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12th Class Chemistry
Coordination Compounds

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Coordination Compounds

These metal compounds which are made by the combination of two or more ions/molecules in which all the ions/molecules do not dissociate into its constituents in aqueous Solution are known as complex compounds.

- **Coordination compounds :-**

These are the compounds in which a central metal atom or ion is linked to a fixed number of ions or molecules through coordinate bonds.

Example :- $[Cr(NH_3)_3Cl_3]$

- **Addition compounds :-**

when two or more Salts are mixed in a fixed proportion and allowed to crystallise then new type of compounds formed is known as Additional compounds.

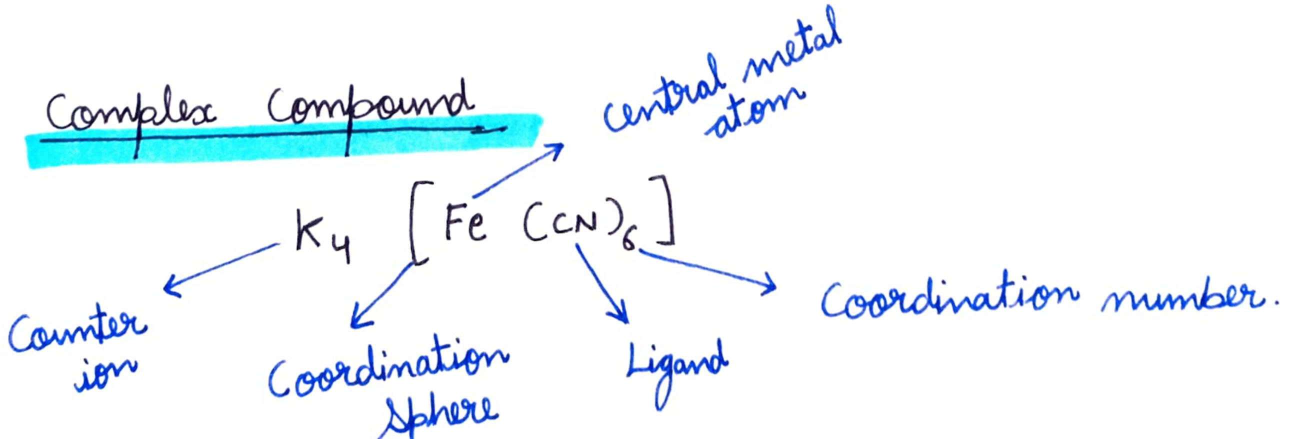
=> Additional compounds have two types

1> Double Salt

2> Complex Salt

Double Salts	Coordination compounds [Complex salts].
=> A double salt is a compound prepared by the combination of two different salt components.	=> A complex salt is a compound composed of a central metal having coordination bonds with ligands around it.
=> Completely dissociate into its ions in water.	=> Do not completely dissociate into its ions in water.
=> They loose its complete identity.	=> They keep some of their identity.
=> They give the tests of all of their constituents.	=> They do not give tests of all constituents.
=> Example :- $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \longrightarrow 2K^+ + SO_4^{2-} + 2Al^{+3} + 24\ H_2O$.	=> Example :- $K_4[Fe(CN)_6]$. $\longrightarrow 4K^+ + [Fe(CN)_6]$

- Complex Compound



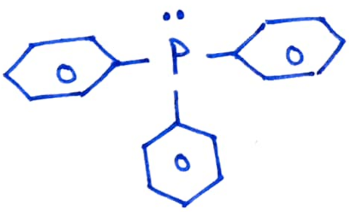
- **Terminology related to coordination compounds :-**

1) **Ligand :-** The donor species [atoms, ions or molecules] which donate a pair of electrons to the central metal atom or ion and form coordinate bonds are called **ligands**.

