

13/2/24

classmate

Date _____

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CHAPTER - 5

COORDINATION COMPOUNDS

★ ADDITION COMPOUNDS

When two salts fuse with each other in a definite proportion.

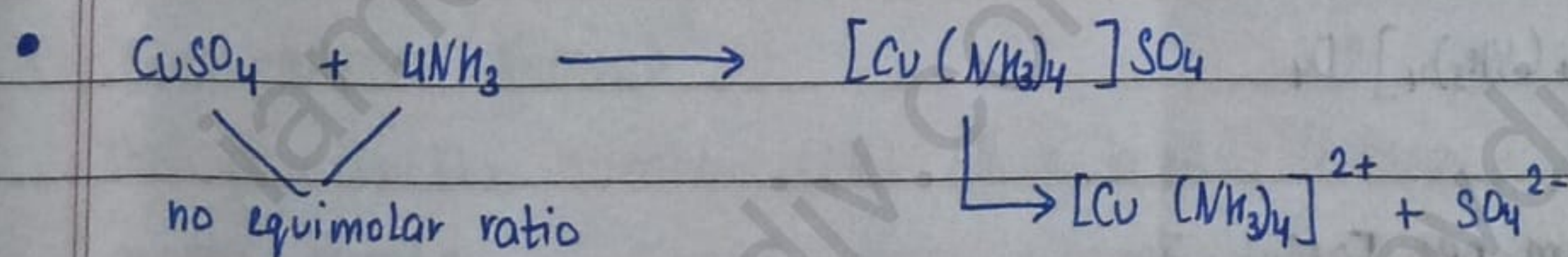
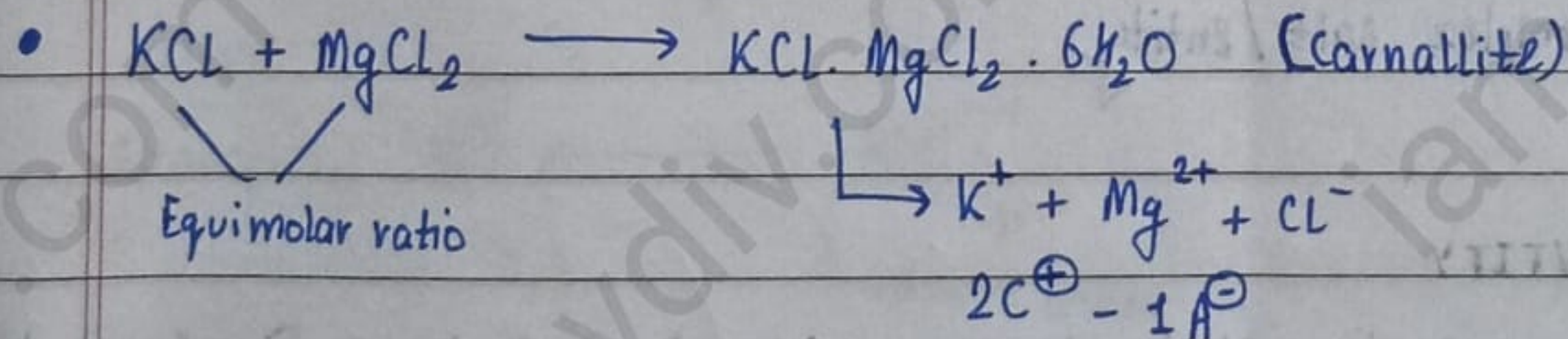
Two types

- (i) Complex salt
- (ii) Double salt

S.No.

DOUBLE SALTCOMPLEX SALT

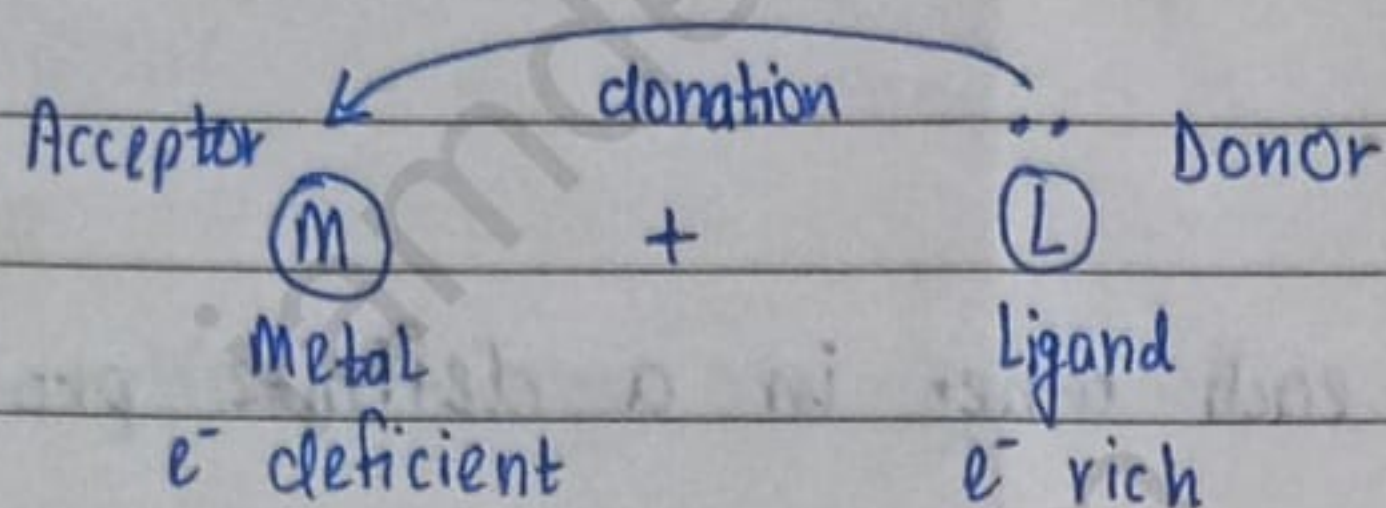
(i)	When two salts fuse together in equal ratio.	When two salts fuse together in unequal ratio.
(ii)	Dissociate completely. ✓	Complete dissociation. X
(iii)	Ratio of cations and anions $2C^{\oplus} - 1A^{\ominus}$ $2A^{\ominus} - 1C^{\oplus}$	
(iv)	Every ion gives its individual test.	Every ion does not give individual test.



★ COMPLEX SALT

Coordination compound \Rightarrow When e^{-} deficient specie (metal atom/ion) is

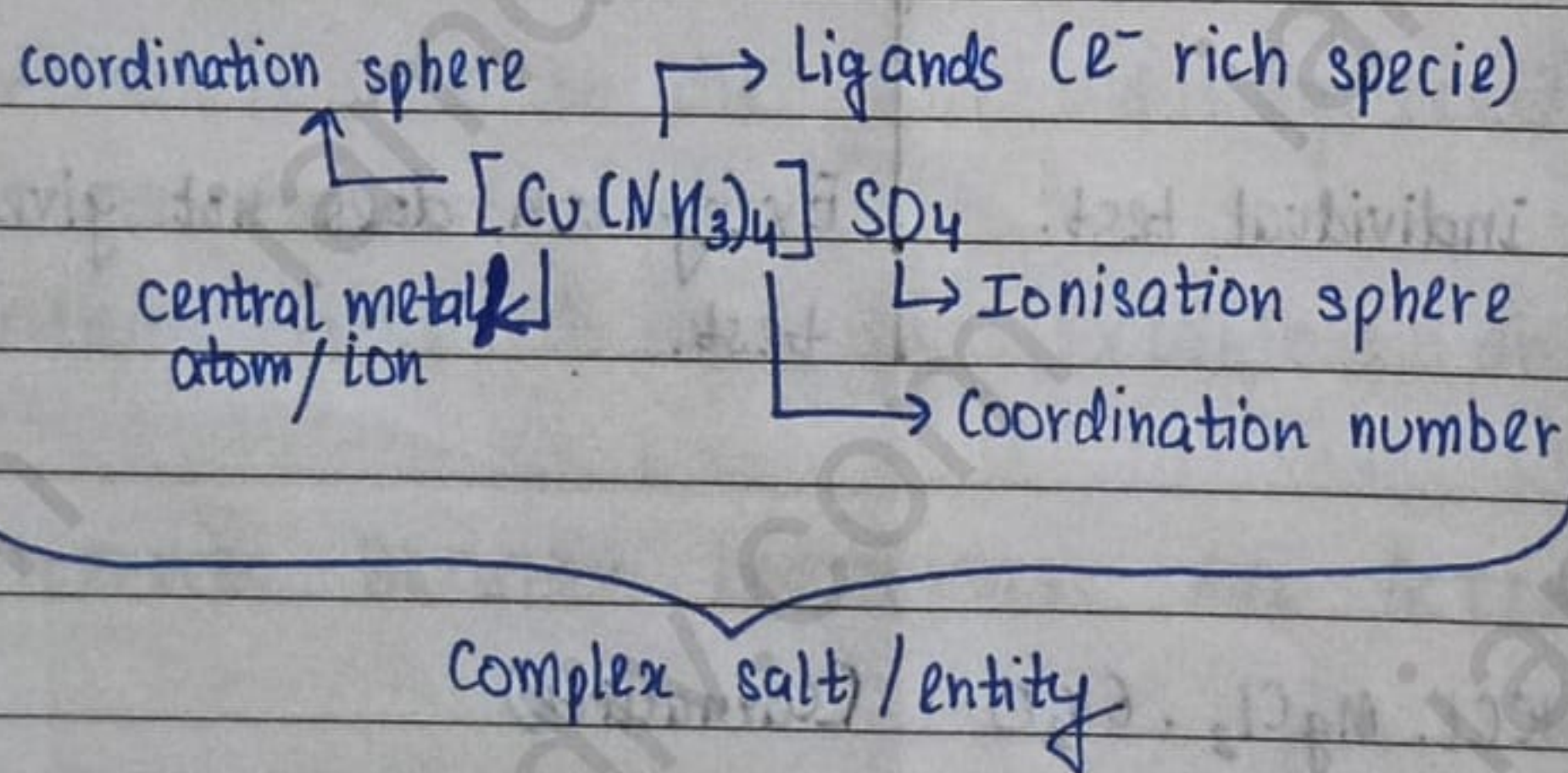
getting complexed with e^- rich specie (Ligand) by forming coordinate bond.



• IMPORTANT TERMS

* COORDINATION COMPOUNDS

- They contain a central atom (or cation) which is coordinated to a suitable number of anions or neutral molecules called ligands and usually retain their identity in solution as well as in solid state.
- They may be positively charged, negatively charged or a neutral species.
 $[Co(NH_3)_6]^{3+}$, $[NiCl_4]^{2-}$, $[Ni(CO)_4]$



* COORDINATION ENTITY

It constitutes a central metal atom or ion bonded to a fixed number of ions or molecules.

Example: $[Cu(NH_3)_4]SO_4$

* CENTRAL ATOM OR ION

In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion.

Example: $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
 \rightarrow central atom

* COORDINATION SPHERE

The central atom/ion and the ligands attached to it are enclosed in square bracket and are collectively termed as the coordination sphere.

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

* COUNTER IONS

The ions present outside the coordination sphere are called counter ions.

Example: $[\text{Cu}(\text{NH}_3)_4]^{2+} + \text{SO}_4^{2-}$
 \rightarrow counter ion

* LIGANDS

A molecule, ion or group that is bonded to the metal atom or ion in a complex or coordination compound by a coordinate bond is called ligand.

It may be neutral, positively or negatively charged.

* DONOR ATOM

An atom of the ligand attached directly to the metal is called the donor atom.

Example: $\text{M} \leftarrow \begin{array}{c} \text{h} \\ \text{O} \\ \text{h} \end{array}$
 \rightarrow donor atom

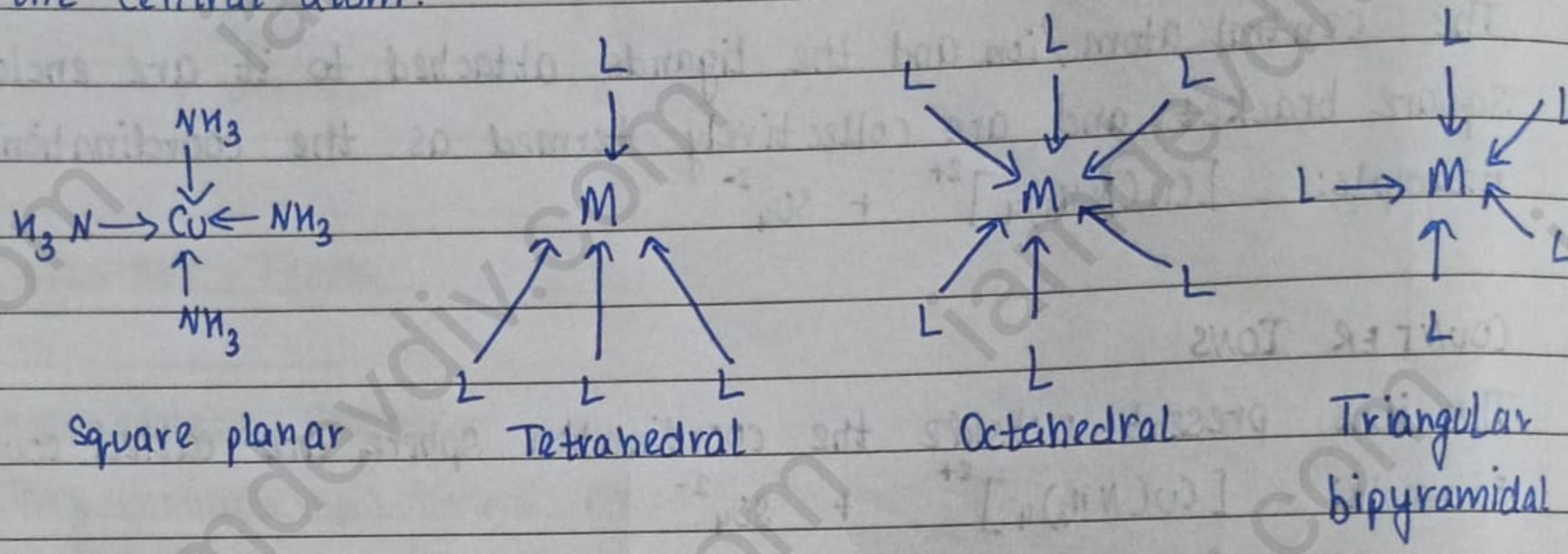
* COORDINATION NUMBER

The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded.

Example: $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
 \rightarrow coordination number

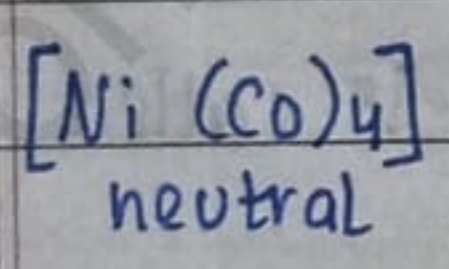
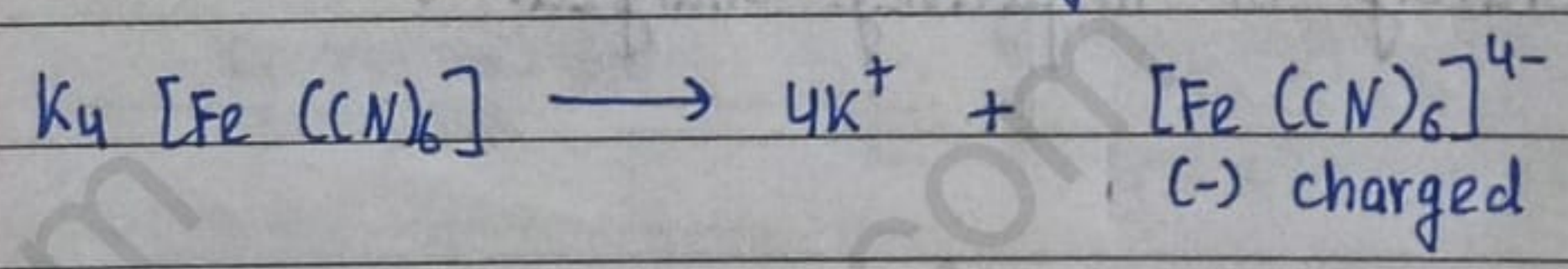
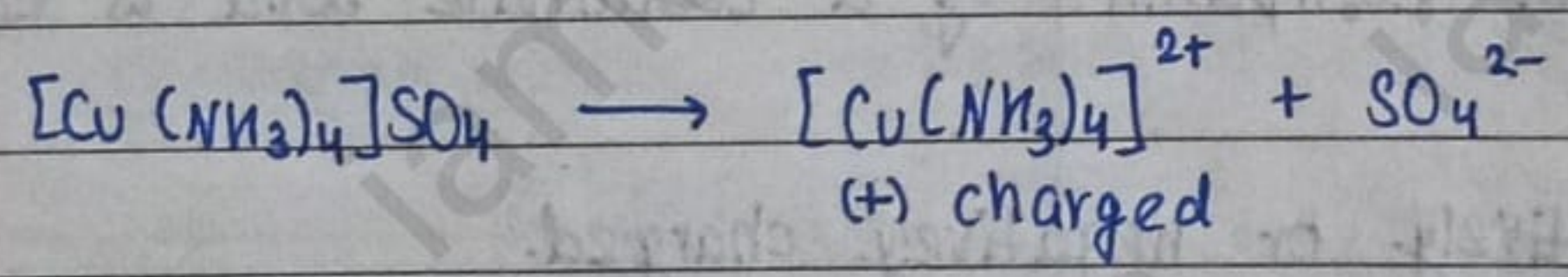
* COORDINATION POLYMERON

The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom.



