (2022)

$CuSO_4$ when reacts with KCN forms CuCN, which is insoluble in water. It is soluble in excess of KCN, due to formation of the following complex:

(A) $K_2[Cu(CN)_4]$

(B) $K_3[Cu(CN)_4]$

(C) $Cu(CN)_2$

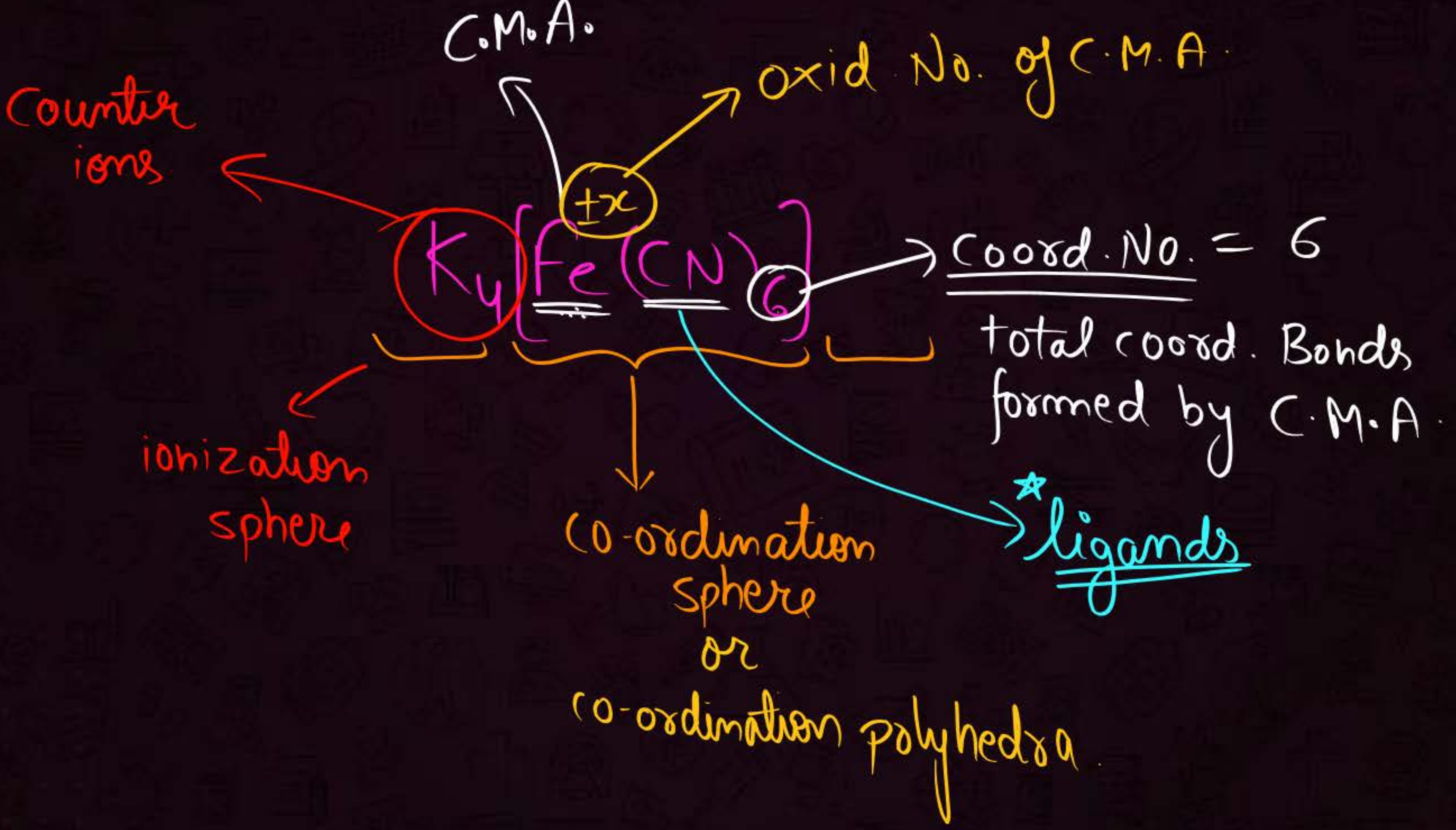
(D) $Cu[KCu(CN)_4]$

$$\overset{+2}{Cu}SO_4 + KC\overset{-1}{N} \longrightarrow \overset{+2}{Cu}(CN)_2 \longrightarrow \overset{+1}{Cu}CN + (CN)_2\uparrow$$

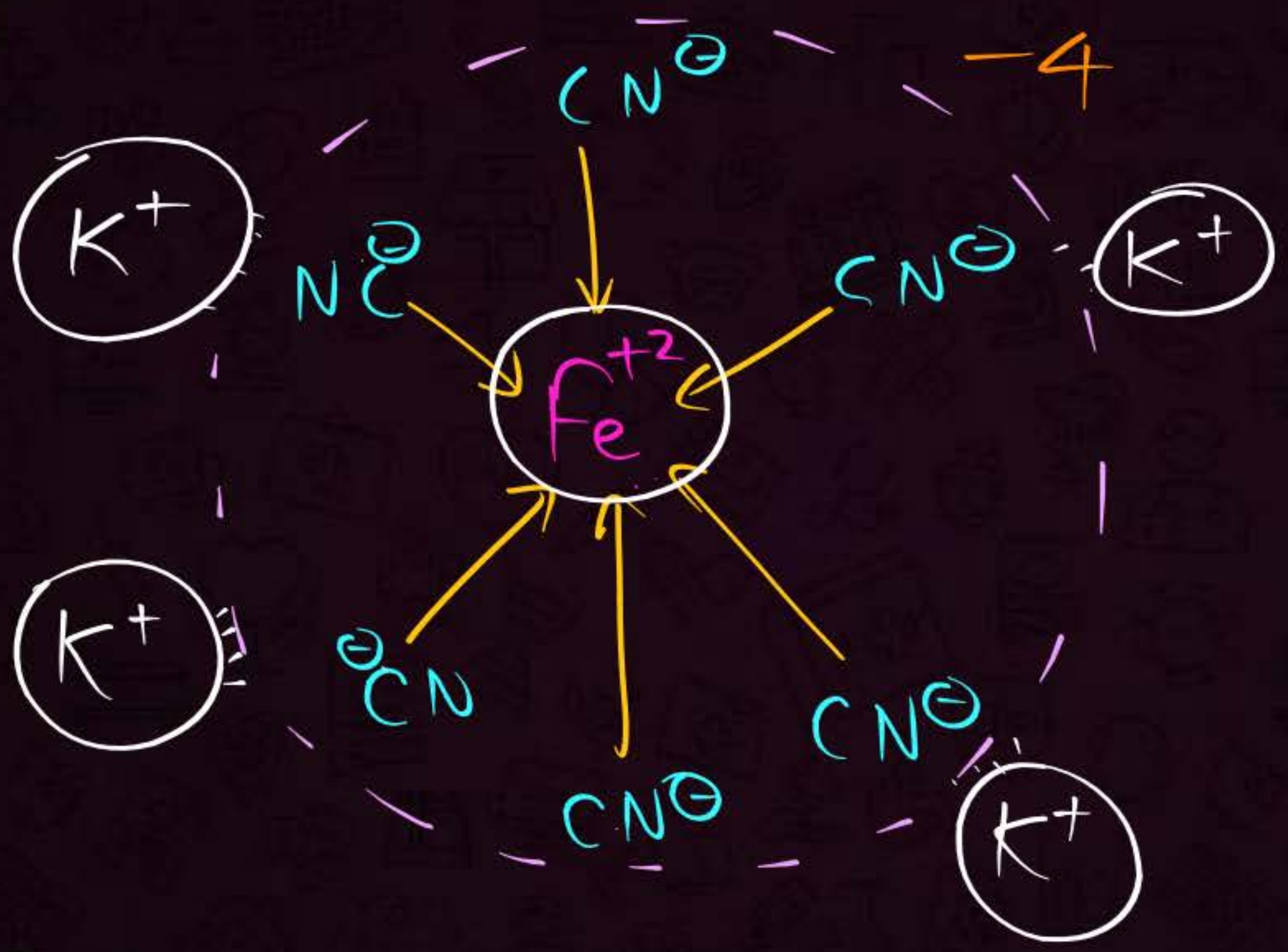
O.A. R.A.

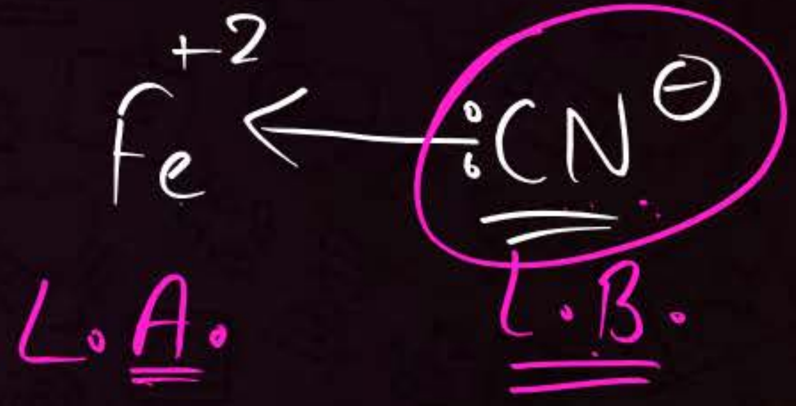
$$\overset{+1}{Cu}CN \xrightarrow{\text{Excess KCN}} K_3[\overset{+1}{Cu}(CN)_4]$$

Few Important Terminologies :



$K_4\overset{+2}{Fe}(CN)_6$ $+2-6=-4$





LIGANDS

any specie which can share an e^- pair (lone pair) with C.M.A & form a coordinate bond is c/d a ligand

L.B. ⟶ Ligand

Ex: $CN^\ominus$ → cyanido

Cl^- → chlorido

O_2^{-2} → peroxido

NH_3 → Ammine

H_2O → Aqua | Aquo

CO → Carbonyl

I) Based On Charge :

Cationic Ligands

- $N_2H_5^{\oplus}$
- O_2^{+}
- NO^{+}

Neutral Ligands

- CO
- en
- NH_3
- H_2O
- N_2H_4

Anionic Ligands

Ex: X^{-} (F^{-}, Cl^{-}, Br^{-}, I^{-})

- CN^{-}
- SCN^{-}
- ox^{-2}
- CO_3^{-2}
- SO_4^{-2}

II) Based on number of donor atoms (Denticity)

Uni

(i) Monodentate ligands :

They have one donor atom in them.

	Formula	Name of ligand	Charge
(i)	$\ddot{N}H_3$	Ammine	0
(ii)	H_2O	Aqua/Aquo	0
(iii)	X^- (F^-, Cl^-, Br^-, I^-)	Halo/Halido	-1
(iv)	OH^-	Hydroxo/Hydroxido	-1
(v)	S^{2-}	Sulphido	-2
(vi)	NH_2^-	Amido	-1

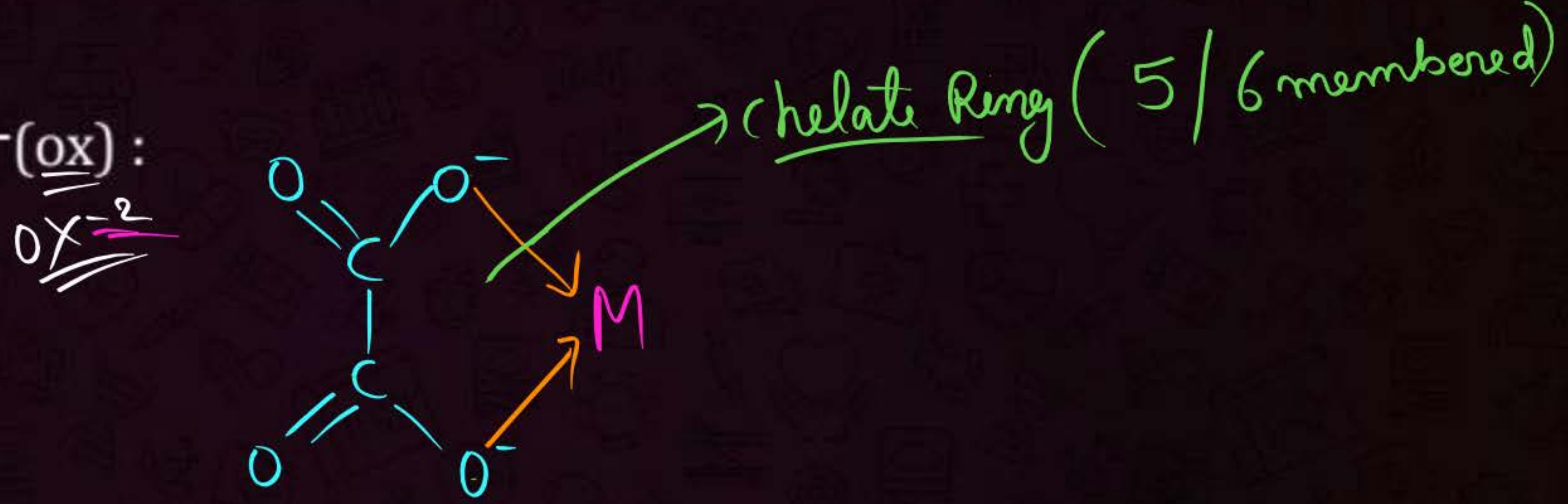
	Formula	Name of ligand	Charge
(vii)	NH^{2-}	Imido	−2
(viii)	N^{3-}	Nitrido	−3
(ix)	N_3^-	Azido	−1
(x)	H^-	Hydrido	−1
(xi)	$\underline{C}O$	Carbonyl	0
(xiii)	$\underline{N}O$	Nitrosyl	0
(xiv)	O^{2-}	oxide	−2
(xv)	O_2^{2-} $\;-\overset{-1}{O}-\overset{-1}{O}-$	peroxide	−2
(xvi)	O_2^- $\;-\overset{-1/2}{O}-\overset{-1/2}{O}-$	Superoxide	−1
(xvii)	C_5H_5N	Pyridine	0
(xviii)	$(\underset{Ph}{C_6H_5})_3P$ / PPh_3	Triphenylphosphine	0

(ii) Bidentate ligands :

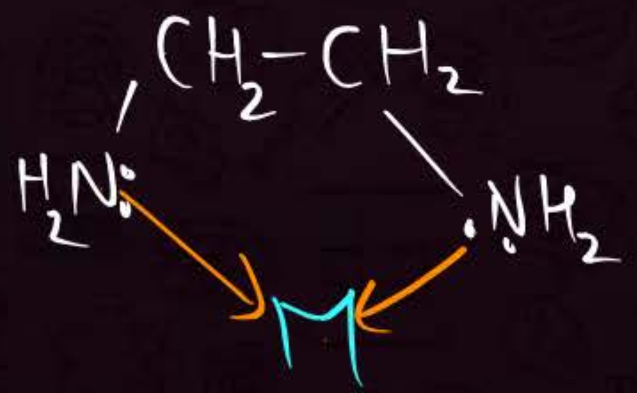
Having two donor atoms/sites.

Examples :

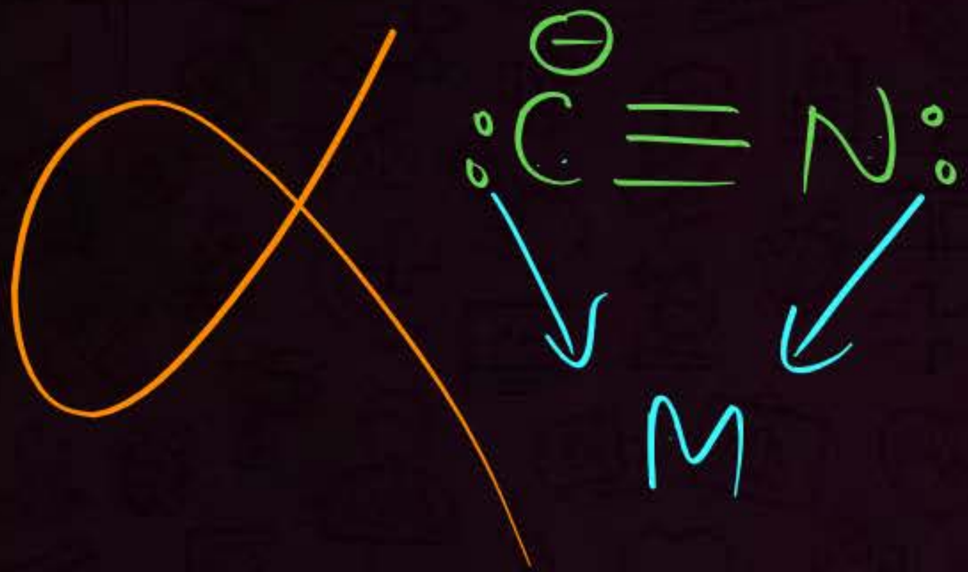
(1) Oxalato ligand : $C_2O_4^{2-}$(ox) :



(2) Ethylene diamine (en)/Ethane -1,2- diamine :



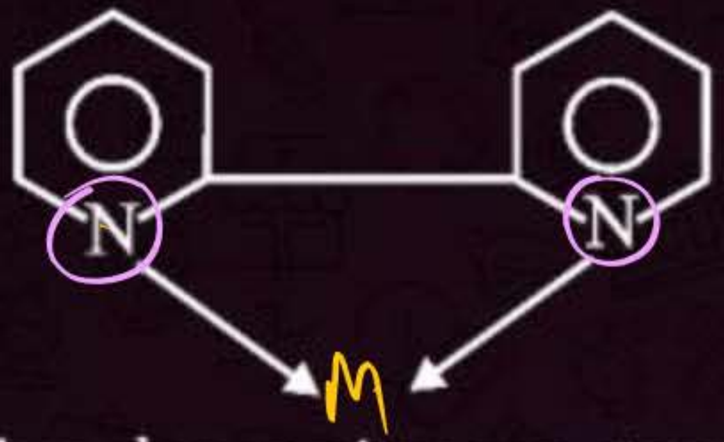
$CN^{\ominus}$



$\leftarrow :\overset{\ominus}{C}\equiv N$

$\leftarrow :N\equiv C^{\ominus}$

(3) Dipyridine (dipy)^{0}



Two donor nitrogen atoms

Py^{0}

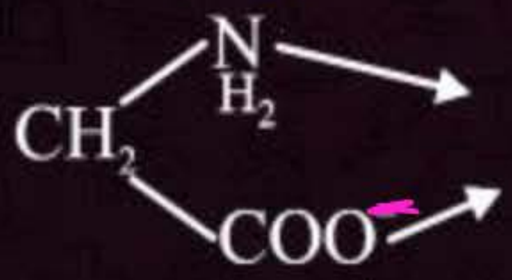
(AA)

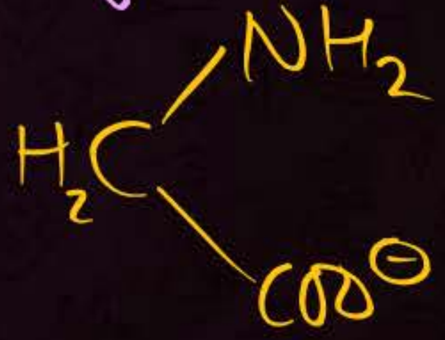
symmetrical Bidentate ligand

(4) Glycinato (gly)$^{-1}$

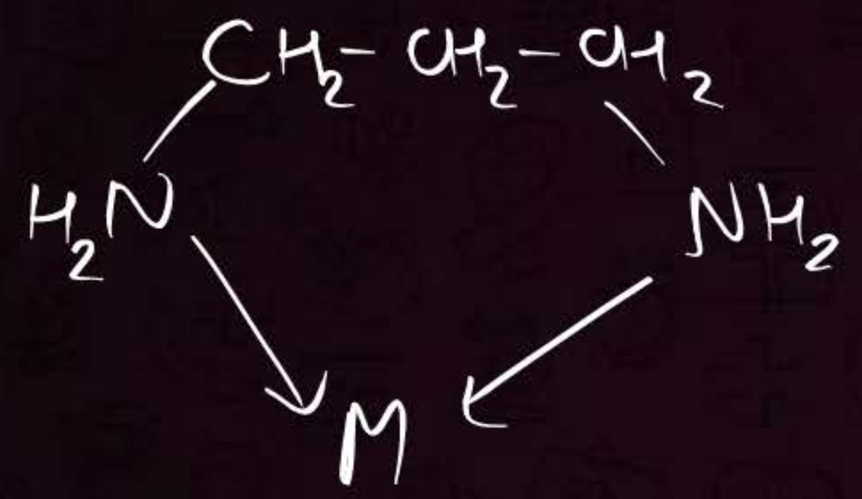
Unsymmetrical Bidentate ligand

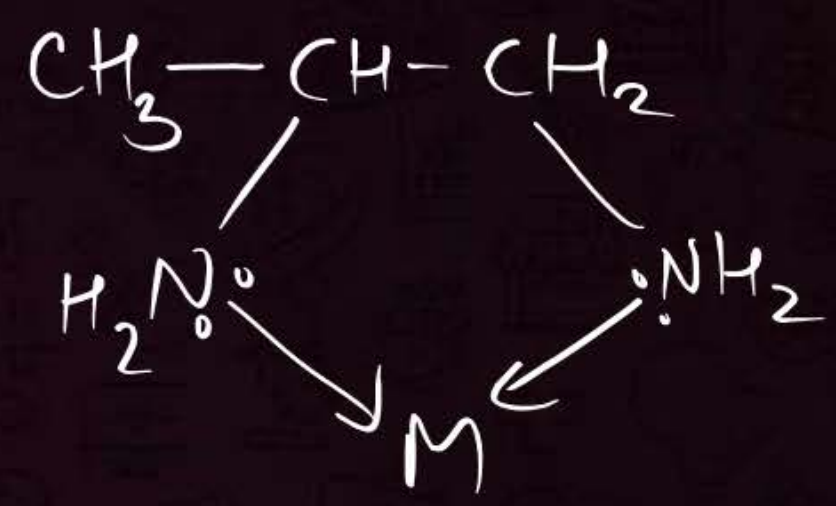
(AB)



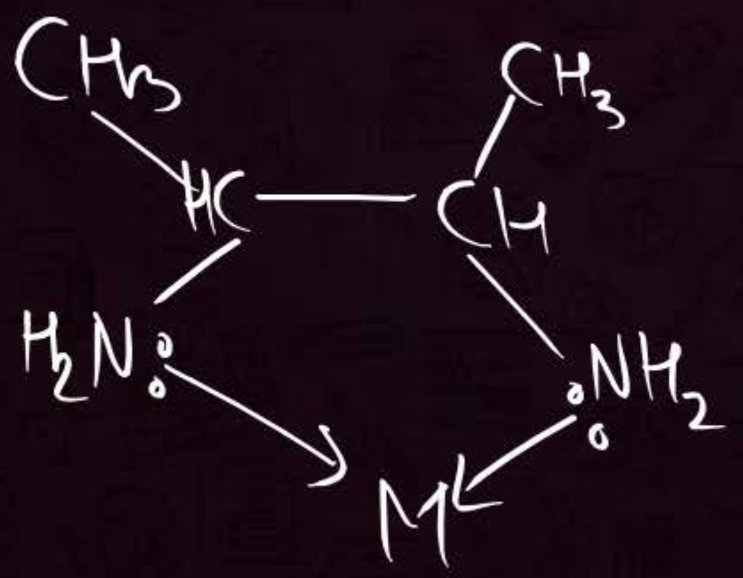


One donor nitrogen atom and one donor oxygen atom tn → trimethylenediamine ; pn → Propylinediamine