⇒ **Types of Ligand :-**

(a) **Monodentate or unidentate Ligand :-**
which have one donor atom

Ligand	Name	Charge.
$H_2\ddot{\underset{\cdot\cdot}{O}}$	aqua	0
$\ddot{N}H_3$	Ammine	0
CN^-	Cyano	−1
X^- $[F^-, Cl^-, Br^-, I^-]$	Halido [Fluorido, Chlorido, Bromido, Idido].	−1
H^-	Hydrido	−1
OH^-	Hydroxo	−1
NO_2^-	Nitro	−1
NO_3^-	Nitrato	−1

Ligand	Name	Charge
NH_2^-	Amido	-1
NH^{2-}	imido	-2
N^{3-}	Nitrido	-3
SO_4^{2-}	Sulphato	-2
O^{2-}	oxo	-2
O_2^{2-}	peroxo	-2
S^{2-}	Sulphido	-2
CH_3COO^-	Acetato	-1
CO	Carbonyl	0
NO	Nitrolsyl	0
	Pyridene (Py)	0
	Triphenyl Phosphine	0
$\ddot{P}H_3$	phosphine	0

2> Bidentate or didentate ligand :-

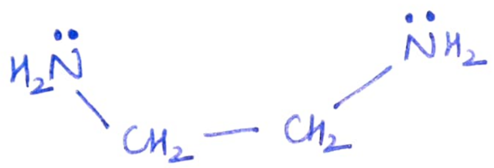
Which have two donor atom.

Example :-

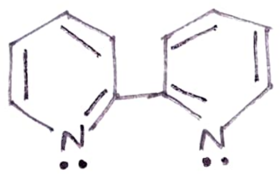
(i) oxalato ligand $[C_2O_4^{2-}]$ (2 donor O- atom).

$$\begin{array}{c} COO^- \\ | \\ COO^- \end{array}$$

(ii) Ethylene diamine (en) or [Ethane- 1,2- diamine]. (2- donor N-atom)



(iii) 2, 2'- bypridine.



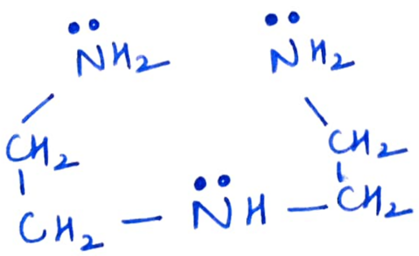
(2 donor N- atom)
Bidentate.

3> Polydentate ligand :-

Which have more than two donor atom.

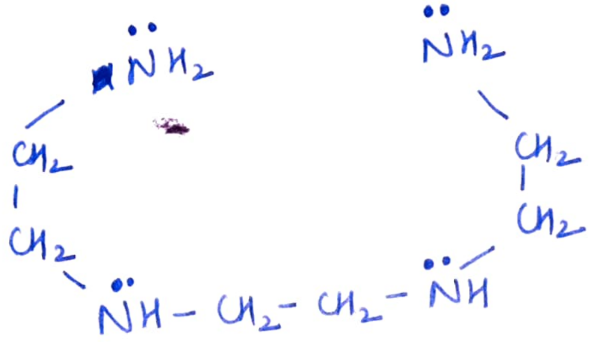
Example :-

(i) Diethylene triamine (dien).



3 donor
N- atom
(Tridentate)

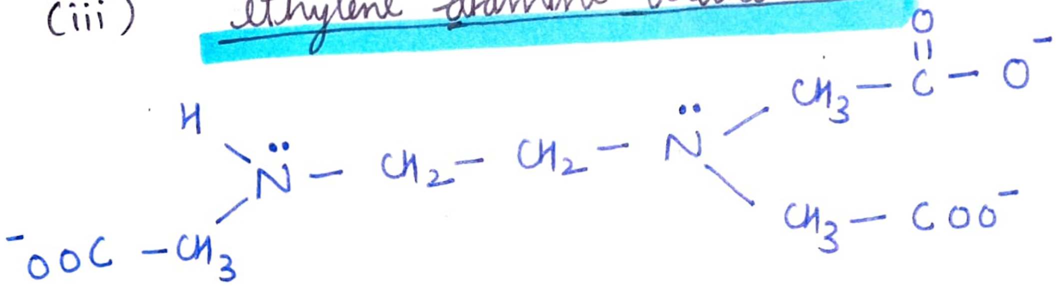
(ii) Triethylene tetramine



(4 donar N-atoms).

