3.0 INTRODUCTION

- (a) The concept of coordination compounds arises from the complex formation tendency of transition elements.
- (b) These compounds play a vital role in our lives. Haemoglobin of blood and chlorophyll of plants are also coordination compounds of Fe, Mg respectively.

3.1 TYPE OF COMPOUNDS

Molecular or Addition Compounds

- (a) When two or more simple salts are chemically combined together in fixed proportion by weight the molecular or addition compounds are formed.
- (b) Some common examples are as follows. $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$ Alum
- (c) Depending upon the behavior in an aqueous solution they are of two types
 (i) Double salt or lattice compound (ii) Coordination or complex compounds.

Double Salt or Lattice Compounds

The addition compounds which lose their identity in aq. solution and get completely ionised in water.

Ex. (i) K_2SO_4 . $Al_2(SO_4)_3$.24 H_2O (Potash Alum) (ii) $FeSO_4(NH_4)_2SO_4.6H_2O$ (Mohr's salt) (iii) $KCl.MgCl_2.6H_2O$ (Carnallite)

Coordination or Complex Compounds

- (a) Those molecular or addition compounds which retain their identity in aq. solution or lose the identity of constituents are called complex salt.
- (b) Complexes retain their identity in aqueous solution. i.e., they do not dissociate into separate ion.

 $K_4[Fe(CN)_6] \xrightarrow{H_2O} 4K^+ + [Fe(CN)_6]^{-4}$

Potassium ferrocyanide Ferrocyanide ion

(c) On the basis of type of ligands complex compounds are divided as follows :

(i) Homoleptic complexes :

Complex in which all the ligands are identical is called homoleptic complex. Ex. $(Co(NH_3)_6]^{+2}$

(ii) Heteroleptic complexes :

Complex in which all the ligands are not identical is known as heteroleptic complex. **Ex.** $[Fe(en)_2Cl_2]^{+1}$

TERMINOLOGY

(a) Complex Ion

An aggregate of metal ion with anions, cation or neutral molecules is called as complex ion.

(b) Central Metal Ion

(i) The metal ion which forms complex ion in .combination with anions, cation or neutral molecules is called as **central metal ion**.

(ii) Central metal ion acts as an electron pair acceptor and forms coordinate covalent bond.

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(c) Coordination Number

The total number of coordinate covalent bonds formed by central metal ion with ligands is called as coordination number.

(d) **Coordination Sphere** – (Entity)

(i) The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere.

(ii) Coordination sphere is written inside square bracket, for example $[Co(NH_3)_6]^{3+}$

(iii) The part outside the bracket is called ionisation sphere.

(iv) The speties present in the coordination sphere are non-ionisable.

(v) The species present in the ionization sphere are ionisable.

Central metal ion Coordination sphere [Cu(NH₃)₄]SO₄ — Ionization sphere Ligand Coordination number

(e) Oxidation State

It is a number which represents the electrical charge on the central metal atom of a complex ion.

Ex. the oxidation number of Fe, Co and Ni in $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$ and Ni(CO)₄ is +2, +3 and zero respectively.

(f) Charge On the Complex Ion

It is the algebraic sum of the total charge of the ligands and central metal ion.

(g) Ligands

(i) The anions, cation or neutral molecules which combine with central metal ion to form complex ion are called as ligands.

(ii) They act as electron pair donor (Lewis bases), but strong crystal field ligands like CO, CN^- etc can accept electron pair from the metal ion, because these ligands are π^- acids.

(h) Naming of ligands

(i) a-suffix is provided to the name of anionic ligands.

(ii) ium-suffix is provided to the name of cationic ligands.

Classification of ligands :

On the basis of denticity

1. **Monodentate ligands :** Which has only one donor site

Neutral monodentate	ligands
NH ₃	ammine
H ₂ O	aqua
NO	nitrosyl
PH ₃	phosphine
PPh ₃	triphenyl phosphine
O ₂	dioxygen
N_2	dinitrogen
CH ₃ –OH	methyl alcohol

CH ₃ –NH ₂	methyl amine
NH ₂ CONH ₂	urea
NH_2NH_2	hydrazine
CH ₃ –O–CH ₃	dimethyl ether
СО	carbonyl
CS	thiocarbonyl
Cationic monodentate	ligands :
O_2^+	oxygenium
NO^+	nitrosylium or nitrosonium
\mathbf{NH}_2^+	nitronium
$H_2N-\overset{+}{NH_3}$	hydrazinium
Anionic monodentate	ligands :
F^-	Fluorido / fluoro
Cl	Chlorido / chloro
Br	bromido / bromo
Г	iodido / iodo
O ⁻²	oxido / oxo
S ⁻²	sulphido / sulpho
OH	hydroxido / hydroxo
CH ₃ -O ⁻	methoxido / methoxo
O_2^-	superoxido / superoxo
O_2^{-2}	peroxido / peroxo
N ⁻³	nitrido
N_3^-	azido
$(NH_2)^-$	amido
NH ⁻²	imido
H	hydrido

2. Bidentate ligands : Ligands which has two donor sites (simultaneously)





Ambidentate ligand : Ligands which have two different donor atoms but at the time of coordination can donate electron pair from any one donor atoms are called ambidentate ligand.

(i)	$M \leftarrow \overline{C} \equiv N$	cyanido (CN)
	$M \leftarrow N \equiv \overline{C}$	isocyanido(NC)
(ii)	M←O–C≡N	cyanato / cyanato-O
	M←N≡C−Ō	isocyanato / cyanato-N
(iii)	$M \leftarrow \overline{S} - C \equiv N$	Thiocyanato / Thiocyanato-S
	$M \leftarrow N \equiv C - \overline{S}$	Isothiocyanato / thiocyanato-N
(iv)	$M \leftarrow \overline{O} - N = O$	Nitrito/ Nitrlto-O

3.

4.

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		1	U
M-	<u> </u>	V<	2.14
		` \	
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)

Nitro / Nitrito-N

5. Flexidentate ligands : Ligands which can change their denticity.

 SO_4^{-2} , $S_2O_3^{-2}$, CO_3^{-2} , NO_3^{-} , CH_3COO^{-} etc are generally act as monodentate ligand but in some compound they can ad as bidentate ligand.

eg. (i) $(Co(NH_3)_5(SO_4)]Cl$ in this complex SO_4^{-2} act as a monodentate ligand.

(ii) $[Co(en)_2(SO_4)]Cl$ in this complex SO_4^{-2} act as a bidentate ligand.

(ii)

6. Chelating ligands : Bidentate or polydentate ligands which attach themselves with central metal ion in such a way that they form a ring, are known as chelating ligands. Number of rings = denticity -1

5 or 6 membered rings are more stable

e.g. (i) [Pt(trien)]SO₄ denticity = 4 chelating rings = 3

Na₂Fe(OH)(EDTA)] denticity of EDTA = 5 chelating rings = 4

On the basis of nature of bonding between central metal atom and ligand.

(i) Normal or classical ligands :

Ligand which only donate electron pair to central metal ion & form coordinate (σ)bond e.g. OH⁻, NH₂⁻, Cl⁻,N⁻³, O⁻² etc.

(ii) Non classical or π -acid or π -acceptor ligands :

Ligand which donate electron pair to central metal ion & form coordinate σ bond but simultaneously they accept electron pair from central metal ion through back bonding or synergic bonding.

 $CO, NO^+, CN^-, R_3P, R_3As$ etc.

The electronic configuration of CO molecule shows that it has lone pair of electrons on carbon and oxygen atom each. Carbon atom can donate its electron pair of a transition metal atom (M), forming $OC \rightarrow M$ coordinate bond.

Since the metal atom in metal carbonyl is in zero oxidation state, the formation of M \leftarrow CO σ bond accumulates a negative charge on the metal atom. The accumulation of negative charge on the metal atom can be counter balanced by transferring some negative charge from the metal atom to CO molecule (ligand). This transfer can be done by making a M \rightarrow CO π . bond by the overlap between an appropriate filled orbital on the metal atom and empty π_y^* or π_z^* molecular orbital on CO molecule. This type of bonding between M and CO is called synergic bonding.



[Schematic of orbital overlaps in metal carbonyls] Conclusion of synergic bonding : due to synergic bonding (a) M–C bond strength increases; M–C bond length decreases; because double bond character increases

(b) C–O bond strength decreases; C–O bond length increases; because bond order of C–O decreases, electron density in ABMO of CO increases.