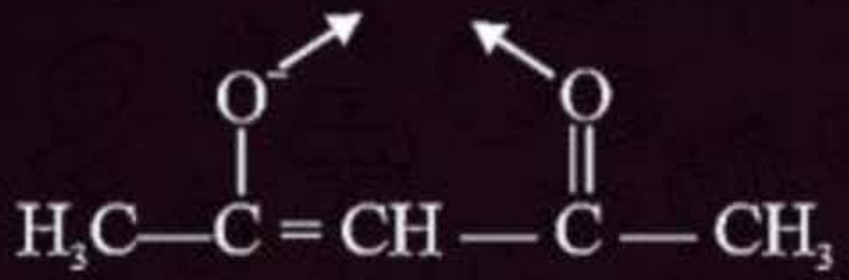




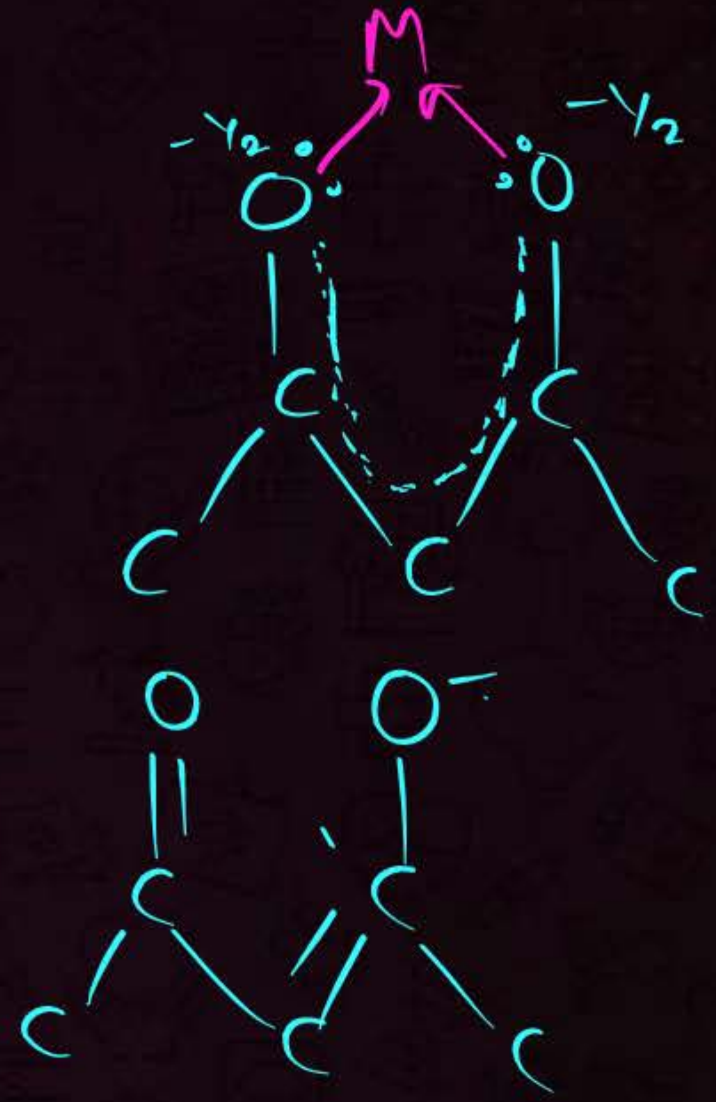
bn → butylene diamine



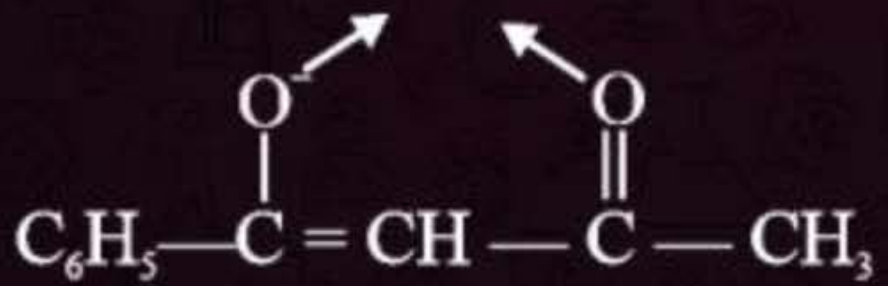
(5) Acetylacetonato (acac)$^{-1}$



Two donor oxygen atoms



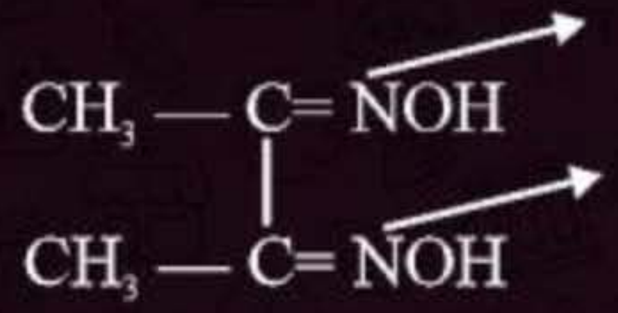
(6) Benzoylacetonato (bcac)



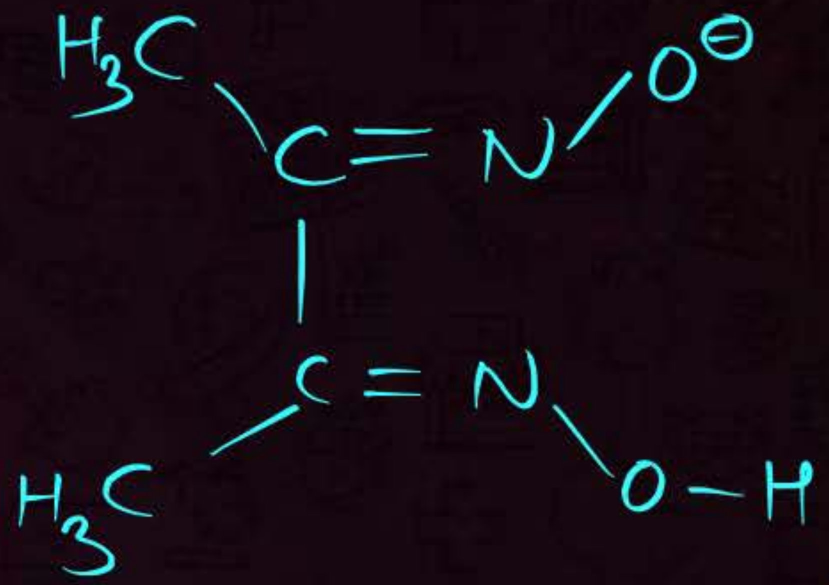
Two donor oxygen atoms

Imp

(7) Dimethylglyoxime (DMG)



Two donor nitrogen atoms



It forms Rosy Red ppt. with Ni^{2+} in basic medium

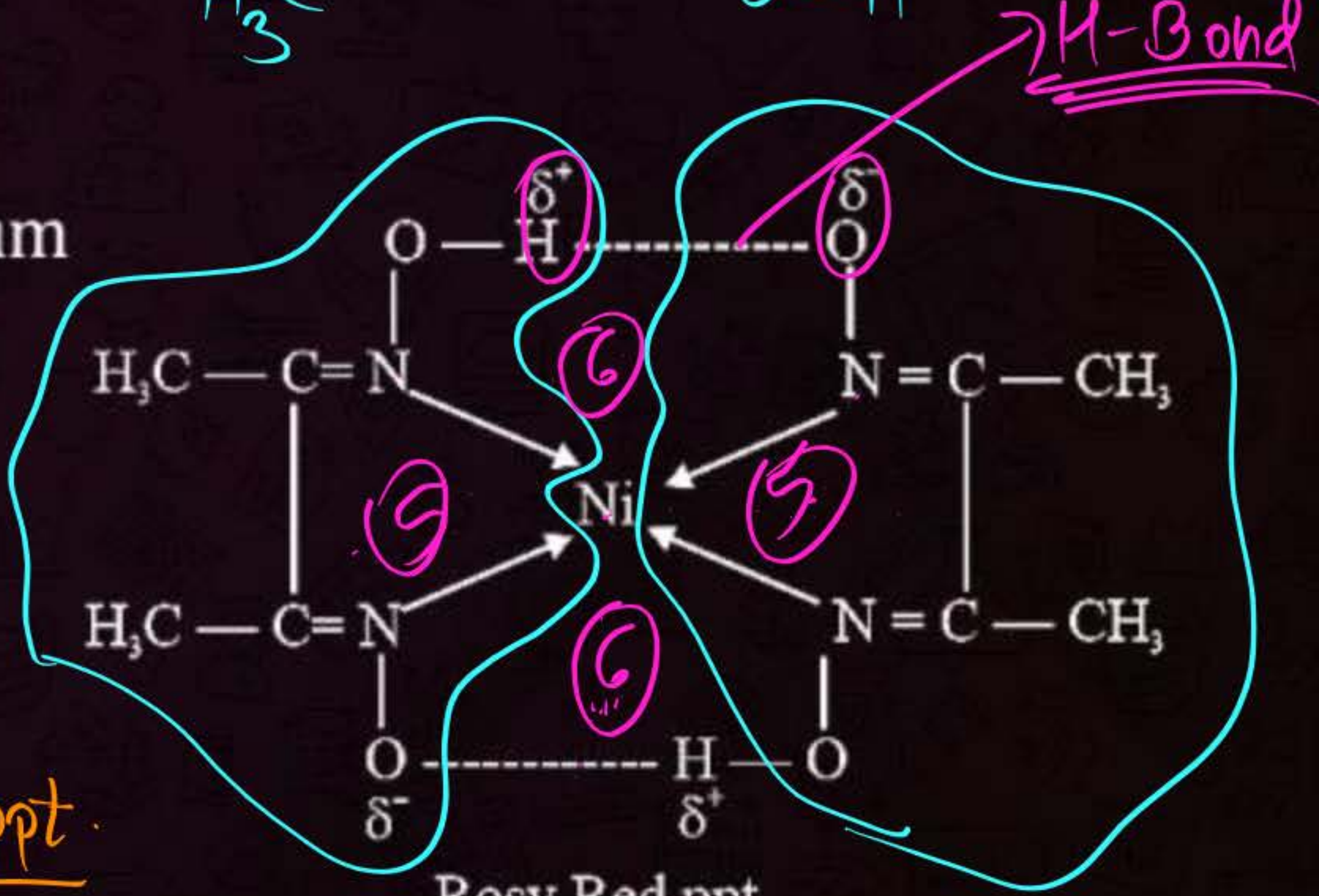
Ni^{2+} + 2DMG + NH_4OH (basic medium)

Ni^{+2} + DMG $\longrightarrow$ $[Ni(DMG)_2]$

नीला नहीं

Rosy / Cherry Red ppt.

लाल गुलाबजामुन

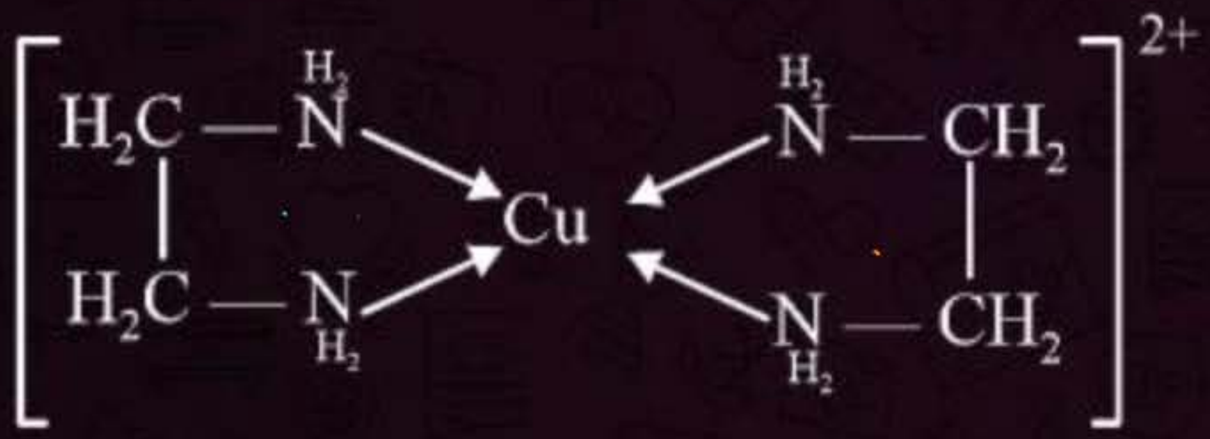


Rosy Red ppt

* dsp^2 hybridization / square planar complex
* Diamagnetic
* Four chelate rings
* Two six membered in in which intramolecular H-bonding is present
* Two five membered rings

Chelation/ Chelate Compounds :

Examples :



CHELATE COMPOUND

Polydentate ligands : Having more than two donor atoms in them

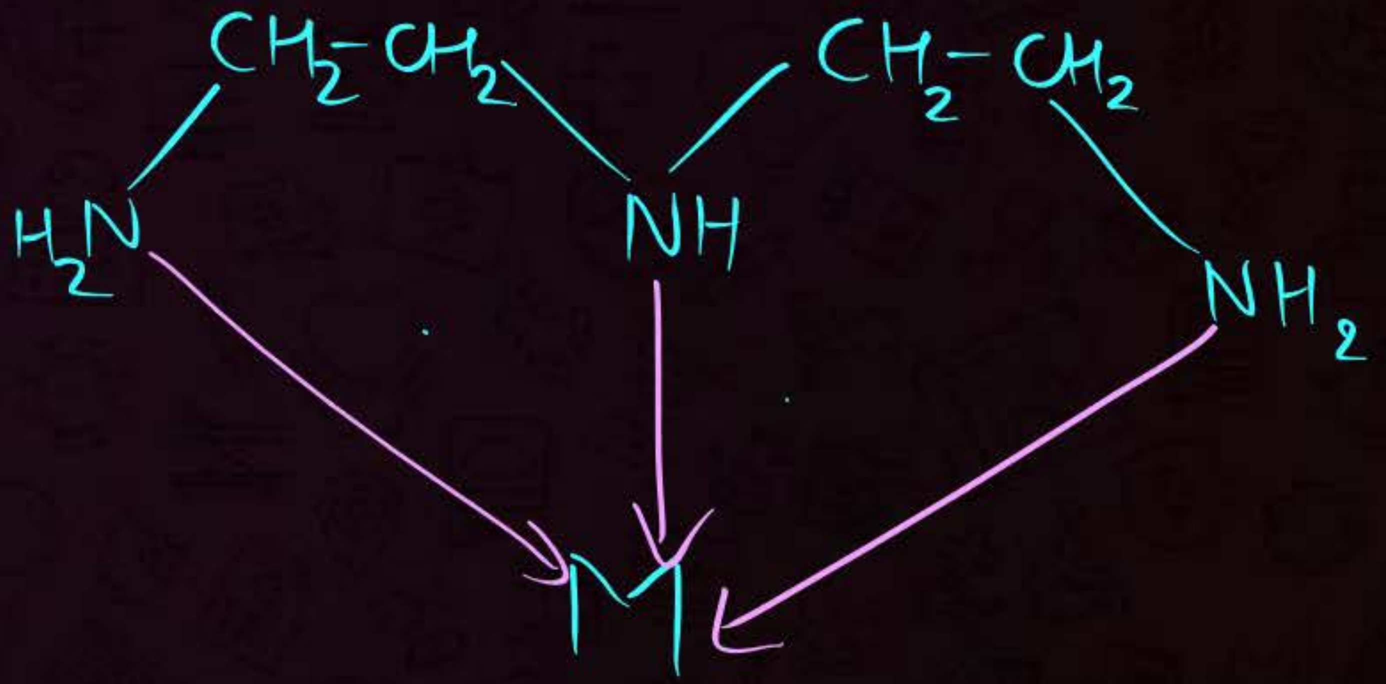
Examples : Tridentate ligand

(1) Diethylene triamine (dien)

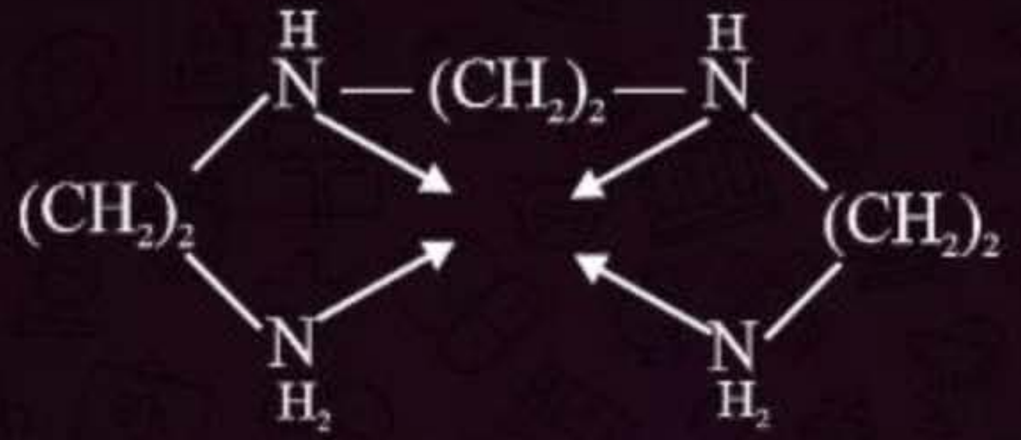
$$H_2\ddot{N}CH_2CH_2-\underset{\underset{H}{|}}{\ddot{N}}-CH_2CH_2\ddot{N}H_2$$

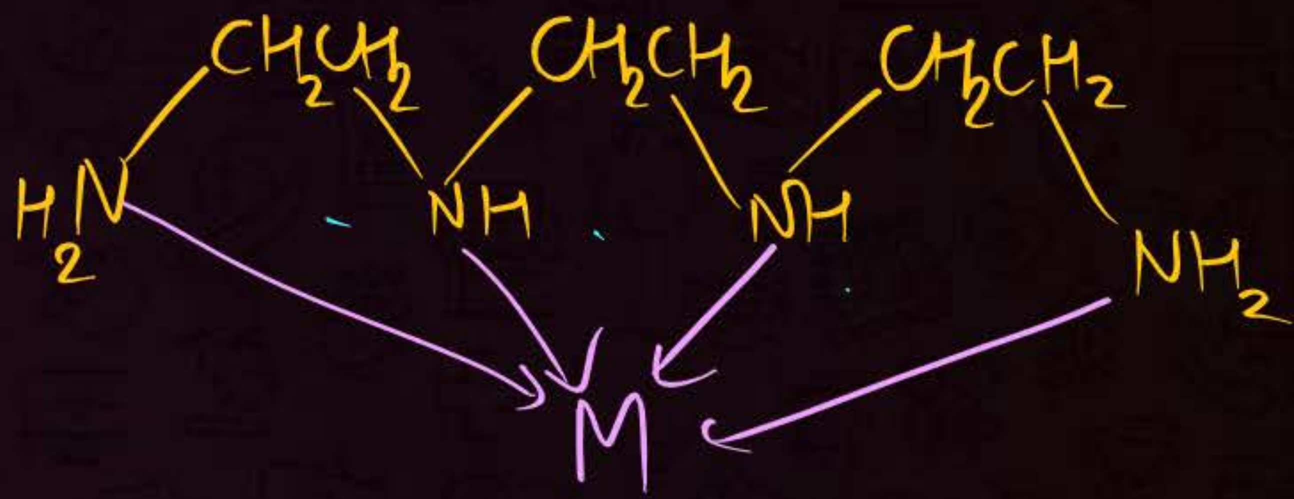
Diethylenetriamine,dien

Three donor nitrogen atoms



(ii) Triethylene tetraamine (trien) Denticity = 4

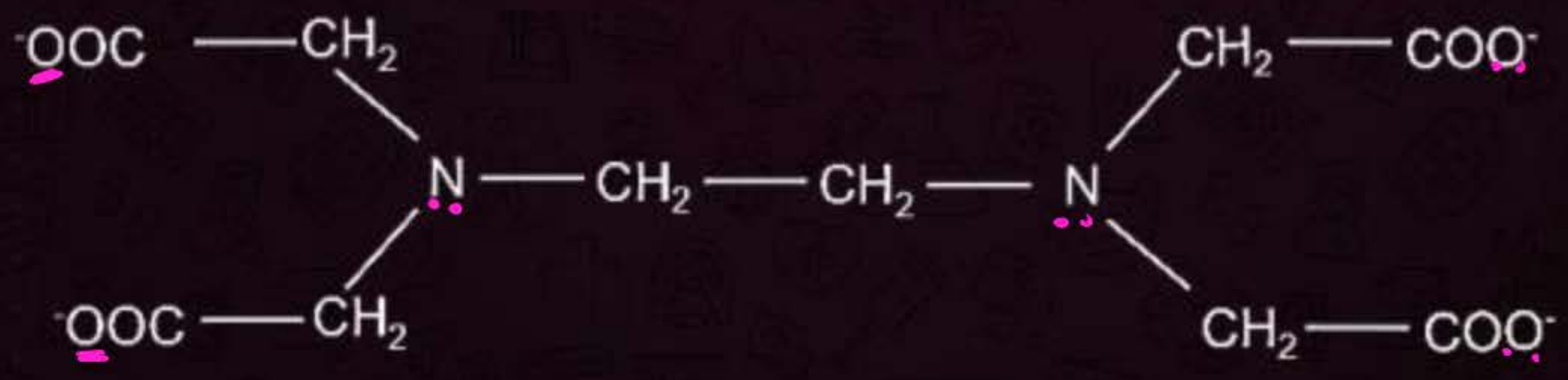




Four donor nitrogen atoms

Imp

(iii) Ethylenediamine tetracetato ion $(EDTA)^{4-}$



Two donor nitrogen and four donor oxygen atoms.

No. of Chelate Rings formed by a Polydentate Ligands (N)

$$N = \text{Denticity} - 1$$

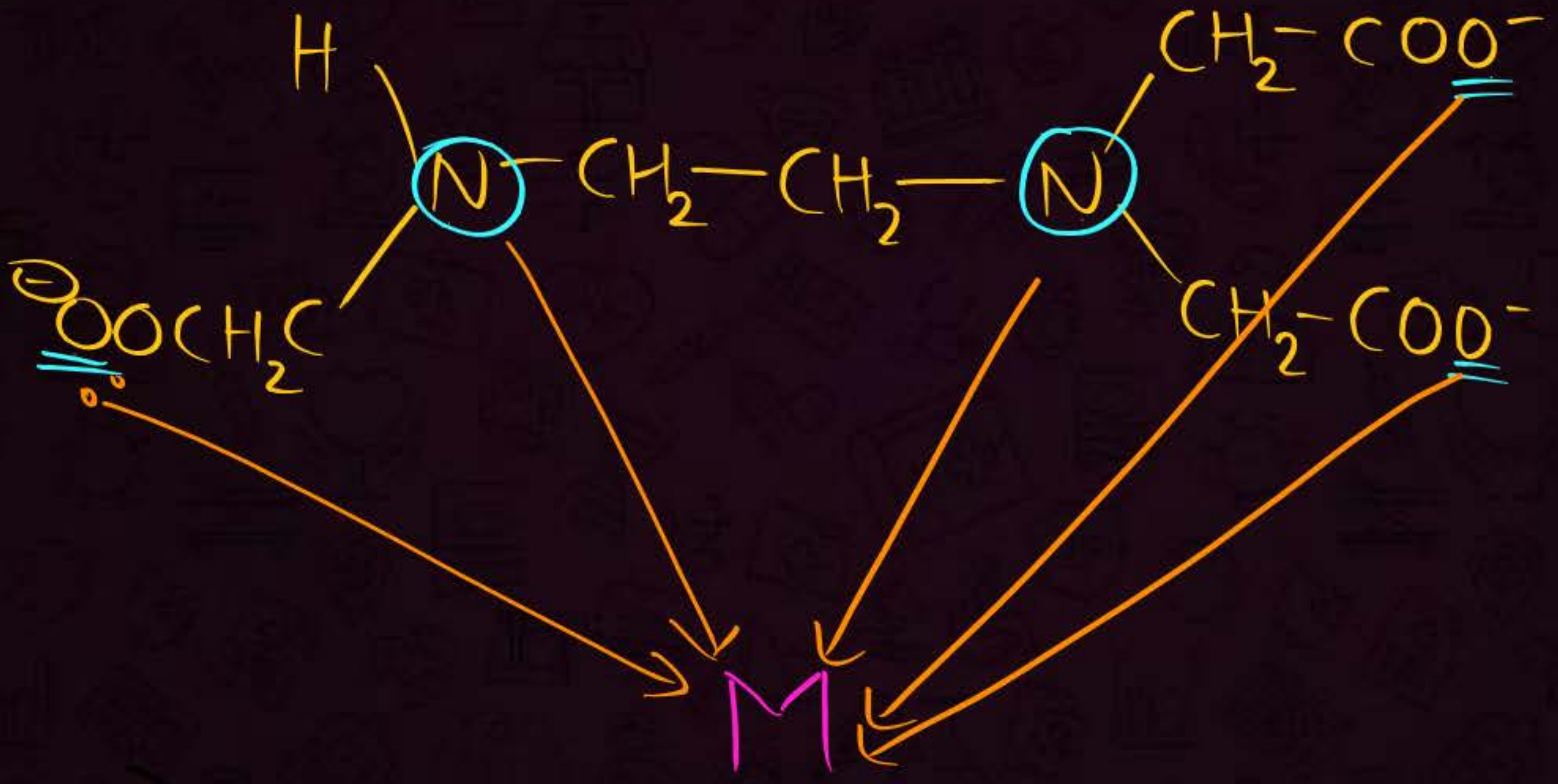
edta^{-3} denticity = 5

No. of chelate Rings = 4

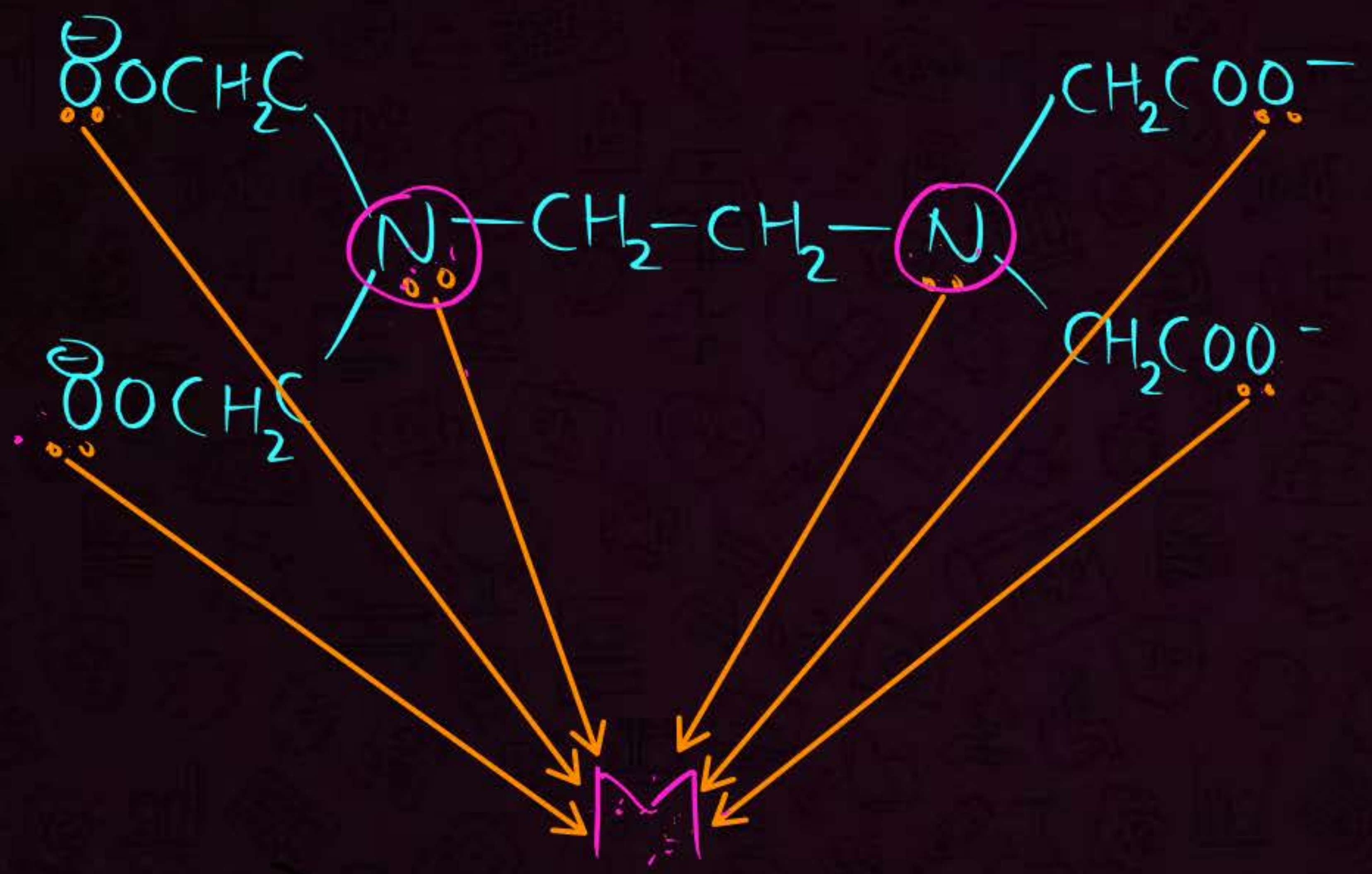
edta^{-4} denticity = 6

No. of chelate Rings = 5

edta^{-3} → ethylendiamine triacetato



* edta^{-4} (denticity = 6)