(teteradentate).

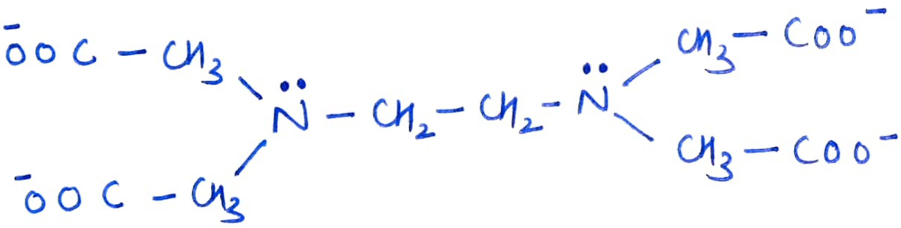
(iii) ethylene diamine triacetate :-



(3 donor O- atom and 2 donor N- atom)

(unsymmetrical) (Pentadentate)

(iv) Ethylene diamine tetracetate :- [EDTA].



[4 donor O- atom and 2 donor N- atom]

(unsymmetrical) (Hexadentate)

4) Ambidentate ligand :-

Those unidentate ligands which have more than one donor atom.

Example :-

$M \leftarrow CN$

Cyano

$M \leftarrow NC$

isocyano

$M \leftarrow SCN$

thiocyanato

$M \leftarrow NCS$

isothiocyanato

nitro

$M \leftarrow O-N=O$

nitrito

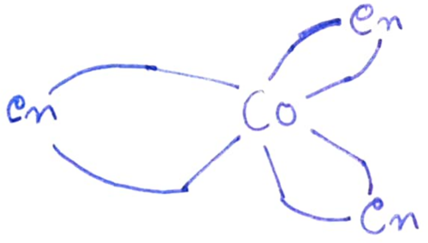
5) Central metal atom or ion :-

Central atom is bonded with ligands through the coordinate bond in which lone pair of ligand is coordinated in the valence shell of central atom.

6) **Chelating Ligand :-**

When a bidentate or a polydentate ligand is attached by two or more atoms to the central atom forming a ring, the ligand is called chelating ligand and the complex is called chelate, the effect is called chelate effect.

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



- **Counter ion :-** The ionizable group which are written outside the coordination sphere.

- **Coordination Sphere :-** Then central metal atom and the ligands are enclosed in Square bracket.

- **Coordination number :-** Total number of coordinate bonds formed with central metal atom by the ligands.

- **Denticity :-** The number of donor atoms present in a ligand is called the denticity of ligand.

- **Nomenclature of coordination compounds.**

=> Rules of Naming of coordination compounds.

(i) The cation is named first in both positively and negatively charged coordination entities.

(ii) The ligands are named in an alphabetical order before the name of the central atom / ion.

(iii) Names of the anionic ligands end in -o. e.g. chloro, cyano etc. Neutral ligands have no special ending like NH_3 (ammine), H_2O (aqua) and positive ligands end in -ium like NO^+ (nitrosonium).

(iv) Prefixes, mono, di, tri etc., are used to indicate the number of individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the term bis, tris, tetrakis are used, that ligand being placed in the parenthesis.

For Example :-

$[NiCl_2(PPh_3)_2]$ is named as dichlorobis (triphenylphosphine) nickel (II).

(v) oxidation State of the metal in cation, anion or neutral Coordination entity is indicated by Roman numeral in parenthesis.

- Write the IUPAC name of :- [CBSE Previous year question].

1> $K_3[CrF_6]$ (CBSE-2011)

=> Potassium hexafluorochromate (III)

2> $[PtCl(NH_2CH_3)(NH_3)_2]Cl$ (CBSE-2011)

=> diamminechloridomethylamine platinum (II) chloride.

3> $[Pt(NH_3)_4Cl_2]Cl_2$ (CBSE- 2011 C)

=> tetraamminedichloridomethylamine platinum (II) chloride.

4> $[Cr(NH_3)_6][Co(CN)_6]$ (CBSE - 2012)

=> hexaamminechromium (III) hexacyanocobaltate (III)

5> $[Pt(NH_3)_3(NO)Cl_2]Br_2$ (CBSE - 2011 C)

=> triamminedichloridonitrosyl platinum (IV) bromide.