π -donor and π -acceptor ligands

ligands which donate n electron to central metal ion & also accept electron density from central metal ion through, synergic bonding,

(i) $H_2C=CH_2$ (η^2 - ethylene) : it Is a 2π electron donor

(ii) $(\eta^6 \text{-benzene})$: it is a 6π electron donor

(iii) $// [C_5H_5]^-$ (η^5 -cyclopentadienyl) : it is a 6π electron donor

For example

(a)
$$[Cr(\eta^6 - C_6H_6)_2]$$

(b) [Fe($\eta^5 - C_5 H_5$)₂]

sandwich compound ferrocene (sandwich compound)

(c) K[PtCl₃(η^2 -C₂H₄)] (Zeise's salt)

The bonding of alkenes to a transition metal to form complexes has two components. First, the π -electron density of the alkene overlaps with a σ -type vacant. orbital. of the metal atom. Second is the back bonding formed by the flow of electron density from a filled d-orbital on the metal into the vacant π^* -antibonding molecular orbital of the carbon atom as shown below:



BEGINNER'S BOX-1

- 1. Which of the following is true about metal-EDT A complex (if it is a 3d metal)
 - (1) The ratio of moles of metal & EDTA In complex is 1:6
 - (2) The1 ratio of moles of metal & EDTA in complex is 6:1
 - (3) The ratio of moles of metal & EDTA in complex is. 1: 1
 - (4) 3d metal ion cannot bonded with EDTA

- 2. CN⁻ is ambidentate ligand because (1) it has multiple bonds (3) it form chelate
- 3. Highest C–O bond length will be in (1) $[Mn(CO)_6]^+$ (3) $[V(CO)_6]$
- 4. The strongest -CO bond is present in (1) $[Cr(CO)_6]^+$ (3) $[V(CO)_6]$
- 5. Match the following

Ligand

- ethylenediamine (A)
- **(B)** hydrazine
- (C) dimethylgyloximato(dmg⁻)
- (D) dien
- [Ans. $A \rightarrow P, B \rightarrow R, C \rightarrow P, D \rightarrow Q$]
- 6. Match the following

Complex

- (A) $[Ni(dmg)_2]$ (P)
- $\left[Ca(EDTA) \right]^{2}$ **(B)** (Q)
- $[Fe(en)_3)Cl_3$ (C) (R)
- $(Ag(S_2P_3)_2)^{2}$ (D) **(S)**
- (T) [Ans. $A \rightarrow P, Q, T; B \rightarrow S; C \rightarrow S; D \rightarrow R$]
- The oxidation state of metal in (Iron in $[Fe(CN)_6]^{3-}$ is 7. (3) - 3(1) - 6(2) + 3
- Coordination number of Co in $[CoF_6]^{-3}$ is 8. (1)4(2)5(3) 6
- 9. The neutral ligand is (1) Chlorido (2) Hydroxide
- 10. H₂N-CH₂-CH₂-NH₂ serves as : (1) Monodentate ligand (2) Chelating ligand (3) Bridging'ligand (4) Cationic ligand

3.2 **IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS**

The present system of nomenclature derived from the suggestions of Alfred Werner and recommended by the Inorganic Nomenclature Committee of the I.U.P.A.C. The main rules of naming of complexes are-

(3)Ammine

(a) Like simple salts, the	positive part of the coordination compound is named first.
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- (2) carbon as a negative charge
- (4) both C & N tan donate lone pair

(2) $[Cr(CO)_6]$

- (4) Same in all
- (2) $[Fe(CO)_5]$
- (4) All have equal strength

Property

- bidentate (P)
- (\mathbf{O}) tridentate
- form hydrazeniurn ion on protonation (\mathbf{R})
- can form dimer **(S)**

Property

- number of 5 member rings = 2
- number of 6 member rings = 2
- coordination number of central metal ion = 2
- coordination number of central metal ion = 6

(4) + 6

(4) 8

(4) Oxalato

intramolecular H-bonding

Ex. $K_4[Fe(CN)_6]$ the naming of this complex starts with potassium.

(b) Then after ligands of the coordination sphere are to be named.

(c) The ligands can be neutral, anionic or cationic.

(i) The neutral ligands are named as the molecule

Ex. C₅H₅N (pyridine), (C₆H₅)₃P (Triphenyl phosphine),

H2N-CH2-CH2-NH2 (ethylene diamine)

The neutral ligands which are not named as the molecule are

CO (carbonyl), NO (nitrosyl), H₂O (Aqua), NH₃ (ammine)

(ii) Anionic ligands ending with 'ide' are named by replacing the 'ide' with suffix 'O'.

Symbol Name as ligand		ol Name as ligand Symbol		
Cl-	Chloro/Chlorido	N ³⁻	Nitrido	
Br	Bromo/Bromido	O2 ²⁻	Peroxo, O ₂ superoxo	
CN-	Cyano	O ₂ H ⁻	Perhydroxo	
O ²⁻	Охо	✓ S ² -	Sulphido	
OH-	Hydroxo	• NH ₂ •	Amido	
H-	Hydrido	NH ²⁻	imido	

Ligands whose names end in 'ite' or 'ate' become 'ito' i.e., by replacing It~ ending 'e' with 'o' as follows.

CO_{3}^{2-}	Carbonate	SO_{3}^{2-}	Sulphito		
$C_2 O_4^{2-}$	Oxalato (Ox) ^{2–}	CH ₃ COO ⁻	Acetato		
SO4 2-	Sulphato	NO ₂ ⁻	(bonded through	n oxygen) nitrite	[Nitrito - N]
NO_3^-	Nitrato		(bonded through	n nitrogen) nitro	\rightarrow [Nitrito – O]
	e service <u>service</u> e service production producti production production production produ				

 $S_2O_3^{-2}$

Thiosulphato

(iii) Positive ligands naming ends in 'ium'

 $NH_2 - NH_3^+$ (Hydrazinium}, NO_2^+ (nitronium); NO^+ (nitrosonium)

(d) If ligands are present more than once, then their repetation is indicated by prefixes like di, tri, tetra etc. However, when the name of the ligand includes a number.

Ex. dipyridyl, ethylene diamine, then bis, tris, tetrakis are used in place of di, tri, tetra, etc (e) In case of chelationg ligands or ligands having di, tri, tetra, etc. in their name the prefixes bis, tris, tetrakis are used before ligands placed in paranthesis.



Bis(ethylenediamine) cobalt(III)- μ -amido- μ -hydroxobis(ethylenediamine) cobalt (III) sulphate (f) When more than one type of ligand is present in the complex, then the ligands are named in the alphabetical order.

(g) After naming of ligands the central metal ion is to be named followed by its oxidation state in Roman numbers in brackets. (as per IUPAC)

If the complex is neutral or provides a cationic complex ion, then the central metal ion is to be named as it is.

If the complex provides anionic complex ion then the name of central metal ion ends in 'ate' (h) After the naming of central metal ion, anion which is in the outer sphere is to be named. The naming of some of the complexes is done as follows- (as per IUPAC)

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IUPAC Name
Potassium hexacyanidoferrate (II)
Potassium hexachloridoplatinate (IV)
Hexamminecobalt (III) chloride
Tetraaquadichlorochromium (III) chloride
Diammine tetrachloroplatinum (IV)
Triamminetrichlorocobalt (III)
Potassium hexanitrocobaltate (III)
Sodium pentacyanonitrosoniumferrate (II)
Tetrachloronickelate (II) ion
Pentamminechlororuthenium (III) ion
Tris (ethylenediamine) iron (III) chloride
Bis (glycinato) nickel (II)

(i) If coordination compound contains 2 coordination spheres then both spheres should have opposite charges. Name of cationic part written first following the name of anionic sphere according to the general IUPAC rule.

Ex. [Fe(NH₃)₆]₃[Co(NO₂)₆]₂ [Hexa amine iron (II) hexa nitro cobaltate(III)]

3.3 BONDING IN COORDINATION COMPOUNDS

(A) Werner's Theory

This was postulated by **Alfred Werner** in 1893. The postulates of Werner's theory of complexes are –

 $\operatorname{Fe}(\operatorname{NH}_{3})_{6}\operatorname{Cl}_{3} \xrightarrow{\operatorname{H}_{2}\operatorname{O}} [\operatorname{Fe}(\operatorname{NH}_{3})_{6}]^{+3} + 3\operatorname{Cl}^{-}$

 $Fe(NH_3)_5Cl_3 \xrightarrow{H_2O} [Fe(NH_3)_5Cl]^{+2} + 2Cl^{-1}$

Every metal forming a complex exhibits two types of valencies - Primary valency and Secondary Valency. In the above complexes chlorine act as primary valency and NH_3 acts as secondary valency.

According to Werner central metal have 2 types of valencies :

Primary valencies	Secondary valencies	
(i) Equal to oxidation state of CMA	(i) Equal to coordination number of CMA	
(ii) Satisfied by anions	(ii) satisfied by ligands	
(iii) Non directional	(iii) Directional	
(iv) Ionisable	(iv) Non-ionisable	
(v) not helpful geometry predictions	(v) helpful in geometry predictions	

Shapes : According to Werner all secondary valencies has shapes arrangement according to coordination number.

Experimental evidence of werner's theory

(a) Precipitation of primary valencies on the addition of a suitable reagent.

Ex. Fe(NH₃)₆Cl₃ forms 3 moles of AgCl in the form of precipitate on addition of AgNO₃ solution. This indicates that the complex ionises as Fe(NH₃)₆Cl₃ $\xrightarrow{\text{H}_2\text{O}}$ (Fe(NH₃)₆]⁺³ + 3Cl⁻

(b) Electrical conductance of complexes : More the number of ions provided greater is the electrical conductance of the complex in aqueous medium. Electrical conductivity \propto number of Ions.

Ex. The electrical conductance of aqueous $[Fe(NH_3)_6]Cl_3$ is greater than that of aqueous solution of $[Fe(NH_3)_5Cl]Cl_2$.