3+2+1=6

Imp

O–M–O linkage = 6

N–M–N linkage = 1

O–M–N linkage = 8

QUESTION- (NEET 2021)

Ethylene diaminetetraacetate (EDTA) ion is:

(A) Unidentate ligand

(B) Bidentate liganid with two "N" donor atoms

(C) Tridentate ligand with three "N" donor atoms

(D) Hexadentate ligand with four "O" and two "N" donor atoms

QUESTION- (NEET 2015)

The sum of coordination number and oxidation number of the metal M in the complex $[M(en)_2(C_2O_4)]Cl$ (where en is ethylenediamine) is:

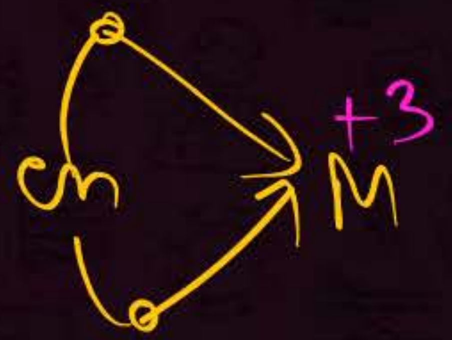
$4 + 2 = 6$

(A) 7

(B) 8

(C) 9

(D) 6

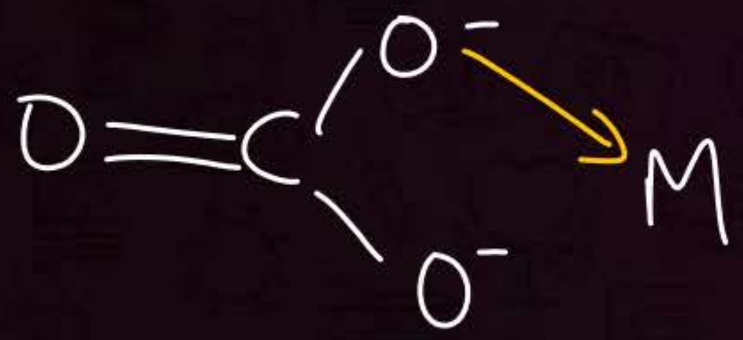


O.S. = +3
C.N = 6

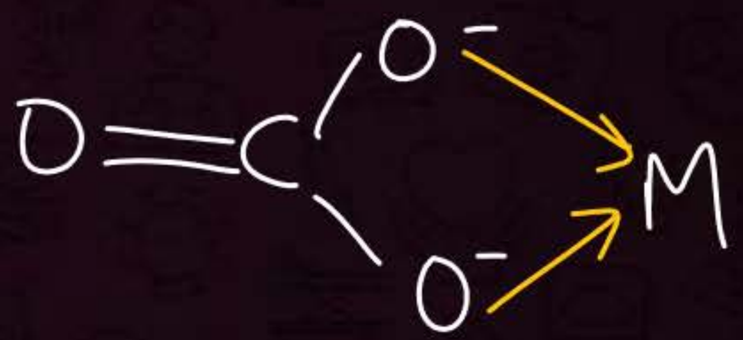
9

FLEXIDENTATE LIGANDS

flexible/Variable denticity



Denticity = 1



Denticity = 2

Ex:- CO_3^{-2}, SO_4^{-2}, SO_3^{-2}, $S_2O_3^{-2}$, $edta^{-3}$, $edta^{-4}$ etc. pH

AMBIDENTATE LIGANDS

Ligands which has more than one donar atoms/sites but at a time only one donar atom/site share its lp.

Ex: $CN^{\ominus}$

cyanido or cyano $\leftarrow :\overset{\ominus}{C}\equiv N:$

$:\overset{\ominus}{C}\equiv \underline{N}: \rightarrow$ isocyanido or isocyano

Example:

$\leftarrow :\overset{\ominus}{\ddot{S}}-C\equiv N:$

(1)	$M \leftarrow \overset{\ominus}{C}N$ cyano	$M \leftarrow N\overset{\ominus}{C}$ isocyano
(2)	$M \leftarrow \overset{\ominus}{S}CN$ thiocyanato-S	$M \leftarrow NC\overset{\ominus}{S}$ thiocyanato- N or isothiocyanato
(3)	$M \leftarrow \overset{\ominus}{O}CN$ cyanato	$M \leftarrow NC\overset{\ominus}{O}$ isocyanato
(4)	$M \leftarrow \overset{\ominus}{N}O_2$ nitrito –N	$M \leftarrow \overset{\ominus}{O}NO$ nitrito –O
(5)	$M \leftarrow SO_3^{2-}$ Sulphito -S	$M \leftarrow OSO_2^{2-}$ Sulphito -O
(6)	$M \leftarrow S_2O_3^{2-}$ thiosulphato – S	$M \leftarrow OS_2O_2^{2-}$ thiosulphato – O

$:\overset{\ominus}{S}-C\equiv N: \rightarrow$

Nitro / Nitrito – O/N

Based on e- pair donating/accepting tendency :

i) Classical ligands :→ $M \xleftarrow{\sigma} :L$

ii) Non Classical ligands :→ (π-acids / π-acceptors)

$M \xleftarrow{\sigma \text{ dative}} :L$ and $M \xrightarrow{\pi \text{ dative}} L$

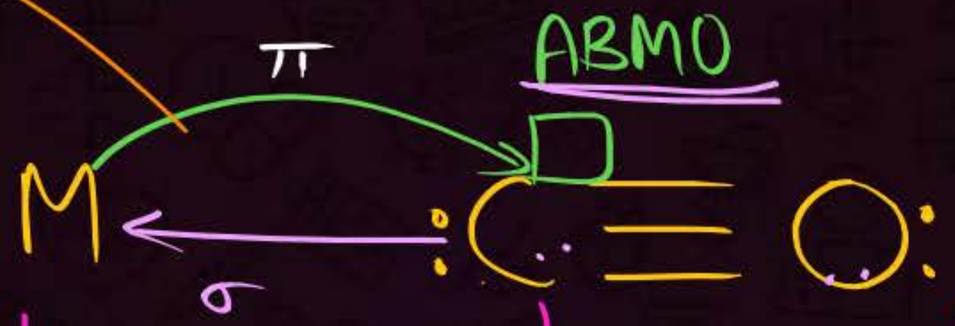
(Atomic orbital): Cl^-, R_3P, R_3As

(ABMO): CO, CN^-, NO, NO^+, C_2H_4, C_2H_2, C_6H_6 etc...

BONDING IN METAL CARBONYL COMPLEXES

$B.O. = \frac{B_{e^-} - AB_{e^-}}{2}$

Synergic Bonding



M–L Bond

Due to synergic Bonding

M–L Bond Order ↑

M–L Bond length ↓

M–L Bond Strength ↑

Stability ↑

B.O. ↑	B.O. ↓
B.S. ↑	B.L. ↑
B.L ↓	B.S ↓

C — O Bond

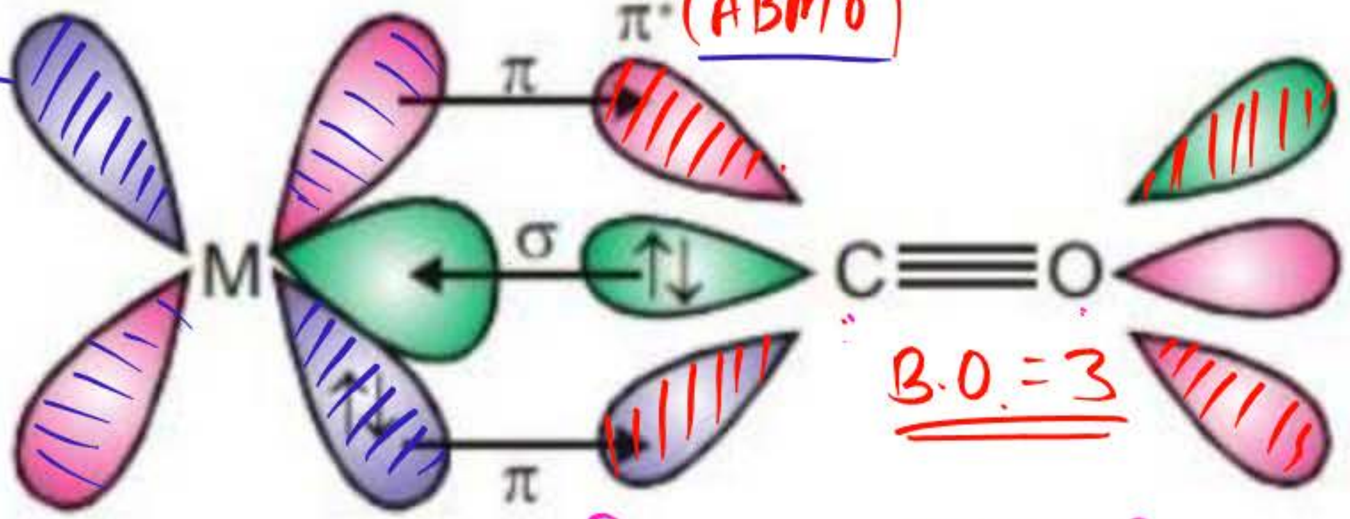
Due to synergic Bonding

C–O B.O. ↓

C–O B.L. ↑

C–O B.S ↓

filled d-orbital of C.M.A.



B.O. ↑
B.S. ↑

ABMO e^- ↑
B.O ↓

B.B.
Stability ↑

Stability ↑

$$B.O. \downarrow = \frac{1}{2}\left(B_{e^-} - AB_{e^-} \uparrow\right)$$

C—O B.L. ∝ synergic Bonding

QUESTION- (NEET 2016)

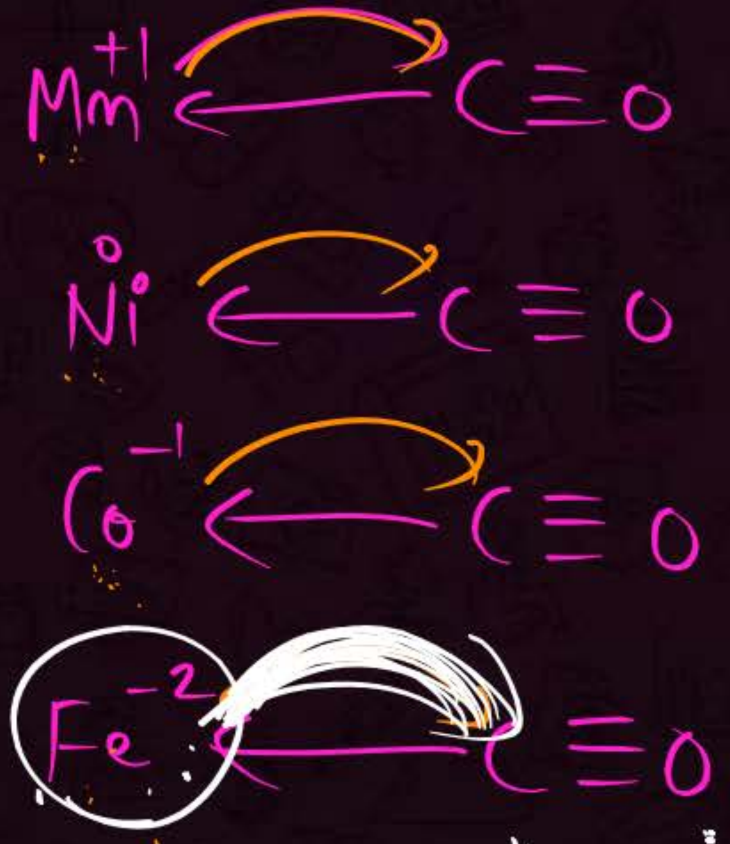
Which of the following has longest C-O bond length? (Free C-O bond length in CO is 1.128 Å)

(A) $[Mn(CO)_6]^+$

(B) $Ni(CO)_4$

(C) $[Co(CO)_4]^-$

(D) $[Fe(CO)_4]^{2-}$



(A) $[\overset{0}{Ni}(CO)_4]$

(B) $[\overset{-1}{Mn}(CO)_5]^-$

(C) $[\overset{+2}{Fe}(CO)_6]^{+2}$

(D) $[\overset{+1}{Fe}(CO)_5]^+$

Max. C — O B.L = B

Max. M — C B.O. = B

QUESTION- (NEET 2011)

B.S. ∝ B.O.

Which of the following carbonyl's will have the strongest C-O bond? [2011 Main]

Max. B.O. ↑

(Min^m. syn. Bonding)

(A) $V(CO)_4^-$ (−1)

(B) $Fe(CO)_5$ (0)

(C) $Mn(CO)_4^+$ (+1) ✓

(D) $Cr(CO)_6$ (0)

* Types of Complex Compounds :-

(I) Based on charge :-

① Cationic Complex :→ $[Co(NH_3)_6]^{+3}Cl_3$, $[Ni(en)_3]^{+2}SO_4$ etc...

② Anionic Complex :→ $K_4[Fe(CN)_6]^{-4}$, $Na_2[Ni(CN)_4]^{-2}$ etc...

③ Neutral Complex :→ $[Ni(CO)_4]$, $[Fe(CO)_5]$, $[Mn(CO)_5]$ etc...

II) Based on ligands :-

I) Homoleptic Complex :→ same type of ligands

Ex: $K_4[Fe(CN)_6]$, $[Ni(en)_3]Cl_2$, $[Co(NH_3)_6]Cl_3$ etc...

II) Heteroleptic Complex :→ have different types of ligands

Ex: $[Co(NH_3)_4Cl_2]Cl$, $[Fe(H_2O)_5\overset{+}{N}O]SO_4$, $[Pt(NH_3)(Cl)(I)(H_2O)]$ etc.

Brown Ring Complex

III) Based on dissociation :-

I) Perfect Complex :→ coordination sphere does not dissociates.

$$Cu^{+2} + KCN \longrightarrow Cu(CN)_2 \longrightarrow CuCN + (CN)_2 \uparrow$$

$$CuCN \xrightarrow{\text{Excess KCN}} K_3[Cu(CN)_4]$$

$K_3[Cu(CN)_4]$ → Perfect Complex w.r.t. H_2S

$$K_3[Cu(CN)_4] \xrightarrow{H_2S\ \text{gas}} Cu_2S \text{ (Black)}$$

~~Cu_2S (Black)~~

II) Imperfect Complex :→ Coordination sphere gets dissociated & C.M.A. can show its presence.

$$Cd^{+2} + KCN \longrightarrow Cd(CN)_2 \xrightarrow[KCN]{Excess} K_2[Cd(CN)_4]$$

$K_2[Cd(CN)_4]$ → Imperfect w.r.t. H_2S

$$K_2[Cd(CN)_4] \xrightarrow{H_2S \text{ gas}} CdS \text{ (yellow)}$$

IUPAC NAMING OF COMPLEX COMPOUNDS

e^-

$\overset{+}{K_4}[Fe(CN)_6]$ Complex $[Co(NH_3)_6]Cl_3$

(I) Cation —— <space> —— Anion

① Simple Cation :→ Same Name

② Complex Cation :→

(i) Ligands

(ii) C.M.A. (English Name)

(iii) oxid^n. State (Roman)

(+1) (+4) (0) (I) (III)

① Simple Anion → Same Name

② Complex Anion :→

(i) Ligand

(ii) C.M.A (Latin Name + "ate")

(iii) oxidation State (Roman)

Cationic Part		Anionic Part
Iron	Fe	Ferrum + ate ⇒ Ferrate
Cobalt	Co	Cobaltate
Platinum	Pt	Platinate
Silver	Ag	Argentate
Chromium	Cr	Chromate
Manganese	Mn	Manganate
Zinc	Zn	Zincate
Gold	Au	Aurate
Mercury	Hg*	*Mercurate

* Naming of Ligands :→

(1) Alphabetical Order :↓

Ex: $[M(H_2O)(NO_2)(Cl)(Br)(I)(O)]$

	H_2O	NO_2	Cl	Br	I	O
	a	n	c	b	i	o
	1	5	3	2	4	6

Ex: $[M(H_2O)_3(NH_3)_3]$

	$(H_2O)_3$	$(NH_3)_3$
	aq.	am
	(2)	(1)

(2) $(\ )_2$ – Di / Bis-( )

$(\ )_3$ – tri / tris-( )

$(\ )_4$ – tetra / tetrakis-( )

$(\ )_5$ – Penta / Pentakis-( )

$(\ )_6$ – hexa / hexakis-( )

⋮

$(CN)_2$ → dicyanido

$(en)_2$ → ~~di~~ ethylenediamine

→ Bis-(ethylenediamine)

or

→ Bis-(ethane-1,2 diamine)

(3) Charge on ligand

Charge on ligand	Ligand Name
(1) −ve / anionic ligand	ligand Name + "O"
(2) +ve / cationic ligand	ligand Name + "ium"
(3) Neutral ligand	Same Name

Ex: CN^- = cyanido

Cl^- = chloro / chlorido

NO_2^- = Nitrito-N

H_2O = Aqua / Aquo

* NH_3 = Ammine

$N_2H_5^+$ = Hydrazenium

NO^+ = Nitrosylium / Nitrosonium

O_2^+ = Oxygenium

en → ethylenediamine / ethane-1,2-diamine

$K_4[Fe(CN)_6]^{-4}$ CN^-

$(+4) + x + (-6) = 0$

Potassium hexacyanidoferrate (II)

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

hexaamminecobalt (III) chloride

Example 5.2 Write the formulas for the following coordination compounds:

(a) Tetraammineaquachloridocobalt(III) chloride
(b) Potassium tetrahydroxidozincate(II)
(c) Potassium trioxalatoaluminate(III)
(d) Dichloridobis(ethane-1,2-diamine)cobalt(III)
(e) Tetracarbonylnickel(0)

Solution (a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ (b) $K_2[Zn(OH)_4]$ (c) $K_3[Al(C_2O_4)_3]$
(d) $[CoCl_2(en)_2]^+$ (e) $[Ni(CO)_4]$

Example 5.3 Write the IUPAC names of the following coordination compounds:

(a) $[Pt(NH_3)_2Cl(NO_2)]$ (b) $K_3[Cr(C_2O_4)_3]$ (c) $[CoCl_2(en)_2]Cl$
(d) $[Co(NH_3)_5(CO_3)]Cl$ (e) $Hg[Co(SCN)_4]$

Solution (a) Diamminechloridonitrito-N-platinum(II)
(b) Potassium trioxalatochromate(III)
(c) Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
(d) Pentaamminecarbonatocobalt(III) chloride
(e) Mercury (I) tetrathiocyanato-S-cobaltate(III)

$\left[\overset{+3}{Co}(NH_3)_4(Cl)(H_2O)\right]^{+2}Cl_2$

am c aq.

Tetraammineaquachloridocobalt (III) chloride

→ $K_2\left[\overset{+2}{Zn}(OH)_4\right]^{-2}$ Potassium tetrahydroxidozincate (II)

→ $K_2\left[\overset{+2}{Hg}I_4\right]$ Potassium Tetraiodidomercurate (II)

→ $\left[Pt(NH_3)_2(Cl)(NH_2CH_3)\right]^{+}Cl^{-}$ ⇒ Diamminechloridomethylamineplatinum (II) chloride

a c m

Intext Questions

5.1 Write the formulas for the following coordination compounds:

(i) Tetraamminediaquacobalt(III) chloride

(ii) Potassium tetracyanidonickelate(II)

(iii) Tris(ethane–1,2–diamine) chromium(III) chloride

(iv) Amminebromidochloridonitrito-N-platinate(II)

(v) Dichloridobis(ethane–1,2–diamine)platinum(IV) nitrate

(vi) Iron(III) hexacyanidoferrate(II)

5.2 Write the IUPAC names of the following coordination compounds:

(i) $[Co(NH_3)_6]Cl_3$

(ii) $[Co(NH_3)_5Cl]Cl_2$

(iii) $K_3[Fe(CN)_6]$

(iv) $K_3[Fe(C_2O_4)_3]$

(v) $K_2[PdCl_4]$

(vi) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

QUESTION- (NEET 2015 Re)

The name of complex ion, $[Fe(CN)_6]^{3-}$ is:

(A) Hexacyanidoferrate (III) ion

(B) Hexacyanoiron(III) ion

(C) Hexacyanoferrate (III) ion

(D) Tricyanoferrate(III) ion

QUESTION- (NEET 2015 Re)

IUPAC name of $[Pt(NH_3)_3(Br)(NO_2)Cl]Cl$ is:

(A) Triammine chlorobromonitro platinum (IV) chloride

(B) Triammine bromonitrochloro platinum (IV) chloride

(C) Triammine bromochloronitro platinum (IV) chloride

(D) Triammine nitrochlorobromi platinum (IV) chloride

QUESTION- (NEET ~~2015 Re~~ 2021)

The IUPAC name of the complex.

$[Ag(H_2O)_2][Ag(CN)_2]$

diaquasilver(I) dicyanidoargentate(I)

(A) diaquasilver(I) dicyanidoargentate(I)

(B) dicyanidosilver(II) diaquaargentate(II)

(C) diaquasilver(II) dicyanidoargentate(II)

(D) dicyanidosilver(I) diaquaargentate(I)

SIDGEWICK'S EAN RULE

$$E.A.N. = Z - O.S. + 2 \times C.N.$$

Z = Atomic No.

O.S. = oxidation state

C.N. = Coord. No.