6> $[Co(CN)_2(NH_3)_4]Cl$ (CBSE -2010)

=> tetraamminedicyanocobalt (III) chloride.

7> $[Cr(NH_3)_5(NCS)][ZnCl_4]$ (CBSE- 2012 C)

=> pentaammineisothiocyanato chromium (III) tetrachlorozincate (II

- Using IUPAC norms write the formulae for the following :-

1> Sodium dicyanidoaurate (I). (CBSE- 2017)

=> $Na[Au(CN)_2]$

2> Tetraamminechloridonitrito-N-Platinum (IV) Sulphate.

=> $[Pt(NH_3)_4Cl(NO_2)]SO_4$.

- Isomerism in coordination compounds.

⇒ This arises due to different structural arrangements (structural isomerism) or spatial arrangements (stereoisomerism) of compounds having same formula.

- Structural isomerism.

1) Ionisation isomerism :-

Compounds which give different ions in solution due to the exchange of ions in coordination sphere and counter ions are called ionisation isomers.

Example:- $[Co\,Br(NH_3)_5]SO_4$.

$[Co\,SO_4(NH_3)_5]Br$.

2) Soluate / Hydrate isomerism :- The isomers which have similar composition but differ in the presence of number of water molecules as ligand, e.g.

$[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ and

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

3) Linkage isomerism :- When complexes differ only in the point of attachment of ambident ligand with central metal atom.

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

4) Coordination isomerism :-

when the interchange of ligands take place between cationic and anionic entities of different metal ions present in a complex.

Example:-

$[Co(en)_3][Cr(CN)_6]$ and $[Cr(en)_3][Co(CN)_6]$.

- **Stereoisomerism :-**

which have same formula but different spatial arrangement.

=> It has two types :-

(i) Geometrical isomerism (ii) Optical isomerism

=> Geometrical isomerism :-

→ when similar groups are present in adjacent position, it is Cis.

→ when they are present in opposite position, it is trans.

=> It occurs in Square planar compound of type $[MA_2B_2]$, $[MA_2BC]$, $[M(AB)_2]$ [AB = unsymmetrical ligand] and octahedral. Complexes of type $[MA_4B_2]$, $[M(AA)_2B_2]$ or $[M(AA)_2BC]$ [AA = Symmetrical bidentate ligand]. and $[MA_3B_3]$ shows fac (facial) and mer (meridional) geometrical isomers.

- Optical isomerism :-

=> This is shown by complexes whose mirror images are non-superimposable. Such complexes are called optical isomers.

=> It is shown by octahedral complexes and exists in two forms laevo and dextro. The isomer which rotates the plane polarised light towards right is called dextro rotatory (d-) and the other rotates towards left is called laevo-rotatory (l-).

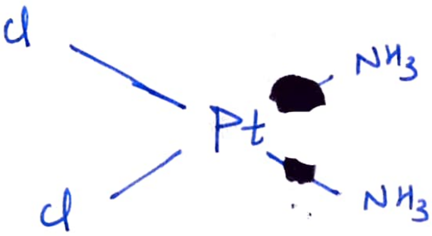
=> It is shown by the complexes of the type $[M(AA)_3]$, $[M(AA)_2B_2]$ [only cis-form shows optical isomerism but not trans form], $[M(AA)_2AB]$ (only cis-form but not trans form) and $M(AA)A_2B_2$. [AA= bidentate ligand like en, ox].

=> Tetrahedral Complexes [MA_4 or MA_3B] do not show geometrical isomerism because the relative positions of unidentate ligands attached with central atom are the same with respect to each other.

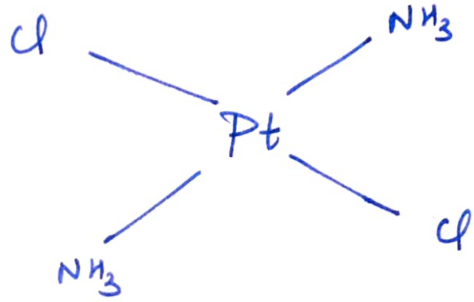
Example :-

1) Geometrical isomers of $[Pt(NH_3)_2Cl_2]$.