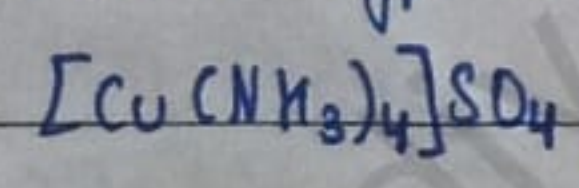
* CHARGE ON THE COMPLEX ION

The charge on the complex ion is equal to the algebraic sum of the charges on all the ligands coordinated to the central metal ion.

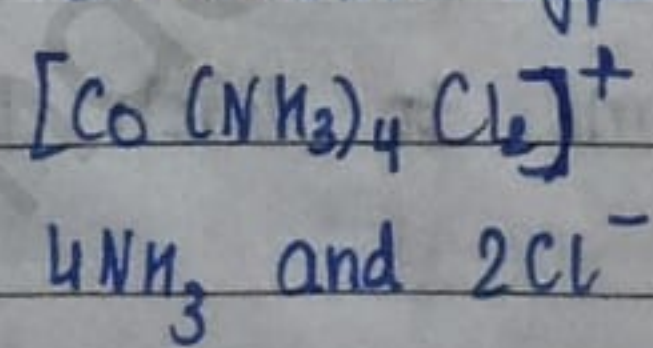


* HOMOLEPTIC AND HETEROLEPTIC COMPLEXES

homoleptic \Rightarrow Same type of ligands



heteroleptic \Rightarrow Different types of ligands



★ LIGANDS

- (i) A ligand is an ion or molecule, which donates a pair of electrons to the central metal atom or ion to form a coordination complex.
- (ii) Ligands can be anions, cations and neutral molecules.
- (iii) Ligands act as Lewis bases (donate electron pairs) and central metal atoms viewed as Lewis acid (electron pair acceptor).
- (iv) The nature of bonding between metal to ligand varies from covalent bond to ionic bond.
- (v) Denticity: The number of ligating (linking) atoms present in ligand is called denticity.

• CLASSIFICATION

* ON THE BASIS OF CHARGE

- | | |
|---|--|
| <p>(i) (-) charge
Suffix \Rightarrow 'o' or 'ido'</p> <p>$F^- \Rightarrow$ fluoro / flourido
 $OH^- \Rightarrow$ Hydroxo / Hydroxido
 $Br^- \Rightarrow$ Bromo / Bromido
 $O_2^- \Rightarrow$ Superoxido
 $O_2^{2-} \Rightarrow$ Peroxido</p> | <p>(ii) (+) charge
Suffix \Rightarrow 'ium'</p> <p>$NO_2^+ \Rightarrow$ Nitronium
 $NO^+ \Rightarrow$ Nitrosonium
 $NH_2-NH_2^+ \Rightarrow$ hydrazinium</p> |
| <p>(iii) Neutral
Self names</p> <p>$H_2O \Rightarrow$ aqua
 $NH_3 \Rightarrow$ Ammine
 $CO \Rightarrow$ carbonyl
 $CS \Rightarrow$ Thio-carbonyl</p> | |

* ON THE BASIS OF DENTICITY

(i) Unidentate Ligands

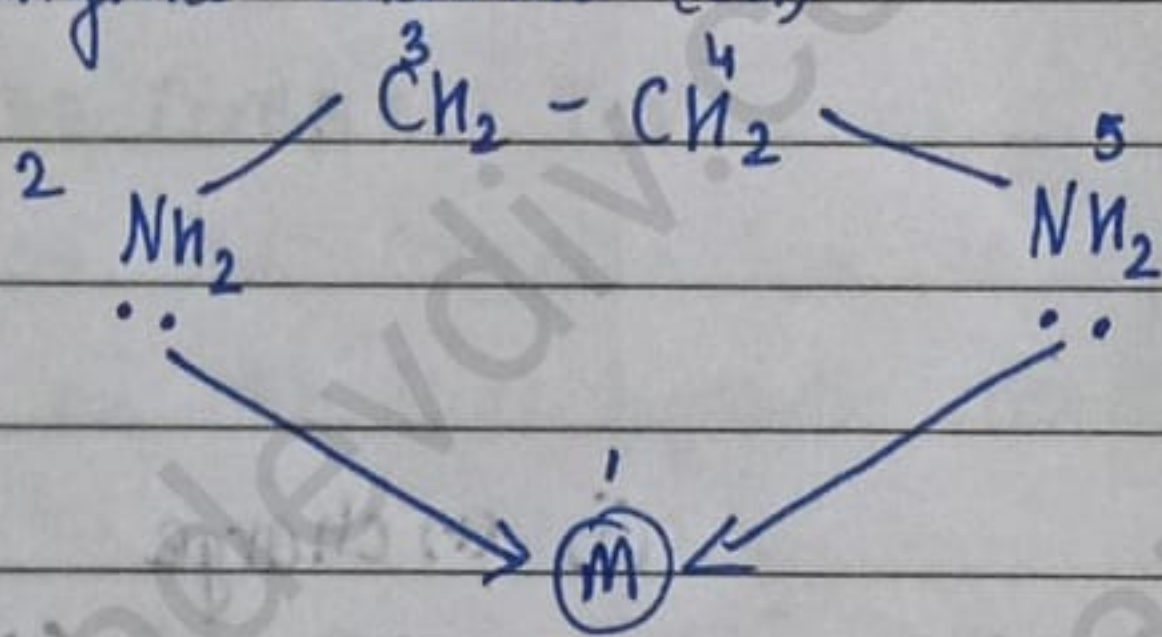
The ligands whose only one donor atom is bonded to metal atom are called unidentate ligands.

Examples: F^{\ominus} , OH^{\ominus} , N_3^{\ominus}
 \rightarrow azido

(ii) Didentate Ligands

The ligands which contain two donor atoms or ions through which they are bonded to the metal ion.

Examples: Ethylene diamine (en)



Ring formation \rightarrow Chelate ring (5 membered)

\downarrow
Chelation

- During complex formation between metal and ligand if ring formation occurs
- Chelation \rightarrow when denticity > 1
- Ring size $\rightarrow 6, 5, 4, 3$
- Stability $\rightarrow 6 > 5 > 4 > 3$
- Complex \rightarrow Chelation rings \propto stability

(iii) Polydentate Ligands

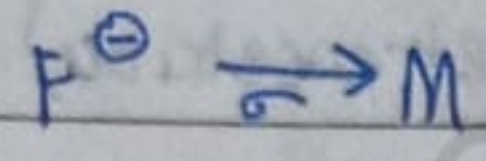
When several donor atoms are present in a single ligand, the ligand is called polydentate ligand

Examples: Tridentate = 3 donor sites

Tetradentate = 4 donor sites

* ON THE BASIS OF BOND FORMED BETWEEN LIGAND AND METAL

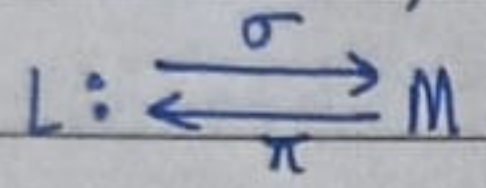
(i) σ -donor



When ligand forms σ bond with metal.

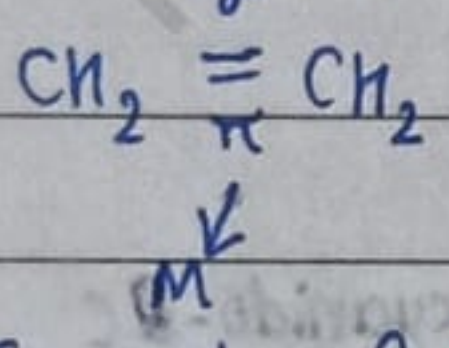
Example: Monodentate ligand

(ii) σ -donor, π -acceptor



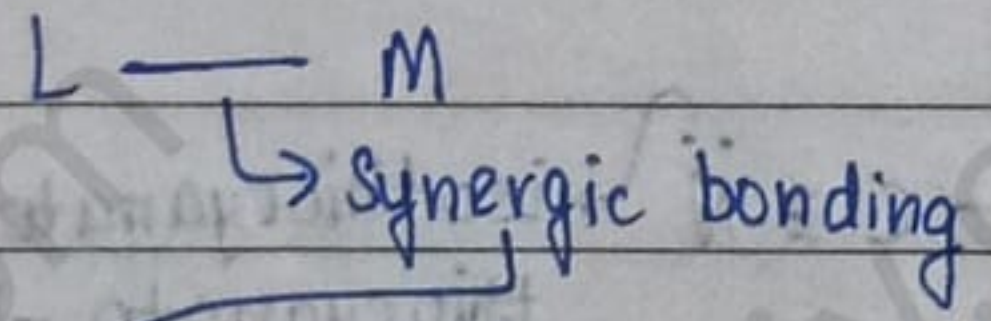
When ligand donates its e^- density to metal and M back donates its e^- density to ligand. Example: CO, CN^- , NO^+ , etc.

(iii) π -donor, π -acceptor

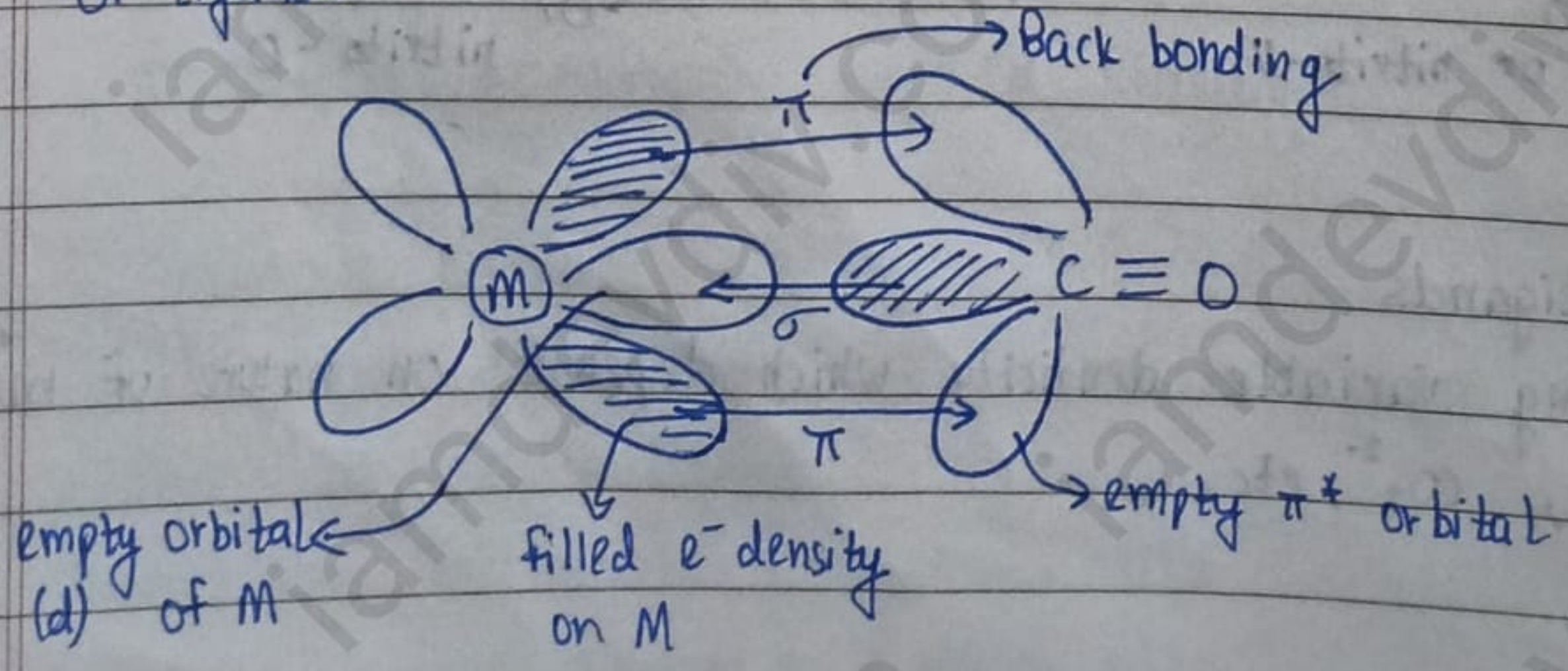


Example: C_2H_4 , Benzene, etc.

• BONDING



When ligand donates its e^- density (filled) into empty orbital of metal and metal back donates its filled e^- density into empty π^* orbital of ligand.



LIST OF LIGANDS

Denticity	Name	Ligand	Name of ligand in complex	Donor atom	
Neutral ligands	Water	H_2O	Aqua / aquo	O	
	Ammonia	NH_3	Ammine	N	
	Carbon monoxide	CO	Carbonyl	C	
	Nitrogen oxide	NO	Nitrosyl	N	
	Thiocarbonyl	CS	Thiocarbonyl	S	
Neutral	Mono-dentate	Pyridine (py)	C_5H_5N	Pyridine (py)	N
		Methyl amine	CH_3NH_2	Methylamine	N
		Dinitrogen	N_2	Dinitrogen	N
		Phosphine	PH_3	Phosphine	P
Bi-dentate	Acetone	CH_3COOCH_3	Acetone	O	
	Ethylene-diamine (en)	$NH_2(CH_2)_2NH_2$	Ethylenediamine (en)	2N-atoms	
(+ve) charged Ligand	Mono-dentate	Nitrosonium ion	NO^{\oplus}	Nitrosonium	N
		Nitronium ion	NO_2^{\oplus}	Nitronium	N
		Hydrazinium ion	$NH_2NH_3^{\oplus}$	Hydrazinium	N
		Hydride ion	H^{\ominus}	Hydrido	H
		Oxide ion	O^{2-}	Oxo	O
		Peroxide ion	O_2^{2-}	Peroxo	O
		Hydroxide ion	OH	Hydroxo	O
		Fluoride ion	F^-	Fluoro (Fluorido)	F
		Chloride ion	Cl^-	Chloro (chlorido)	Cl
		Bromide ion	Br^-	Bromo (bromido)	Br

(-) ve charged ligands

Iodide ion	I^-	Iodo (Iodido)	I
Acetate ion	CH_3COO^\ominus	Acetato (acetatido)	O
Cyanide ion	CN^\ominus	Cyano (cyanido)	C
Isocyanide ion	NC^\ominus	Isocyano	N
Sulphite ion	SO_3^{2-}	Sulphito	O
Imide ion	NH^{2-}	Imido	N
Sulphide ion	S^{2-}	Sulphido or thio	S
Amide ion	NH_2^\ominus	Amido	N
Nitrate ion	NO_3^\ominus	Nitrato	N
Nitro ion	NO_2^\ominus	Nitro (nitrito-N)	N
Nitrite ion	ONO^\ominus	nitrito	O
Nitride ion	N^{3-}	Nitrido	N
Azide ion	N_3^\ominus	Azido	N
Cyanate ion	CNO^\ominus	Cyanato	O
Isocyanate ion	OCN^\ominus	Isocyanato	N
Thiocyanate ion	SCN^\ominus	Thiocyanato	S
Iso thiocyanate ion	NCS^\ominus	Isothiocyanato	N
Acetyl acetonate ion	$CH_3C(=O)-CH=C(O^-)-CH_3$	Acetylacetonato (acac)	2 O-atom
Glycinate ion	$NH_2-CH_2-COO^\ominus$	Glycinato (gly)	1 N-atom and 1 O-atom
Sulphate ion	SO_4^{2-}	Sulphato	2 O-atom
Dimethylglyoxime	$CH_3-C(=N-OH)-C(=N-OH)-CH_3$	Dimethylglyoximato	2 N-atoms
Hexa-dentate	Ethylenediamine tetraacetate ion	EDTA ⁴⁻	2 N-atoms and 4 O-atoms

★ WERNER'S THEORY

Werner is also known as the father of Coordination chemistry.

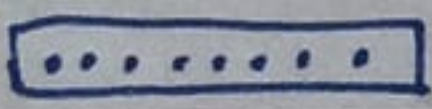
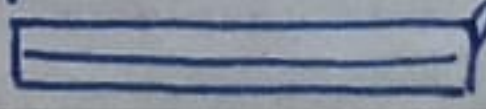
He proposed some theoretical concepts to explain how the coordination compounds are formed.