$K_4[\overset{+2}{Fe}(CN)_6]$

$EAN = 26 - 2 + 2 \times 6 = 36$ (Kr)

* Sidgewick's EAN Rule :–

If E.A.N. of C.M.A. in any complex is equal to the atomic No. (Z) of Next Noble gas, then the complex will be stable

$K_4[Fe(CN)_6] \Rightarrow EAN = 36 \rightarrow Kr$

$[Ni(CO)_4] \Rightarrow EAN = 28 - 0 + 2 \times 4 = 36$ ✓

$[Fe(CO)_5] \Rightarrow EAN = 26 - 0 + 2 \times 5 = 36$ ✓

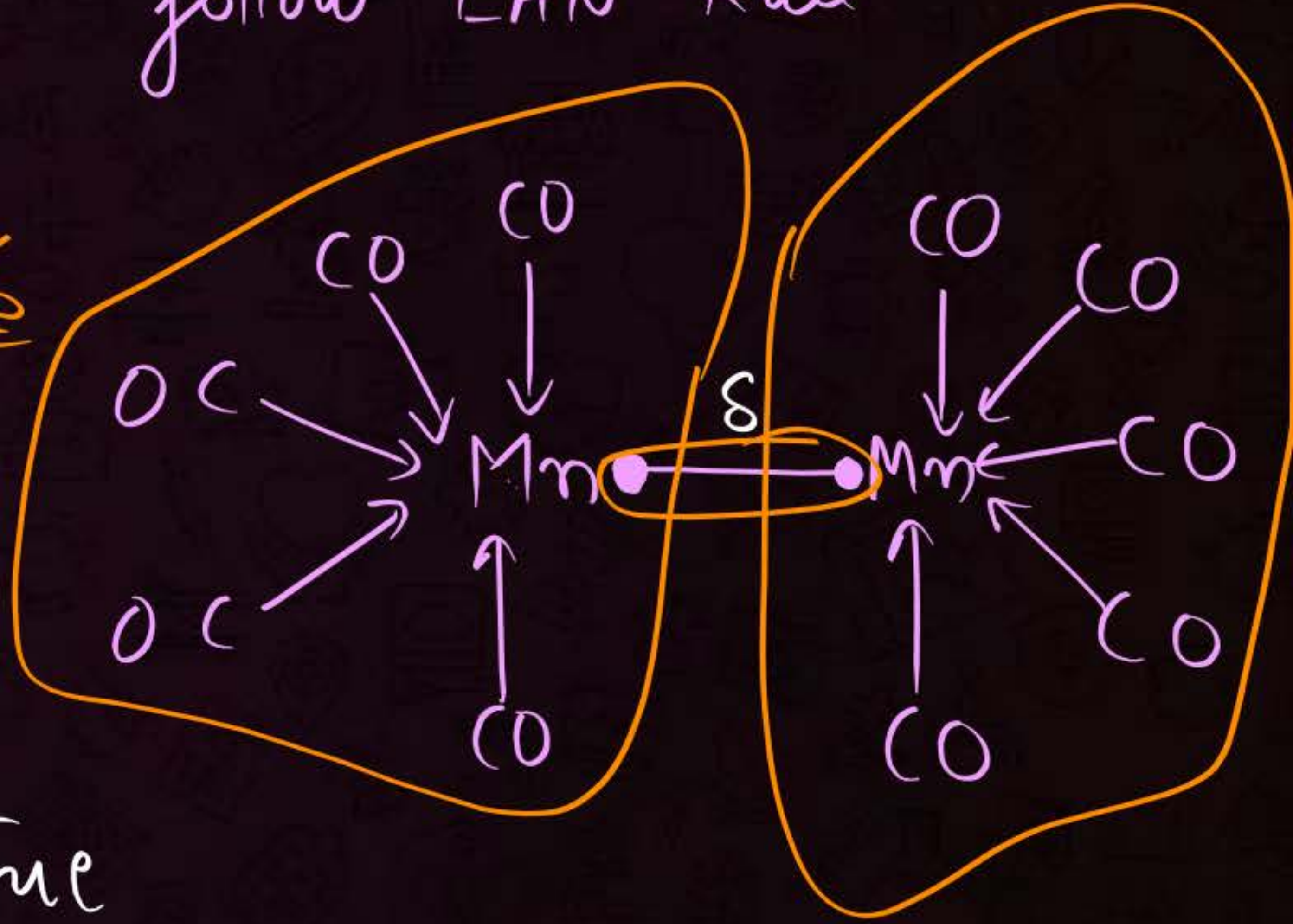
e^- → $[Mn(CO)_5] \Rightarrow 25 - 0 + 2 \times 5 = 35 \xrightarrow{+e^-} 36$

$[Ni(en)_2(\overset{-2}{ox})]Cl_2$

$EAN = 28 - 4 + 2 \times 6 = \underline{\underline{36}}$ ✓ follow EAN Rule

$[Mn(CO)_5] \rightarrow EAN = 35 \xrightarrow{+e^-} \underline{\underline{36}}$

(O.A.)



① $Mn(CO)_5$ is an O.A. ⇒ True

② $Mn(CO)_5$ has tendency to dimerise ⇒ True

ORGANOMETALLIC COMPOUNDS

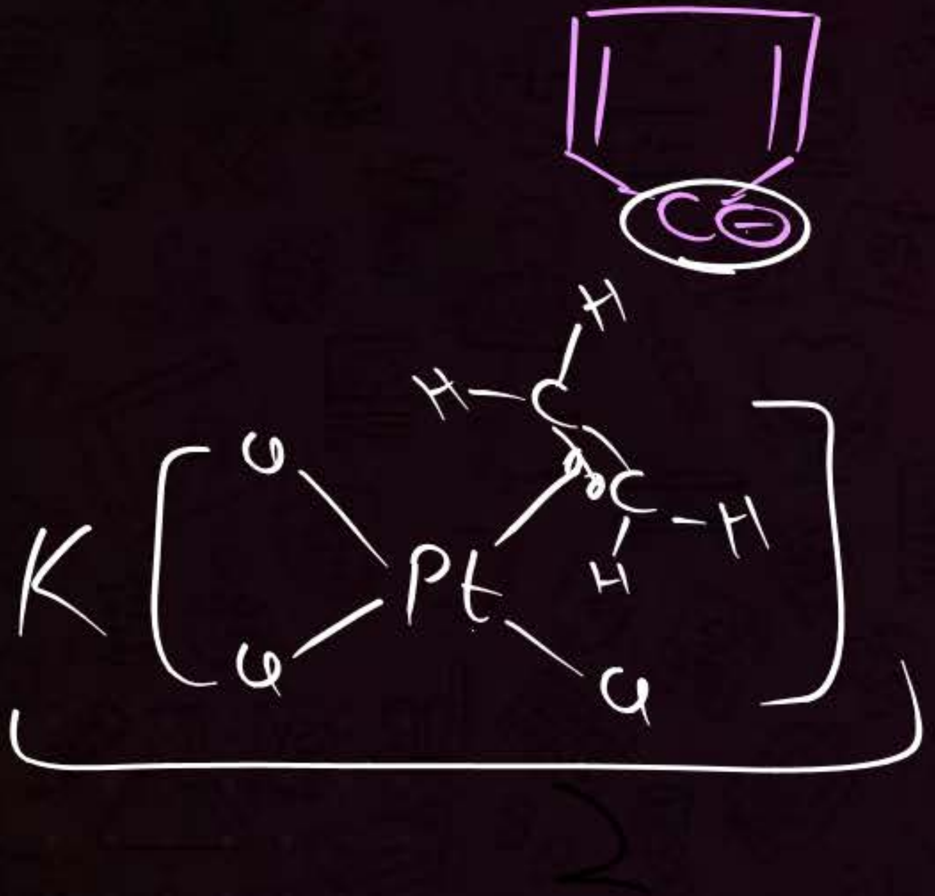
M — C → Polar

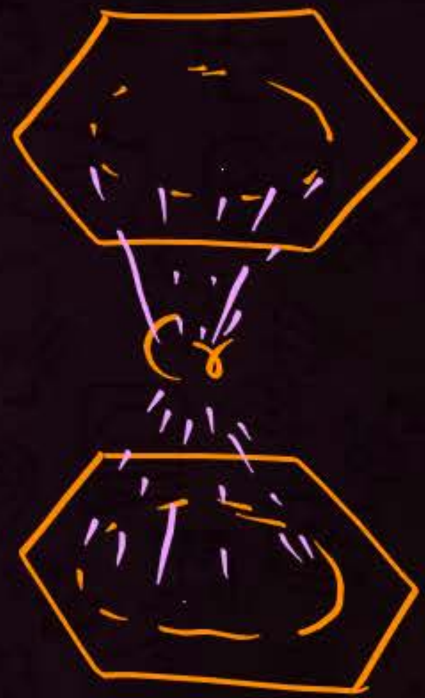
O.M.C.

- σ-Bonded
  - Ex: R–MgX
  - R_2Zn
- π-Bonded
  - $K[PtCl_3(C_2H_4)]$ (Zeise's salt)
  - $[Cr(C_6H_6)_2]$ Dibenzene chromium
  - $[Fe(C_5H_5)_2]$ Ferrocene
- σ & π-Bonded
  - $[Ni(CO)_4]$
  - $[Fe(CO)_5]$
  - etc...

$[Fe(\pi\text{-}C_5H_5)_2]$

$[Cr(C_6H_6)_2]$





Break

WERNER'S THEORY

Acc. to Werner C.M.A. in a complex has 2 types of valencies.

1. Primary Valence
2. Secondary Valence

$[\overset{+3}{Co}(NH_3)_6]\overset{-}{Cl_3}$

P.V.

Primary Valency	Secondary Valency
(1) It is ionizable	(1) It is non ionizable.
(2) It is satisfied by -ve ions	(2) It can be satisfied by -ve ions as well as neutral species
(3) Equal to oxidation No.	(3) Equal to Coordination No.
(4) It is Non Directional in nature	(4) It is directional in Nature.
(5) Not responsible for geometry of the complex.	(5) It is responsible for geometry of the complex.
(6) Represented by "--------"	(6) Represented by "———"

*Note :→ According to Werner :

Metal	S.V.
Co^{+3}	6
Cr^{+3}	6
Fe^{+2}/Fe^{+3}	6
Sc^{+3}	6
Ti^{+3}	6
Mn^{+3}	6
Rh^{+3}	6
Ir^{+3}	6
Ni^{+2}/Ni^{+4}	6
Pt^{+4}	6
Pt^{+2}	4
Pd^{+2}	4
Cd^{+2}	4
Hg^{+2}	4
Cu^{+1}	4
Ag^{+1}	2
Au^{+3}	4

Table 5.1: Formulation of Cobalt(III) Chloride-Ammonia Complexes

Colour	Formula	Solution conductivity corresponds to	Moles of AgCl
Yellow	$[Co(NH_3)_6]^{3+}3Cl^-$	1:3 electrolyte	3 mol
Purple	$[CoCl(NH_3)_5]^{2+}2Cl^-$	1:2 electrolyte	2 mol
Green	$[CoCl_2(NH_3)_4]^{+}Cl^-$	1:1 electrolyte	1 mol
Violet	$[CoCl_2(NH_3)_4]^{+}Cl^-$	1:1 electrolyte	1 mol

$[Co(NH_3)_6]Cl_3$

$$CoCl_3 \cdot 6NH_3 \Rightarrow [Co(NH_3)_6]Cl_3 + AgNO_3 \longrightarrow 3\ AgCl$$

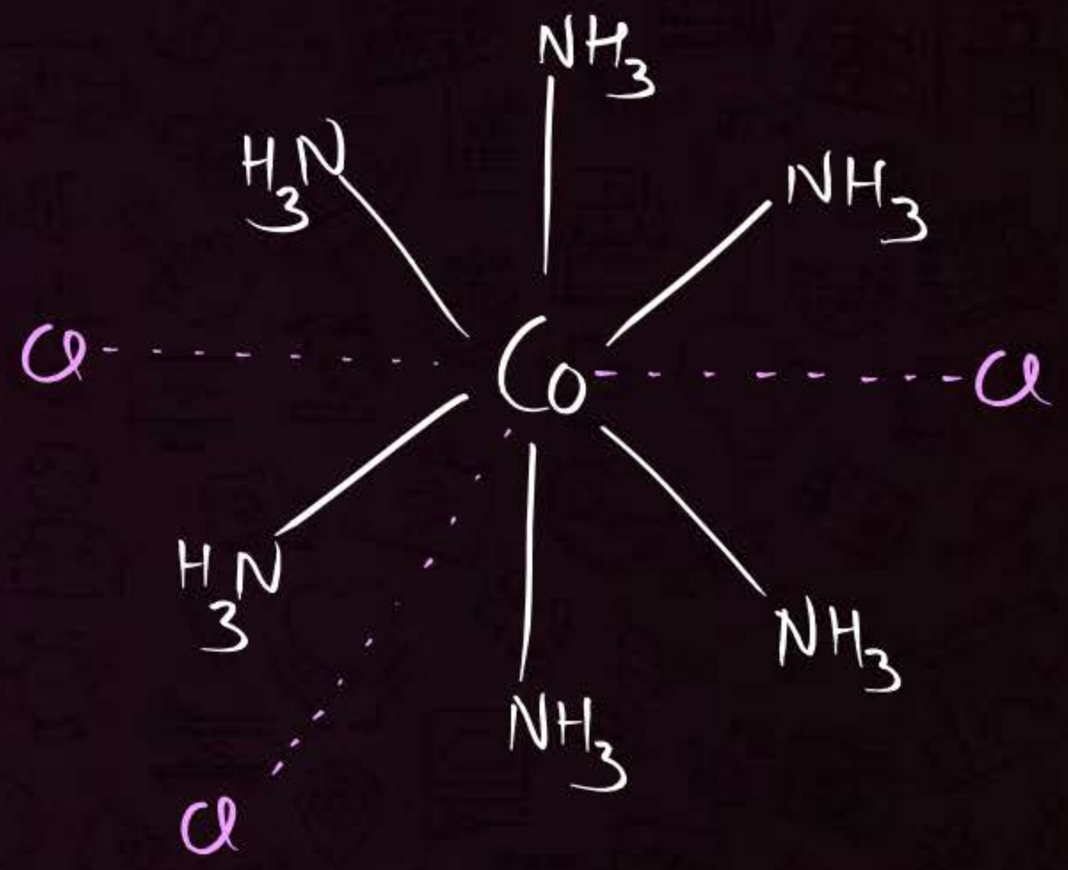
$$1AgNO_3 + 1Cl^- \longrightarrow 1\ AgCl$$

White ppt.

$\overset{+3}{Co}Cl_3 \cdot 6NH_3 \Rightarrow [Co(NH_3)_6]Cl_3$

$P.V. = +3$

$S.V. = 6$

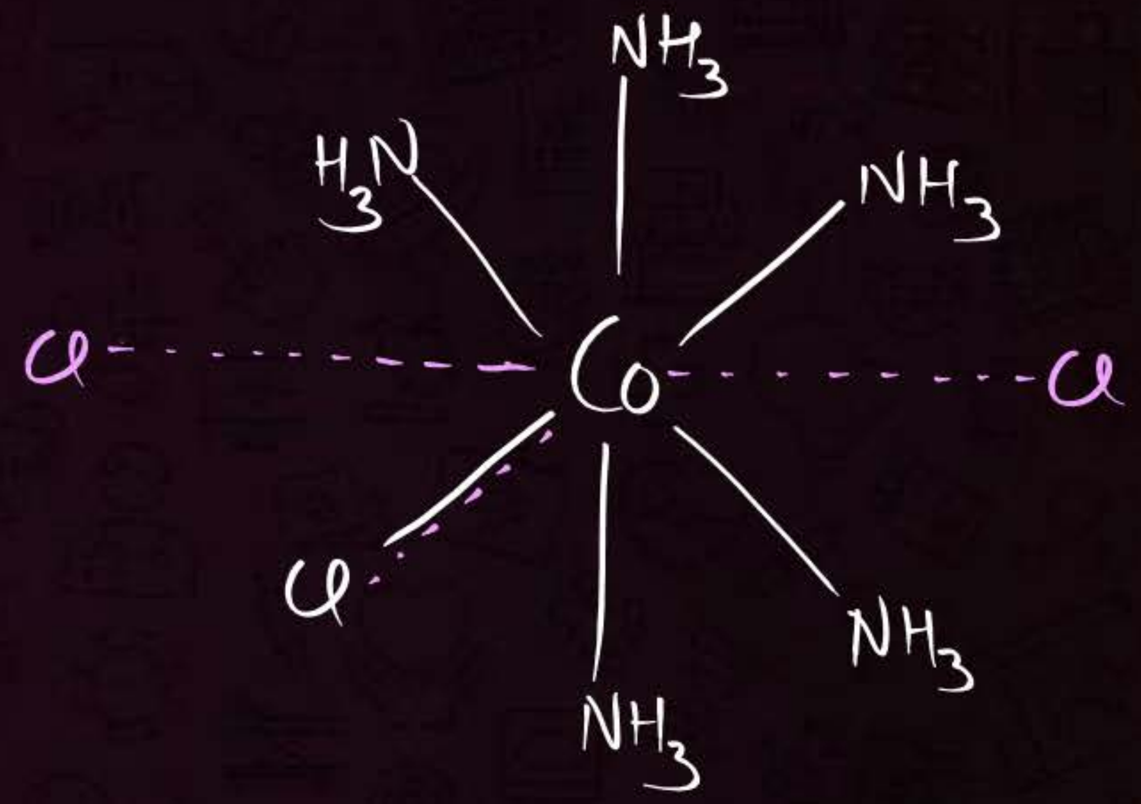


$CoCl_3 \cdot 5NH_3 \Rightarrow [Co(NH_3)_5Cl]Cl_2$

P.V. = 3

S.V. = 6

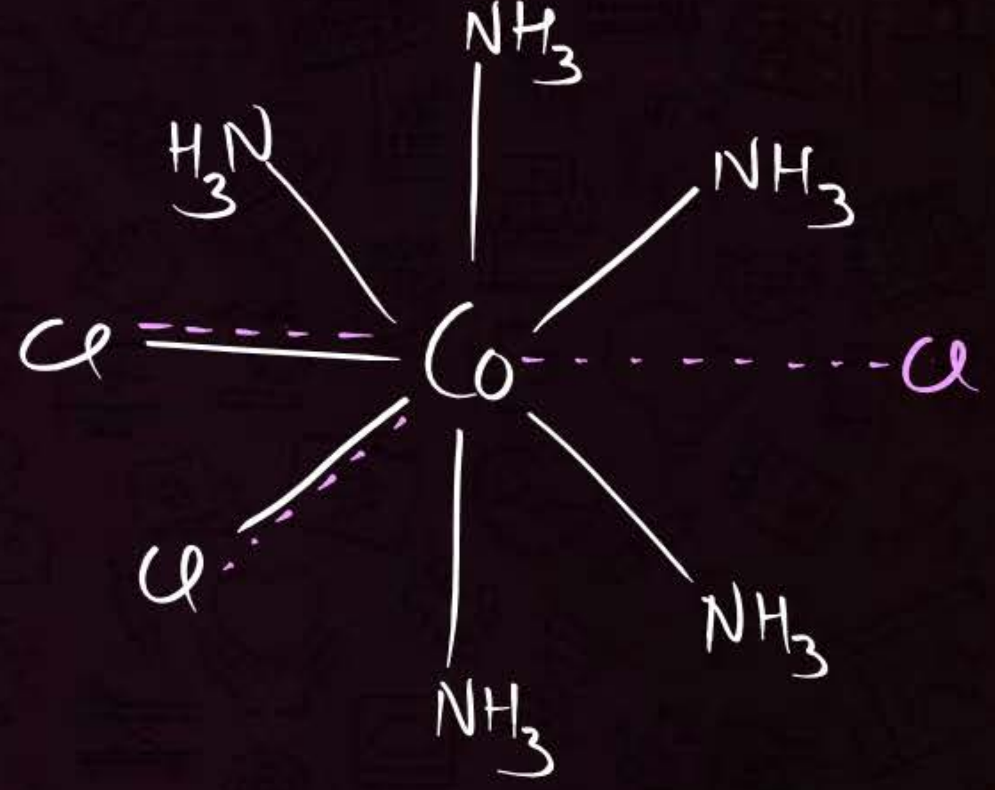
P.V. as well as S.V. = 1



$CoCl_3 \cdot 4NH_3 \Rightarrow [Co(NH_3)_4Cl_2]Cl$

P.V. = 3
S.V. = 6

P.V. as well as S.V. = 2



2

$CoCl_3 \cdot 3NH_3 \Rightarrow [Co(NH_3)_3(Cl)_3]$

P.V. = 3

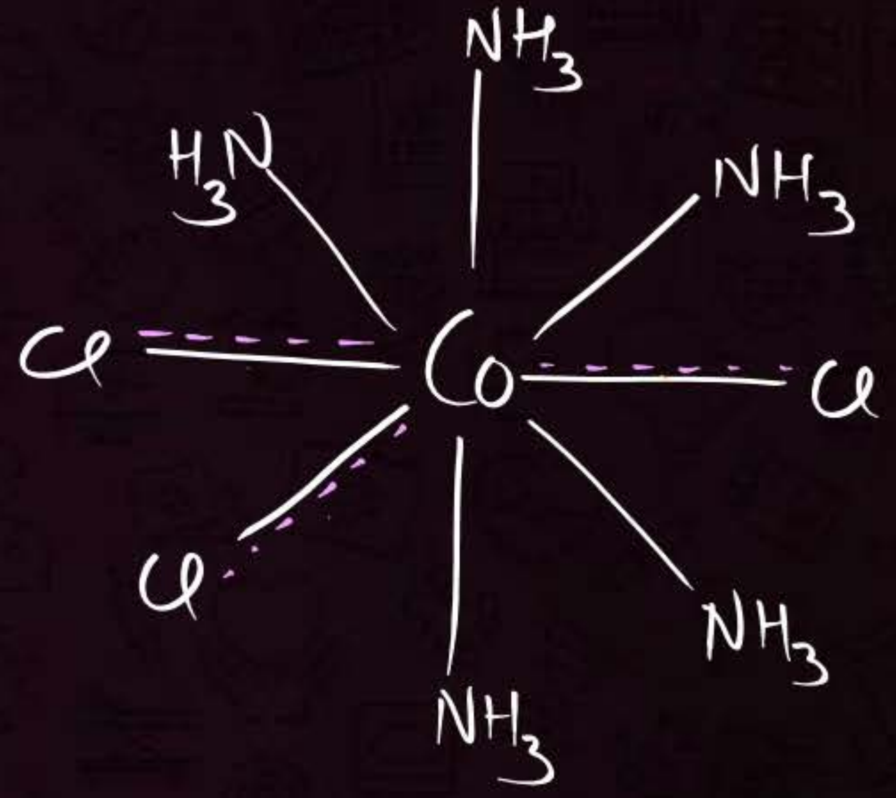
S.V. = 6

P.V. as well as S.V. = 3

$AgNO_3$ (excess)

~~AgCl?~~

No ppt



Example 5.1

On the basis of the following observations made with aqueous solutions, assign secondary valences to metals in the following compounds:

Formula	Moles of AgCl precipitated per mole of the compounds with excess $AgNO_3$
(i) $PdCl_2.4NH_3$	2
(ii) $NiCl_2.6H_2O$	2
(iii) $PtCl_4.2HCl$	0
(iv) $CoCl_3.4NH_3$	1
(v) $PtCl_2.2NH_3$	0

Solution

(i) Secondary 4 (ii) Secondary 6

(iii) Secondary 6 (iv) Secondary 6 (v) Secondary 4

QUESTION- (NEET 2017 DELHI)

The correct order of the stoichiomerics of AgCl formed when $AgNO_3$ in excess is treated with the complexes: $CoCl_3.6NH_3$+ $CoCl_3.5NH_3$ $CoCl_3.4NH_3$ respectively is:

$[Co(NH_3)_6]Cl_3$ $[Co(NH_3)_5Cl]Cl_2$ $[Co(NH_3)_4(Cl)_2]Cl$

(A) 2AgCl, 3AgCl, 1AgCl

(B) 1AgCl, 3AgCl, 2AgCl

(C) 3AgCl, 1AgCl, 2AgCl

(D) 3AgCl , 2AgCl, 1AgCl

QUESTION- (NEET 2015)

Cobalt(III) chloride forms several octahedral complexes with ammonia. which of the following will not give test for chloride ions with silver nitrate at 25°C?

(A) $CoCl_3.4NH_3$

(B) $CoCl_3.5NH_3$

(C) $CoCl_3.6NH_3$

(D) $CoCl_3.3NH_3$ $[Co(NH_3)_3Cl_3]$

QUESTION- (NEET 2001)

Which of the following will exhibit maximum ionic conductivity?

No. of ions ↑

(A) $K_4[Fe(CN)_6]$ ⇒ 5

(B) $[CoNH_3)_4]Cl_3$ ⇒ 4

(C) $[Cu(NH_3)_4]SO_4$ ⇒ 2

(D) $[Ni(CO)_4]^0$ ⇒ Nonelectrolytic soln

0 ions

VALENCE BOND THEORY

C.N.	Hybridization	Geometry
2	sp	linear
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral
	dsp^2 ($d_{x^2-y^2}$)	sq. planar
5	sp^3d (d_{z^2})	Trigonal Bipyramidal
	dsp^3 ($d_{x^2-y^2}$)	sq. pyramidal

6 → sp^3d^2 / d^2sp^3 → octahedral

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

Q. $K_4[Fe(CN)_6]$

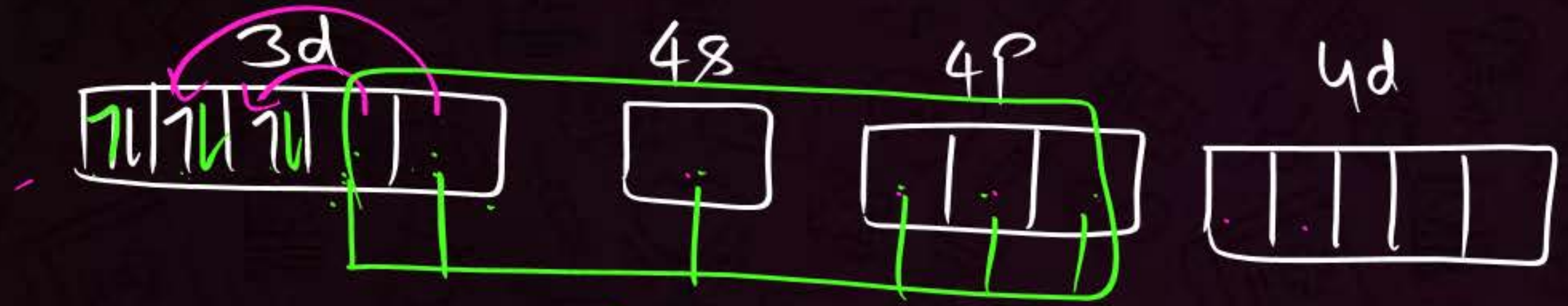
$\leftarrow :CN$

fufaji

(C, N.) S.F.L. → pairing

(X, O, S...) W.F.L. → No pairing

$Fe^{+2} \rightarrow [Ar]\, 4s^0\, 3d^6$



d^2sp^3, octahedral

Diamagnetic

inner orbital complex.