C.NO:- 4 (Square Planar arrangement)



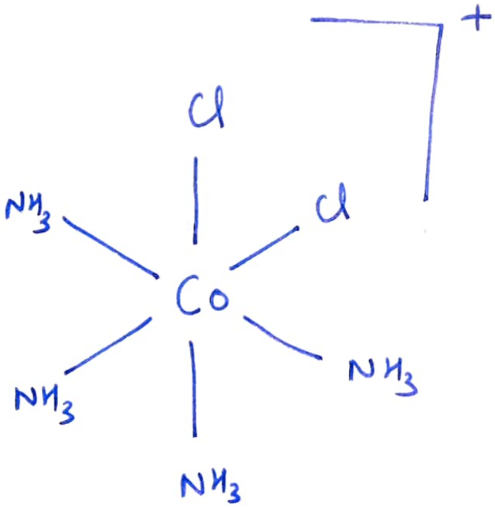
cis



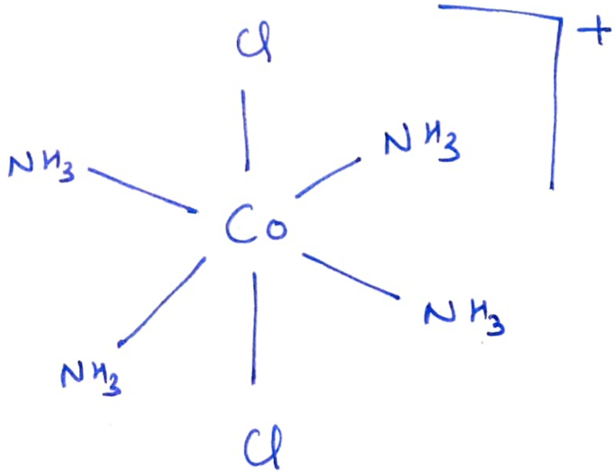
tran

2> Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]^+$

C.NO:- 6 [octahedral structure].