$[Fe(NH_3)Cl]Cl_2 \longrightarrow$	$[Fe(NH_3)_5Cl]^+$	$^{2} + 2Cl^{-}$ Total	number of i	ons = 3
$_{\rm L}Fe(NH_3)CI_{\rm I}CI_2 \longrightarrow$	$[Fe(NH_3)_5CI]$	-+2CI Total	number of 1	ons = z

Complex	Modern formula	No. of Cl ⁻ lons precipitated	Total number of lons
PtCl ₄ ·6NH ₃	[Pt(NH ₃) ₆]Cl ₄	4	5
$PtCl_4 \cdot 5NH_3$	[Pt(NH ₃) ₅ Cl]Cl ₃	3	4
PtCl ₄ ·4NH ₃	[Pt(NH ₃] ₄ Cl ₂]Cl ₂	2	3
PtCl ₄ ·3NH ₃	[Pt(NH ₃) ₃ Cl ₃]Cl	1	2
$PtCl_4 \cdot 2NH_3$	[Pt(NH ₃) ₂ Cl ₄]	- 3 0 4 Alar	0 (non-electrolyte)

Werner's Representation of complex

(i) Fe(NH₃)Cl₃ → [Fe(NH₃)₆]Cl₃
 Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.



(ii) $Fe(NH_3)_5Cl_3 \longrightarrow [Fe(NH_3)_5Cl]Cl_2$

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In this complex 'a" groups act as primary valencies and one of the 'Cl' acts as secondary valency also. Thus Werner's representation of this complex-



(iii) $Fe(NH_3)_4Cl_3 \longrightarrow [Fe(NH_3)_4Cl_2]Cl$

In this complex 'Cl' Groups act as primary valency and two of the 'Cl' group act as secondary valencies also. Thus Werner's representation of this complex-



E.A.N. = (No. of electron in the metal ion) + (No. of electrons gained from the ligands)

OR

Atomic number – (Oxidation state) + $(2 \times \text{Coordination number})$

Example:

Complex	Metal	Atomic	Coordination	Effective atomic number
	(Oxidation State)	Number of Metal	number	(E.A.N.)
[Cu(NH ₃) ₄]SO ₄	+2	29	4	$(29 - 2) + (4 \times 2) = 35$
[Co(NH ₃) ₆]Cl ₃	+3	27	6	(27 – 3) t (6 × 2) – 36 [Kr]
K₂[Hgl₄]	+2	80	4	$(80 - 2) + (4 \times 2) = 86$ [Rn]
[Ag(NH ₃) ₂]Cl	+1	47	2	$(47 - 1) + (2 \times 2) = 50$

BEGINNER'S BOX-2

- **1.** The IUPAC name of $Fe(CO)_5$ is
 - (1) Pentacarbonyl ferrate (0)(3) Pentacarbonyl Iron (0)
- (2) Pentacarbonyl Ferrate (III)
- (4) Pentacarbonyl Iron (II)
- **2.** The compound $Na_2[Fe(CN)_5NO]$ is called
 - (1) Sodium pentacyanonitrosonium ferrate (II)
 - (2) Sodium nitroprusside
 - (3) Sodium nitrosoferrocyanide
 - (4) 1 & 2 both
- **3.** FeCl₃.4H₂O is actually :-(1) [Fe(H₂O)₄]Cl₃ (3) [Fe(H₂O)₄Cl₂]Cl

- (2) $[Fe(H_2O)_3Cl]Cl_2.H_2O$ (4) $[Fe(H_2O)_3Cl_2]Cl.H_2O$
- 4. Which of the following compound does not give test of sulphate ion in aqueous solution

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	(1) K ₂ SO ₄ .Al ₂ (SO ₄) ₃ (3) [CoSO ₄ (NH ₃) ₅]E	.24H ₂ O Br	(2) [Cu(H ₂ O) (4) FeSO ₄ .(N	4]SO4.H2O H4)2SO4.6H2O	
5.	Which of the follo solution:-	wing compound is	expected to yie	ld a white precipitate with AgNO	3
	(a) PtCl ₄ . 4NH ₃	(b) CoCl ₃ .2	3NH ₃	(c) Impure chloroform	
	(d) Vinyl chloride	(e) (O)		(f) Carnallite	
	(1) a, c, f, e	(2) a, d, e	(3) a, b, c, f	(4) a, b, e, f	
6.	Which of the follow	ing is most likely f	ormula of platinu	m complex, if $\frac{1}{4}$ of total chlorine o	f
	the compound is pred (1) PtCl ₄ .6H ₂ O	cipitated by adding A (2) PtCl ₄ .5H ₂ O	AgNO ₃ to its aque (3) PtCl ₂ .2H ₂	Four solution O (4) PtCl ₄ .3H ₂ O	
7.	The Effective atomic (1) 36	c number of Cr in Cr (2) 38	(CO) ₆ is (3) 28	(4) 54	
8.	According to the rule (1) Inert gas configur (3) Pseudo inert elec	e of effective atomic ration tronic configuration	number, central a (2) Duplet (4) Quartet	ntom acquires:	
9.	The Effective atomic (1) 35	e number of iron in F (2) 34	K ₄ [Fe(CN) ₆] is : (3) 36	(4) 38	
10.	The formula of the c (1) $[Co(en)_2SO_4]$ (3) $[Co(en)_3)SO_4$	omplex tris (ethylen	e diamine) cobalt (2) [Co(en) ₃ S (4) [Co(en) ₃]	(III) sulphate is O ₄] ₂ (SO ₄) ₃	
(B)	VALENCE BOND This theory was main (a) Every metal ion	THEORY nly developed by Li when it forms a co	nus Pauling. The	main features of this theory are - d undergoes formation of coordinate	2

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(b) During this bond formation, the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals.

(c) The number of vacant orbitals provided is equal to the coordination number of metal ion.

Ex. In the formation of $[Fe(NH_3)_6]^{3+}$, Fe^{+3} ion provides six vacant orbitals.

In $[Cu(NH_3)_4]^{2+}$, Cu^{+2} ion provides four vacant orbitals.

(d) The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.

(e) The vacant hybrid orbitals of metal ion get overlapped by orbitals of ligands containing lone pair of electrons.

(f) The number of such overlappings is equal to the coordination number of metal ion.

- (g) The empty 'd' orbitals involved in hybridisation may be inner (n–1)d or outer "nd" orbitals.
- (h) These complexes are called as **Inner orbital complexes** and **outer orbital complexes** respectively. It is applicable for coordination number = 6 (complexes).

(i) If inner 'd' orbitals are involved in hybridisation, then it is through the pairing of unpaired electrons in the (n-1)d orbitals of metal ion.

(j) Then such type of complexes will be **diamagnetic** or **less paramagnetic** and will be called as **Low spin complexes**.

(k) Generally outer orbital complexes have **paramagnetic** nature and they are called as **High spin complexes**.

Applications of valence bond Theory

(a) To 6-coordimited complexes :

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



Due to presence strong ligand electrons get paired up so metal ion provides vacant '3d' orbitals for hybridisation.



- This is a **diamagnetic complex**.
- As inner 'd' orbitals are involved in hybridisation, hence it is an **inner orbital complex**.
- It is a **low spin complex**.



- This is a **paramagnetic** complex and **high spin** complex.
- The outer 'd' otbitals are involved in hybridisation, hence it is an outer orbital complex. $[Co(NH_3)_6]Cl_2$

Co ²⁷	1/1/111 3d	$ \begin{array}{c c} 1 \\ 4_s & 4p \end{array} $	4d
Co ²⁺ ion	11 11 1 1 1		
		\sim	n./*
Co ⁺² in [Co(NH ₃) ₆] ²⁺			
가 가지 않는 것을 가지 못했다. 성격과 가 성격을 가져 있다.		d ² sp ³	

(b)	4-coordinated complex : [NiCl ₄] ²⁻
	Ni^{+2} 11111 11
•	The unpaired electrons remain as such because Cl ⁻ is a weak ligand as it is a paramagnetic complex.
	Ni ²⁺ in [NiCl ₄] ²⁻ $1/1/1/1 = 1$ 3d $4s = 4p$ sp ³ hybridisation
•	$[NiCl_4]^{2-}$ has tetrahedral geometry. It is a high spin complex. $[Ni (CN)_4]^{2-}$
	Ni ⁺² $1/1/1/1/1$ $4s$ $4p$
•	dsp hybridisation CN is strong field ligand. Thus the complex has square, planar geometry
•	The unpaired electrons in '3d' orbitals of Ni ²⁺ get paired up; So $[Ni(CN)_4]^{2-}$ is diamagnetic in nature.
•	This Ni^{2+} complex. is an inner orbital complex and a low spin complex. $[Zn(NH_3)_4]^{2+}$
	$\frac{1}{30}$ Zn $\frac{1}{30}$ $\frac{1}{30}$ $\frac{1}{4s}$ $\frac{1}{4p}$
	$Zn^{2+} \text{ in } [Zn(NH_3)_4]^{2+} \underbrace{1 \hspace{.1cm} 1 .1cm$
•	Because the complex is formed by sp^3 hybridisation, hence it is tetrahedral
•	Since all electrons are paired, hence it is diamagnetic [Ni(CO) ₄]
	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
	Ni after rearrangement $1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/$
	sp ³ hybridisation
•	CO is a strong ligand. So it is low spin complex.
•	The empty one 4s and three 4p orbitals mix to form, four new sp3 hybridised orbitals.