The major postulates of Werner's Coordination theory are given below:

- The central metal atom of the coordination compounds show two types of valencies -

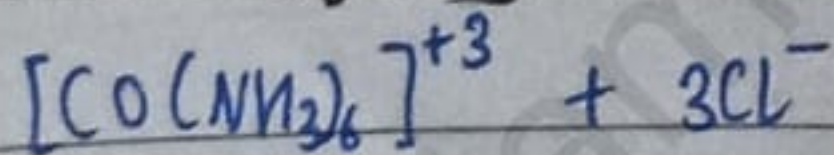
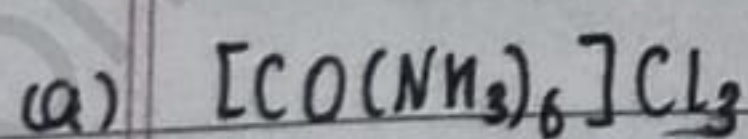
primary valency AND secondary valency
 (oxidation state) (coordination no.)

- The primary valency is ionizable but secondary valency is not ionizable.
- Every metal atom has a fixed number of secondary valencies, i.e., it has a fixed number of coordination number.
- The primary valency of the central metal atom is satisfied by negative ions, but secondary valencies may be satisfied by negative ions or neutral molecules.
- The secondary valencies of the metal are always directed towards fixed position in space and this leads to definite geometry of the coordination complex. It means the primary valencies are not directional in nature but the secondary valencies are directional in nature.

	PRIMARY VALENCY	SECONDARY VALENCY
(i)	Oxidation State	Coordination number
(ii)	Ionisable	Non-ionisable
(iii)	Do not provide geometry	Provide geometry
(iv)	Non-directional	Directional
(v)	Represented by 	Represented by 

★ IUPAC NOMENCLATURE

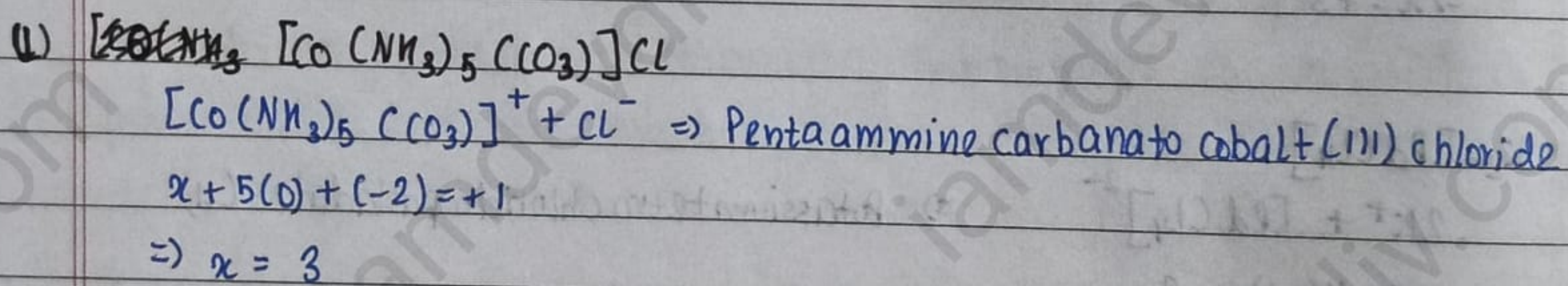
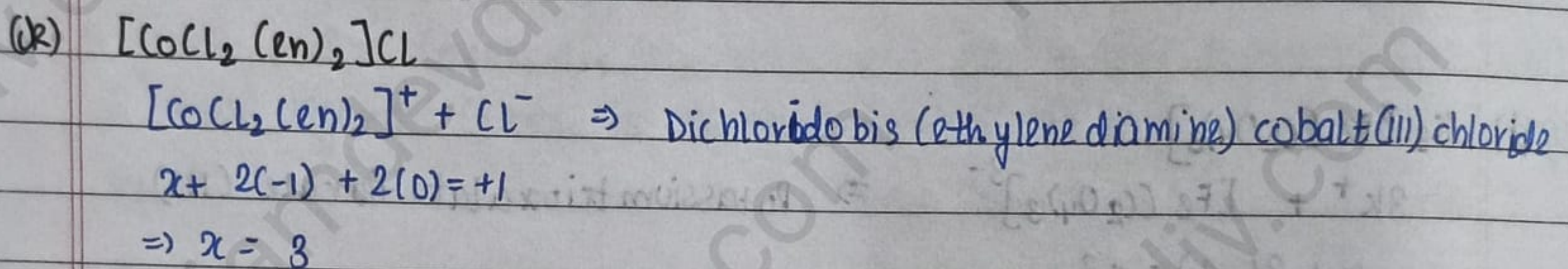
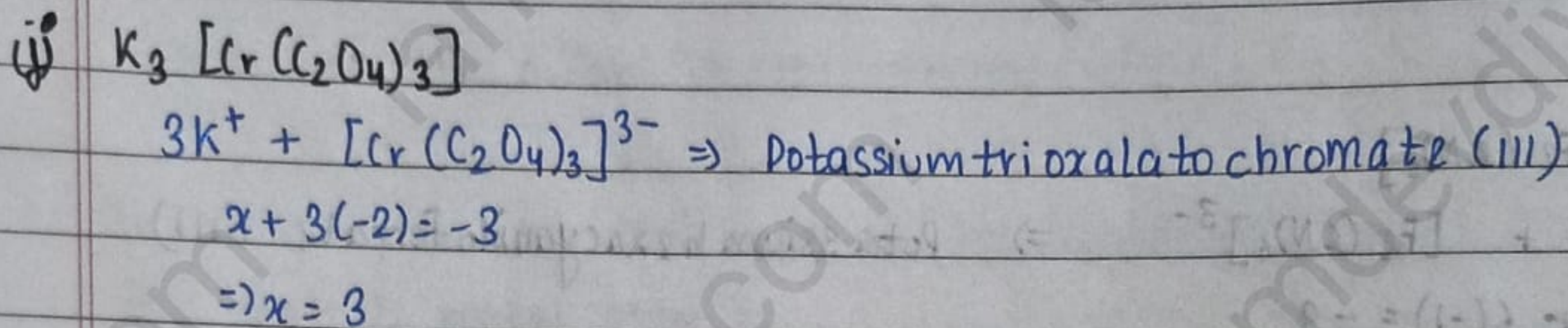
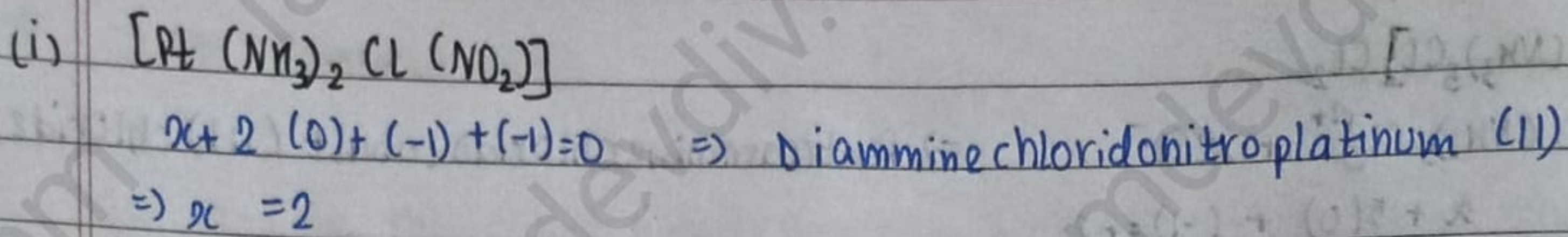
1. In naming the entire complex, the name of the cation is given first and the anion second (just as for sodium chloride), no matter whether the cation or the anion is the complex species.
2. In the complex ion, the name of the ligand or ligands precedes that of the central metal atom.
3. A greek prefix (mono, di, tri, tetra, penta, hexa, etc.) indicates the number of each ligand (mono is usually omitted for a single ligand of a given type).
4. If the name of the ligand itself contains the terms mono, di, tri, eg triphenyl phosphine, then the ligand name is enclosed in parentheses and its number is given with the alternate prefixes bis, tris, tetrakis instead.
5. A Roman numeral or a zero in parentheses is used to indicate the oxidation number of the central metal atom.
6. If the complex ion is negative, the name of the metal ends in 'ate' for example, ferrate, cuprate, nickelate, cobaltate, etc.
7. If more than one ligand is present in the species, then the ligands are named in alphabetical order regardless of the number of each. For example, NH_3 (ammine) would be considered an 'a' ligand and come before Cl^- (chloro).



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

\Rightarrow Hexammine cobalt (III) chloride

- (b) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^- \Rightarrow$ Pentaamminechlorido cobalt (III) chloride
 $x + 5(0) + (-1) = +2$
 $\Rightarrow x = +3$
- (c) $\text{K}_3[\text{Fe}(\text{CN})_6]$
 $3\text{K}^+ + [\text{Fe}(\text{CN})_6]^{3-} \Rightarrow$ Potassium hexacyanido ferrate (III)
 $x + 6(-1) = -3$
 $\Rightarrow x = +3$
- (d) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
 $3\text{K}^+ + [\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} \Rightarrow$ Potassium trioxalato ferrate (III)
 $x + 3(-2) = -3$
 $\Rightarrow x = +3$
- (e) $\text{K}_2[\text{PdCl}_4]$
 $2\text{K}^+ + [\text{PdCl}_4]^{2-} \Rightarrow$ Potassium tetrachlorido palladate (II)
 $x + 4(-1) = -2$
 $\Rightarrow x = +2$
- (f) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]\text{Cl}$
 $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NH}_2\text{CH}_3)]^+ + \text{Cl}^- \Rightarrow$ Diamminechlorido methylamine platinum
 $x + 2(0) + (-1) + 0 = +1$ (II) chloride
 $\Rightarrow x = +2$
- (g) $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$
 $x + 3(0) + 3(-1) = 0 \Rightarrow$ Triammine trichlorido chromium (III)
 $\Rightarrow x = +3$
- (h) $[\text{CoBr}_2(\text{en})_2]^+$
 $x + 2(-1) + 2(0) = +1 \Rightarrow$ Dibromidobis(ethylene diamine)cobalt (III) ion
 $\Rightarrow x = +3$



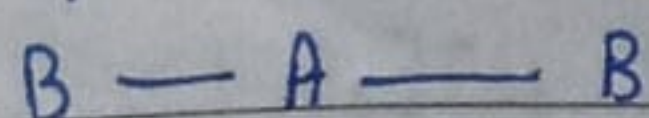
★ VALENCE BOND THEORY

- Metal and Ligand ~~they~~ form coordinate bond with each other.
- Ligand donates its e^- density to empty orbital of metal.
- Orbitals of metal overlap with each other and undergo hybridisation.

• HYBRIDISATION

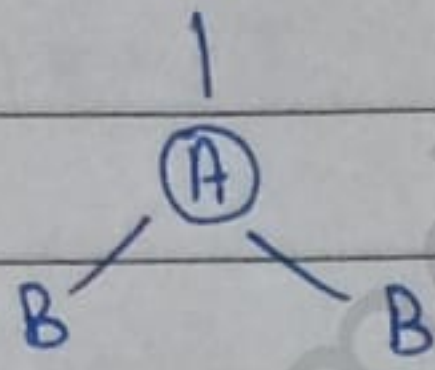
* LINEAR

sp (Coordination number = 2)

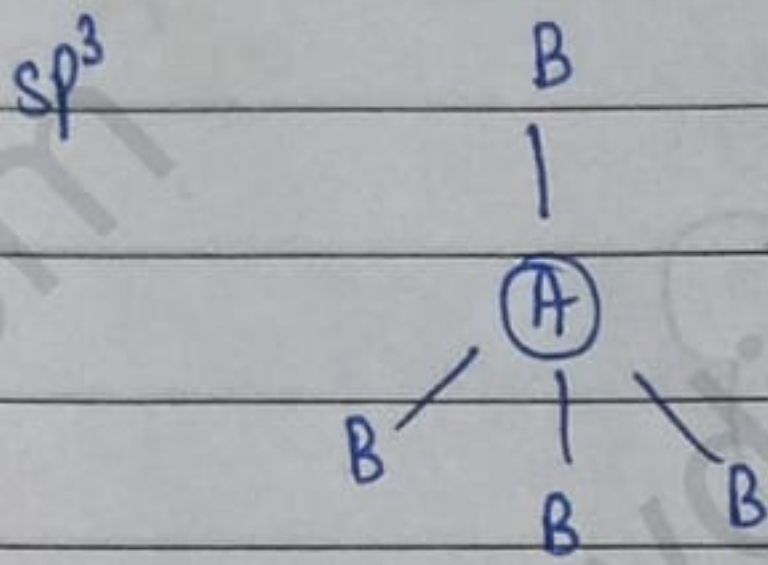


* TRIANGULAR PLANAR

sp^2 B (Coordination number = 3)

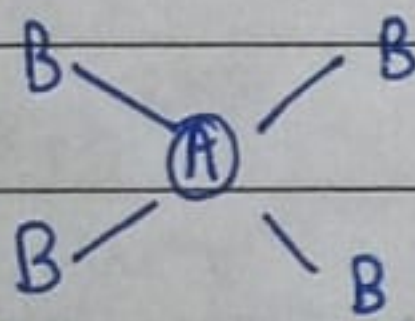


* **TETRAHEDRAL** (Coordination number = 4)



* **SQUARE PLANAR**

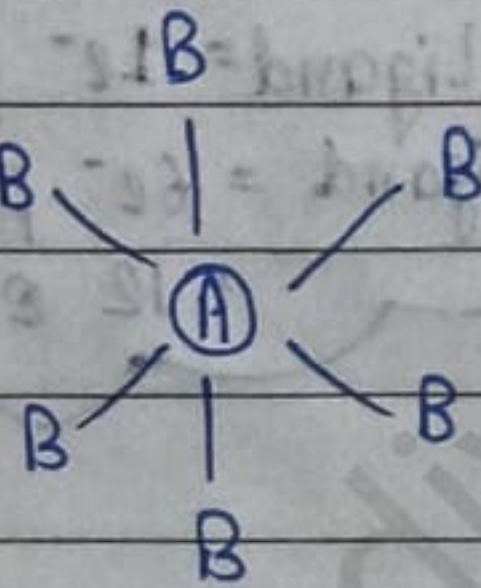
dsp^2 / sp^2d (Coordination number = 4)



* **OCTAHEDRAL** \rightarrow outer orbital complex

$d^2 sp^3 / sp^3 d^2$ (Coordination number = 6)

inner
orbital
complex



• **MAGNETISM**

PARAMAGNETIC

- (i) Strongly attracted by magnetic field
- (ii) No. of unpaired e^- s $\neq 0$

DIAMAGNETIC

- Weakly attracted by magnetic field
- No. of unpaired e^- s = 0

\rightarrow Bohr Magneton

Magnetic moment = $\sqrt{n(n+2)}$ B.M

(n = no. of unpaired e^- s)

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

$$\sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$

$$\sqrt{2(2+2)} = \sqrt{8} = 2.84 \text{ BM}$$

$$\sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$$

$$\sqrt{4(4+2)} = \sqrt{24} = 4.90 \text{ BM}$$

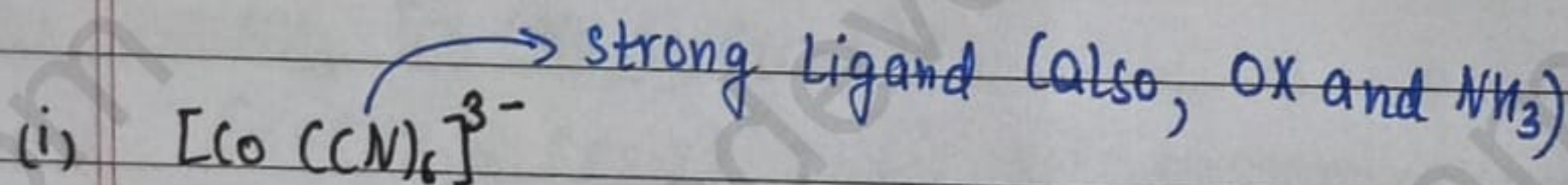
$$\sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ BM}$$