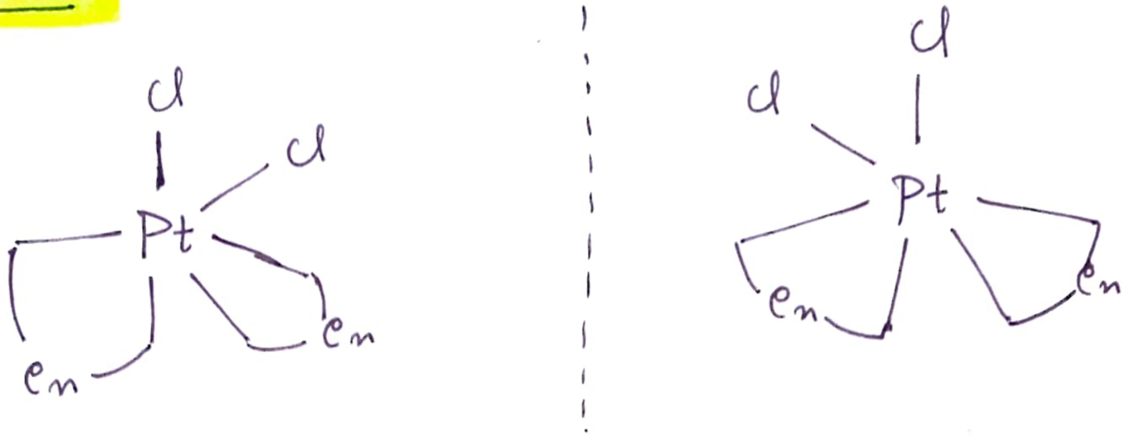


cis



trans

Example :-

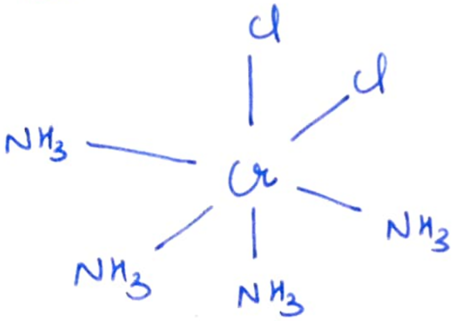


optical isomers of (d and l) of cis-$[Pt Cl_2 (en)_2]^{2+}$

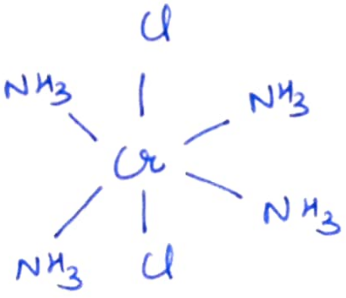
Ques = Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. What type of isomerism does it exhibit ? [CBSE- 2014, 2017].

=> IUPAC name = tetraamminedichlorido chromium (III) ion.

=> It shows geometrical isomerism and has two isomers cis and trans that can be represented as :-



cis - form



trans- form.

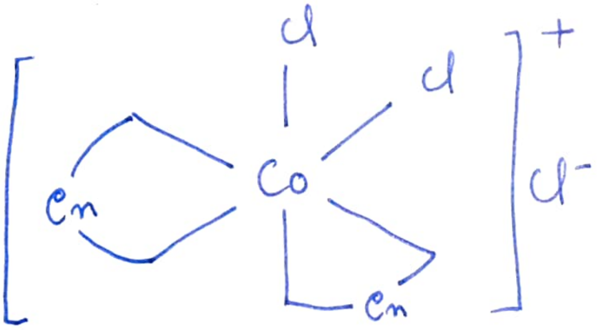
Ques = Draw the structures of isomers, if any and write the names of the following complesc.

(CBSE-2011)

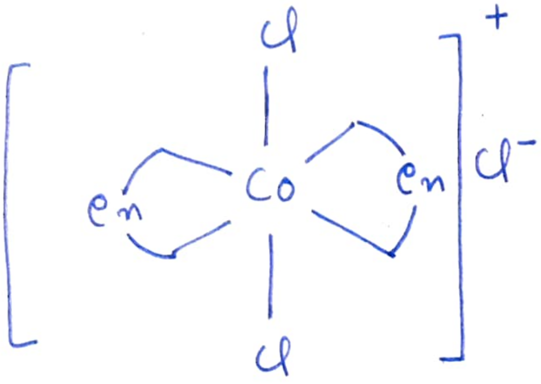
(i) $[Co\,Cl_2\,(en)_2]\,Cl$

=> IUPAC name = dichlorido bis (ethane-1,2-diamine) Cobalt (III) chloride.

Structure :- There are two possible structures of $[Co\,Cl_2\,(en)_2]\,Cl_2$, one is cis and other is trans that can be represented as:-



cis-form

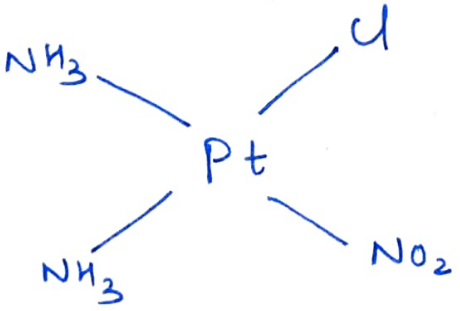


trans-form.

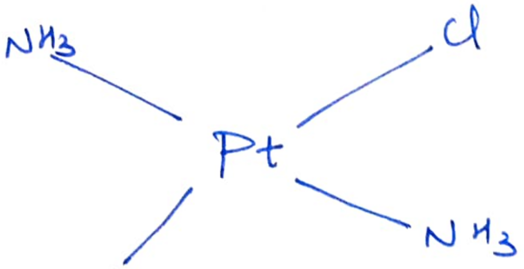
(ii) $[Pt\,(NH_3)_2\,Cl\,(NO_2)]$

=> IUPAC Name = diamminechloridonitrito-N-platinate (II)

Structure :- There are two structures



cis form.



trans-form.

- **Werner's Theory of Coordination Compounds**

=> According to werner's theory, metals consist of two types of valencies called Primary valency and Secondary valency.