• Each orbital accepts one electron pair from Carbon monoxide molecule forming [Ni(CO)₄]

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• It is **diamagnetic** in nature, the shape of nickel tetra carbonyl is **tetrahedral** as shown above. eg. $[Cu(NH_3)_4]^{2+}$



Note : In case if metal belongs to 4d & 5d series all ligand will act' as a strong field ligand . e.g. $[RhF_6]^{3-}$, $[Rh(NH_3)_6]^{3+}$

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Coordination Number	Hybridised orbital	Geometrical shape of the Complex	Examples of Complex
2	sp	Linear	[Ag(NH ₃) ₂] ⁺ [Ag(CN) ₂] ⁻
3	sp²	L L Trigonal planer	[HgI ₃]-
4	sp³	L 109°28' L L L L L L L L L L L L	$[CuCl_{4}]^{2}$ $[ZnCl_{4}]^{2}$ $[FeCl_{4}]^{2}$ $[Ni(CO)_{4}]$ $[Zn(NH_{3})_{4}]^{*2}$
4	dsp² (d _{x²-y²} orbital)	L 90 90 90 90 90 L L Square plannar	$[PdCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$ $[Pt(NH_3)_4]^{+2}$ $[Cu(NH_3)_4]^{+2}$ $[PtCl_4]^{2-}$
5	sp³d	L 90 DE L Trigonal bipyramidal	[CuCl ₅] ⁻³
5	dsp³	CO CO Trigonal bipyramidal	[Fe(CO) ₅]
6	d ² sp ³ When d-orbitals are(n - 1)d-orbitals (Inner orbital comlexes) or sp ³ d ² When d-orbitals are nd orbitals(Outer orbital complexes) In both cases d-orbitals are d _{x²} and d _{x²,u²} orbitals	Lo Octahedral	[Cr(NH ₃) ₆]* ³ [Ti(H ₂ O) ₆]* ³ [Fe(CN) ₆] ⁻³ [Co(NH ₃) ₆]* ³ [PtCl ₆]* ² ,[CoF ₆] ⁻³

BEGINNNER'S BOX-3

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		Edubul	Ĺ		
1.	Complex ion square planar geometry:-	(2) [C] (C) [1 - 2]			
	(1) $[N_1(CN)_4]^2$ (3) $[Cu(NH_3)_4]^{+2}$	(2) $[Cu(CN)_4]^2$ (4) All			
2.	Which is low spin complex ?				
	(1) $[Fe(CN)_4]^{3-}$	(2) $[Co(NO_2)_6]^{3-}$			
	(3) $[Mn(CN)_6]^{3-}$	(4) All			
3.	For the complex $[Fe(CO)_x]$ what is wrong	g :-			
	(1) It is σ - π bonded organometallic compound (2) In the complex value of $\mu = 6$				
	(2) In the complex Value of $x = 0$ (3) In the complex CO is π -acid ligand				
	(4) It is trigonal bipyramidal shape				
4.	In the complex ion ML_6^{n+} , M^{n+} has five crystal field theory, the magnetic proper unpaired electrons	d-electrons and L is weak field ligand. Accordinenties of the complex ion corresponds to how r	ng to nany		
	(1) 0 (2) 5	(3) 2 (4) 3			
5.	Among $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$ and $[NiCl_4]^{2-}$ are diamagne (2) $[NiCl_4]^{2-}$ and $[Ni(CN)l-$ are diamagne (3) $[Ni(CO)_4]$ and $[Ni(CN)l-$ are diamagn (4) $[Ni(CO_4)]$ is diamagnetic and $[NiCl_4]^{2-}$	$[1]_4]^{2-}$: etic and $[Ni(CN)_4]^{2-}$ is paramagnetic tic and $[Ni(CO)_4]$ is paramagnetic etic and $[NiCl_4]^{2-}$ is paramagnetic $^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic			
6.	Which is correct geometry in the case of (1) Tetrahedral (2) Octahedral	$[NiCl_4]^{2-}$ complex? (3) Square planar (4) Pyramidal			
7	For K [CoE] incompatigation to the second				
/.	For $K_3[COF_6]$, incorrect statement is.	(2) Its magnetic moment is $\sqrt{24}$ DM			
	(3) Primary valency of Co is six	(4) Hybridisation state of CoF_6^{3-} is sp^3d^2			
8.	Which of the following compound is squa	are planar and does not have any unpaired electron	ı.		
	(a) $[Cu(NH_3)_4]^{+2}$ (b) XeF_4 (c) [$[Ni(CO)_4]$ (d) $[NiCl_4]^{-2}$			
	(e) $[Ni(CN)_4]^{-2}$ (f) CuSO ₄ .5H ₂ O				
	(1) a, e, f (2) a, b, c	(3) b, e (4) b, c, f			
9.	Which of the following complex does not	t have chelation.			
	(1) $K_3[Al(C_2O_4)_3]$ (2) $[Pt(en)_2]Cl_2$	(3) $[Ag(NH_3)_2]Cl$ (4) $K_2(Ni(EDTA)]$			
10.	Match list - I with list - II and choose the	correct answer from the cod~ given below			
	List - I (complex)	List-II (geometry)			
	(A) $[Pt((V1)/4]]$ (B) $[Pt((NH_3)_6]^{+4}$	(a) Octachedian (b) Squareplanar			
	(C) $[Ag(NH_3)_2]^+$	(c) Tetrahedral			
	(D) $[Zn(NH_3)_4]^{+2}$	(d) Linear			
	A B C D				

(2)	а	b	c	d
(3)	c	d	b	a
(4)	b	c	d	а

(C) Crystal field theory

Crystal Field Theory : This is model of electronic structure of transition-metal complexes that considers how the energies of the d-orbitals of a metal ion are affected by the electric field of the ligand. According to this theory.

(a) The ligands in a transition-metal complex are treated as point charges.

(b) A ligand anion becomes simply a point of negative charge. A neutral molecule, with its electron pair that it donates to the metal atom, is replaced by a negative charge, representing the negative end of the molecular dipole.

(c) In the electric field of these negative charges, the fived orbitals of the metal atom no longer have exactly same energy. Splitting of five degenerated-orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting.

(d) The extent of splitting of metal d-orbitals depends upon the nature and number of ligands surrounding it and the charge on the central metal ion.

(e) The extent of splitting of metal d-orbitals determines the magnetic and spectroscopic properties of the complexes.

SPLITTING IN OCTAHEDRAL COMPLEXES

In a octahedral complex, the co-ordination number is 6. The metal ion is at the centre and the ligands occupy the six corners of the octahedron as shown in figure.

We know that two orbitals, $d_{x^2-y^2}$ and d_{z^2} are oriented along the axis while the remaining three orbitals, viz, d_{xy} , d_{yz} , d_{zx} and d are oriented in between the axis.



The two orbitals $d_{x^2-y^2}$ and d_{z^2} are designated as e_g orbitals while the three orbitals d_{xy} , d_{yz} and d_{zx} are designated as t_{2g} orbitals. As the six ligands approach the central ion along the axis, e_g orbitals, is repelled more by the ligand than in the t_{2g} orbitals.

In other words, the energy of the d_{z^2} and $d_{x^2-y^2}$ orbitals increases much more then the energy d_{xy} , d_{yz} and d_{zx} orbitals.

Thus, in octahedral complexes, the five d-orbitals split up into two sets : one set consisting of two orbitals $(d_{x^2-y^2} \text{ and } d_{z^2})$ of higher energy (eg orbitals) and the other set consisting of three orbitals $(d_{xy}, d_{yz}, \text{ and } d_{zc})$ of lower energy (t_{2g} orbitals).



Splitting in tetrahedral complex

The co-ordination number for tetrahedral complexes is 4. The tetrahedral arrangement of four ligands surrounding a metal ion may be visualized by placing ligands at the alternate comers of a cube, as shown in figure.



Tetrahedral arrangement of four lignads

It can be shown that in a tetrahedral structure, none of the d-orbitals points exactly towards the ligands. When ligand approaches it is more dose d_{xy} , d_{yz} , d_{xz} in comparison of $d_{x^2-y^2}$ and d_{z^2} because d_{xy} , d_{yz} , d_{zx} are between the axis and d_{z^2} and $d_{x^2-y^2}$ are along the. So d_{xy} , d_{yz} , d_{zx} feels more repulsion as compare to d_{z^2} and $d_{x^2-y^2}$.

Thus, the d orbitals are also splitted into two groups but in a reverse order. The three orbitals, d_{xy} , d_{yz} and d_{xz} , designated as t_2 orbitals, now have higher energy than the two orbitals $d_{x^2-y^2}$ and d_{y^2} designated as eg-orbitals.



Calculation of crystal field stablizing energy (CFSE)

(i) For octahedral CFSE = $[-0.4(n_{t_{2a}}) + 0.6(n_{eg})]\Delta_0$ + Pairing energy (**P.E.**)

where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals

 n_{eg} = number of electron in eg orbitals

$\Delta_0 = crystal field splitting energy$

(ii) For tetrahedral CFSE = $[-0.6(n_e) + 0.4(n_{t_1})] \Delta_t$ + Pairing energy (**P.E.**)

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where n_{t_2} = number of electron in t₂ orbitals

 n_e = number of electron in e orbitals.