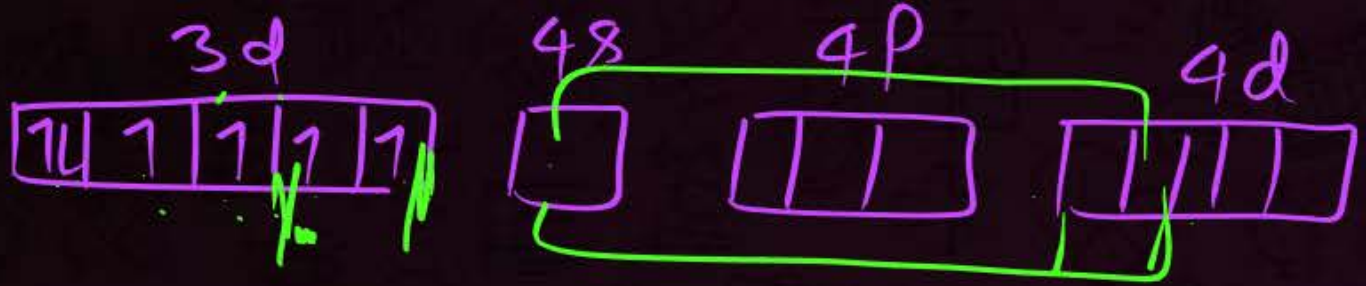
low spin complex

Q. $K_4[FeF_6]$

$F^{\ominus} \longrightarrow$ (W.F.L.)

$Fe^{+2} \rightarrow [Ar]\,4s^0 3d^6$

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



sp^3d^2, octahedral

para, $\mu = 4.89$ B.M

outer orbital complex

high spin complex

QUESTION- (NEET 2001)

Match the coordination number and type of hybridisation with distribution of hybrid orbitals in space based on Valence bond theory.

Select the correct option:

(A) A-iii, B-iv, C-i, D-ii

(B) A-iv, B-i, C-ii, D-iii

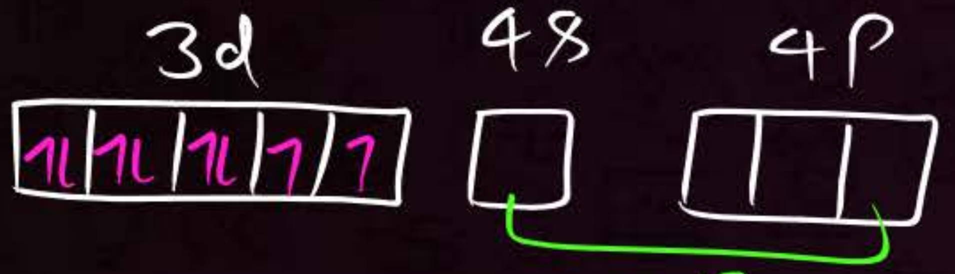
(C) A-iii, B-i, C-iv, D-ii

(D) A-ii, B-iii, C-iv, D-i

Coordination number and type of hybridization		Distribution of hydrid orbitals in space	
A.	4, sp^3	i.	Trigonal bipyramidal
B.	4, dsp^2	ii.	Octahedral
C.	5, sp^3d	iii.	Tetrahedral
D.	6, d^2sp^3	iv.	Square planar

$[NiCl_4]^{-2}$ $Cl^- \rightarrow$ WFL

$Ni^{+2} \rightarrow [Ar]\,4s^0\,3d^8$



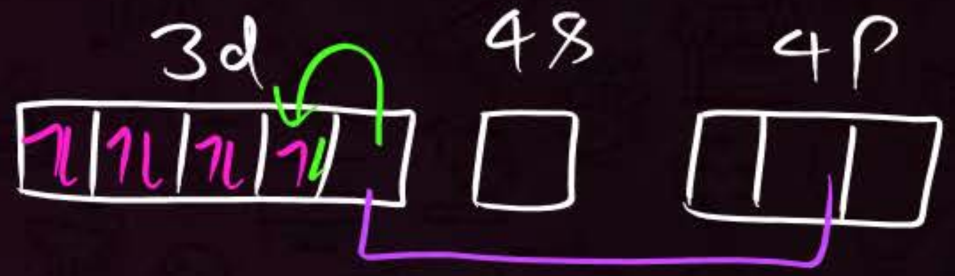
sp^3

Tetrahedral

para. (2.8 BM)

$[Ni(CN)_4]^{-2}$ $CN^{\ominus} \rightarrow$ SFL

$Ni^{+2} \rightarrow [Ar]\,4s^0\,3d^8$

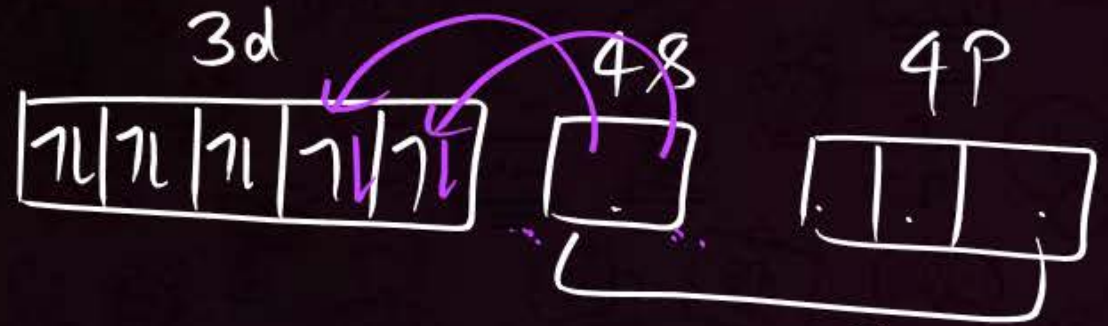


dsp^2, sq. planar

Dia.

$[Ni(CO)_4]$ $CO \rightarrow$

$Ni^0 \rightarrow [Ar]\, 4s^2 3d^8$



sp^3, Tetrahedral

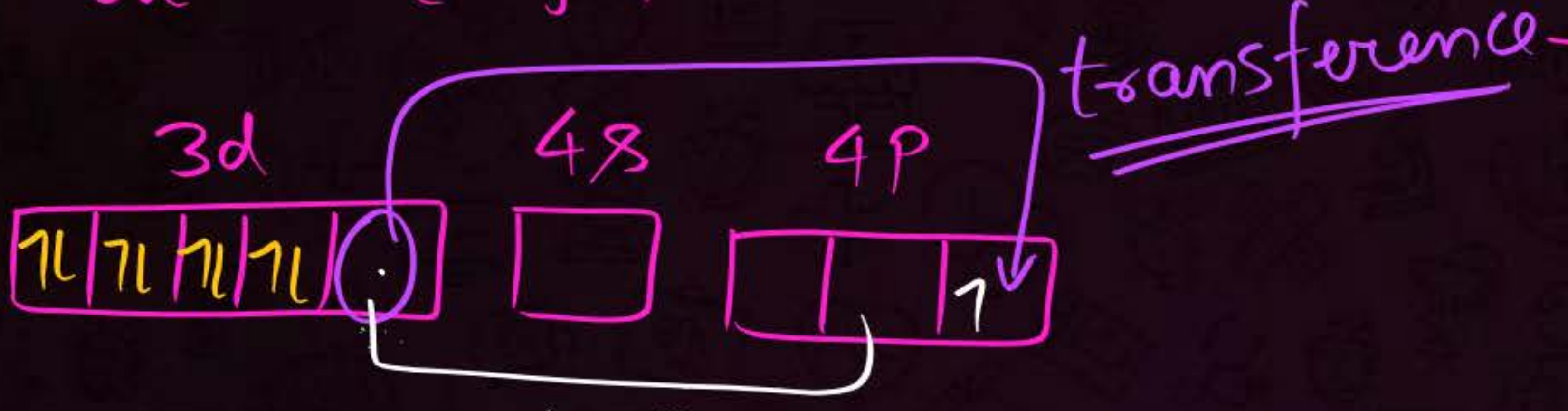
Diamagnetic

Low spin.

* Imp * $[Cu(NH_3)_4]SO_4$

$\ddot{N}H_3$ (SFL)

$Cu^{+2} \rightarrow [Ar]\, 4s^0 3d^9$

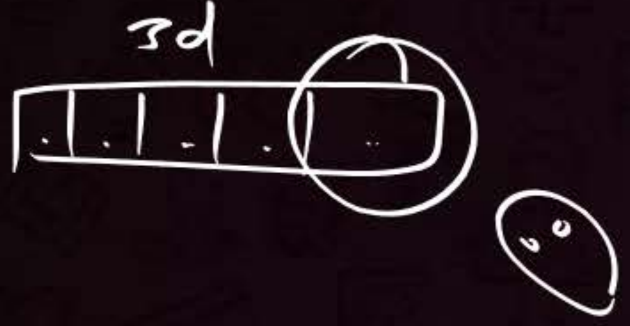


dsp^2 sq. planar

$C.N. = 4 + d^9 + SFL$

$C.N. = 6 + d^7 + SFL$

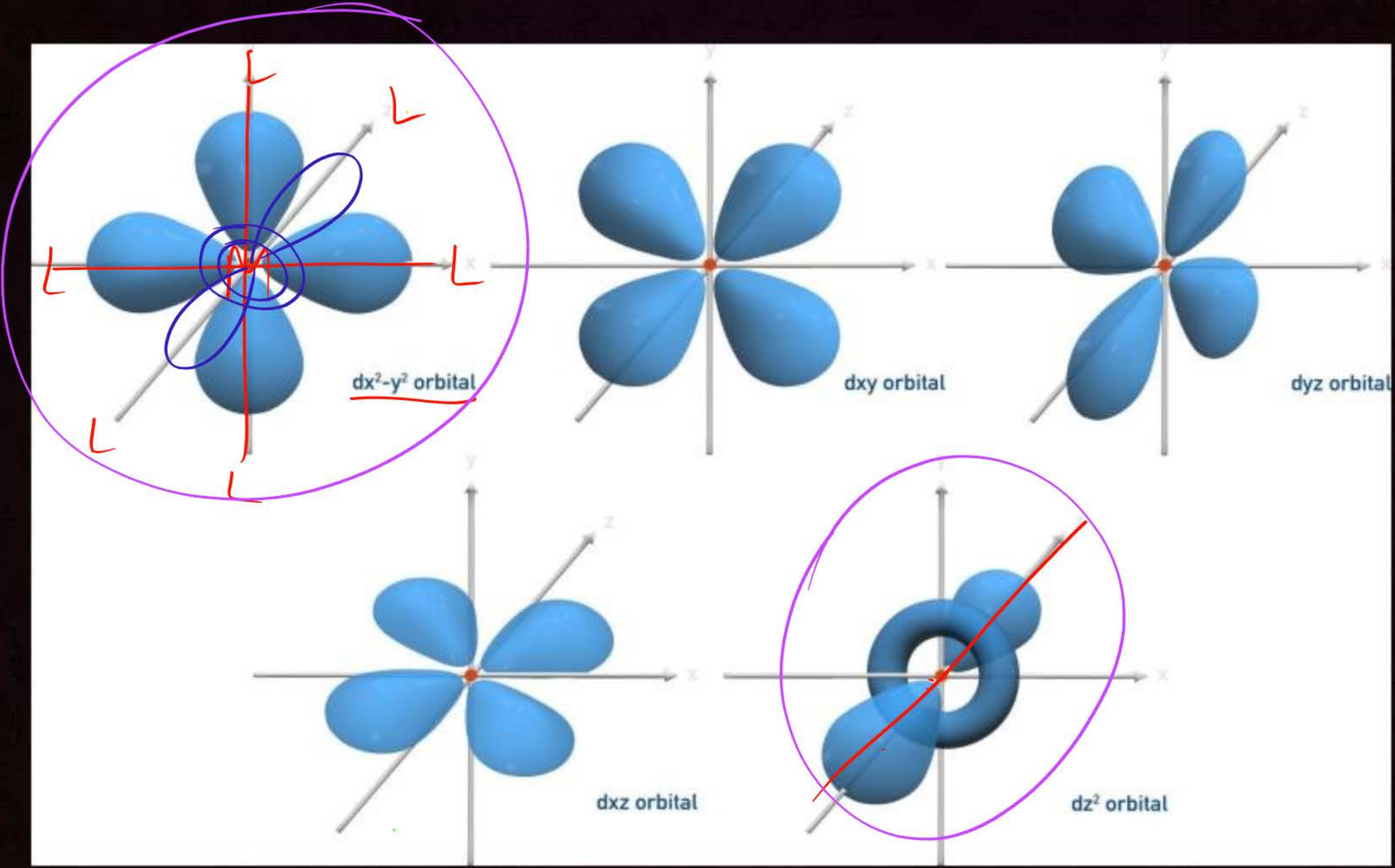
CRYSTAL FIELD THEORY



C.M.A ⇒ +ve point charge

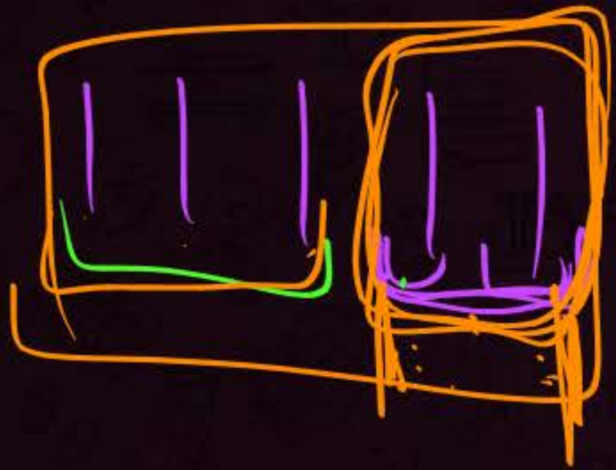
Ligands ⇒ −ve point charge
or
point dipoles

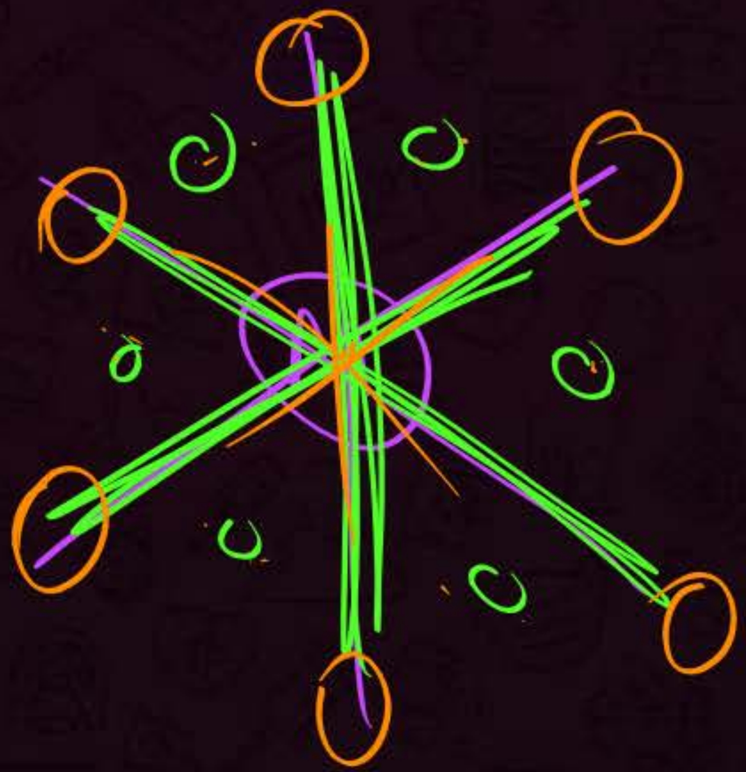
while ligand approach towards metal the d-orbitals of Metal gets repelled by lp (field) & the degeneracy of d-orbitals gets lifted | disturbed

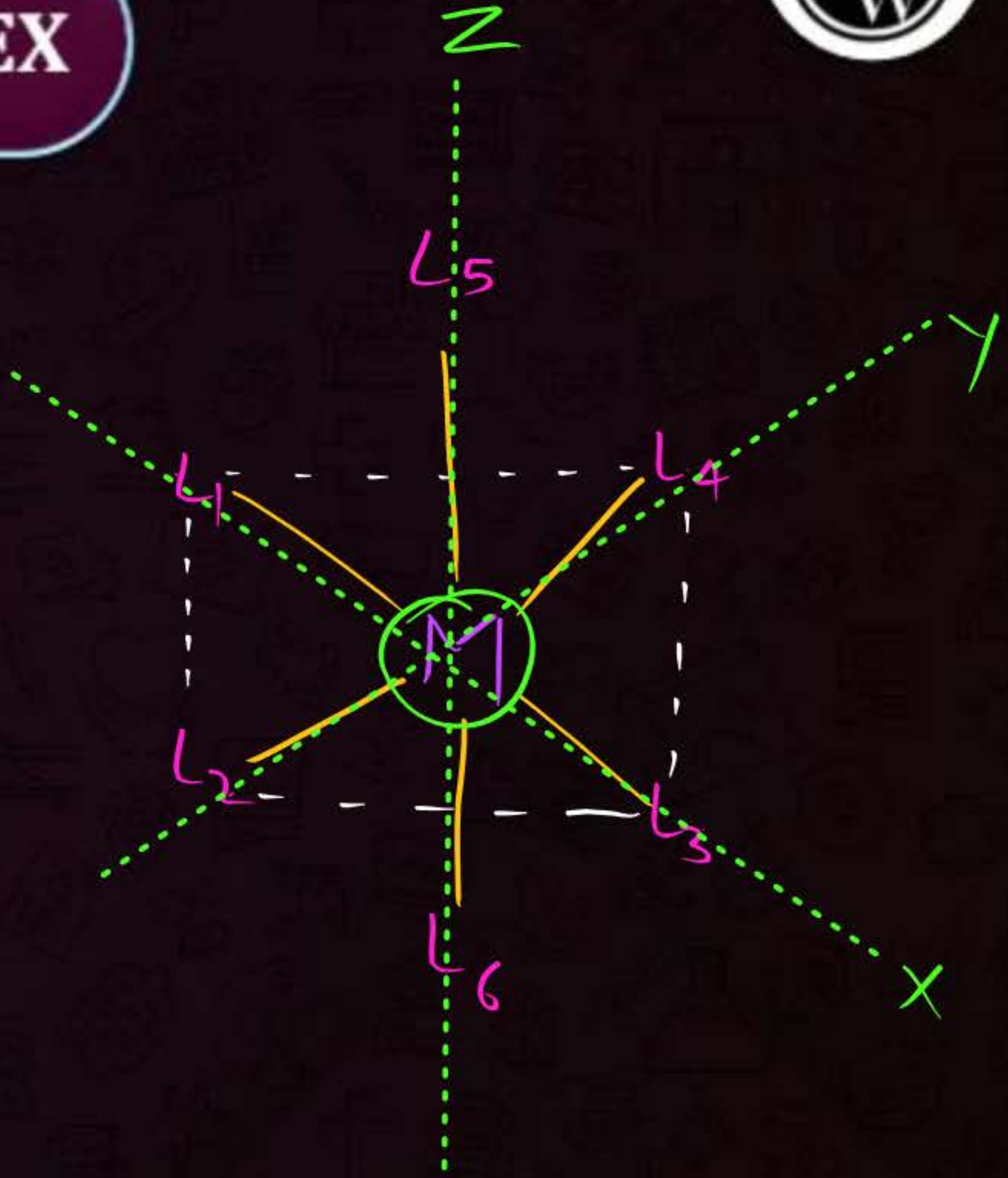

dx²-y² orbital
dxy orbital
dyz orbital
dxz orbital
dz² orbital

SPLITTING IN OCTAHEDERAL COMPLEX

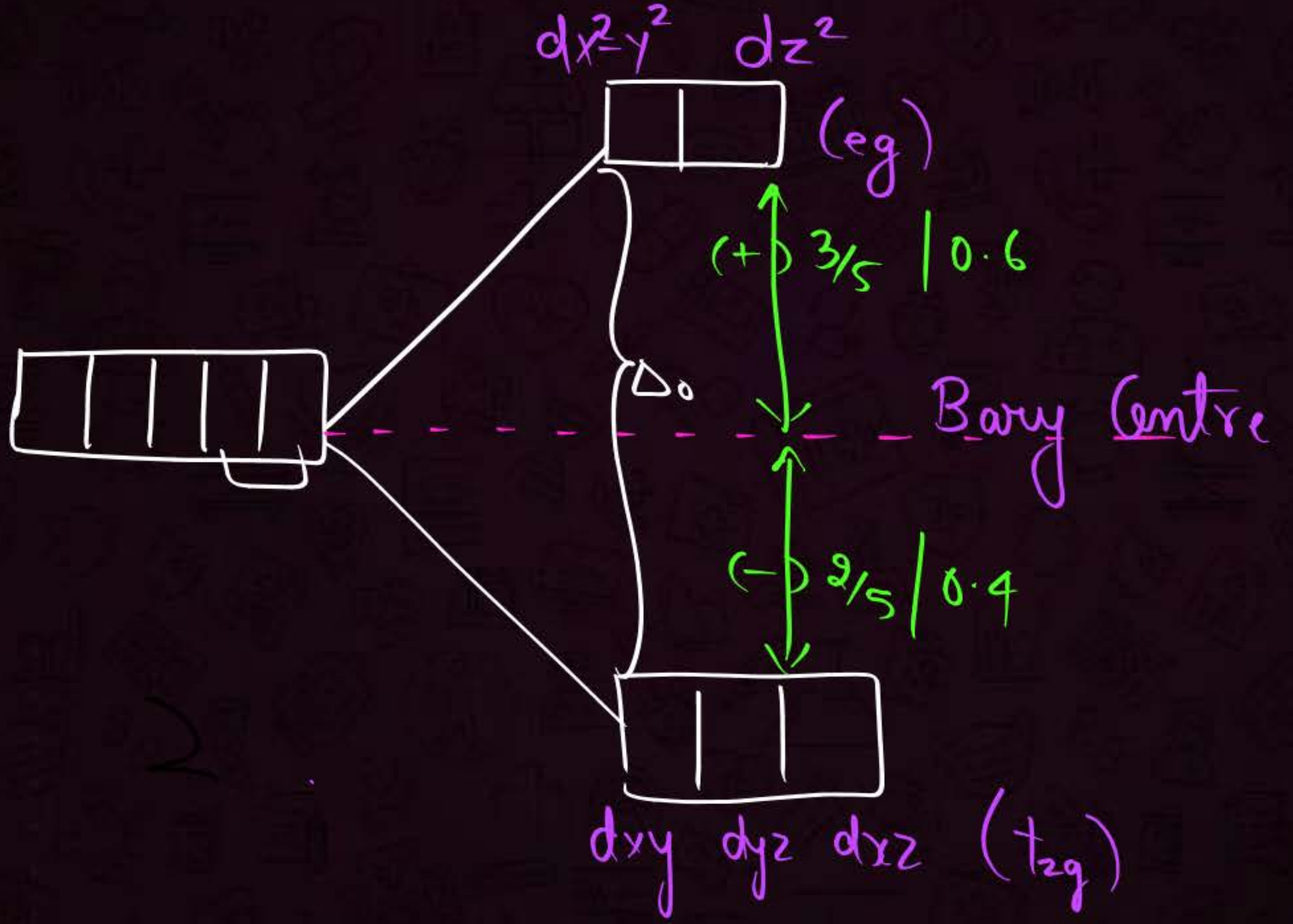
In octahedral geometry ligands approach towards the metal along the axis.