Strong Ligands \Rightarrow e^- 's pairing \checkmark

Weak Ligands \Rightarrow e^- 's pairing \times

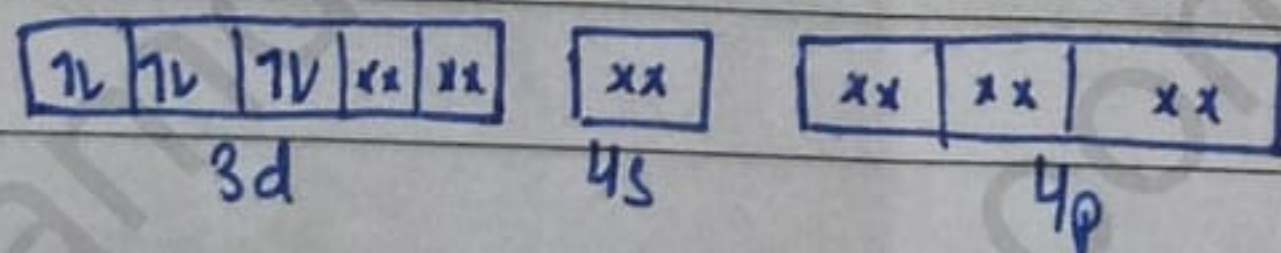
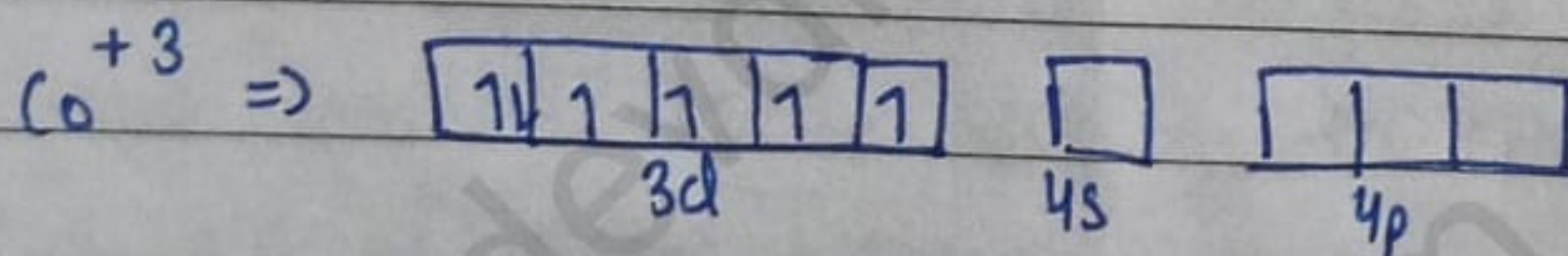
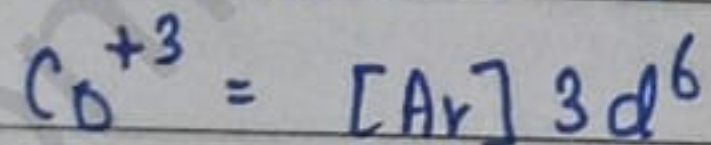
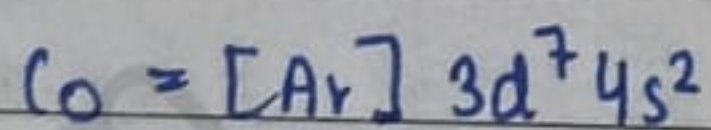
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QUESTIONS



Oxidation State (O.S) $\Rightarrow x + 6(-1) = -3$

$\Rightarrow x = +3$

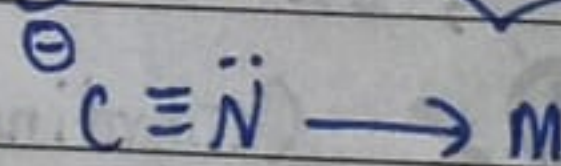
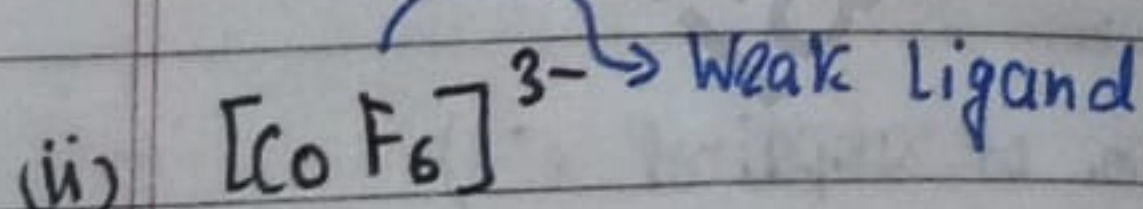


$= d^2 sp^3$

Inner orbital complex

$= n = 0$

Diamagnetic



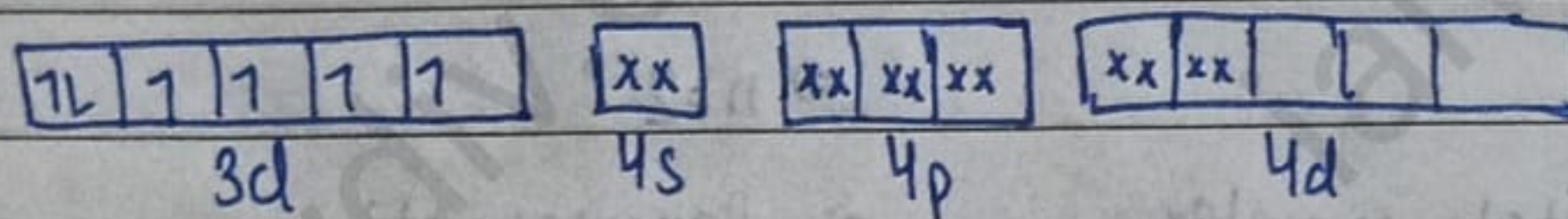
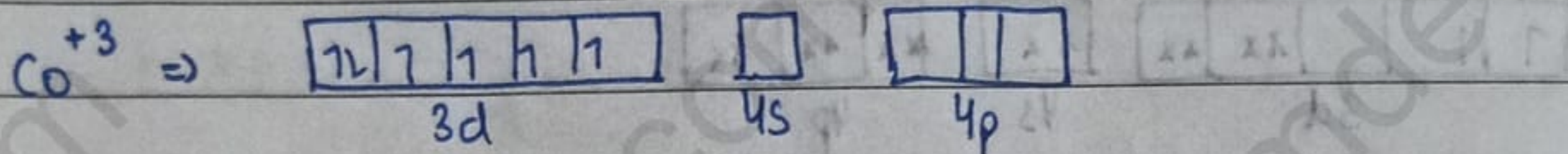
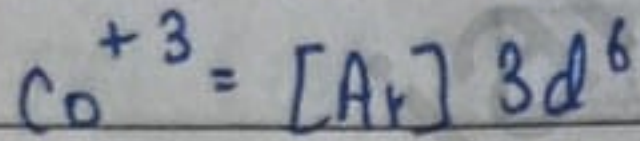
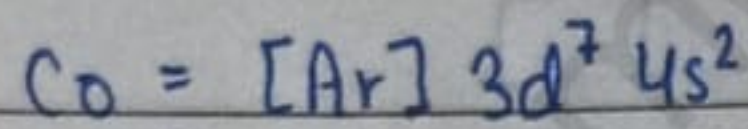
1 Ligand = 1 e^- pair

6 Ligand = 6 e^- pair

= 12 e^- 's

$$O.S \Rightarrow x + 6(-1) = -3$$

$$\Rightarrow x = +3$$



$$\Rightarrow sp^3d^2$$

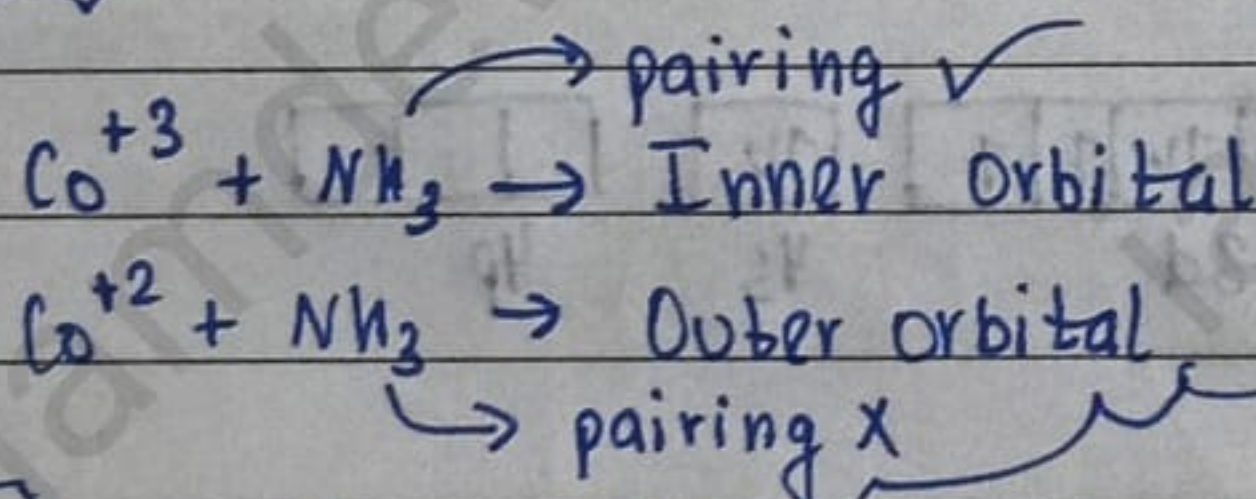
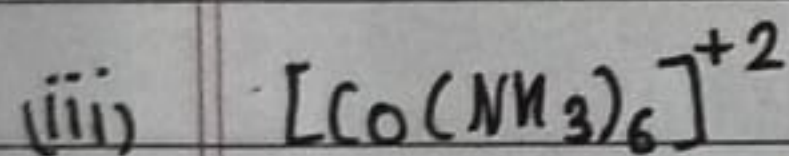
\Rightarrow Outer orbital complex

\Rightarrow Octahedral

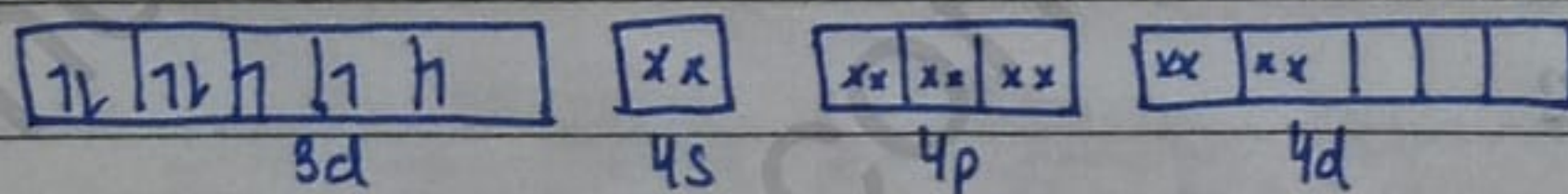
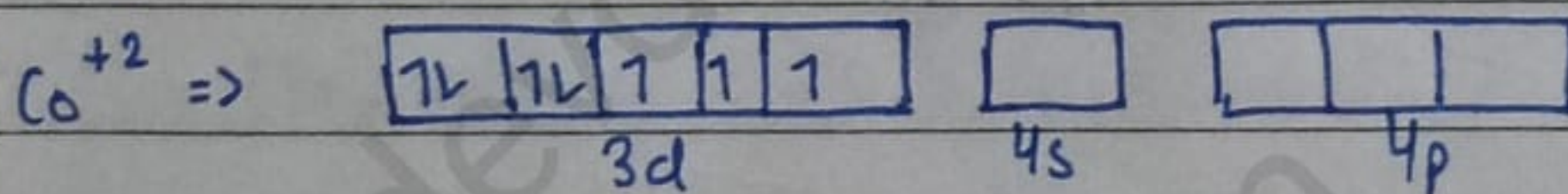
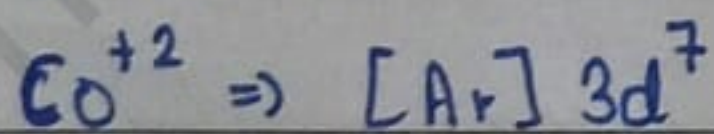
$$\Rightarrow n = 4$$

\Rightarrow Paramagnetic

$$\Rightarrow \sqrt{4(4+2)} = 4.90$$



$$O.S \Rightarrow x + 6(0) = +2$$



$$\Rightarrow sp^3d^2$$

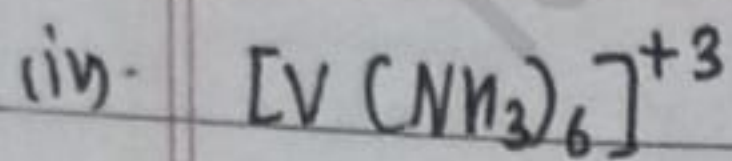
\Rightarrow Octahedral

\Rightarrow Outer orbital complex

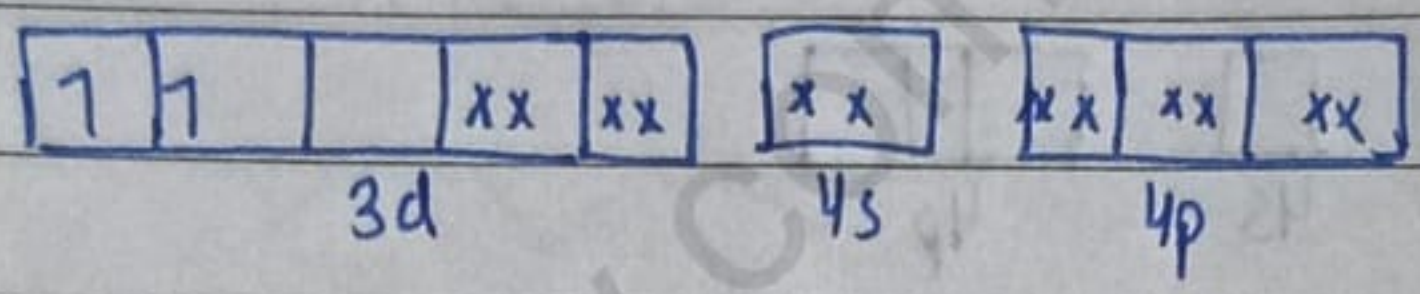
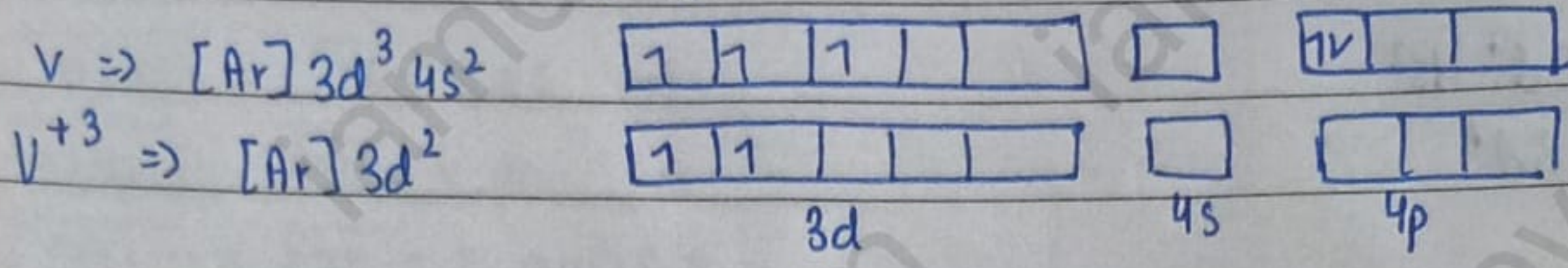
$$\Rightarrow n = 3$$

\Rightarrow Paramagnetic

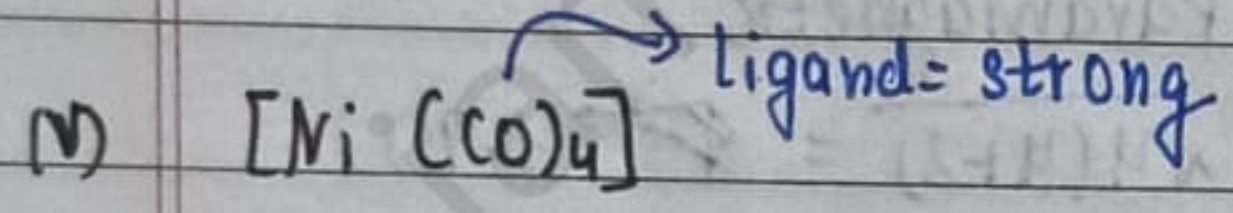
$$\Rightarrow \sqrt{3(3+5)} = 3.87 \text{ BM}$$



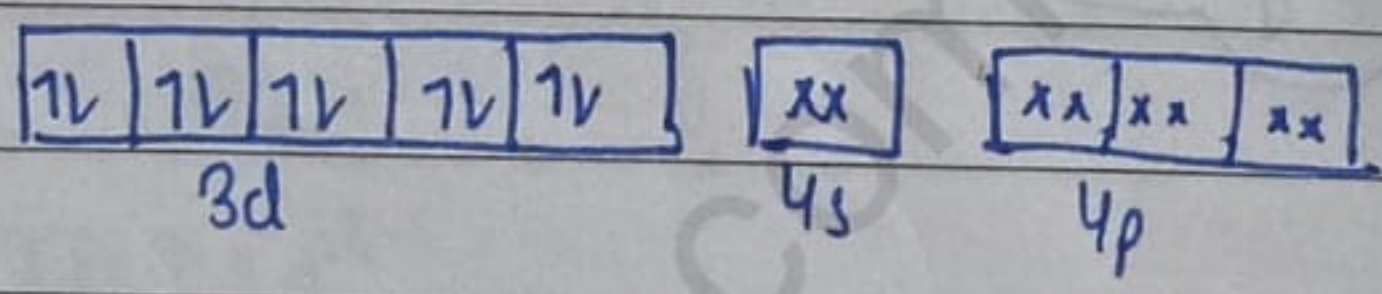
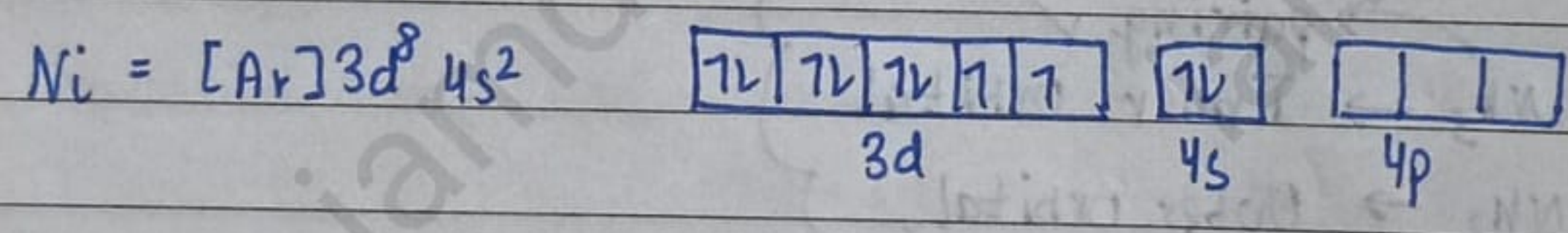
Oxidation state $\Rightarrow x + 6(0) = +3$
 $\Rightarrow x = 3$