 Δ_t = crystal field splitting energy

- **Ex:** Explain the formation of $Na_4[Fe(CN)_6]$ and $Na_4[FeF_6]$? Show which is low spin and which is high is high spin complex and also calculate, the Crystal field stablisation energy (CFSE)?
- **Sol.** In given compounds CN^- is strong field ligands and F^- is weak field ligand and in both compounds ions is in +2 oxidation state d^6 configuration.

So in $Na_4[Fe(CN)_6]$ Na[FeF₆] $e_{a}(d_{x^{2}-y^{2}}, d_{z})$ $e_{q}(d_{x^{2}-y^{2}}, d_{z})$ 3d 3d $1_{1} 1_{1} t_{2g}(d_{xy}, d_{yz}, d_{zx})$ In presence In presence of ligand of ligand For octahedral CFSE = $[-0.4 (n_{t_{\gamma_e}}) + 0.6 (t_{eg})]\Delta_0 + P.E.$ where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals. n = number of electron in e_g orbitals Na₄(Fe(CN)₆] CFSE = $-2.4 \Delta_0 + 3P$. $[n_{t_{2}} = 6, n_{eg} = 0]$ $[n_{t_{2}} = 4, n_{eg} = 2]$ Na₄[Fe(F)₆] CFSE = $-0.4 \Delta_0 + P$ where $P = pairing energy to pair up electron; \cdot$

Factors affecting Δ

factor affecting splitting

(i) Strength of ligand

- (ii) Oxidation state of central metal ion
- (iii) Transition series. (d-series)
- (iv) Geometry (nurriber of ligands)

$$\Delta_{\rm sp} = \frac{4}{3} \Delta_0 \qquad ; \qquad \Delta_{\rm t} = \frac{4}{9} \Delta_0 \; ; \qquad [\Delta_{\rm sp} = 1.3 \Delta_0]$$

Factors affecting strength of ligands

Strength of ligand depends upon :

(i) good σ donor (ii) good π acceptor (iii) high negative charge (iv) Small in size

[C.F.S.E. is more in case of S.F.L. as compared to W.F.L.]

[C.F.S.E. oc oxidation state]

(C.F.S.E., 5d > 4d > 3d]

 $[\Delta sq > \Delta_0 > \Delta_t]$

Spectro-chemical series for ligands

Series which shows the relative strength of ligands.

I (weakest) < Br⁻ < SCN < Cl⁻ < S²⁻ > NO₃⁻ < F⁻ < OH⁻ < C₂O₄²⁻ < H₂O < NCS⁻

$$cedta^{4-} < NH_3 < en < NO_2^- < CN^- < CO (strongest)$$

APPUCATION OF CRYSTAL FIELD THEORY

Applications of C.F.T. are

- (i) To predict the geometry that the compound is either trater orbital or outer orbital complex.
- (ii) To calculate the magnitude of paramagnetism.
- (iii) To show flhe colour property.

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- (i) d⁴ high spin octahedrat (iii) d⁵ high spin octahderal
- $(v) d^{6}$ high spin octahedral
- (v) d high spin octand (vii) d^7 tetrahderal
- (V_{11}) d tetranderal

Sol.

- (i) four unpaired electron
- (iii) five unpaired electron
- (v) four unpaired electron
- (vii) three unpaired electron
- (ii) d^4 low spin octahedral (iv) d^5 tetrahedral (vi) d^5 tetrahedral (vii) d^8 low spin octahedral (viii) d^7 high spin octahedral. (ii) two unpaired electron. (iv) five unpaired electron (vi) two unpaired electron (viii) three unpaired electron





- **Ex.** $[Ti(H_2O_6)]^{+3}$ is violet in colour explain using CFT.
- **Sol.** In $[Ti(H_2O_6]^{3+}$ d-robitals of Ti³⁺ lost their degeneracy in the presence of octahedral ligand field and produce t_{2g^1} & eg⁰. orbital of different energy complex absorbed visible light for excitation

of electron from t_{2g^0} to eg¹ (d-d transition) and show complimentary violet colour.

- **Ex.** How the complex compounds show the colour?
- **Sol.** When d-electrons absrobs energy from visible region they will get excited. Absorbed energy is related to a particular wavelength.

 $E(\Delta) = \frac{hc}{\lambda_{absorbed}}$

when electrons fall into lower energy level it will show colour whose wavelength (λ) is the complimentary of absorbed wavelength ($\lambda_{absorbed}$).

- **Ex.** Why violet coloured $[Ti(H_2O)_6]Cl_3$ becomes colourless when heated ?
- Sol. When $[Ti(H_2O)_6]Cl_3$ is heated water molecules are removed and in the absence of ligand crystal field splitting does not occur and hence the substance is colourless.
- **Ex.** $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?
- **Sol.** It is due to difference in power of ligands.
- **Ex.** What will be the correct order for the wavelengths of absorption in the visible region for the following : $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?

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Sol. $[Ni(H_2O)_6]^{2+} > [Ni(NH_3)_6]^{2+} > [Ni(NO_2)_6]^{4-}$

GOLDEN KEY POINTS

- Red colour of ruby is due to presence of small amount of Cr^{+3} in atomsphere of Al_2O_3 .
- Green colour of emerald is due to presence of Cr^{+3} in atmosphere of $Be_3Al_2Si_6P_{18}$ [beryl]
- Complex become colourless in absence of ligand field because in absence df ligand d-d-transition does not occur.
- $[Ti(H_2O_6]^{3+}$ become cofourfess on heating due to removal of water molecules.
- Anhydrous $CuSO_4$ is colourless but hydrated $CuSO_4$ is blue due to moisture.
- Halogens are coloured due to the HOMO-LUMO transition.
- KMnO₄, K₂Cr₂O₇, CrO₂Cl₂ are coloured due to charge transfer spectra.

3.4 STABILITY OF CO-ORDINATION COMPOUNDS IN SOLUTION

According to thermodynamic stability, the reaction between a metal ion and the ligands may be considered as a Lewis acid base reaction in solution. If the equilibrium constant is high then the complex obtained is theromodynamically stable in solution. The reaction can be written as follows : $M + nL \div \dot{\uparrow}$ (ML_n]

The stability constant K, of the complex $[ML_n]$ is given by the relation, $K = \frac{[ML_n]}{[M][L]^n}$. The

greater the value of K, more stable is the complex.

The strength of a complex ion also depends upon -

- (i) Higher charge of the central metal ion.
- (ii) Greater base strength of the ligand.
- (iii) Ring formation (chelation) in structure of complexes.

BEGINNER'S BOX-4

1. Consider the following statements $S_1 : [Cr (NH_3)_6]^{3+}$ is a inner orbital complex with crystal field stabilization energy equal to - $1.2 \Delta_0$

 S_2 : The complex formed by joining the CN⁻ ligands to Fe³⁺ ion has theoretical value of 'spin only' magnetic moment equal to 1.73 B.M.

 $S_3: Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS],$

In reactant and product the oxidation states of iron are same and arrange in the order of true/false.

(1) FTF (2) TTF (3) TTT (4) FFF

- 2. For the $t_{2g}^6 e_g^2$ system, the value of magnetic moment (µ)is : (1) 2.83 B.M. (2) 1.73 B.M. (3) 3.87 B.M. (4) 4.92 B.M.
- 3. Which of the following compound is not coloured :-(1) Na₂[CuCl₄] (2) Fe₄[Fe(CN)₆]₃ (3) Na₂[CdCl₄] (4) Na₂CrO₄
- 4. The stability constants of the complexes formed by a metal ion M^{2+} with NH₃, CN⁻, H₂O are of the order of 10^{15} , 10^{27} , 10^{11} respectively. Then :- (1) NH₃ is the strongest ligand

	(3) These values cannot predict the strength of the ligand(4) All the ligands are equally strong								
5.	The value for crystal field stabilisation energy (1) $K_2(MnF_6]$ (2) $K_3[Fe(CN)_6]$	ergy is zero for (3) $K_3[FeF_6]$ (4) $K_4[Fe(CN)_6]$							
6.	Match the following Complexes (i) $(CoCl_6)^{3-}$ (ii) $[Co(OX)_3]^{3-}$ (iii) $(Co(H_2O)_6]^{2+}$ (c) (iv) $[Fe(CN)_6]^{4-}$ [Ans. i-d, ii-b, iii-a,d iv-c]	Property (a) No. of electrons in $t_{2g} = 5$ (b) No. of electrons in $e_g = 0$ No. of electrons in $t_{2g} = 6$ (d) No. of electrons in $e_g = 2$							
7.	Which order is correct (1) $[NiC1_6]^{4-} > [NiCl_4]^{2-}$ (2) $[Cr(en)_3]Cl_3 > [Cr(H_2O)_6]Cl_3$ (3) $[Co(CN)_6]^{4-} > [Co(CN)_6]^{3-}$ (4) All of these	splitting energy & $\Delta 0$ crystal field stabilisation energy reducing behaviour							
8.	Which is inner d-complex (1) $[Co(H_2O)_6]^{3+}$ (3) $(IrF_6]^{3-}$	(2) $[RhF_6]^{3-}$ (4) All							
9.	Which stability order is incorrect (1) $[Fe(C_2O_4)_3]^{3-} > [Fe(H_2O)_6]^{3+}$ (3) $[Ni(en)_2]^{2+} > [Ni(dmg)_2]$	(2) $(Fe(EDTA)]^{2-} > [Fe(en)_3]^{3+}$ (4) $(Fe(CN)_6]^{3-} > [Fe(CN)_6]^{4-}$							

10. The complex exhibit lowest energy absorption bond is (1) $[NiCl_4]^{2-}$ (2) $[Ni(CO)_4]$ (3) $(Ni(CN)_4]^{2-}$ (4) $[Ni(H_2O)_6]^{2+}$

3.5 ISOMERISM IN COMPLEXES

(2) CN^{-} is the strongest ligand

(a) Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as **Isomers**.