=> **Primary valency :-** It is equal to oxidation state of central metal atom.

=> **Secondary valency :-** It is equal to coordination number.

- **Valence Bond theory (VBT) :-**

=> Its Postulates are :-

1> Metal ligand bond is formed by the donation of electrons by ligand to metal.

2> Metal atom/ion must have vacant orbitals of equal energies, equal to the number of ligands to be attached.

3> Sometimes unpaired $(n-1)d$ electrons pair up to create empty orbitals

4> Depending upon the type of hybridisation d^2sp^3 (or sp^3d^2), dsp^2 and sp^3, the shapes of the complex are octahedral, square planar and tetrahedral respectively.

5> If no unpaired electron is present, then complex is **diamagnetic**. If unpaired electrons are present, complex is **paramagnetic**.

6> If coordination number is 6, complex is octahedral with **sp^3d^2** or **d^2sp^3** hybridisation.

7> In strong field ligand forces, the d- electrons of central metal are pair up against Hund's rule. The strong field ligand which causes this are CO, NO, CN^-, NO_2^-, NH_3, en. Some weak field ligands are H_2O, X^-, NO_3^-, ROH etc.

8> If complex formed involves inner (n-1) d orbitals for hybridisation, it is called inner orbital or low spin or spin paired complex, e.g. $[Ni(CN)_4]^{2-}$. whereas, if complex formed involves outer (n)d orbitals for hybridisation, it is called outer orbital, high spin. or spin free complex e.g. $[Ni(H_2O)_6]$.

=>

Coordination Number	Type of hybridisation	Geometry
4	sp^3 →	Teterahedral
	dsp^2 →	Square planar
5	dsp^3 →	Trigonal bipyramidal
	sp^3d →	Square pyramidal
6	d^2sp^3 →	octahedral (Inner complex)
	sp^3d^2 →	octahedral (outer complex).

• Limitations of Valence bond theory :-

1) It does not give quantitative interpretation of magnetic data.

2) It does not explain the colour of coordination Compounds.

3) It does not give an exact explanation of thermodynamics or Kinetic Stabilities of coordination compounds.

4) It does not distinguish between weak and strong ligands.

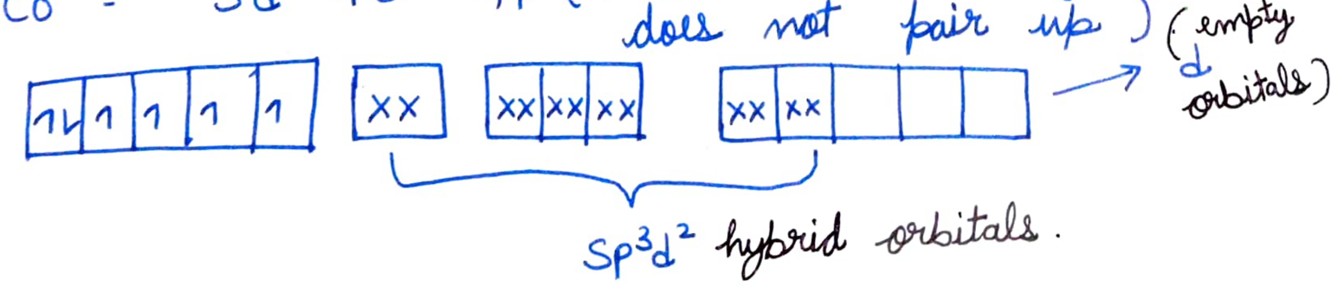
5) It does not predict the tetrahedral or Square planar Structures for 4- Coordinate complexes.

Ques = Write the hybridisation and shape of the following complexes :- (CBSE - 2014 C).

(i) $[CoF_6]^{3-}$

=> oxidation of Co = +3.

Co^{+3} = $3d^6\ 4s^0\ 4p$ (Flourine is weak ligand, it does not pair up)



=> Hybridisation = sp^3d^2

=> Geometry = octahedral.