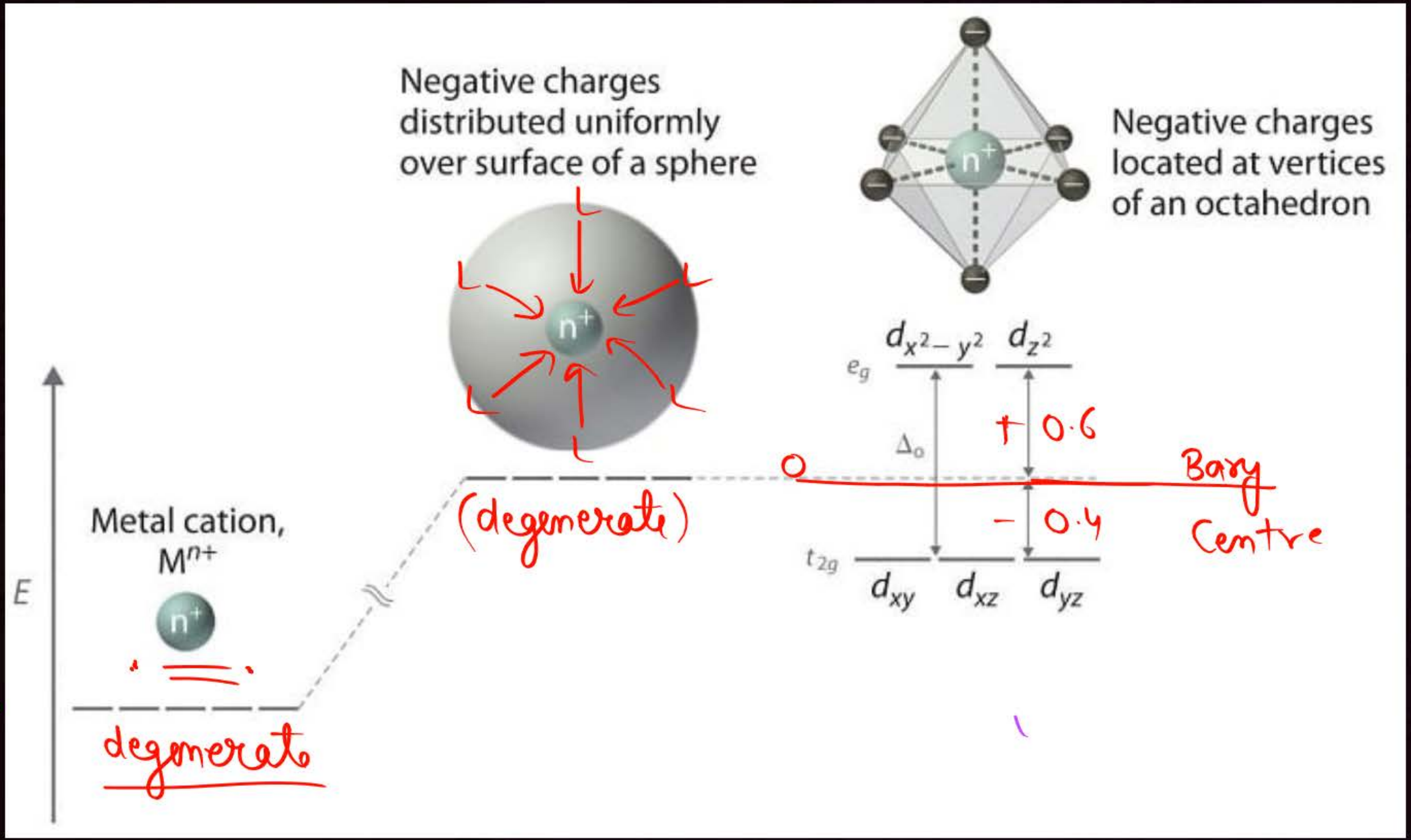






$\Delta_o \rightarrow$ Crystal field splitting energy gap for Octahedral Complex





$$\Delta_o = 0.6 \times n_{eg} - 0.4 \times n_{t_{2g}}$$

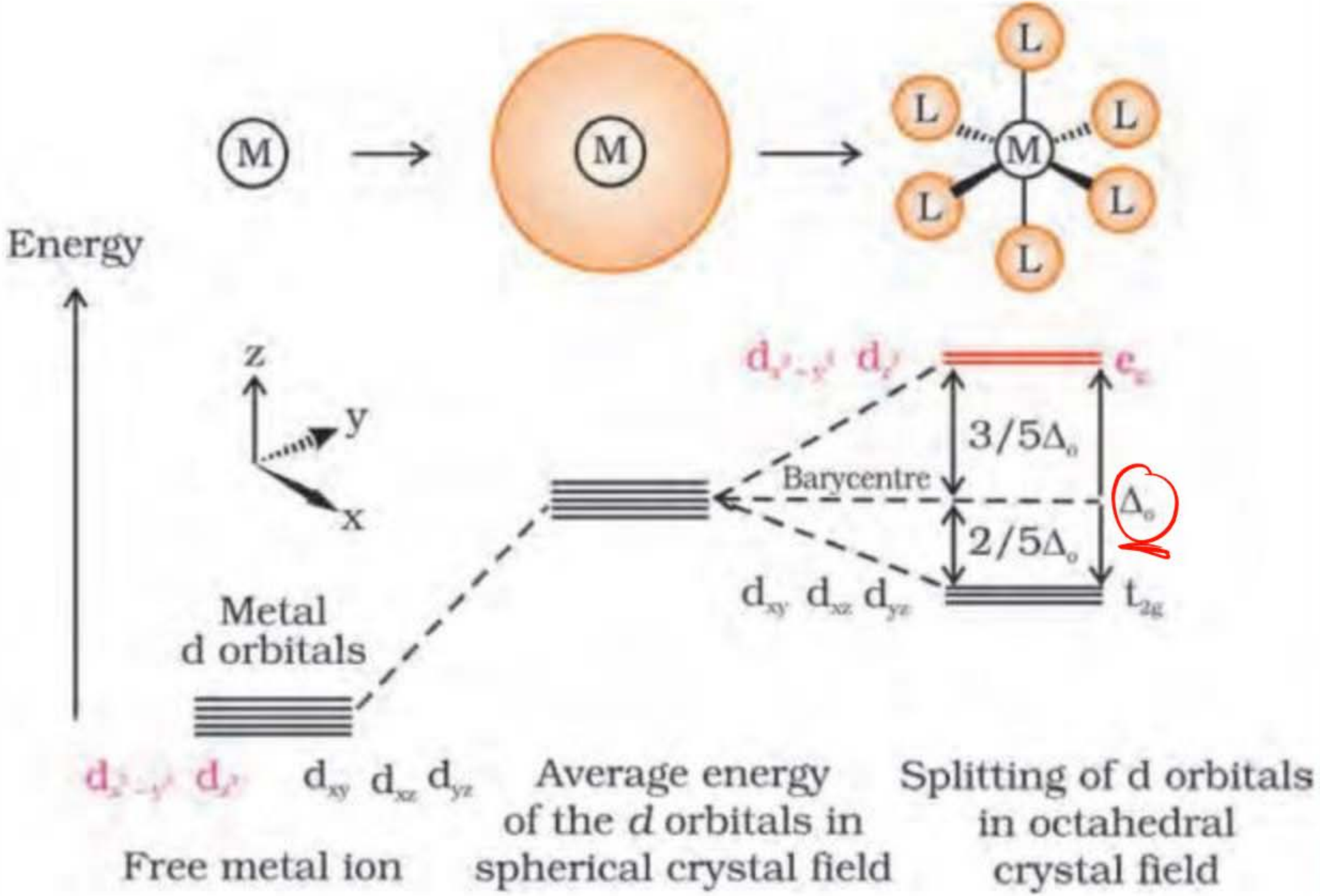


Fig.5.8: *d orbital splitting in an octahedral crystal field*

* Spectrochemical Series *

In general, ligands can be arranged in a series in the order of increasing field strength as given below:

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$$

$$I^- < Br^- < SCN^- < Cl^- < S^{-2} < F^- < OH^- < ox^{-2} < H_2O < NCS^- < EDTA^{-4} <$$

$$NH_3 < Py < en < Dipy < NO_2^- < CN^- < CO$$

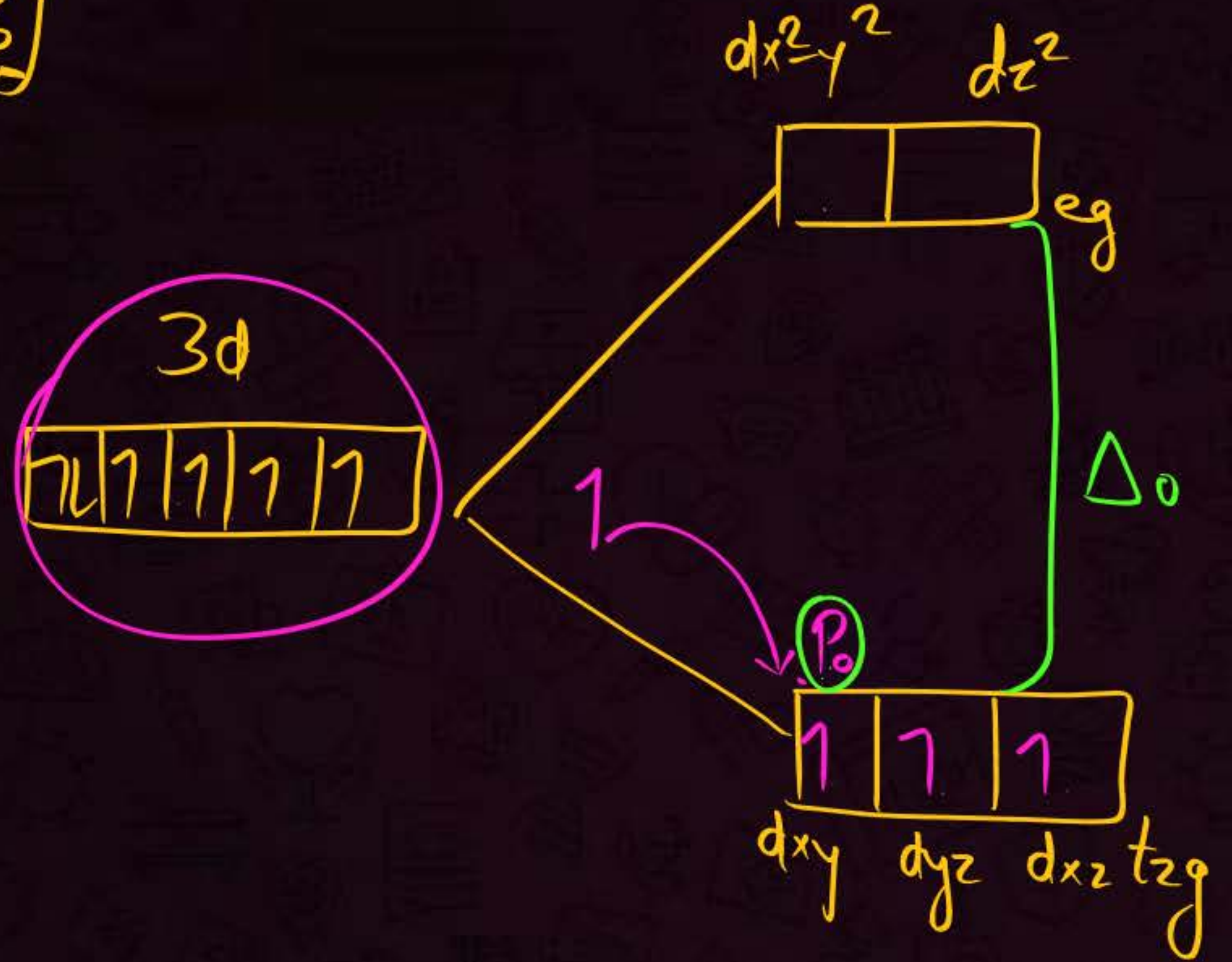
Spectrochemical Series

I^-	Br^-	SCN^-	Cl^-	S^{-2}	F^-	OH^-	ox^{-2}	H_2O	NCS^-	$EDTA^{-4}$
आई	बाहर	सानिया	कल	से	फिर	ओह	ox	पानी में	नाचो	इतना

NH_3	Py	en	Dipy	NO_2	CN^-	CO	
अम्मा	प्यारी	इन	दो पैसे से	नाइट में	सुनने	को	(आई)

$K_4[Fe(CN)_6]$

$Fe^{+2} \Rightarrow 3d^6$



SFL → { $\Delta_o > P_o \Rightarrow$ pairing

WFL → { $\Delta_o < P_o \Rightarrow$ No pairing

$P_o \rightarrow$ Pairing Energy

d^1, d^2, d^3

SFL ($\Delta_o > P_o$)

WFL ($\Delta_o < P_o$)

↑↓	↑

↑↓	↑

↑

↑↓	↑↓	↑↓

↑↓	↑↓	↑↓

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

$d^6 \rightarrow$ WFL $\rightarrow t_{2g}^4 e_g^2$

d^8

C.N. = 6 (Hitrick)

$d^1, d^2, d^3 \longrightarrow d^2sp^3$, para.

$[\overset{+3}{Cr}(H_2O)_6]Cl_3 \Rightarrow 3d^3$, d^2sp^3, 3 unpaired e^-, para.

$[\overset{+3}{Cr}(CN)_6]^{-3} \Rightarrow 3d^3$, d^2sp^3, 3 unpaired e^-, para.

$[\overset{+3}{Ti}(H_2O)_6]Cl_3 \Rightarrow 3d^1$, d^2sp^3, 1 unpaired, para.

C.N. = 6

d^{4-7}

S.F.L. → d^2sp^3 (low spin)

W.F.L. → sp^3d^2 (high spin)

$d^{8-10} \Rightarrow sp^3d^2$, d^8, d^9 (para.)

d^{10} → (Dia.)

$K_4[\overset{+2}{Fe}(CN)_6] \rightarrow d^6$, SFL, d^2sp^3, Dia.

$K_3[\overset{+3}{Fe}(CN)_6] \rightarrow d^5$, SFL, d^2sp^3, para

$K_3[\overset{+3}{Fe}F_6] \rightarrow d^5$, WFL, sp^3d^2, para.

$[\overset{+2}{Ni}(H_2O)_6]Cl_2 \rightarrow d^8$, sp^3d^2, para.

$[\overset{+2}{Zn}(NH_3)_6]SO_4 \rightarrow d^{10}$ sp^3d^2, Dia.

QUESTION- (NEET 2020)

Which of the following is the correct order of increasing i field srength of ligands to form coordination compounds?

(A) $SCN^- < F^- < CN^- < C_2O_4^{3-}$

(B) $F^- < SCN^- < C_2O_4^{3-} < CN^-$

(C) $CN^- < C_2O_4^{3-} < SCN^- < F^-$

(D) $SCN^- < F^- < C_2O_4^{3-} < CN^-$

QUESTION- (NEET 2020)

What is the correct electronic configuration of atom in $K_4[Fe(CN)_6]$ based on crystal field theory?

(A) $t^4_{2g}e^2_g$

(B) $t^6_{2g}e^0_g$

(C) $e^3t^3_2$

(D) $e^4t^2_2$

QUESTION- (NEET 2020)

The geometry and magnetic behavior of the complex $[Ni(CO)_4]$ are?

(A) Square planar geometry and diamagnetic

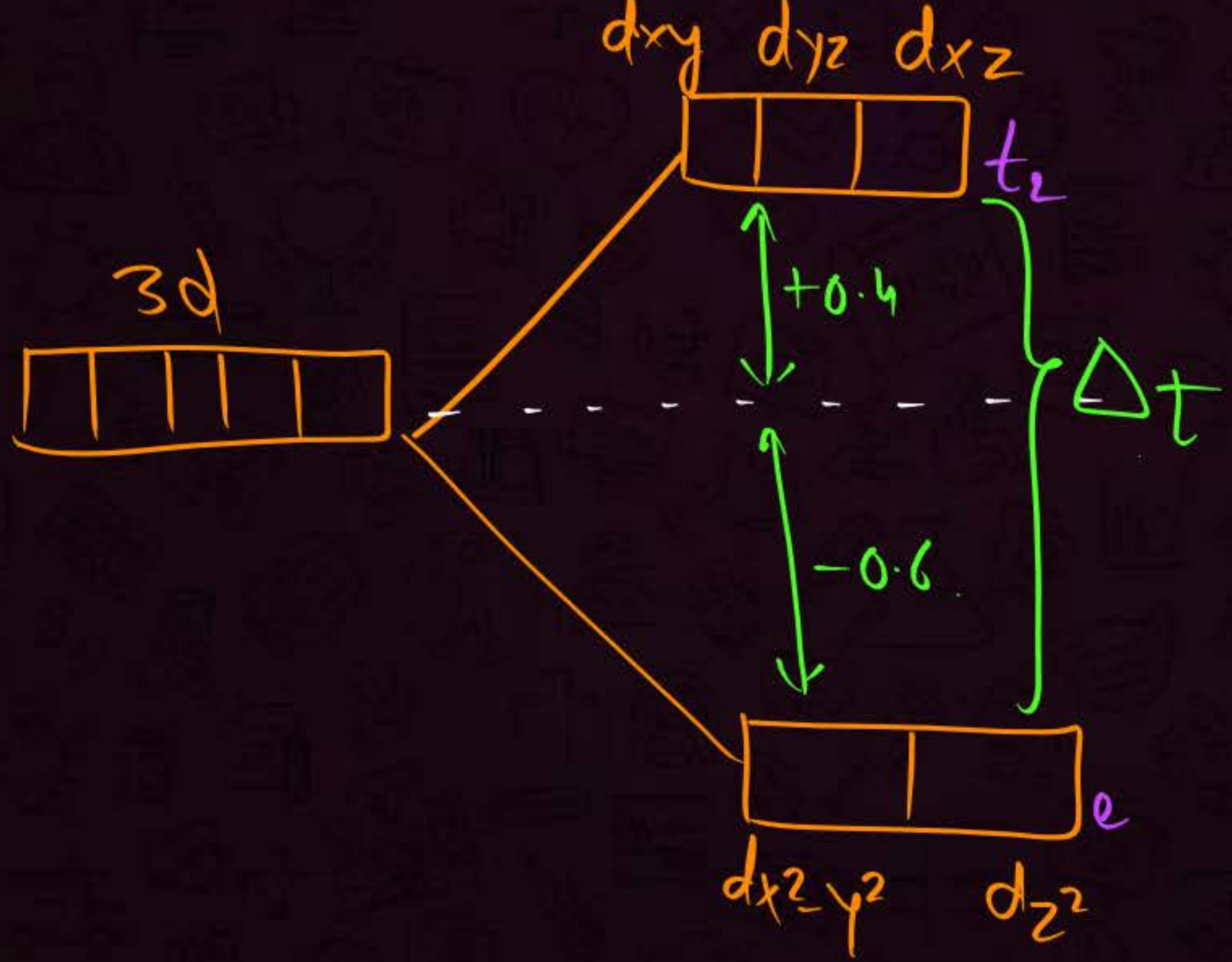
(B) Tetrahedral geometry and diamagnetic

(C) Tetrahedral geometry and paramagnetic

(D) Square planar geometry and paramagnetic

SPLITTING IN TETRAHEDERAL COMPLEX

In tetrahedral complex ligands approach b/w the axis.



$$\Delta_t = 0.4(n_{t_2}) - 0.6(n_e)$$

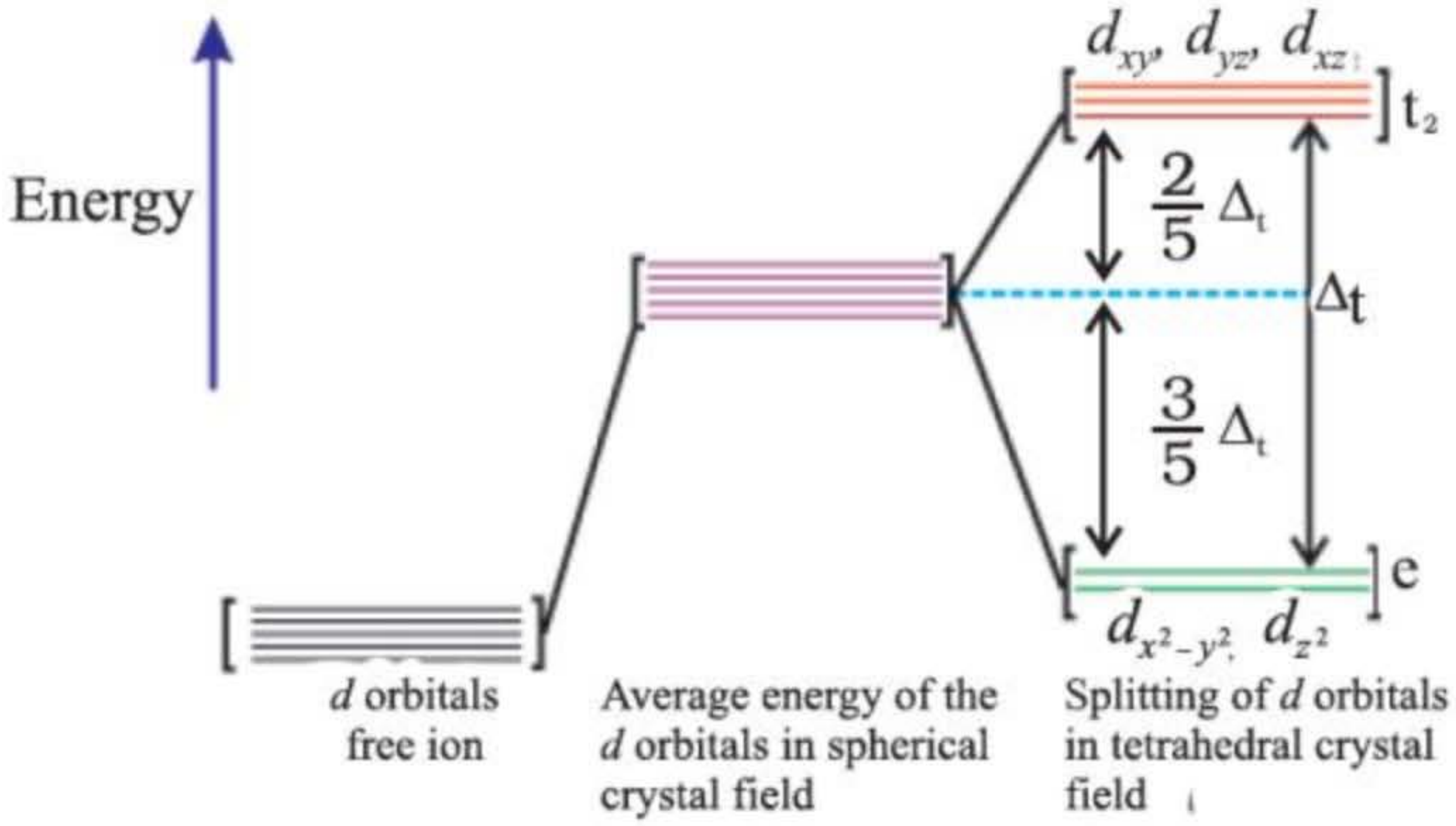
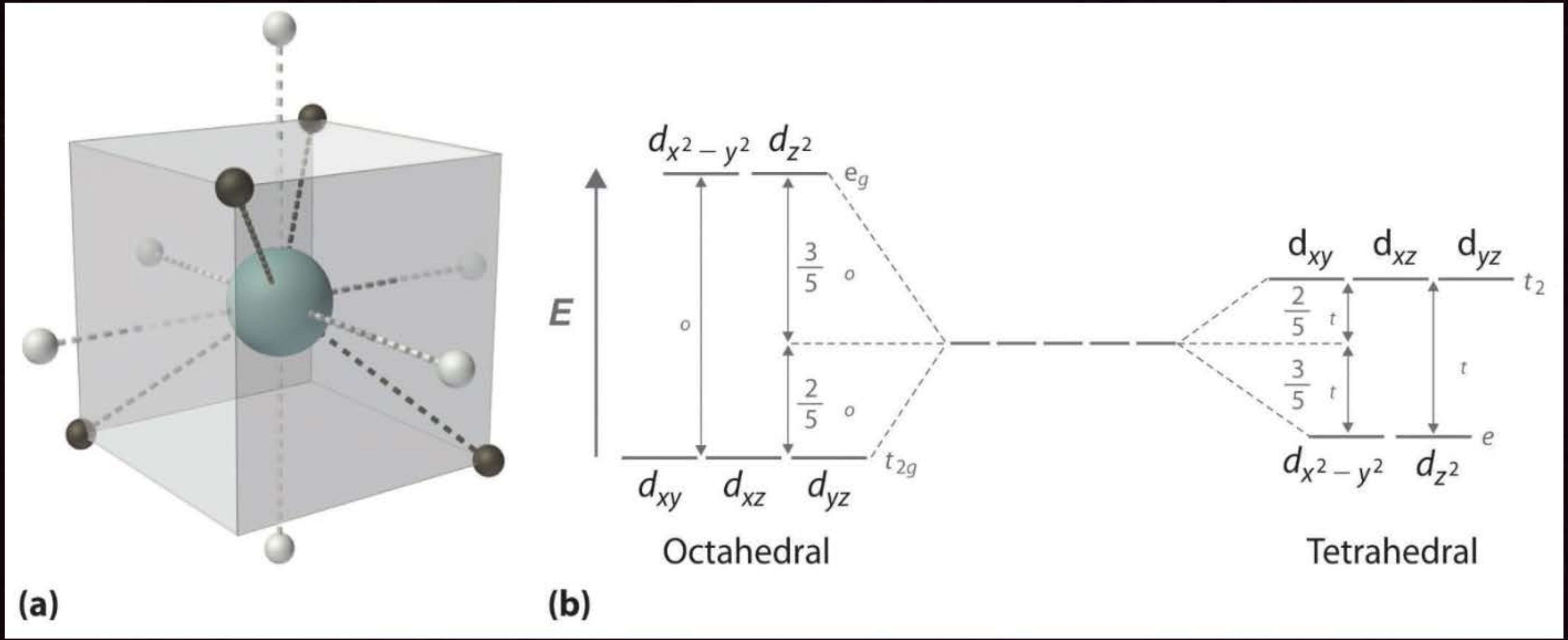
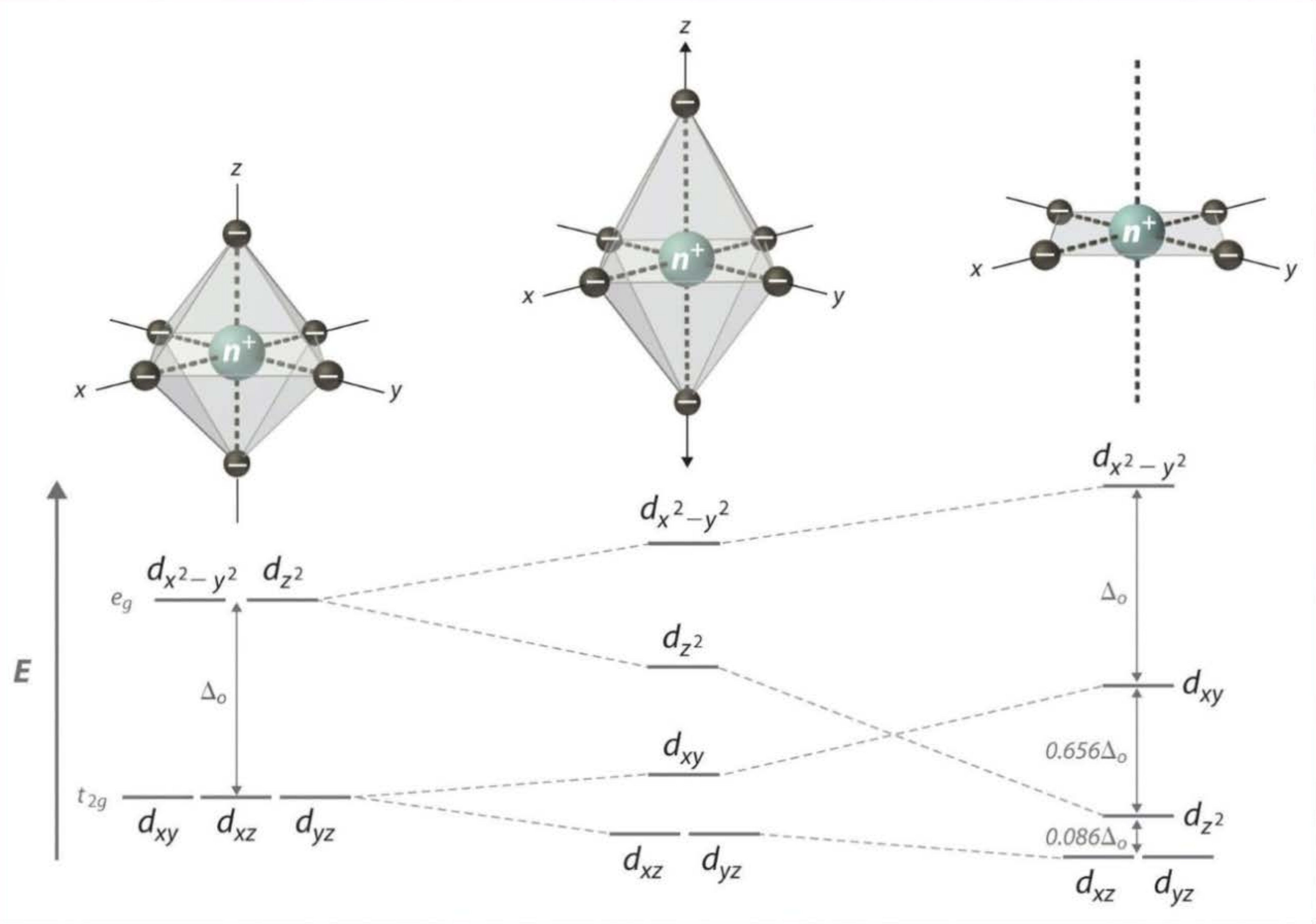


Fig.5.9: d orbital splitting in a tetrahedral crystal field.