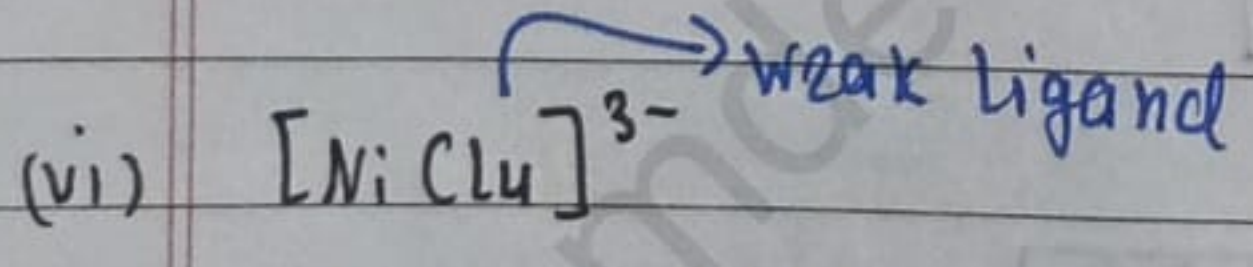
- ⇒ $d^2 sp^3$
- ⇒ $n = 2$
- ⇒ Inner orbital complex
- ⇒ Paramagnetic
- ⇒ Octahedral
- ⇒ $\sqrt{2(2+2)} = 2.84 \text{ BM}$



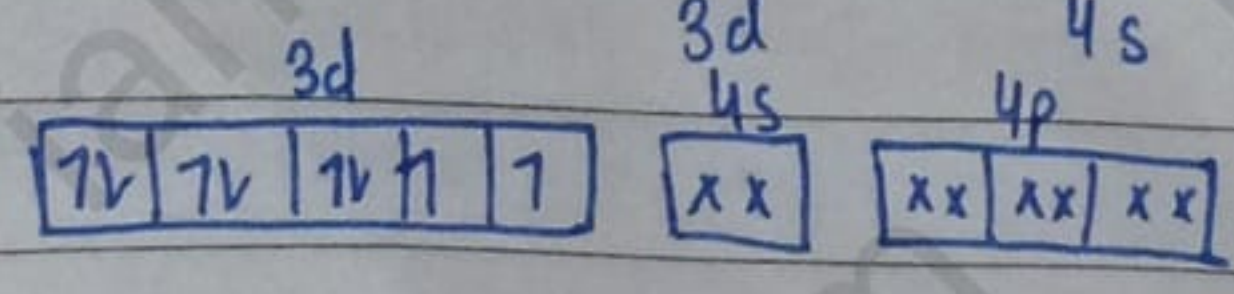
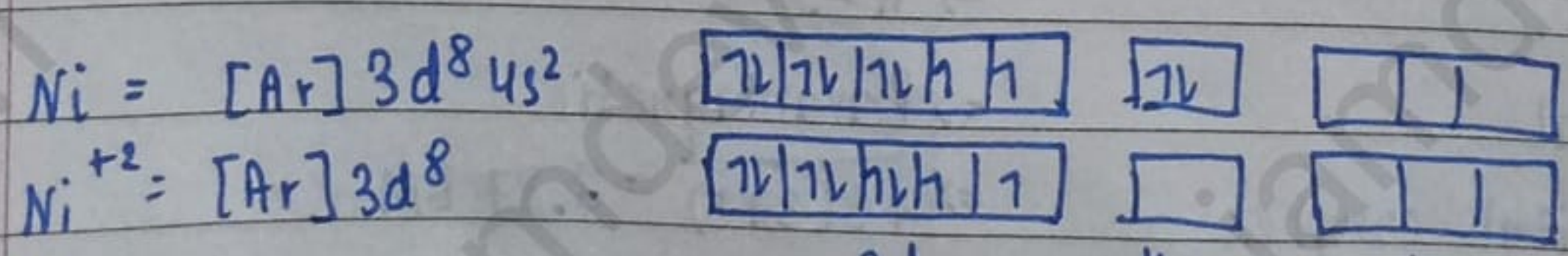
O.S $\Rightarrow x + 4(0) = 0$
 $\Rightarrow x = 0$

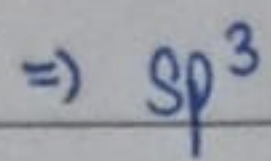


- ⇒ sp^3
- ⇒ $n = 0$
- ⇒ Tetrahedral
- ⇒ Diamagnetic



O.S $\Rightarrow x + 4(-1) = -2$
 $\Rightarrow x = +2$





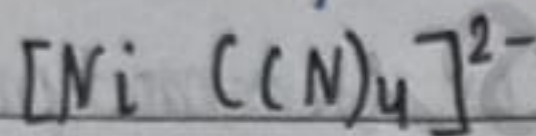
\Rightarrow Tetrahedral

$\Rightarrow n=2$

\Rightarrow Paramagnetic

$\Rightarrow \sqrt{2(2+2)} = \sqrt{8} = 2.84 \text{ BM}$

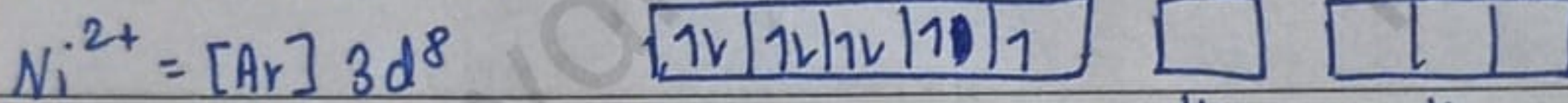
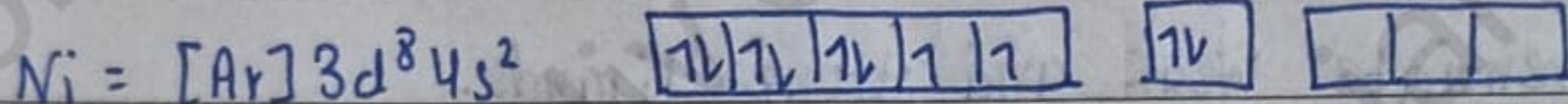
(vii)



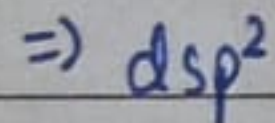
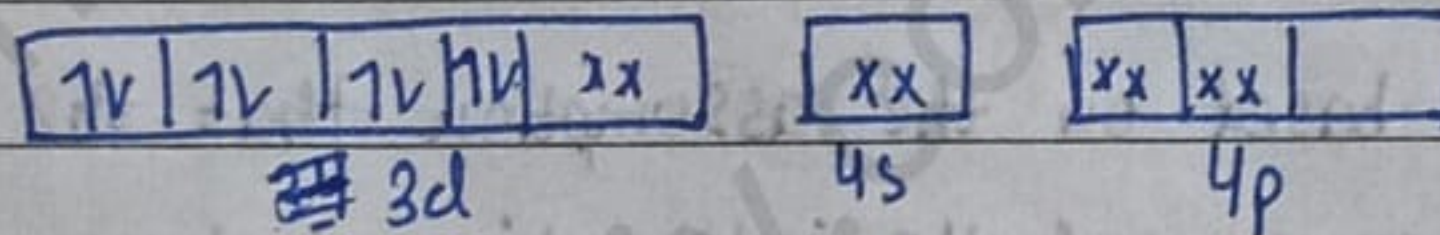
\rightarrow strong ligand

O.S $\Rightarrow x + 4(-1) = -2$

$\Rightarrow x = +2$



3d 4s 4p

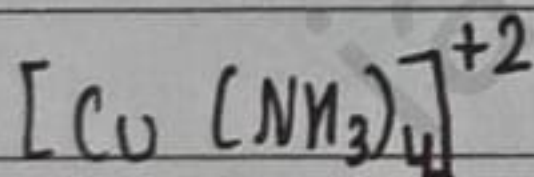


\Rightarrow Square planar

$\Rightarrow n=0$

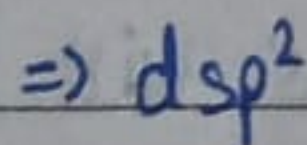
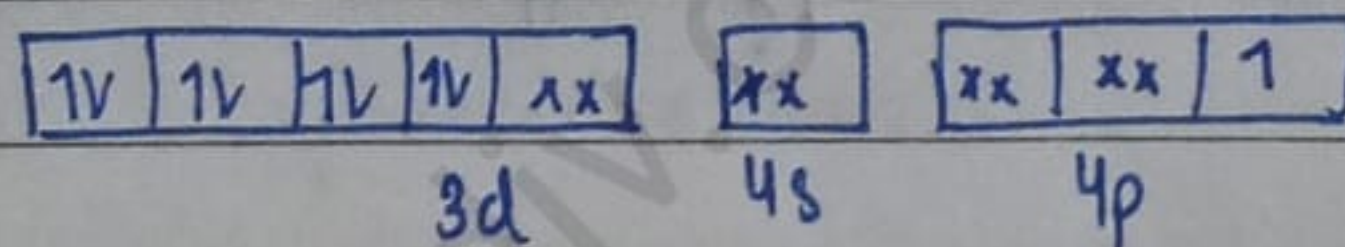
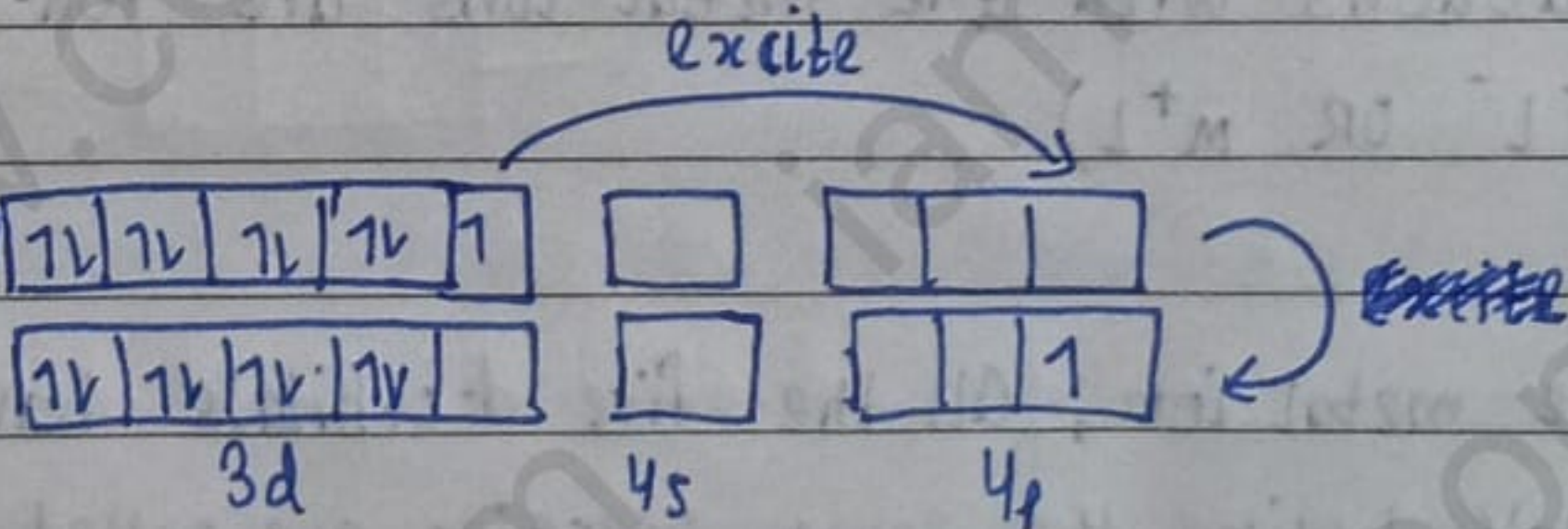
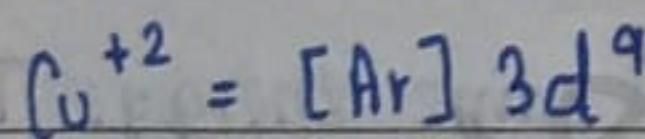
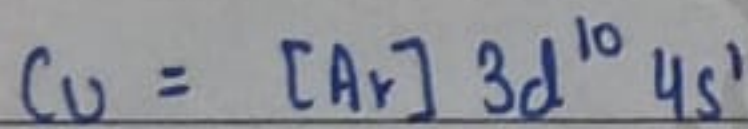
\Rightarrow Diamagnetic

(viii)



O.S $\Rightarrow x + 4(0) = +2$

$\Rightarrow x = +2$



\Rightarrow Square planar

$\Rightarrow n=1$

\Rightarrow Paramagnetic

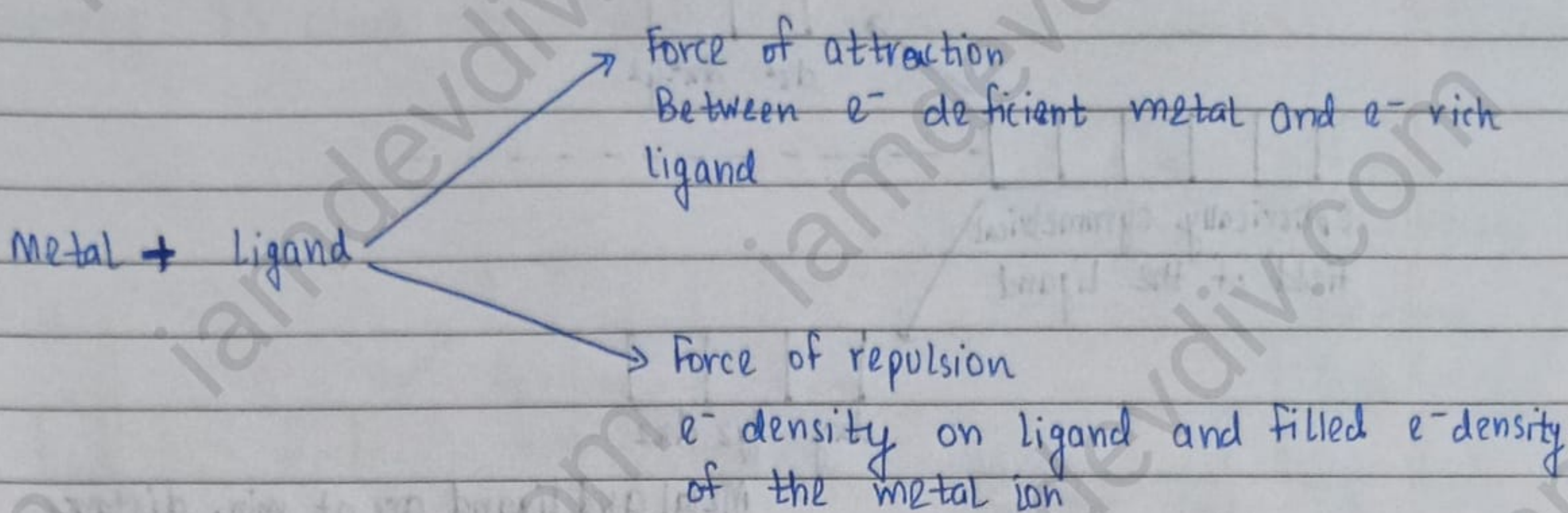
$\Rightarrow \sqrt{1(1+2)} = 1.73 \text{ BM}$

• LIMITATIONS OF VALENCE BOND THEORY

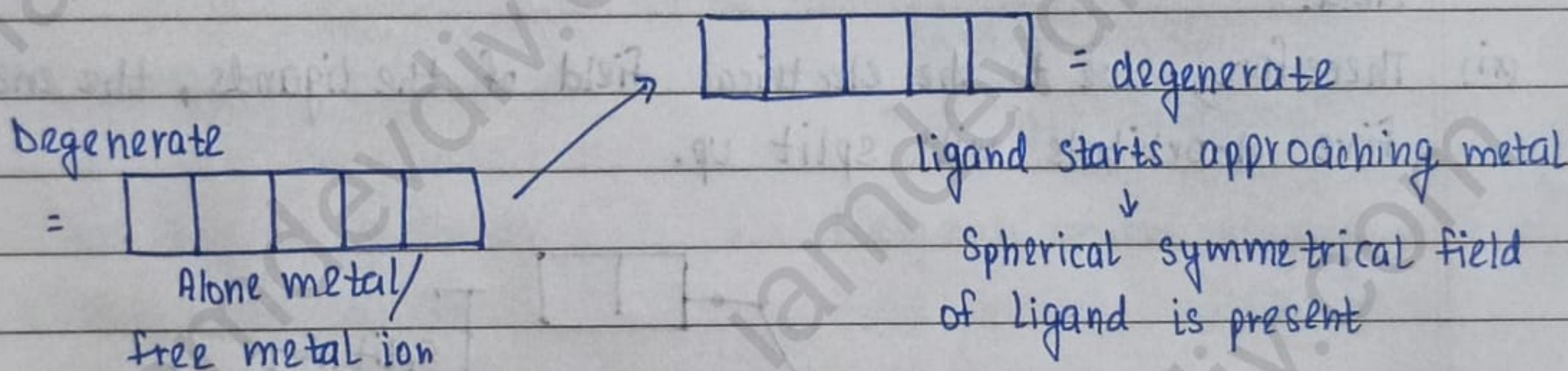
- (i) Does not give quantitative interpretation of magnetic data.
- (ii) Does not explain colour of coordination compounds.
- (iii) Does not give quantitative interpretation of kinetic or thermodynamic stabilities of coordination compounds.
- (iv) Cannot determine exact predictions regarding tetrahedral and square planar complexes in $C.N=4$
- (v) Does not differentiate weak and strong ligands.