(b) Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.(c) Classification of isomerism :

Type of isomerism Structural isomerism Figure 1 isomerism Stereo isomerism Figure 2 isomerism Figure

• Structural Isomerism

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

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• Ionisation Isomers

The type of isomerism which is due to the exchange of groups or ion between the coordinating sphere and the ionisation sphere.

Ex. (a) $Co(NH_3)_4$ Br₂SO₄ can represent

(i) $[Co(NH_3)_4Br_2]$ SO₄ (red violet)

(ii) $[Co(NH_3)_4SO_4)Br_2$ (red).

These complexes give sulphate ion and bromide ion respectively

(b) $[Pt(NH_3)_4 Cl_2] Br_2$ and $[Pt(NH_3)_4 Br_2]Cl_2$

(c) $[Co(NH_3)_4(NO_3)_2]SO_4$ and $[Co(NH_3)_4SO_4](NO_3)_2$

• Hydrate Isomers

This type of isomerism is due to presence of different number. of water molecules inside a coordination sphere.

Ex. (a) $Cr(H_2O)_6Cl_3$ has three possible structures

(i) [Cr(H₂O)₆]Cl₃ violet

(ii) $[Cr[H_2O)_5Cl] Cl_2 .H_2O$ green

(iii) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ dark green.

These complexes differ from one another with respect to the number of water molecules acting as ligands. Other hydrate isomers are

(i) $[Co(NH_3)_4 H_2O Cl]Cl_2$

(ii) [Co(NH₃)₄Cl₂]Cl. H₂O

Linkage or Salt Isomers

(a) This type of isomerism arises due to presence of ambidentate ligands like NO_2^- , CN^- and SCN^-

(b) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.

(c) Such type of isomers are distinguished by infra red (I.R.) spectroscopy.

Ex. (i) $(Co(NH_3)_5NO_2]Cl_2$ and $(Co(NH_3)_5 ONO]Cl_2$

(ii) In NO_2^- ligand, The coordinating sites are nitrogen (i.e., NO_2^- Nitro ligand) or through oxygen (i.e. ONO Nitrito ligand)

(iii) The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.

• Coordination Isomers

(a) This type of isomerism is exhibited when the complex has two complex ions in it- 'Cationic and Anionic'.

(b) This type of isom1erism is caused by the interchange of ligands between the two complex ions of the same complex.

Ex. (i) $[Co(NH_3)_6] [Cr(CN)_6]$	(ii)	$[Co(NH_3)_6] [Cr(C_2O_4)_3]$
$[Cr(NH_3)_6]$ (Co(CN) ₆]		$[Cr(NH_3)_6] [Co(C_2O_4)_3]$

• Stereo Isomerism

(a) They have same molecular formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion.

(b) The two stereo isomers which are possible are - Geometrical and optical.

(A) Geometrical or cis - Trans Isomers

(a) The ligands occupy different positions around the central metal ion.

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(b) When two identical ligands are coordinated to the metal ion from same side then it is **cis isomer**. (Latin, cis means same).

(c) If the two identical ligands are coordinated to the metal ion from opposite side then it is Trans isomer (in Latin, Trans means across).

(d) These geometrical isomers differ in physical as well as in chemical properties.

(e) Geometrical isomerism is most important in compounds with coordination numbers 4 and 6.

(f) 4-coordinated complexes with tetrahedral geometry do not exhibit cis-Trans isomerism, because relative position of ligands remain same for each other.

(g) It is exhibited by 4-coordinated complexes with square planar geometry.

Note : There are orally 5 possible cases which shows geometrical isomerism is square planar complex. Such as Ma₂b₂, Ma₂bc, Mabcd, M(AB)₂, M(AB)cd

Geometrical Isomers With Coordination Number = 4 (Square Planar Complexes)

(i) Complexes with general formula, Ma_2b_2 (where both a and b are monodentate) can have Cisand trans.





(iv) Diglycinato platinum (II) complexes

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Note : Other 6-Coordinated geometrical isomers are-

General formula	Total No. of geometrical isomers					
Mabcdef	15(30 optical isomers)					
Ma ₂ bcde	9					
Ma ₂ b ₂ cd	6					
$Ma_2b_2c_2$	5					
Ma ₃ bcd	4					
$Ma_3b_2c_3$	3					
Ma ₃ b ₃	2					
Ma ₄ bc	2					
Ma_4b_2	2					
Ma ₅ b	Nil					
Ma ₆	Nil					

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Here M = central atom; a, b, c, d, e. f = Monodentate ligands -

(B) Optical Isomers

(a) Optically active complexes arc those which are non-superimposable over the mirror image structure.

(b) An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.

(c) The complex which rotates plane polarised light to left hand side is laevo rotatory i.e. λ' or '-' and if the complex rotates the plane polarised light to right hand side then it is dextrorotatory, 'dt 'or '+'.

(d) Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as optical isomers.

(e) The 'd' and ' λ ' -isomers of a (X) compound are called as Enantiomers or Enantioniorphs.

Optical isomers with coordination number = 6 $[Ma_2b_2c_2]^{n+} \rightarrow [Pt(py)_2(NH_3)_2Cl_2]^{2+}$ (i) py Cl NH. H₃N NH, NH, Cis-d-isomer Cis- *l*-isomer Mirror (ii) $[Mabcedf] \rightarrow [Pt(py)NH_3NO_2ClBrI]$ Br NO NO, H_aN \mathbf{c} NH₃ l-isomer d-isomer Mirror $[M(AA)_3]^{a_+} \rightarrow [Co(en)_3]^{3_+}$ (iii) 3+ 3+ en en en en en Mirror ℓ-form d-form

(iv) $\left[M(AA)_2ab\right]^{2+}$

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BEGINNER'S BOX-5

- 1. Which of the following sets is/are example of co-ordination isomerism in complexes?
 - (1) $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $(Co(CN)_6]$ $[Cr(NH_3)_6]$
 - (2) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and $[Cr(H_2O)_4Cl_2)Cl_2H_2O$
 - (3) $[Co(NH_3)_5Br]SO_4$ and $(Cr(NH_3)_5SO_4]Br$
 - (4) $[Pt(NH_3)_2CI_2]$ and $[Pt(NH_3)_4]$ $[PtCl_4]$

2.	Which of the followin (1) Tetrahedral comp (3) Octahedral compl	ng does/do not exhibit lexes exes	t optical isomerism (2) Square planar complexes (4) Polynuclear complexes						
3.	The number of geome (1) 0	etrical isomers of [Co((2) 2	NH) ₃ (NO) ₃) are: (3) 3	(4) 4					
4.	Which of the follow concentration (1) $[Cr(OX)_2]^{3-}$ (3) $[Co(en)Cl_4]^{-}$	ing coordination entit	(2) [Co(en) ₂ Cl ₂] ⁺ (4) All						
5.	The number of isome (1) 2	ric forms∙ in which [C (2) 3	$[Co(NH_3)_4Cl_2]^{1+}$ ion can occur is (3) 4 (4) 1						
6.	The total number of p (1) 3	oossible isomer for the (2) 6	complex comp. :- [Cu (<mark>3)</mark> 5	$(NH_3)_4]$ [PtCl ₄] (4) 4					
7.	The complexes [Co(N (1) Coordination ison (3) Geometrical isom	NO ₂)(NH ₃) ₅] Cl ₂ and [Onerism merism	[Co(ONO)(NH ₃) ₅] Cl ₂ are the examples of (2) Ionisation isomerism (4) Linkage isomerism						
8.	The type of isomerism (1) Linkage	n exhibited [Rh(en) ₂ Cl (2) Coordination	2][Rh(en)Cl4] and [Rh (3) Ligand	(en) ₃][RhCl ₆] is (4) Ionisation					
9.	Which of the following will give maximum number of isomers : (1) $[Co(py)_3(NH_3)_3]^{3+}$ (2) $[Ni(en)(NH_3)_4]^{2+}$ (3) $[Fe(C_2O_4)(en)_2]^{2-}$ (4) $[Cr(NO_2)_2(NH_3)_4]^+$								
10.	The Complexes given	h below are :-							

 $en \underbrace{M}_{A} en \underbrace{M}_{en} A$ (1) Geometrical isomers

(3) Optical isomers

(2) Position isomers(4) Identical

3.6 ORGANOMETALLIC COMPOUNDS

Compounds in which C-atom is directly bonded with less electronegative element. (Ge, Sb, B, Si, P, As) Also form organometallic compounds.