(a)
(b)
E
$d_{x^2-y^2}$ d_{z^2}
e_g
$\frac{3}{5}$ o
o
$\frac{2}{5}$ o
t_{2g}
d_{xy} d_{xz} d_{yz}
Octahedral
d_{xy} d_{xz} d_{yz}
t_2
$\frac{2}{5}$ t
$\frac{3}{5}$ t
t
e
$d_{x^2-y^2}$ d_{z^2}
Tetrahedral



z
x
y
n+
E
e_g
$d_{x^2-y^2}$
d_{z^2}
Δ_o
t_{2g}
d_{xy}
d_{xz}
d_{yz}
$d_{x^2-y^2}$
d_{z^2}
d_{xy}
d_{xz}
d_{yz}
$d_{x^2-y^2}$
Δ_o
d_{xy}
$0.656\Delta_o$
d_{z^2}
$0.086\Delta_o$
d_{xz}
d_{yz}

* Stability of Complex :→

Crystal field Stablization Energy = $\Delta_o + n P_o$ → n = no. of pairs

(C.F.S.E)

d^5

SFL

$K_3[\overset{+3}{Fe}(CN)_6] \Rightarrow [(0.6\times 0)-(0.4\times 5)]\Delta_o + 2P_o$

$= -2\Delta_o + 2P_o$

↑↓	↑↓	↑

QUESTION- (NEET 2010)

WFL

Crystal field stabilization energy for high spin d^4 octahedral complex is:

d^4, WFL

(A) $-0.6\,\Delta_a$

(B) $-1.8\,\Delta_a$

(C) $-1.6\,\Delta_a$

(D) $-1.2\,\Delta_a$

$\Delta_o = 0.6 \times 1 - 0.4 \times 3$

$= 0.6 - 1.2$

$= -0.6$

Factors Affecting Stability :

Stability ∝ splitting

① Nature of ligand :→

$\Delta_o \propto$ strength of ligand

Ex:

$[Fe(H_2O)_6]^{+3} < [Fe(NH_3)_6]^{+3} < [Fe(NO_2)_6]^{-3} < [Fe(CN)_6]^{-3}$

(2) Charge on C.M.A. :→

$\Delta_0 \propto$ +ve charge on C.M.A.

Ex: $K_4[\overset{+2}{Fe}(CN)_6] < K_3[\overset{+3}{Fe}(CN)_6]$

(3) Zeff of C.M.A. :→

$\Delta_0 \propto Z_{eff}$ of CMA

Ex: $[\overset{+2}{Ni}Cl_4]^{-2} < [\overset{+2}{Pd}Cl_4]^{-2} < [\overset{+2}{Pt}Cl_4]^{-2}$

4d, 5d series metals

↓

WFL ⟹ SFL

(4) Geometry of Complex :-

$$\Delta_{sq.} > \Delta_o > \Delta_t$$

$$\Delta_t = \frac{4}{9}\Delta_o$$

$$\Delta_{sq} = 1.3\,\Delta_o$$

dsp^2 (sq. pl.)

$[Ni(CN)_4]^{-2} > [NiCl_4]^{-2} < [Ni(NH_3)_6]^{+2}$

(1)	(2)	(3)
Δ_{sq}	Δ_t	Δ_o

(1) > (3) > (2)

(5) Chelation :→ (Most dominating factor)

CN^-
CO

Stability ∝ Chelation

Ex: $[Ni(H_2O)_6]^{+2} < [Ni(en)_3]^{+2} < [Ni(dien)_2]^{+2} < [Ni(edta)]^{-2}$

Chelate Rings = 0, 3, 4, 5

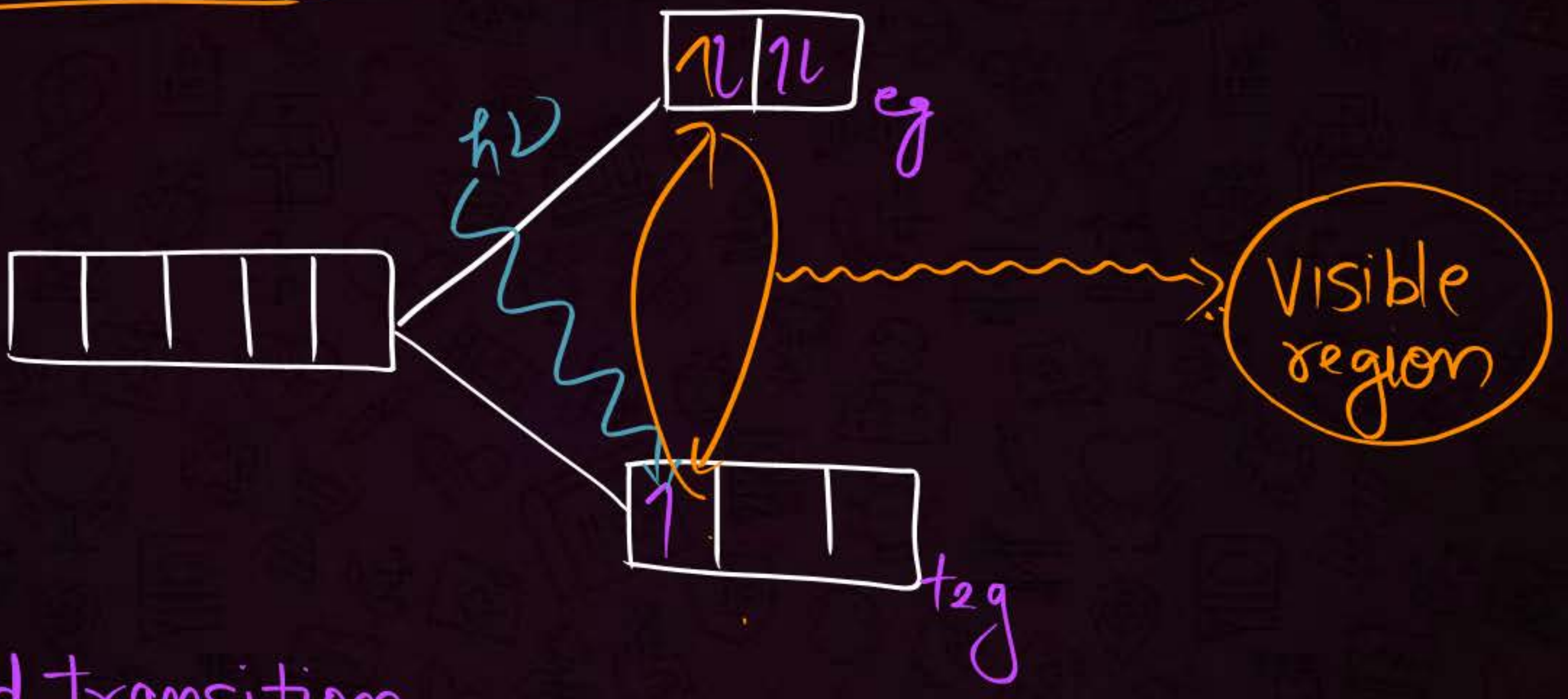
$[Ni(H_2O)_6]^{+2} < [Ni(ox)_3]^{-3}$

Chelation

* Colour of Complexes :-

Reason → d-d transition

[FeF_6]$^{-3}$
colourless



d^0, d^{10} → No d-d transition

d^{1-9} → d-d transition ✓

⇓

Coloured

d^0 → Coloured (Charge transfer)

$K_2\overset{+6}{Cr_2}O_7$, $K\overset{+7}{Mn}O_4$ } d^0 → Coloured due to charge transfer.

QUESTION- (DELHI 2017)

Pick out the correct statement with respect to $[Mn(CN)_6]^{3+}$

H.W.

(A) It is dsp^2 hybridised and square planar

(B) It is sp^3d^2 hybridised and octahedral

(C) It is sp^3d^3 hybridised tetrahedral

(D) It is d^2sp^3 hybridised and octahedral

QUESTION- (DELHI 2013)

An magnetic moment of 1.73 BM will be shown by one among the following:

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

(B) $[Ni(CN)_4]^{3-}$

(C) $TiCl_3$

(D) $[CoCl_4]^{4-}$

H.W.

QUESTION- (DELHI 2013)

The order of energy absorbed which is responsible for the color of complexes

A. $[Ni(H_3O)_2(en)_2]^{3+}$

B. $[Ni(H_2O)_6(en)]^{3+}$

C. $[Ni(en)_3]^{3-}$ is

(A) B > A > C

(B) A > B > C

(C) C > B > A

(D) C > A > B

QUESTION- (DELHI 2017)

Imp

Correct increasing order for the wavelengths of absorption in the visible region for the compelxes of Co^{3+} is:

(A) $[Co(NH_3)_3]^{2+}$, $[Co(en)_3]^{3+}$, $[Co(H_2O)_3]^{3+}$

(B) $[Co(en)_3]^{2+}$, $[Co(NH_3)_3]^{3+}$, $[Co(H_2O)_3]^{3+}$

(C) $[Co(H_2O)_3]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(NH_3)_3]^{2+}$,

(D) $[Co(H_2O)_3]^{3+}$, $[Co(NH_3)_3]^{2+}$, $[Co(en)_3]^{3+}$,

$\lambda \propto \frac{1}{E}$

$E = H_2O < NH_3 < en$

$\lambda = \quad > \quad >$

Q. Colourless?

$d^{10} \rightarrow$ colourless

① $[\overset{+3}{Ti}(H_2O)_6]Cl_3$ — d^1 ✓

② $[\overset{+2}{Cu}(NH_3)_4]SO_4$ — d^9 ✓

③ $[\overset{+2}{Zn}(H_2O)_4]SO_4$

④ $K_4[\overset{+2}{Fe}(CN)_6]$ — $d^6 \rightarrow$ ✓

Colour of Some Gem Stones

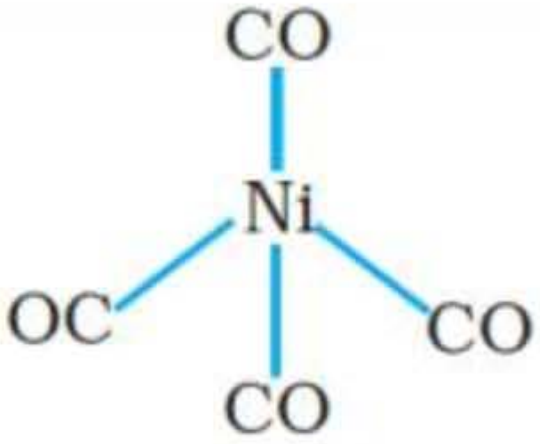
The colours produced by electronic transitions within the *d* orbitals of a transition metal ion occur frequently in everyday life. Ruby [Fig.5.12(a)] is aluminium oxide (Al_2O_3) containing about 0.5-1% Cr^{3+} ions (d^3), which are randomly distributed in positions normally occupied by Al^{3+}. We may view these chromium(III) species as octahedral chromium(III) complexes incorporated into the alumina lattice; *d*–*d* transitions at these centres give rise to the colour.

In emerald [Fig.5.12(b)], Cr^{3+} ions occupy octahedral sites in the mineral beryl ($Be_3Al_2Si_6O_{18}$). The absorption bands seen in the ruby shift to longer wavelength, namely yellow-red and blue, causing emerald to transmit light in the green region.

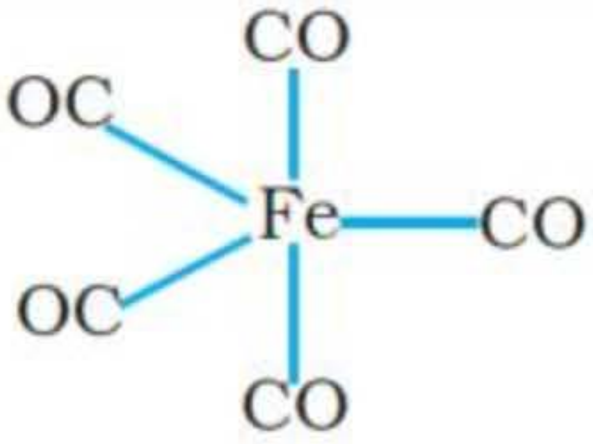
(a) 

(b) 

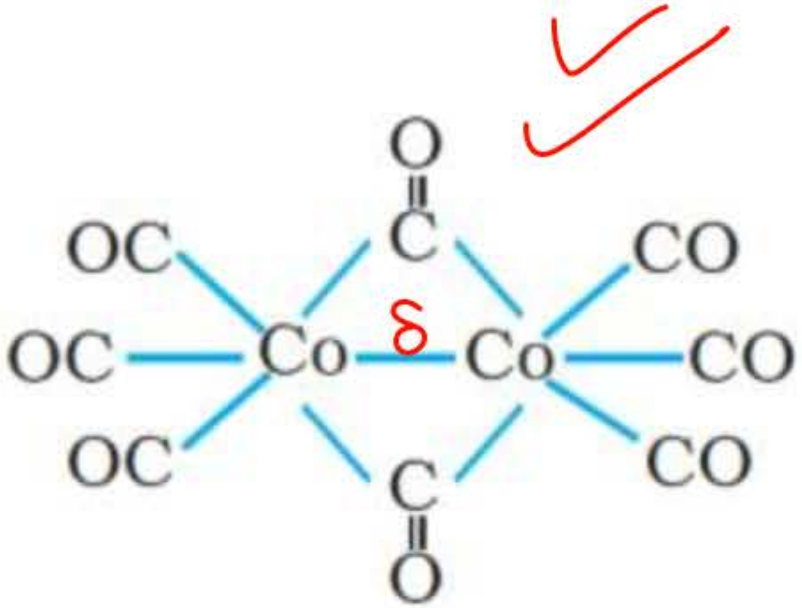
Fig.5.12: (a) Ruby: this gemstone was found in marble from Mogok, Myanmar; (b) Emerald: this gemstone was found in Muzo, Columbia.



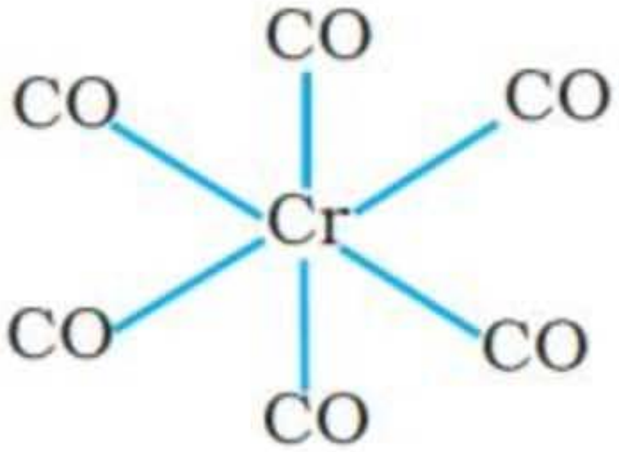
$Ni(CO)_4$
Tetrahedral



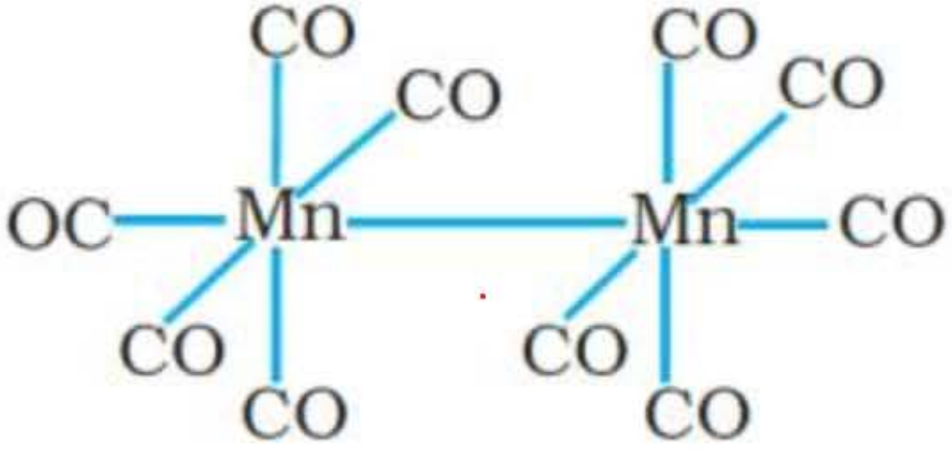
$Fe(CO)_5$
Trigonal bipyramidal



$[Co_2(CO)_8]$



$Cr(CO)_6$ Octahedral



$[Mn_2(CO)_{10}]$

ISOMERISM

Isomerism

- **Structural**
  - Ionization Isomerism
  - Hydrate | Solvate Isomerism
  - Linkage Isomerism
  - Coordination Isomerism
- **Stereo**
  - G.I.
  - O.I.

Break
10 min.

* Structural Isomerism *

I) Ionization Isomerism :-

$[Co(NH_3)_5Br]SO_4$ & $[Co(NH_3)_5SO_4]Br$ ✓

$[Co(H_2O)_4Cl_2]Br$ & $[Cr(H_2O)_4ClBr]Cl$ ✗

2)

(II) Hydrate Isomerism :→ (Solvate Isomerism)

$[Co(H_2O)_6]Cl_3$

$[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$

$[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$

} Solvate / Hydrate isomerism

III) Linkage Isomerism :→ ambidentate ligands

Ex: $[Co(NH_3)_5(NO_2)]SO_4$ & $[Co(NH_3)_5(ONO)]SO_4$

IV) Co-ordination Isomerism ↓

Ex:

$[\overset{+2}{Pt}(NH_3)_4]^{+2}[\overset{+2}{Zn}Cl_4]^{-2}$

$[\overset{+2}{Pt}(NH_3)_3Cl]^{+1}[Zn(NH_3)Cl_3]^{-1}$

~~$[\overset{+2}{Pt}(NH_3)_2Cl_2]^{0}[Zn(NH_3)_2Cl_2]^{0}$~~

$[Pt(NH_3)Cl_3]^{-1}[Zn(NH_3)_3Cl]^{+1}$

$[PtCl_4]^{-2}[Zn(NH_3)_4]^{+2}$

Hitrick

(I) for Monodentate ligands:

Total Coord. Isomers = ① If C.M.A. are same = $C.N/2$
② If CMA are Diff = C.N.

II) for Bidentate ligands :→

Total Coord. Isomers = ① If C.M.A. are same = $C.N/2 - 1$
② If CMA are Diff. = $C.N/2 + 1$

$[Co(NH_3)_6][CrCl_6] \Rightarrow 6$

$[Co(NH_3)_6][CoCl_6] \Rightarrow 3$

$[Co(NH_3)_6][Cr(ox)_3] \Rightarrow 6/2 + 1 = 4$

$[Co(en)_3][Co(ox)_3] \Rightarrow 6/2 - 1 = 2$

2

Stereo Isomerism

G.I.

- C.N. = 4
  - sp^3 Tetrahedral

G.I ✗

  - dsp^2 (squar planar)

- C.N. = 6 (Octahedral)

O.I. (C.N. = 4)

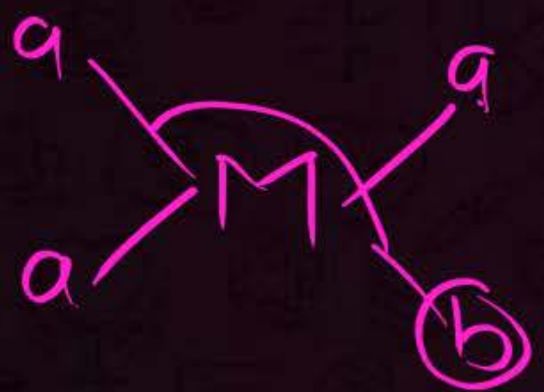
- Tetrahedral
  - O.I ✓
  - ✓ M_{abcd}
  - ✓ $M(AB)_2$
- Sq. planar
  - O.I ✗

C.N. = 4 (sq. planar)