★ CRYSTAL FIELD THEORY [FOR OCTAHEDRAL] $\rightarrow C.N=6$

- (i) Crystal field theory is based on the assumption that the metal ion and the ligands act as point charges and the interactions between them are purely electrostatic.
- (ii) In negative ligands, anions such as Cl^- , Br^- , CN^- , the interactions with metal ions are ion-ion interactions. ($M^+ L^-$)
- (iii) If the ligands are neutral molecules (such as NH_3 , H_2O , CO), the interactions with the metal ions are ion-dipole interactions. ($M^+ L^-$ OR $M^+ L$)
- (iv) In free metal ion, all the five d-orbitals have the same energy. These orbitals having the same energies are called degenerate orbitals. This means that an electron can occupy any one of these five-d orbitals with equal ease.
- (v) On the approach of the ligands, the orbital electrons will be repelled by the lone pairs (or negative charges) of the ligands. The repulsion will raise the energy of the d-orbitals.



(vi) If all the ligands approaching the central metal ion are at equal distance from each of the d-orbitals, the energy of each orbital will increase by the same amount, due to spherical field or symmetrical field of ligands.



(vii) These orbitals will still remain degenerate, but they will have higher energy than that of the free ion.

(viii) d-orbitals have different orientations and, therefore, these orbitals will experience different interactions from the ligands.

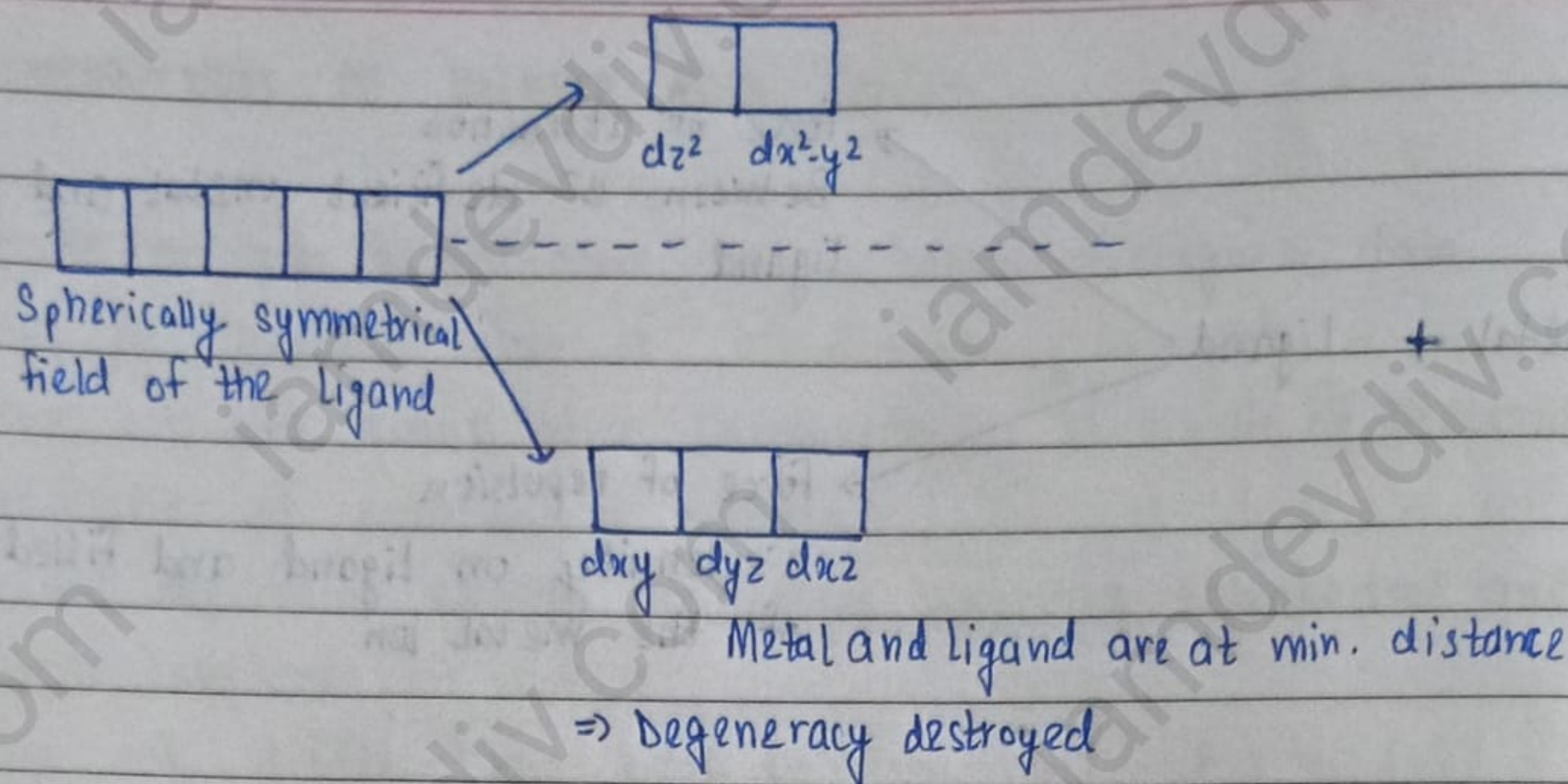
(ix) The orbitals lying in the direction of the ligands, will experience greater repulsion and their energies will be raised relative to their positions in a symmetrical field.

d_{xy}, d_{yz}, d_{zx}
(e^- density between axis)

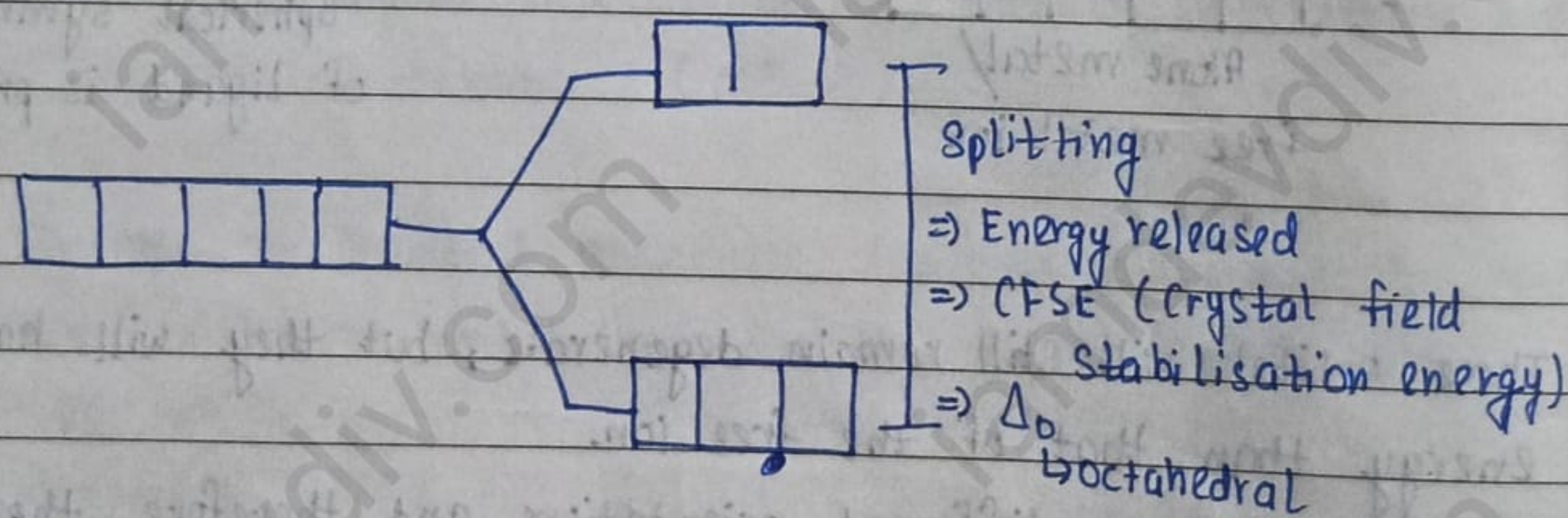
Repelled (↓) = Energy (↓)

$d_{z^2}, d_{x^2-y^2}$
(e^- density on the axis)

Repelled (↑) = Energy (↑)

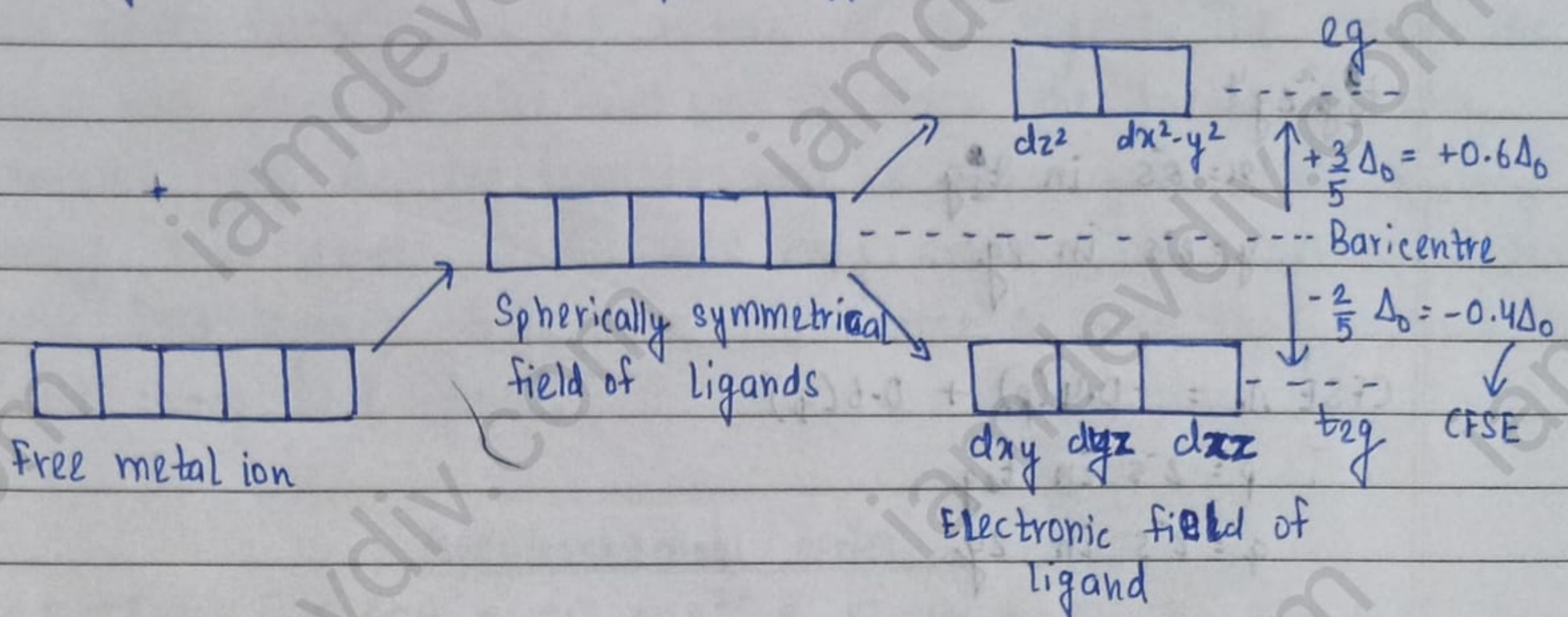


- (x) The orbitals lying away from the approach of the ligands will have lesser interactions with the negative charge of donor atoms (ligands) and therefore, their energies will be lower than they would be in a spherical field.
- (xi) Therefore, due to the electrical field of the ligands, the energies of the five d-orbitals will split up.



- (xii) This conversion of five degenerate d-orbitals of the metal ion into different sets of orbitals having different energies in the presence of electrical field of ligands is called crystal field splitting.
- (xiii) The crystal field splitting occurs in such a way that the average energy of the d-orbitals does not change.
- (xiv) This is known as barycentre rule.
- (xv) This means that the three orbitals lie at an energy that is $2/5$ below the average d-orbital energy and the two d-orbitals lie at an

Energy $\frac{3}{5}$ above the average energy.



Ligand + Metal \longrightarrow Bond

Stable complex

$$L + M = fA \uparrow$$

(Low spin complex)

First t_{2g} is completely filled and then e^- goes towards eg

Less stable complex

$$L + M = fA \downarrow$$

(High spin complex)

First each orbital of t_{2g} is singly filled then each orbital of eg singly filled after that pairing starts, first in t_{2g} then in eg

(xvi) The actual configuration adopted by the complex is decided by the relative values of CFSE and P represents the energy required for electron pairing in a single orbital.

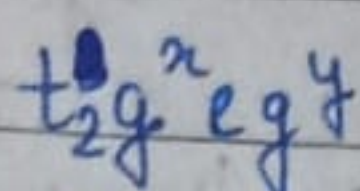
(a) If $CFSE < P$, we have weak field, the fourth electron will enter one of the eg orbitals giving the configuration, $t_{2g}^3 \cdot eg^1$. It will be high spin complex.

(b) If $CFSE > P$, we have strong field and the pairing will occur in the t_{2g} orbitals with eg orbitals remaining unoccupied giving the configuration t_{2g}^4 . It will be low spin complex.

Strong field ligand form = Low spin complex

Weak field ligand form = High spin complex

ELECTRONIC CONFIGURATION



$x = e^-s$ in t_{2g}

$y = e^-s$ in e_g

$$CFSE \Delta_o = -0.4(p) + 0.6(q)$$

$p = e^-s$ in t_{2g}

$q = e^-s$ in e_g

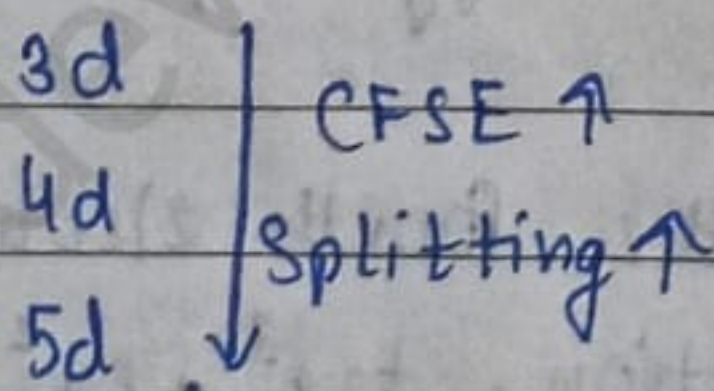
FACTORS DETERMINING THE MAGNITUDE OF THE ORBITAL SPLITTING ENERGY [CFSE]

* OXIDATION STATE OF THE METAL ION

The higher the ionic charge on the central metal ion, the greater the value of CFSE. Therefore, the metal ion with higher oxidation state causes larger CFSE, than is done by the ion with lower oxidation state.

* NATURE OF THE METAL ION

The coordination entities of second and third transition series have a greater tendency to form low spin complexes as compared to the first transition series.