Ex.
$$\begin{cases} R - Zn - R & \text{dialkyl zinc (Frankland reagent)} \\ R - Mg - X & \text{Alkyl Magnesium halide (Grignards reagent)} \\ \end{cases}$$
(b)
$$\begin{cases} U \\ Sodium acetate \\ Sodium ethoxide \\ Sodium ethoxide \\ Sodium Mercaptide \\ H_3C - SNa \end{cases}$$
These are not organometallic compounds because in these compounds metal is not directly attached with carbon atom. (c)
$$\begin{cases} R - Zn - R & \text{dialkyl zinc (Frankland reagent)} \\ U \\ Sodium acetate \\ H_3 - C - ONa \\$$

(d) Carbides and carbonates are not considered OMC because in these compounds metal carbon bond has ionic nature.

Classification of Organometallic Compounds

OMC can be classified into three main categories-

 σ - bonded OMC : These compounds are formed mostly by non transition and metalloid elements.

Ex. R-Mg-X (Grignard's reagent)

 $(CH_3)_2$ Zn (Dimethyl zinc or Frankland's reagent)

R₂Cd (Dialkyl cadmium)

 $(C_2H_5)Pb$ (Tetra ethyl lead)- used as antiknocking agent in petrol.

 $(C_2H_5)_4Al + TiCl_4$ (Ziegler natta catalyst)-Heterogeneous catalyst, used in polymerisation of alkene.

 π - bonded OMC : These are usaully formed by transition metals.

Ex. Ferrocene [Fe($\eta^2 - C_5H_5$)₂] where η = No. of carbon atoms combined with metal atom.

Zeise's salt $K[PtCl_3(\eta^2 - C_2H_4)]$

Dibenzene chromium [$Cr(\eta^6 - C_6H_6)_2$]

 σ and π - bonded OMC : Transition metals of gp. 6, 7, 8, 9 and 10 in their zero oxidation state form such type of OMC. The carbonyl compounds of these metals have both σ and π bonds.

Ex. [Ni(CO)₄], [Fe(CO)₅], [Mn₂(CO)₁₀] [M(CO)₆], [M = Cr, Mo, W]

3.7 APPUCATION OF COORDINATION CHEMISTRY

(a) Test of Ni^{+2} : Ni^{+2} ion give rosy red ppt when react with dmg in weak alkaline medium.

 $Ni^{2+} + 2dmg \xrightarrow{NH_4OH} [Ni(dmg)_2]$ 3d⁸ SFL $dsp^2 sq. planar$ (b) Test of S^{2-} : Na₂S + Na₂[Fe(CN)₅(NO)] \rightarrow Na₄(Fe(CN)₅(NOS)] sodium nitro prousside violet colour (c) Test of Fe^{+2} & Fe^{+3} : $\xrightarrow{K_3[Fe(CN)_6]} 3KFe[Fe(CN)_6]$ $Fe^{+2} + K_3 [Fe(CN)_6] \rightarrow Fe_3 [Fe(CN)_6]_2$ 1,2-drops turn bull blue salt colloidal solution $\xrightarrow{K_4[Fe(CN)_6]} 4KFe[Fe(CN)_6]$ $Fe^{-3} + K_4[Fe(CN)_6] \rightarrow Fe_4[Fe(CN)_6]_3$ salt 1, 2-drops prussiun blue colloidal solution (d) Test of Fe^{+3} $FeCl_3 + 3K SCN$ $Fe(SCN)_3 + 3KCl$ Power by: VISIONet Info Solution Pvt. Ltd Mob no. : +91-9350679141 Website : www.edubull.com

Potassium thiocyanate Blood red colour (e) Test of Cu^{+2} $2Cu^{+2} + K_4[Fe(CN)_6] \rightarrow Cu_2[Fe(CN)_6$ Chocolate brown (f) Brown ring test : Test for Nitrate ion

$$NO_{OA}^{-} + Fe^{+2} + 4H^{+} \xrightarrow{\text{redox}} Fe^{+3} + NO + 2H_{2}O$$

$$[Fe(H,O), 1SO_{A} + NO = \sum_{n=1}^{\infty} [Fe(H,O), (NO)]SO_{A}$$

 $[Fe(H_2O)_6]SO_4 + NO \longrightarrow \left[\begin{array}{c} Fe(H_2O)_5 \\ brown ring complex \end{array} \right] SO_4$ (g) If excess of KCN & KI is added in CuSO₄ insoluble CuCN & Cui is formed which later turn into soluble complex.

$$2 \underset{\text{salt}}{\text{KCN}} + \underset{\text{salt}}{\text{CuSO}_{4}} \xrightarrow{-\kappa_{2} \text{SO}_{4}} Cu(\text{CN})_{2} \xrightarrow{\underset{\text{redox}}{\text{CN}^{-}\text{RA}}} Cu^{+}\text{CN}^{-} + \frac{1}{2}(\text{CN})^{2}$$

$$\downarrow 3 \underset{\text{K}_{3}}{\downarrow} \text{Cu}(\text{CN})_{4}]$$

$$\underset{\text{soluble complex}}{\text{soluble complex}}$$

(h) AgCl or AgBr ppt (Not AgI) are soluble in ammonia & NH₄OH

$$\underset{ppt}{\operatorname{AgCl}} \xrightarrow{2\operatorname{NH}_{3}} \left[\underset{\text{soluble complex}}{\operatorname{Ag(NH}_{3})_{2}} \right] \operatorname{Cl}^{-1}$$

(i) In photography : undecomposed AgBr is removed from photography film by using hyposolution $[Na_2S_2O_3.5H_2O]$

$$AgBr \xrightarrow{hv} Ag + \frac{1}{2}Br_2$$

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3 \left[Ag(S_2 O_3)_2 \right]^{3-} + NaBr$$
soluble complex

(j) Light blue colour of aqueous solution of $CuSO_4$ turn into dark blue in presence of ammonia

 $[Cu(H_2O)_4]SO_4 \xrightarrow{4NH_3} [Cu(NH_3)_4]SO_4$ Light blue dark blue

But in the presence of add in above there is no co four change

 $NH_3 + HCl \longrightarrow NH_4^+Cl^-$

basic acid

(k) Rusting spots of iron [Fe₂O₃.XH₂O) can be removed by using oxalic acid.

(l) cyano complex are used for electroplating of Ag or Au due to high stability.

e.g. [Ag(CN)₂]⁻

(m) Wilkinson catalyst (RhCl(PPh₃)₃ is used for hydrogenation of alkene. (Homogeneous catalysis)

- (n) [EDTA)]^{4–} is used for estimation of hardness of water.
- (o) $[Ca(EDTA)]^{2-}$ is used to remove Pb poison.

 $[Ca(EDTA)]^{2-} + Pb^{+2} \rightarrow [Pb(EDTA)]^{2-} + Ca^{+2}$

(p) **Biological importance**

Chlorophyll (Mg)haemoglobin (Fe^{+2})Myoglobin (Fe^{+2})Vit $B_{12}(Co)$ Corboxypeptide (Zn)Insulin (Zn)

JAHN TELLER EEFFECT

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In octahedral field if the d electrons are symmetrically arranged, they will repel all six ligands equally. Thus the structure will be a completely regular octahedron.

If the d electrons are unsymmetrically arranged, they will repel some ligands in the complex more than others. Thus the structure is distorted. The e_g orbitals point directly at the ligands. Thus unsymmetric filling of thee orbitals results n some ligands being repelled more than others. This causes a significant distortion of the octahedral shape. In contrast the t_{2g} orbitals do not point directly at the ligands, but point in between the ligand directions. Thus unsymmetric filling of the t_{2g} orbitals has only a very small effect on the stereochemistry. Distortion caused by unsymmetric filling of the t_{2g} orbitals is usually too small to measure.

If the d_{z^2} orbital contains one more electron than the $d_{x^2-y^2}$ orbital then the ligands approaching along +z and -z will face greater repulsion than the other four ligands. The repulsion and distortion result in elongation of the octahedron along the z-axis. This is called tetragonal distortion or tetragonal elongation.

If the $d_{y^2-y^2}$ orbital contains the extra electron, then elongation will occur along the x and y

axes. This means that the ligands approach more closely along the z axis. Thus there will be four long bonds and two short bonds. This is equivalent to compressing the octahedron along the z-axis, and is called tetragonal compression.

Example-I

Many Cu(+II) salts and complexes also show tetragonally distorted octahedral structures. Cu²⁺ has a d⁹ configuration:

$$\begin{array}{c} t_{2g} & e_{g} \\ \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \\ \hline \end{array}$$

To minimize repulsion with the ligands, two electron occupy the d_{z^2} orbital and one electron occupies of $d_{x^2-y^2}$ orbital.

Thus the two ligands along +z and -z are repelled more strongly than are the other four ligands. Therefore according to Jahn Teller effect distortion in regular octahedral geometry occurs when unsymmetrical configuration is present in e_g orbitals of central metal ion/atom.

Example-II

High spin complexes in which J.T. effect is i.e. d^1 , d^2 , d^3 (neglegible), d^4 , d^6 , d^7 , d^9 observed.

TRANS EFFECT (The kinetic trans effect)

The kinetic trans effect, defined as the relationship between the rate of substitution of square planar complexes and the nature of the species trans to the ligands being displaced.