① Ma_4

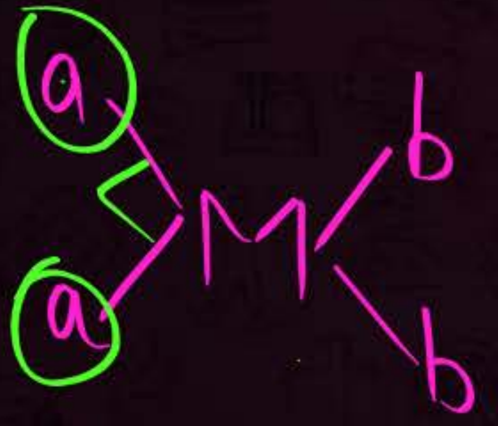
G.I ✗ O.I ✗

② Ma_3b

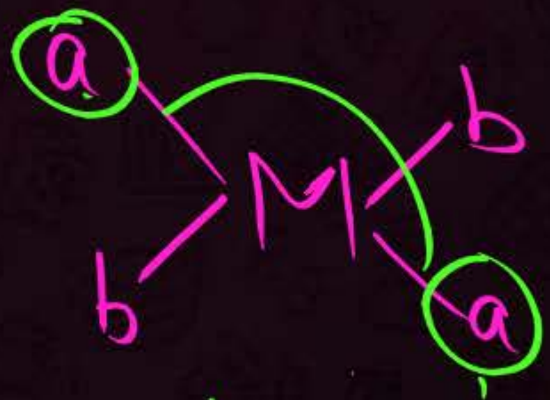


G.I ✗ O.I ✗

③ Ma_2b_2

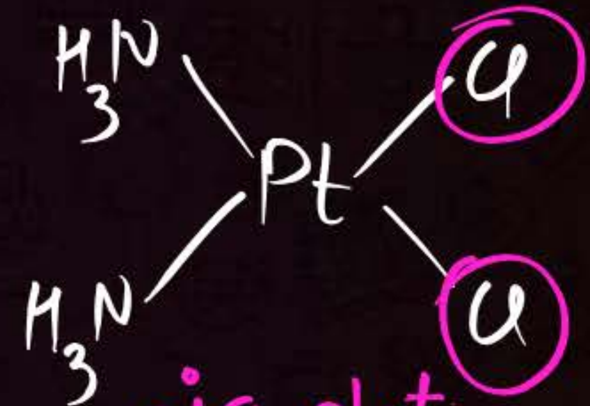


cis



trans

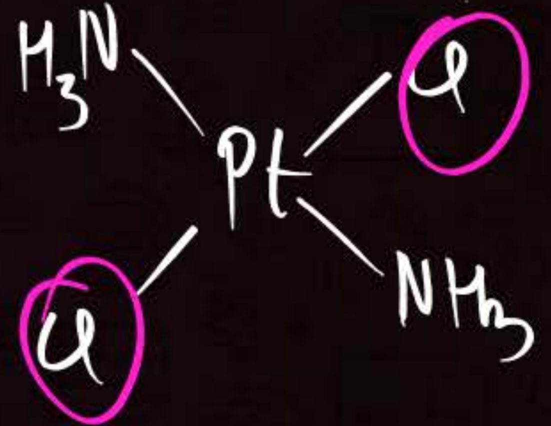
cancer treatment



cis platin

Ma_2b_2

$[Pt(NH_3)_2Cl_2]$

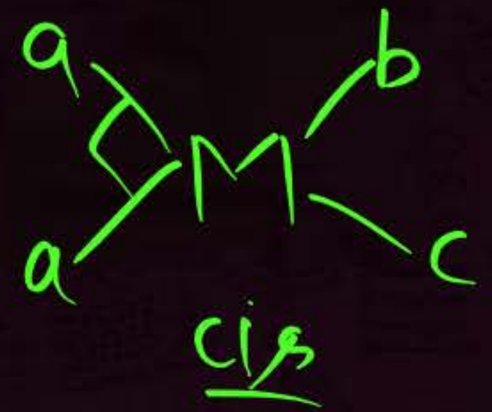


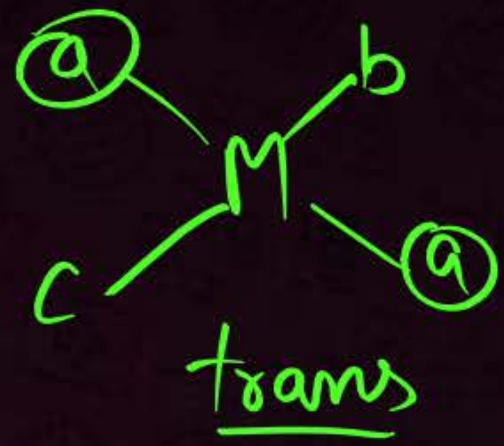
(4) Ma_2bc

G.I. = 2

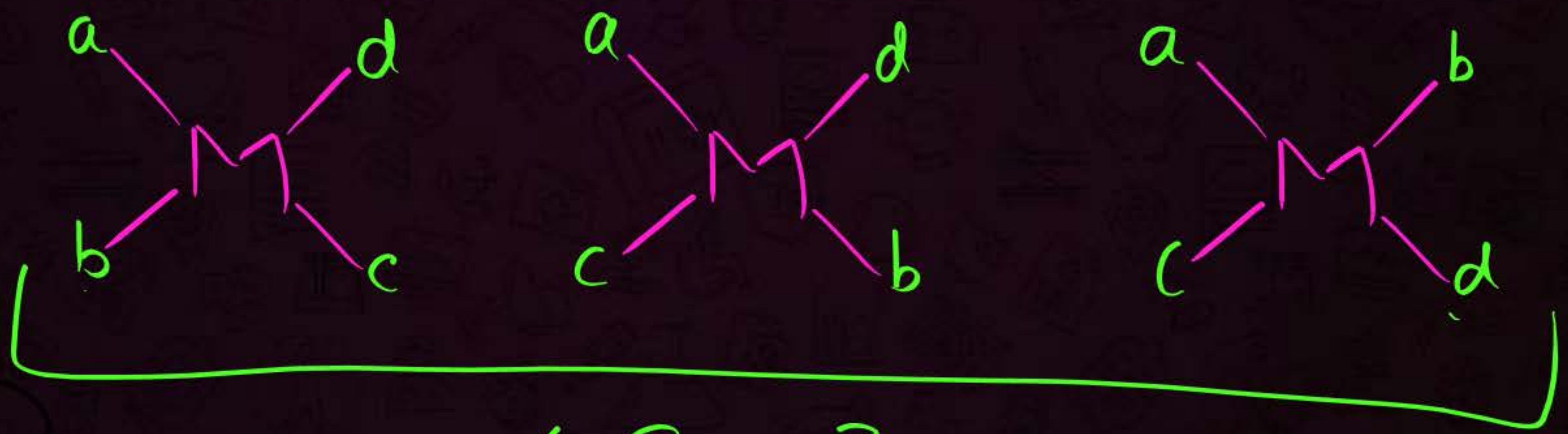
P.O.E. = 0

Stereo = 2





* (5) Mabcd

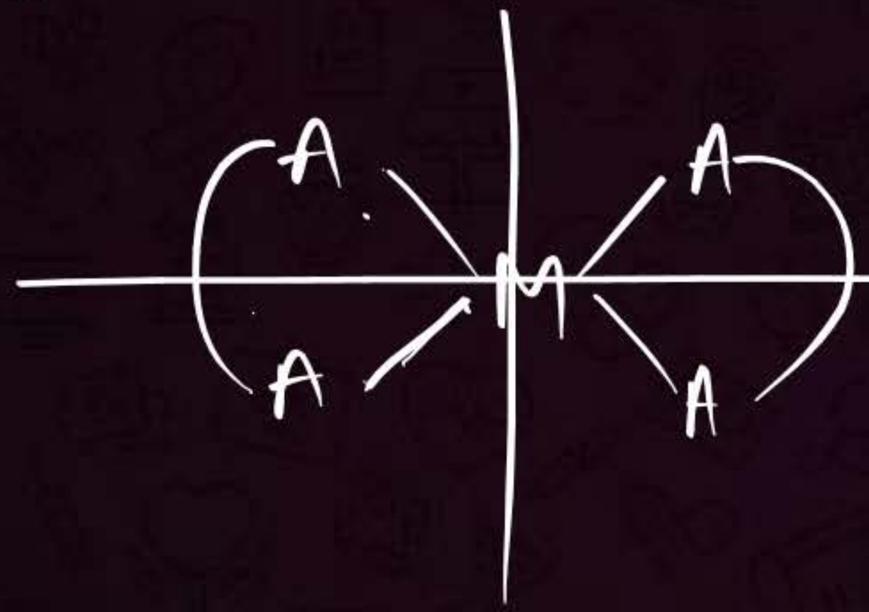


G.I = 3

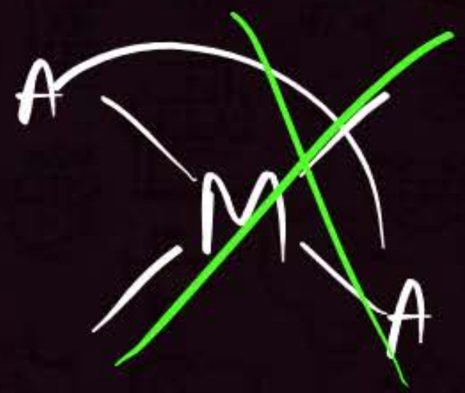
ox, en, DMG, bn   AA → symmetrical Bidentate ligand

Gly⁻, AB → Unsymmetrical Bidentate ligand

$M(AA)_2$



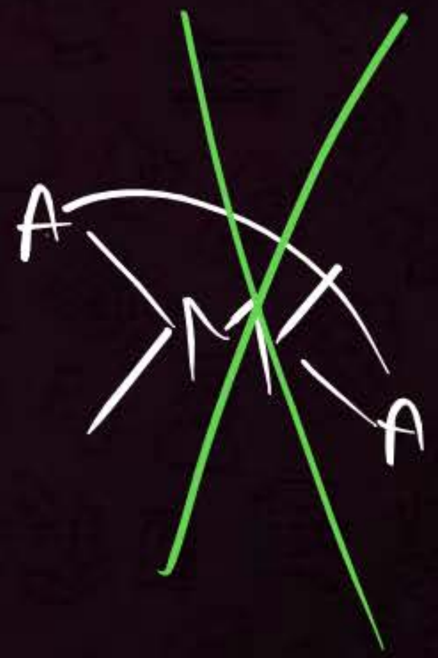
G I X



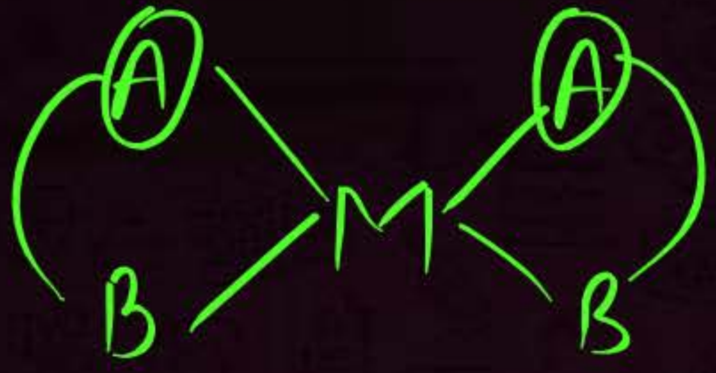
$M(AA)b_2$

G I X

O I X

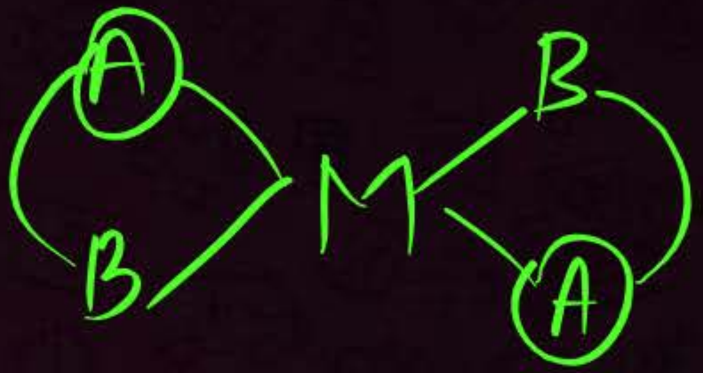


$M(AB)_2$



cis

O I X



trans

O I X

$M(AB)c_2$

G. I X

O. I X

$M(AB)cd$

G I = 2

symm.

E O

G X

Unsymm.

en

C.N. = 6

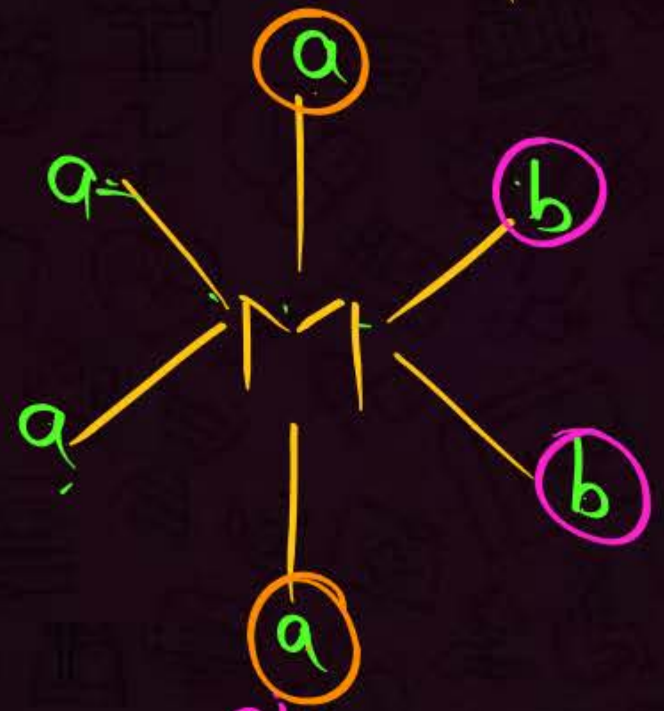
Ma_6 = G.I ✗ O.I ✗

Ma_5b = G.I ✗ O.I ✗

cis = 12

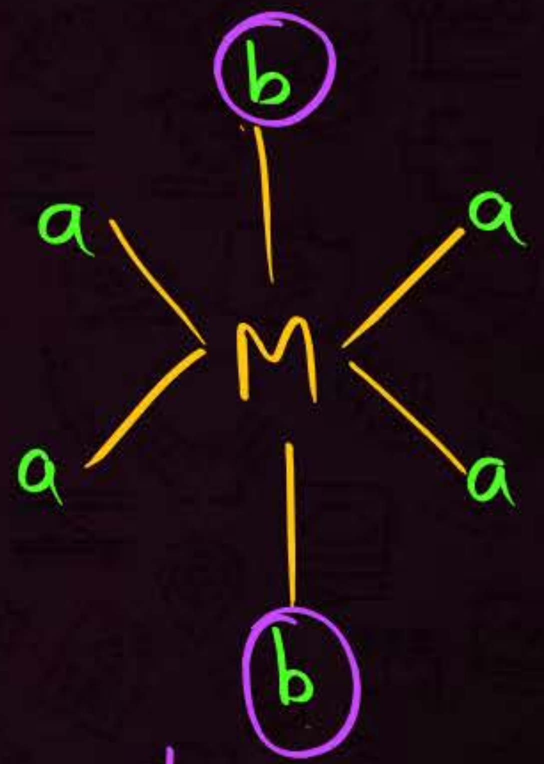
trans = 3

Ma_4b_2 =



cis

O.I ✗



trans

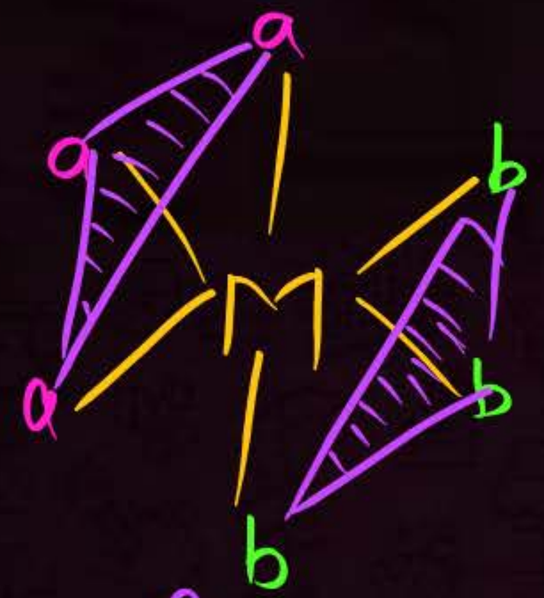
G.I = 2

P.O.E = 0

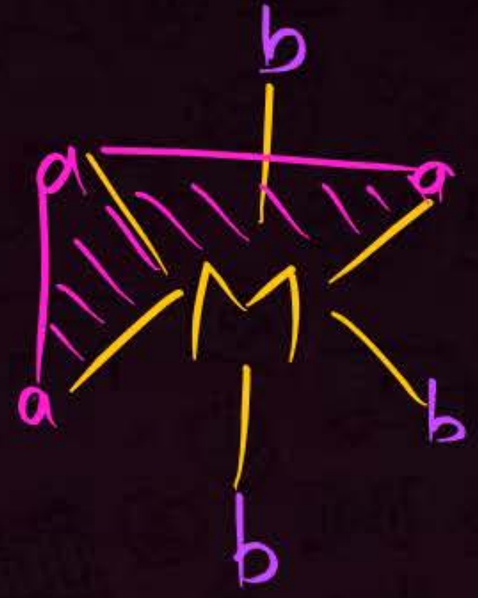
stereo = 2

Complex	G.I	P.O.E	Stereo
Ma_6 —	×	×	–
Ma_5b —	×	×	—
Ma_4b_2 —	2	0	2
Ma_4bc —	2	0	2
Ma_3b_3 —	2	0	2
Ma_3b_2c —	3	0	3
Ma_3bcd —	4	1	5
$Ma_2b_2c_2$ —	5	1	6
Ma_2b_2cd —	6	2	8
Ma_2bcde —	9	6	15
$Mabcdef$ —	15	15	30

Ma_3b_3



fac.



Mer.

G.I = 2

P.O.E = 0

Stereo = 2

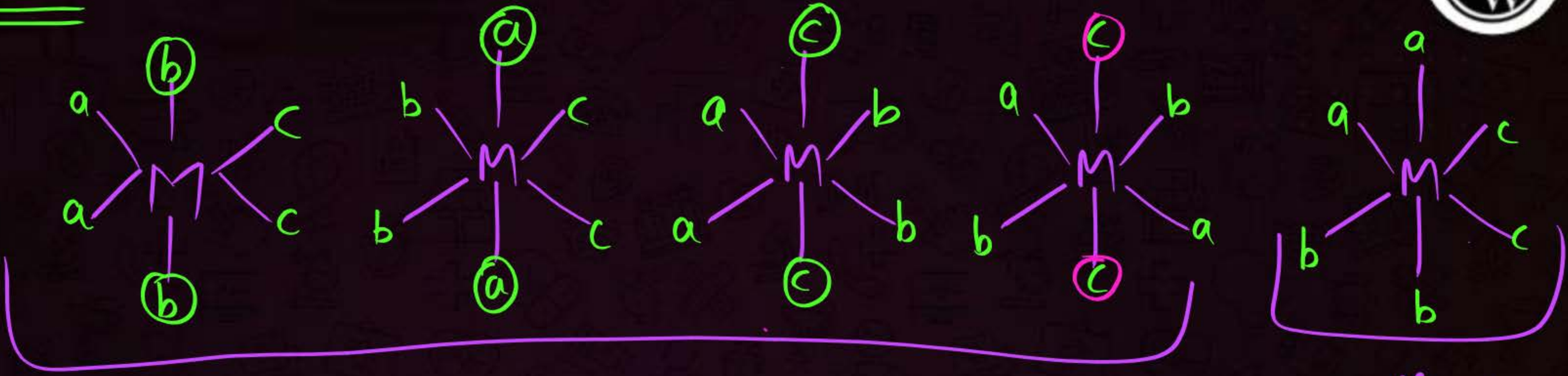
$[Co(NH_3)_3Cl_3]$

Stereo = ?

G.I = ?

P.O.E. = ?

$Ma_2b_2c_2$

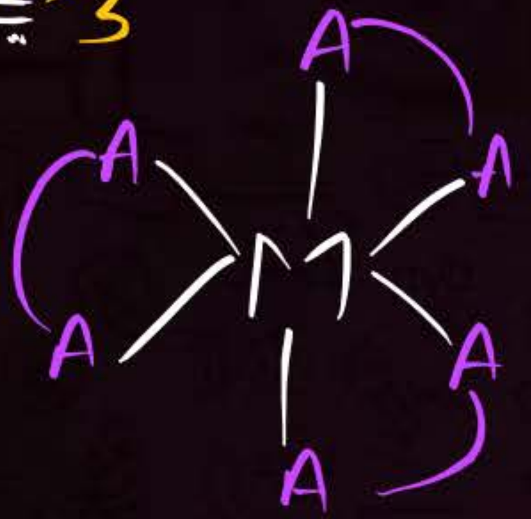


O. I ✗

all cis

O. A ✓✓

$M(AA)_3$



G.I ✗

O.A ✓

Stereo = 2

3 Rings → O.A ✓

2 Ring → same plane O.I ✗

diff plane O.A ✓

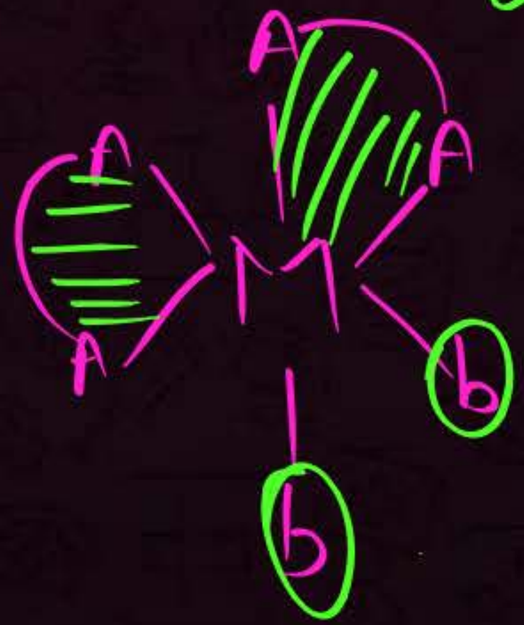
$M(AA)_2b_2$ / $M(AA)_2bc$

G.I = 2

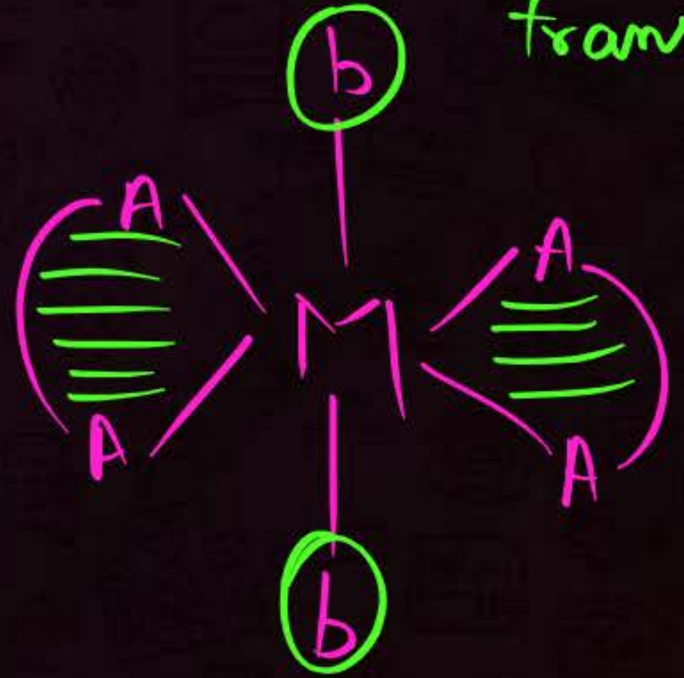
P.O.E = 1

Stereo = 3

cis ✓



trans. O.I ✗



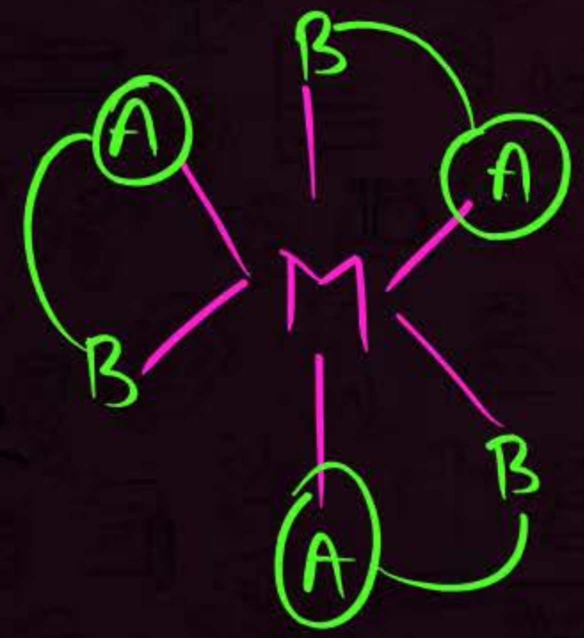
$[Co(en)_2Cl_2]$ $M(AA)_2b_2$

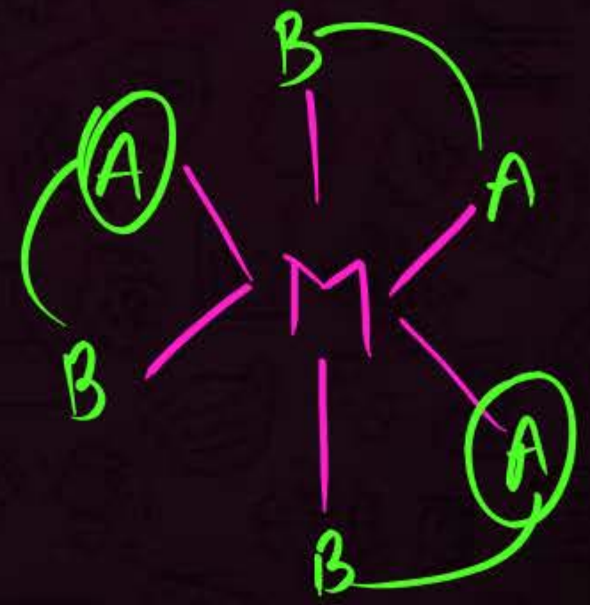
Stero isomers = ? 3

G.I = ? 2

P.O.E = ? 1

$M(AB)_3$





G.I = 2

P.O.E = 2

Stereo = 4

Intext Questions

5.3 Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

(i) $K[Cr(H_2O)_2(C_2O_4)_2]$

(ii) $[Co(en)_3]Cl_3$

(iii) $[Co(NH_3)_5(NO_2)](NO_3)_2$

(iv) $[Pt(NH_3)(H_2O)Cl_2]$

5.4 Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$ are ionisation isomers.

QUESTION- (DELHI 2006)

$[Co(NH_3)_6(NO_2)_2]Cl$ exhibits:

(A) Linkage isomerism, ionization isomerism and optical isomerism

(B) Linkage isomerism, ionization isomerism and geometrical isomerism

(C) Ionization isomerism, geometrical isomerism and optical isomerism

(D) Linkage isomerism, geometrical isomerism and optical isomerism

QUESTION- (2003)

Which one of the following octahedral complexes will not show geometric isomerism? (A and B are monodentate ligands)?

(A) $[MA_5B]$

(B) $[MA_3B_2C]$

(C) $[MA_4B_2]$

(D) $[MA_3B_3]$

QUESTION- (2003)

Which of the following complexes is used to be as an anticancer agent?

(A) cis-$[PtCl_2(NH_3)_2]$

(B) cis-$K_2[PtCl_2Br_2]$

(C) $Na_2[CoCl_4]$

(D) mer-$[Co(NH_3)_3Cl_3]$

H.W.

- Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α–nitroso–β–naphthol, cupron, etc.
- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.
- Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc.

$$Ag_2S + \overset{+}{K}CN^- \longrightarrow [Ag(CN)_2]^-$$

soluble

$\big\downarrow$ Zn

$$[Zn(CN)_4] + Ag \downarrow$$

soluble

- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.

$Ni + CO \rightarrow [Ni(CO)_4]\uparrow \xrightarrow{\Delta} Ni + CO\uparrow$

For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

- Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B_{12}, cyanocobalamine, the anti–pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).
- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.
- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ than from a solution of simple metal ions.
- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.
- There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D–penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: *cis*–platin and related compounds.

V-B_{12} → Co

Chlorophyll → Mg

Haemoglobin → Fe

Wilkinson Catalyst

$[RhCl(PPh_3)_3]$

$Na_2S_2O_3$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