* GEOMETRY OF THE COORDINATION ENTITY

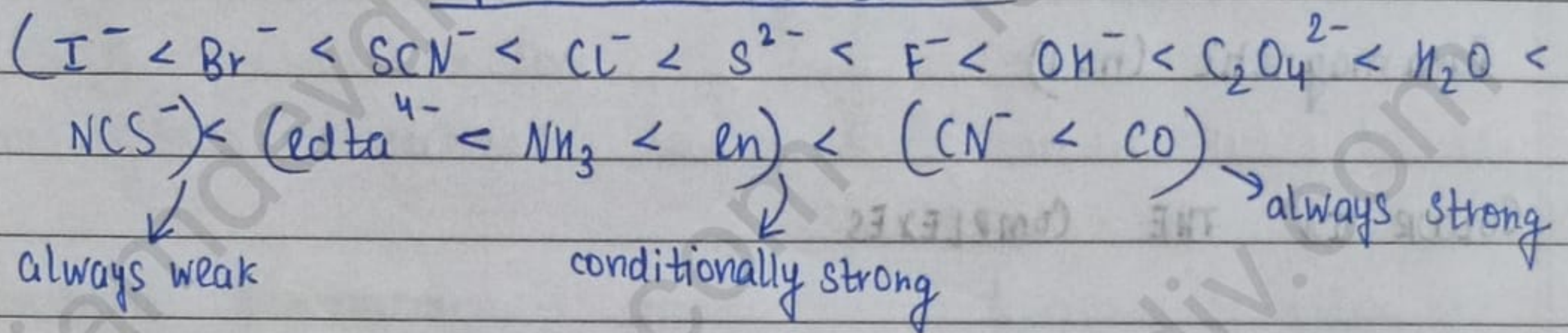
The CFSE value for tetrahedral coordination entities is about half the CFSE value for octahedral entities.

i.e. $C.N. \text{ of } M \propto CFSE \propto \Delta_o \propto \text{Splitting}$

* NATURE OF LIGAND

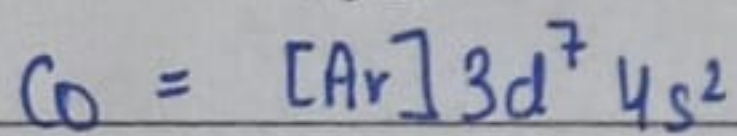
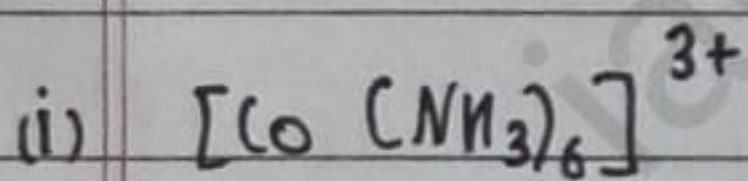
The CFSE depends upon the nature of the ligand. The greater the ease with which the ligands can approach the metal ion and interact with it, the greater will be the crystal field splitting energy. The ligands which cause only small CFSE values are called weak field ligands. While those which cause a large CFSE values are called strong field ligands.

Spectrochemical series.



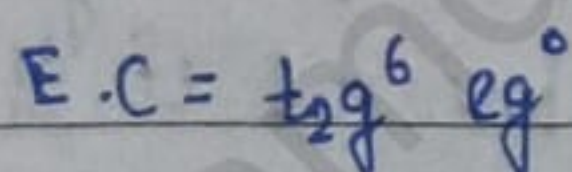
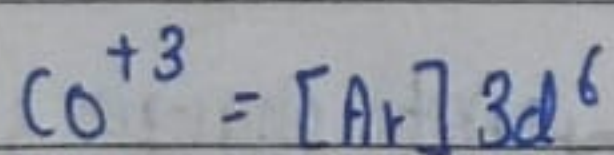
—————→ Ligand field strength ↑

• QUESTIONS



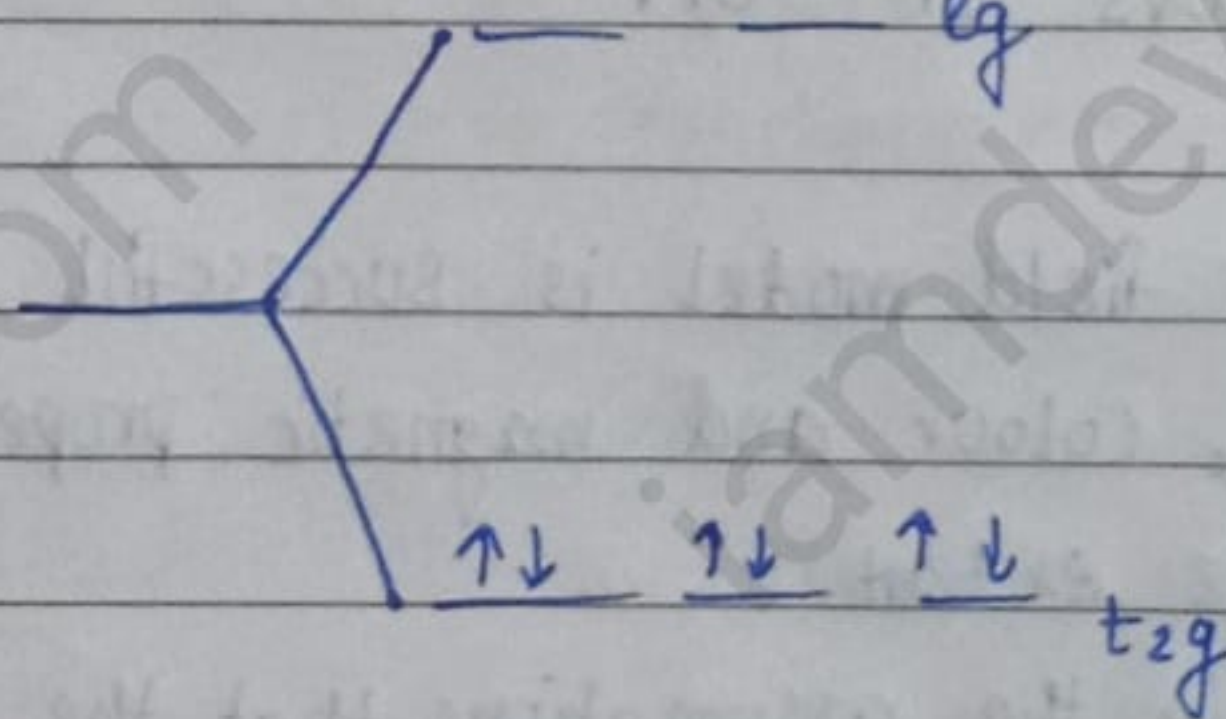
$$x + 6(0) = +3$$

$$x = +3$$

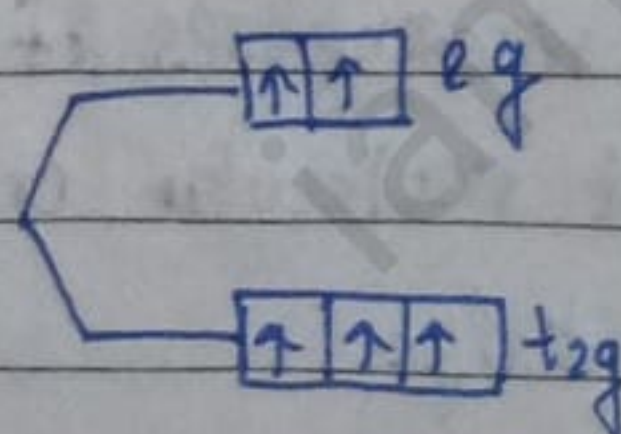
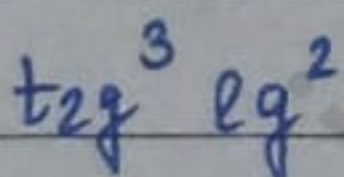
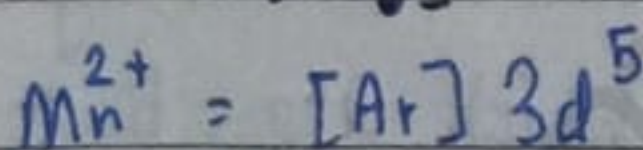
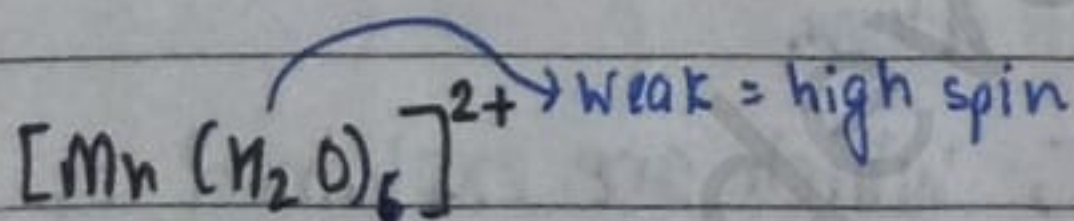


$$\text{CFSE} = -0.4(0) \Delta_0 = -2.4 \Delta_0$$

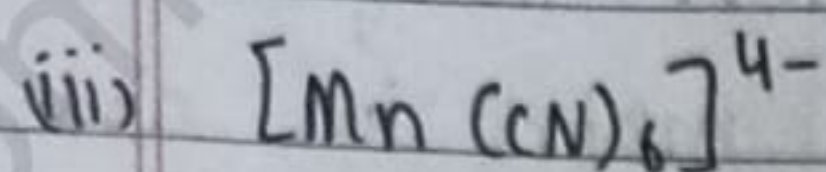
Diamagnetic ($n=0$)



(ii)

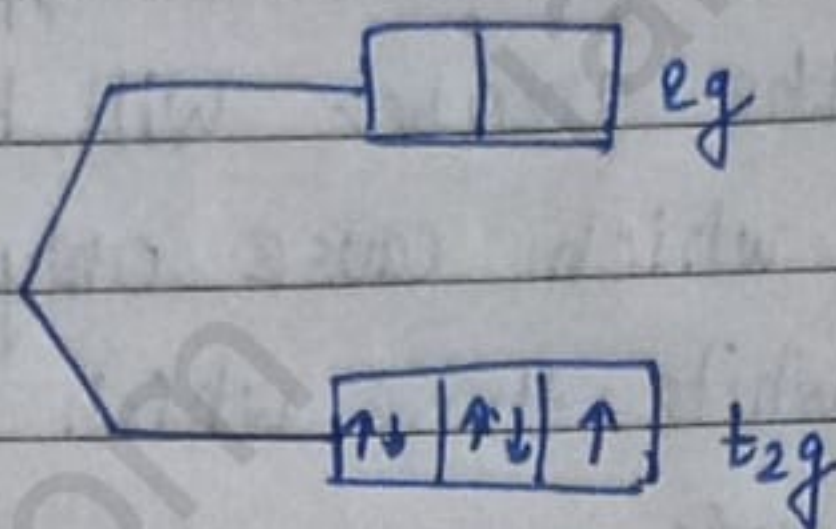
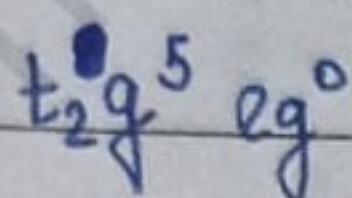
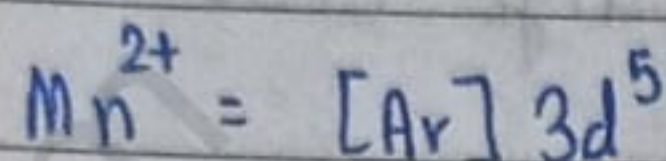


Paramagnetic ($n=5$)



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

$$\Rightarrow x = +2$$



Paramagnetic ($n=1$)

• COLOUR IN THE COMPLEXES

Coordination compounds show colour due to

- (i) d-d transitions
- (ii) Ligand to metal charge transfer
- (iii) Polarisation

• LIMITATIONS OF CFT

- (i) The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of coordination compounds to a large extent.
- (ii) However, from the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. The anionic ligands actually are found at the low end of the spectrochemical series.
- (iii) Further, it does not take into account the covalent character of bonding between the ligand and the central atom.
- (iv) These are some of the weaknesses of CFT, which are explained by ligand field theory (LFT) and molecular orbital theory which are beyond the scope of the present study.

★ ISOMERISM IN COORDINATION COMPOUNDS

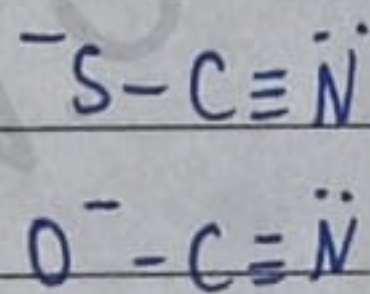
STRUCTURAL ISOMERISM	STEREO ISOMERISM
It gives different structures with respect to linkage between Metal and Ligand.	Different structures are obtained with respect to spatial arrangement of ligands.
(i) Linkage isomerism (ii) Coordination isomerism (iii) Ionisation isomerism (iv) Solvate isomerism	(i) Geometrical isomerism (ii) Optical isomerism

• STRUCTURAL ISOMERISM

* LINKAGE ISOMERISM

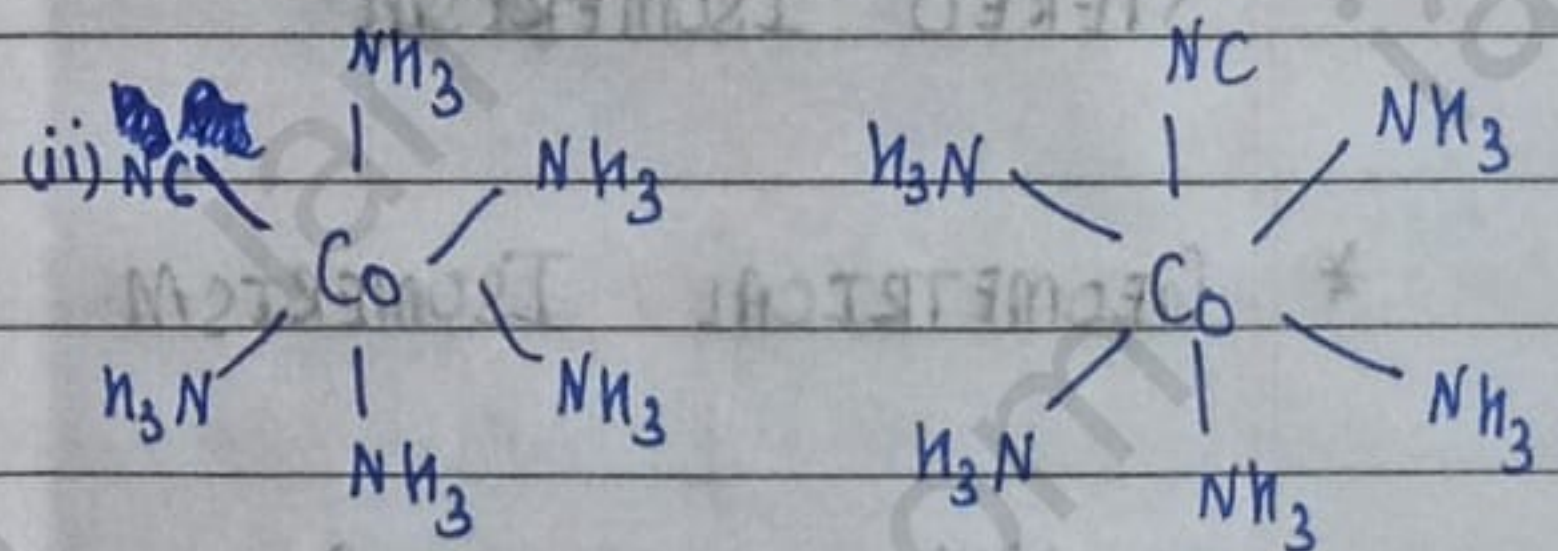
Linkage isomerism occurs in a coordination containing ambidentate ligand i.e. when more than one atom in a unidentate ligand may function as donor atom.

Ambidentate ligands: $\begin{matrix} -C \equiv \ddot{N} \\ N = O \\ \searrow O \end{matrix}$



(i) $[Co(NH_3)_5(CN)_2]Cl$

$[Co(NH_3)_5(NC)_2]Cl$



* COORDINATION ISOMERISM

(i) Coordination isomerism occurs when both positive and negative ions of a salt are complex ions.

(ii) It arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

Example: $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

* IONISATION ISOMERISM

Same chemical formula but give the test of different type of ions in aqueous solution.

Example: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$

* SOLVATE ISOMERISM

i) Isomers having same molecular formula but differ by whether or not a solvent molecule is directly bonded to the metal (i.e., as ligand in coordination sphere) or merely present as free solvent molecules in the crystal lattice (i.e., present outside the coordination sphere).

(ii) If water is involved as a solvent, isomerism is known as 'hydrate isomerism'.