A trans-directing series, such as the one shown below, can be constructed:

 $[H_2O \sim OH^- \sim NH_3 \sim py < Cl^- < Br^- < I^- \sim NO_2^- < C_6H_5^- < CH_3^- < PR_3 \sim H^- << CO - CN^- C_2H_4]$



In a substitution reaction in which there is more than one possibility as to which chloride will be replaced, the trans directing series is used to predict which structure will be possible

	BEGINNI	ER'S BOX-6								
1.	$K_4[Fe(CN)_6]$ reacts with $FeCl_3$ to form : -									
	(1) $K_3[Fe(CN)_6]$	$(2) K_4[Fe(CN)_3Cl_3]$								
	$(3) \mathbf{K}_{3}[Fe(\mathbf{CN})_{5}\mathbf{CI}]$	(4) $KFe[Fe(CN)_6]$								
2.	A blue colouration is not obtained when :									
	(1) NH ₄ OH is added to CuSO ₄	(2) CuSO ₄ solution reacts with $K_4(Fe(CN)_6]$								
	(3) FeCl ₃ reacts with $K_4(Fe(CN)_6]$	(4) Anhydrous white $CuSO_4$ is dissolved in water								
•										
3.	A reagent used for identifying nickel ion is	: (2) Phonolphalin								
	(1) Folassium refrocyanide (3) Dimethyl glyoxime	(2) FIDTA								
	(3) Dimetriyi giyoxine									
4.	Match the. following									
	Complex Prop	erty								
	(A) $[Pt(NH_3)_4Cl_2]$ (P) reacts	with H ₂ S gas								
	(B) $K_3(Cu(CN)_4]$ (Q) estimation	ation of hardness								
	(C) $[Ca(EDTA)]^2$ (R) remove (D) $V_1[Cd(CN)]$ (S) anti a	val of lead poisoning								
	(D) $K_2[Cd(CN)_4]$ (S) and C (1)(A) S T (B) T (C) O P (D) P T	ancer drug in coordination number of metal is = 4 (2) (A) S (B) T (C) O P (D) P T								
	(1)(A)-5,1, (D) 1, (C) Q, R(D) 1, 1 (3) (A)-P. (B) T. (C) Q. R (D) P. T.	(2) (A)-S (D) 1, (C) Q, (D) 1, 1 (4) (A)-R (B) T (C) Q R (D) P T								
	(3)(11)(1,(D)(1,(C)(Q,(C(D)(1,((D)(1,((D)(1,(((((((((((1)(1)(1)(1)(1)(1)(1)(1)(1)(1)(1)(1)(1)(
5.	A person suffering from lead poisoning sho	ould be fed with :-								
	(1) Hypo (2) Cis-platin	(3) $[Ca(EDTA))^{2-}$ (4) DMG								
6	Zeigler patta catalyst is:									
0.	(1) $[RhCl(PPh_2)_2]$	(2) Al(C_2H_5) ₂ + TiCl ₄								
	(1) $[(1 + 1)^{3}]$ (3) $K(PtC)_{2}(n^{2} - C_{2}H_{4})]$	(2) Pt/Rh								
7.	In which of the following process OMC is :	formed with the help of other OMC :								
	(1) $SnCl_4 + Butyl lithium \longrightarrow Bu_4Sn + 4L$	iCl								
	(2) $C_2H_5I + 4Pb/Na \text{ (alloy)} \longrightarrow (C_2H_5)Pb$	+4NaI $+3$ Pb								
	$(3) \operatorname{Ni} + 4\operatorname{CO} \longrightarrow [\operatorname{Ni}(\operatorname{CO})_4)$									
	$(4) K_2[PtCl_4) + CH_2 = CH_2 \longrightarrow K(PtCl_3)$	$C_2H_4)] + KCl$								
8	Which is/are organomatallia compound									
0.	(I) Grignard reagent (II) Sodium methoxi	de (III) trimethyl boron (IV) TEI								
	(1) Only I (2) I & II	(3) I. II. IV (4) I. III. IV								
9.	Which of the following is an organometalli	c compound:								
	(1) $Ti(OCOCH_3)_4$	(2) $Ti(OC_6H_5)_4$								
	$(3) \operatorname{Ti}(\operatorname{OC}_{2}\operatorname{H}_{5})\operatorname{C}_{2}\operatorname{H}_{5}$	$(4) \operatorname{Ti}(\operatorname{OC}_2\operatorname{H}_5)_4$								
	AIND W.									

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BEGINNER'S BOX-1													
1.	(3)	2.	(4)	3.	(3)	4.	(1)	5.	()	6.	()	7.	(2)
8	(3)	0	(2)	10	(2)		(-)						(-)
0.	(\mathbf{J})	9.	(2)	10.	(2)								
					BF	EGINN	ER'S B	OX-2					
1.	(3)	2.	(4)	3.	(3)	4.	(3)	5.	(1)	6.	(4)	7.	(1)
8	$\hat{(1)}$	9	(3)	10	(4)				~ /		, í		
0.	(1)		(\mathbf{J})	10.	(1)								
_					DI								
					BF	GINN	ER'S B	OX-3					
1.	(4)	2.	(4)	3.	(2)	4.	(2)	5.	(3)	6.	(1)	7.	(3)
8.	(3)	9.	(3)	10.	(1)								
	(-)		(-)										
					DI	CINN	ED'S D	OV 1					
4	(2)	-		-	BE	JGINN	EK S B	UA-4	(2)	-			
1.	(3)	2.	(1)	3.	(3)	4.	(2)	5.	(3)	6.	()	7.	(4)
8.	(4)	9.	(3)	10.	(1)								
					BF	GINN	ER'S B	OX-5					
1	(1)	2	(2)	2	(2)	1	(1,2)	5	(1)	6	(A)	7	(4)
1.	(1)	<i>4</i> .	(2)	J.	(2)	4.	(1,2)	5.	(1)	0.	(4)	/.	(4)
8.	(2)	9.	(4)	10.	(4)								
					BF	EGINN	ER'S B	OX-6					
1.	(4)	2.	(2)	3.	(3)	4.	(1)	5.	(3)	6.	(2)	7.	(1)
8	(4)	9	(3)		(-)				(-)		~ /		
0.	(ד)		(\mathbf{J})										

NCERT QUESTIONS (REASONING)

- Q.1 Explain the term Degenerate orbitals :
- Ans. Orbitals which have same energy in a subshell are known as degenerate orbitals.
- **Q.2** What is crystal field splitting ?
- **Ans.** According to CFt the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and negative charge of ligand.

As a ligand approaches the metal ion, the electrons of ligand will be closer to some of the dorbitals and farther away from other causing a loss of degeneracy.

The electrons in the d-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus the d-electrons closer t the ligands will have a higher energy than those further away as a results in the d-orbitals splitting in energy.

This loss of degeneracy of d-orbital is known as crystal field splitting.



The state I represents degeneracy of all the five d-orbitals in the isolated central ion. The state II represents hypothetical degeneracy of all the orbitals at a higher energy level if the negative charge of all the ligands is assumed to be uniformly affecting the electrons in the d-orbitals of the metal ion. The state III represents crystal field splitting.

Q.3 Define (a) crystal field stablisation energy (b) Pairing energy ?

Ans. (a) Crystal field stablisation energy : The lowering in the energy of a transition metal ion in a given ligand environment due to crystal field effects.
(b) Pairing energy : The energy required to pair the electrons.

- **Q.4** Explain the term
 - (a) Inner orbital complex and outer prbital complexes ?
 - (b) Low spin and high spin complexes ?
- Ans. (a) The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and these complexes are called as **Inner orbital complexes** and **outer orbital complexes** respectively.

For example in d^2sp^3 hybridlsation (n–1)d, ns and np orbitals are mixed it forms inner orbital complex and in sp^3d^2 ns, np and nd orbitals are mixed so it forms outer orbitals complex,

(b) When the strong field ligand approaches to metal ion value to splitting energy (Δ) is greater than, pairing energy, so it is unfavourable to put electron into high energy orbitals. Therefore, the tower energy orbitals are completely filled before population of the upper sets starts according to the Aufbau principle. Such type of complexes are called low spin complex.

For low spin complexes

splitting energy (Δ > pairing energy (P)

Weak field ligand causes a small splitting of the d-orbitals where splitting energy is less than pairing energy. It is easier to put electrons into the higher energy set of orbital than to pair up in the same low energy orbitals because two electrons in the same orbitals repel each other. So one electron is put into each of the five d-orbitals before any pairing occur in accordance with hund rule.

Such complexes are known as high spin complex.

For high spin complexes splitting energy (Δ) < pairing energy (P)

- **Q.5** In octahedral complex if central metal have configuration d^1 , d^2 , d^3 always make inner orbital complex, Why ?
- Ans. Central metal ion which have d^1 , d^2 , d^3 configuration have at least two vacant orbitals in any ligand environment or with any central metal ion with any oxidation state. So always make inner orbital complex.
- **Q.6** Explain the formation of Na₄(Fe(CN)₆] and Na₄[FeF₆] ? Show which is low spin and which is high spin complex and also calculate the Crystal field stablisation energy (CFSE) ?
- Ans. In given compounds CN^- is strong field ligands and F^- is weak field ligand and in both compounds ions is in +2 oxidation state d⁶ configuration. So in Na₄[Fe(CN)₆] Na₄[FeF₆]



Q. 8 Why the d⁸ configuration always shows paramagnetism 2.83 B.M in octahedral complex?
 Ans. In given d⁸ configuration for octahedral complex for both strong field lignad and weak field lignad is always have two unpaired electron.