Example:

$[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$	}	hydrate isomers
$[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$		
$[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$		
$[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$ X		

• STEREO ISOMERISM

* GEOMETRICAL ISOMERISM

Condition \Rightarrow Plane of symmetry

Types $\begin{cases} \rightarrow \text{cis} \\ \rightarrow \text{trans} \end{cases}$

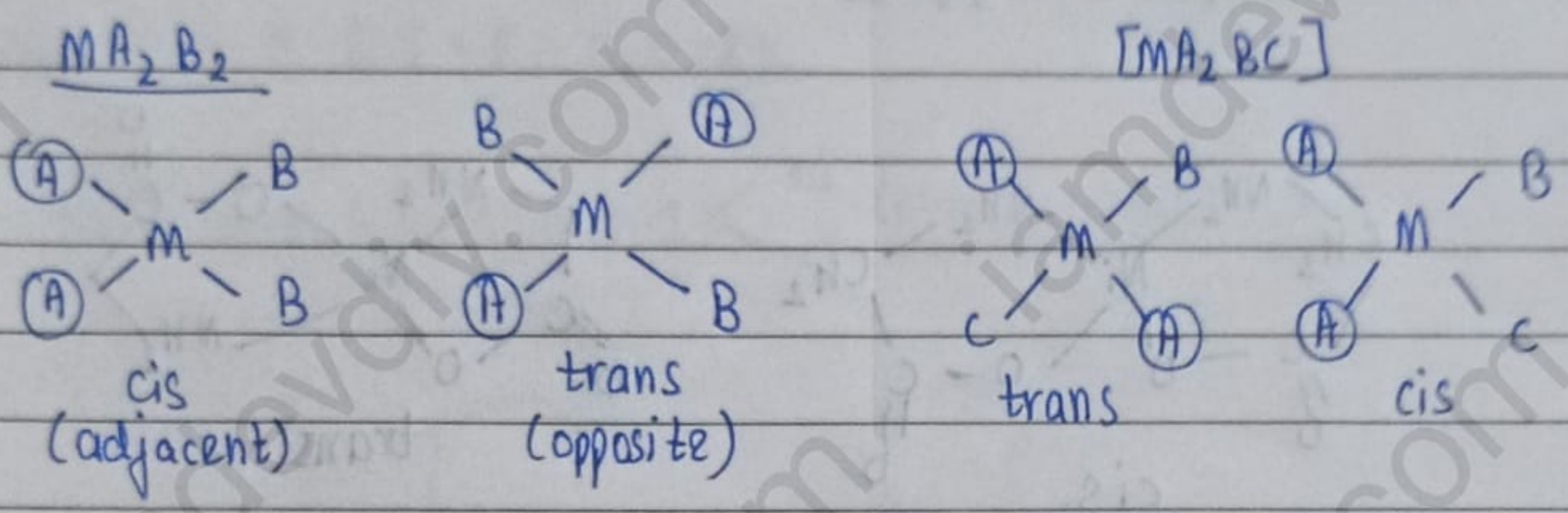
(i) Tetrahedral complexes

Plane of symmetry (X)

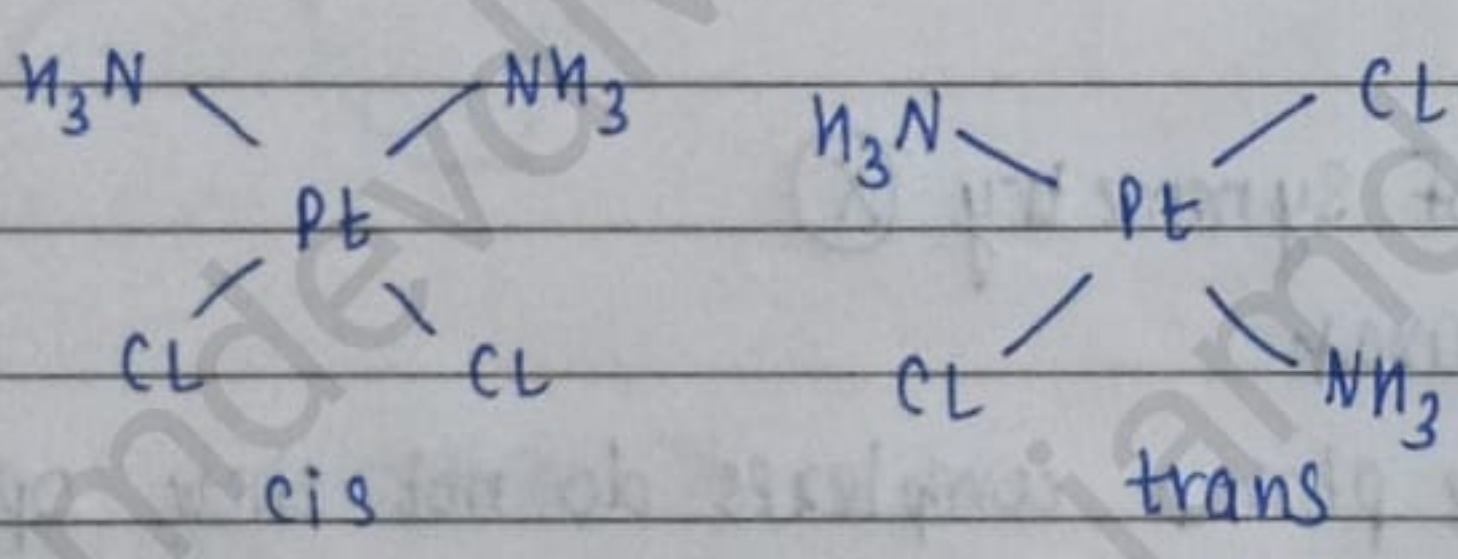
They do not show geometrical isomerism

iii) Square planar
 Plane of symmetry ✓
 They show geometrical isomerism

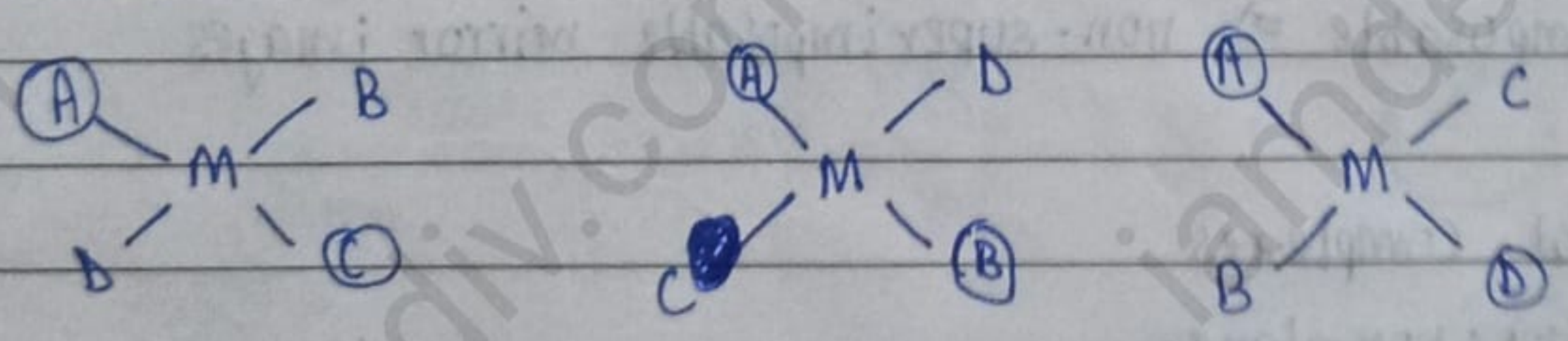
$M(AA)_2, MA_4, MA_3B$ (X)



Example: $[Pt(NH_3)_2Cl_2]$



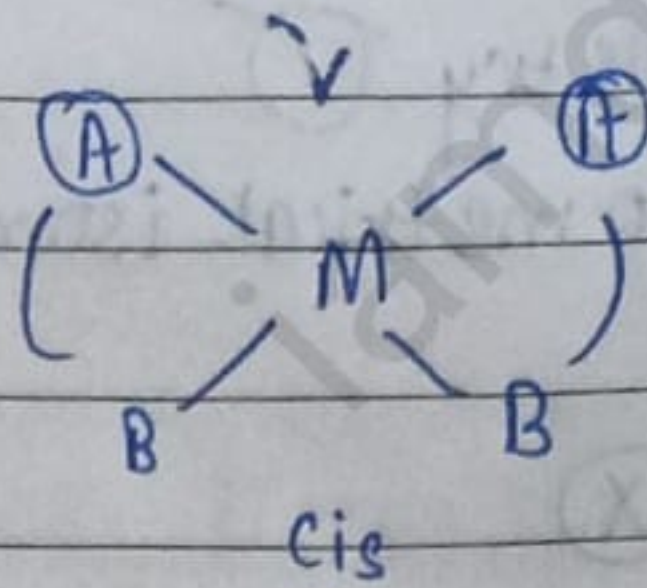
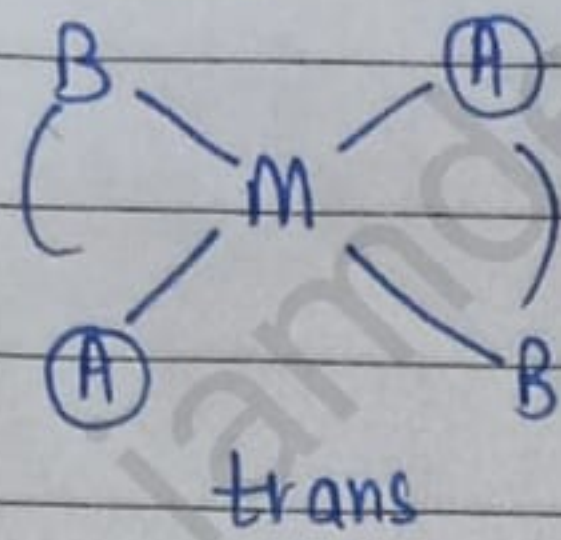
$[M(ABCD)]$



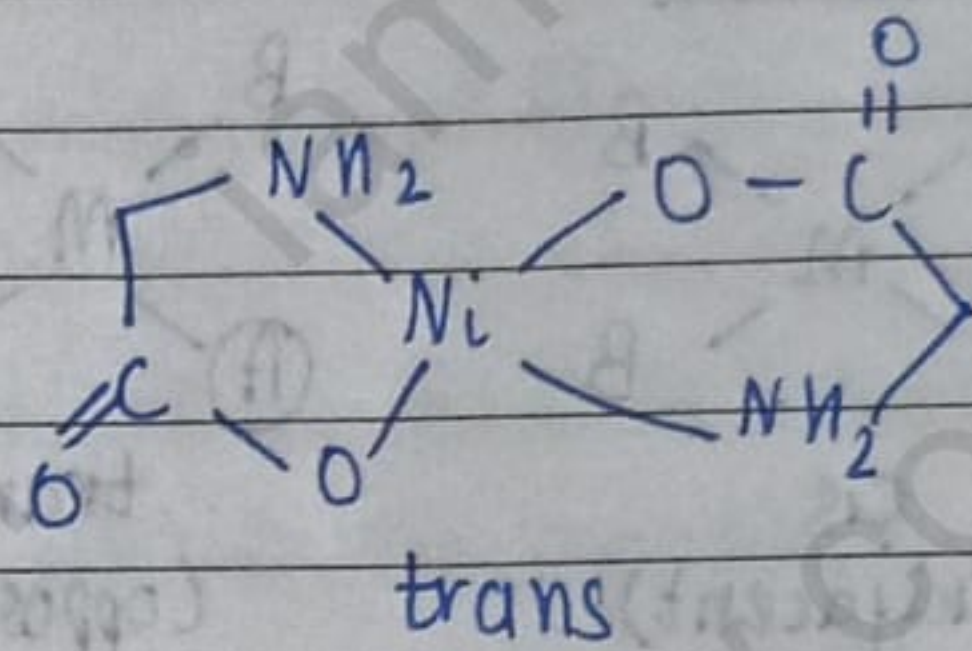
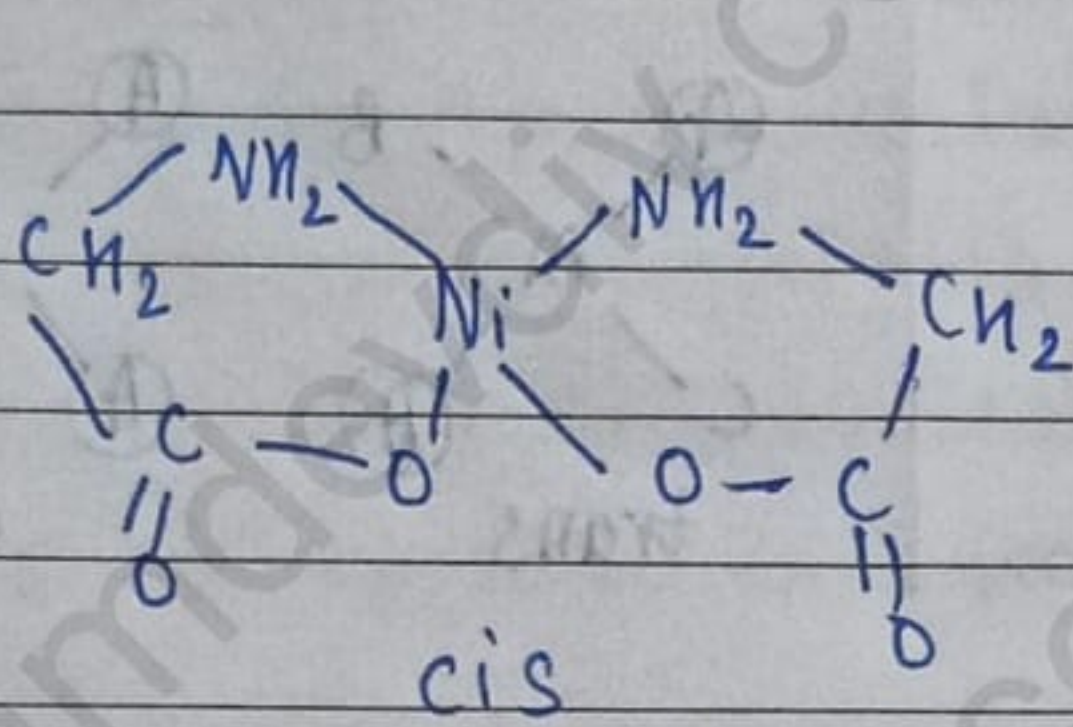
(AA) Symmetrical bidentate ligand
 $n = (AA)$

(AB) Unsymmetrical bidentate ligand
 $gly = (AB)$

$[M(AB)_2]$



Example: $[Ni(gly)_2]$



* OPTICAL ISOMERISM

Condition \Rightarrow Plane of symmetry (X)
Non-planar

(Square planar complexes do not show optical isomerism)

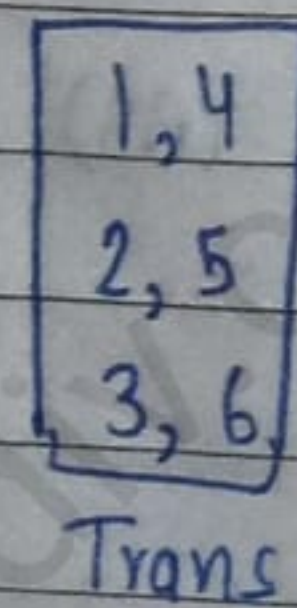
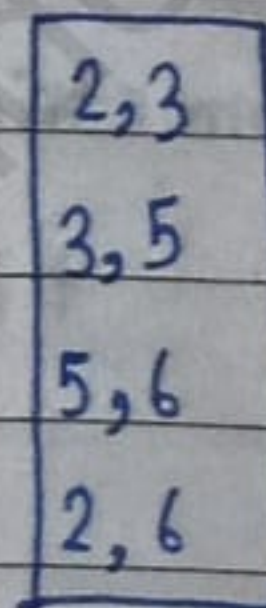
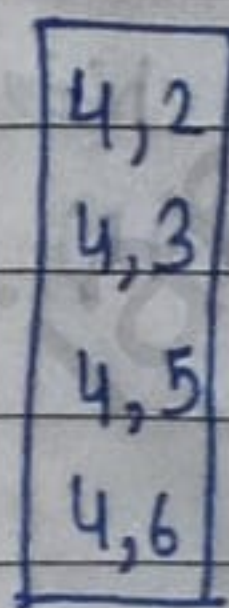
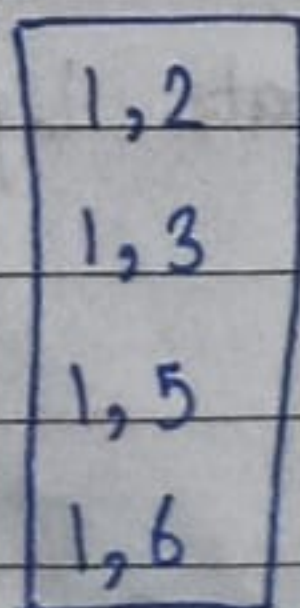
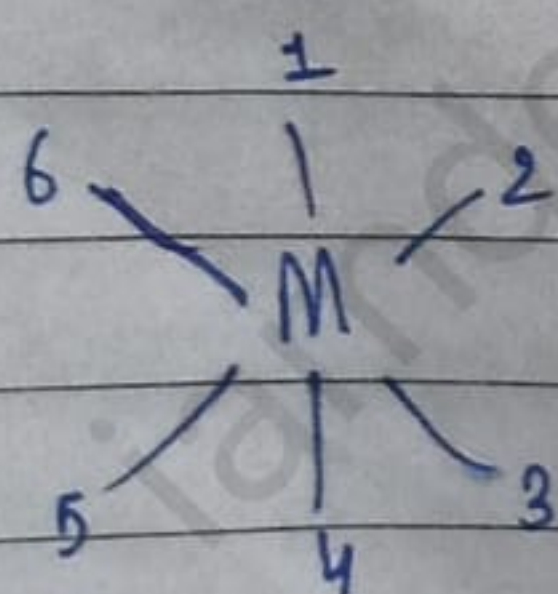
Isomers should show:

Superimposable \Rightarrow non-superimposable mirror images

(i) Tetrahedral complexes
Geometry = non-planar

Condition \Rightarrow MABCD \Rightarrow all ligands different

(ii) Octahedral complexes



Cis-forms \longrightarrow

Trans