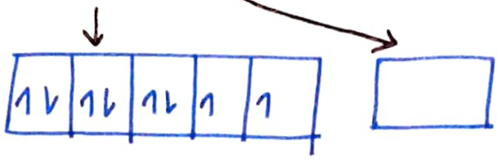
(outer orbital complex).

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

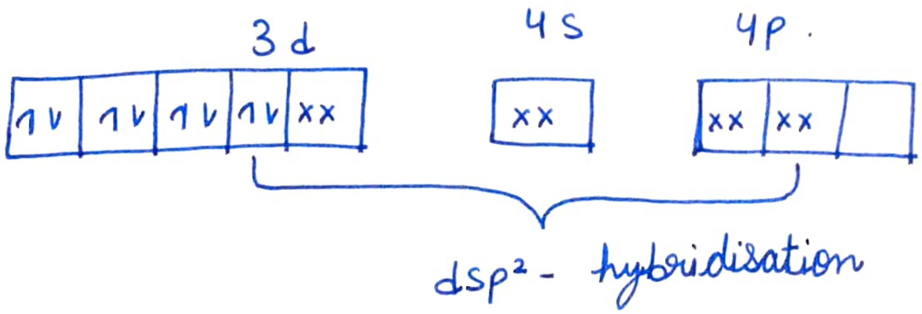
=> oxidation State of nickel = +2.

(Ni = 28)

$Ni^{+2} = 3d^8\ 4s^0$



(CN is strong ligand. it pair up the electrons in d-orbital).



Hybridisation = dsp^2.

Geometry = octahedral.

CRYSTAL FIELD THEORY [CFT]

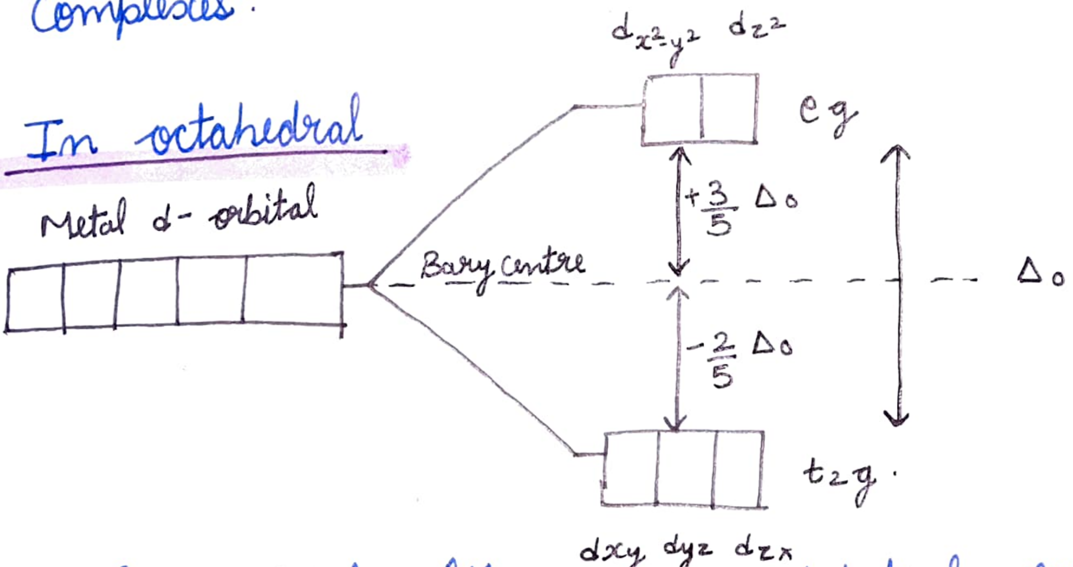
=> Crystal field theory is more appropriate theory than valence band theory (VBT). According to CFT, under the influence of ligand field, degeneracy of the d-orbital is destroyed and it Splits into two or more energy levels. The extent of Splitting depends upon the strength of ligand. A strong ligand causes greater Spilliting. While a weak ligand causes smaller Spilliting.

=> The difference of energy between the two sets of d- orbitals (in octahedral complexes) is called **Crystal field Spilliting Energy.** [CFSE] or Δ_o

=> Geometry of the Complex :-

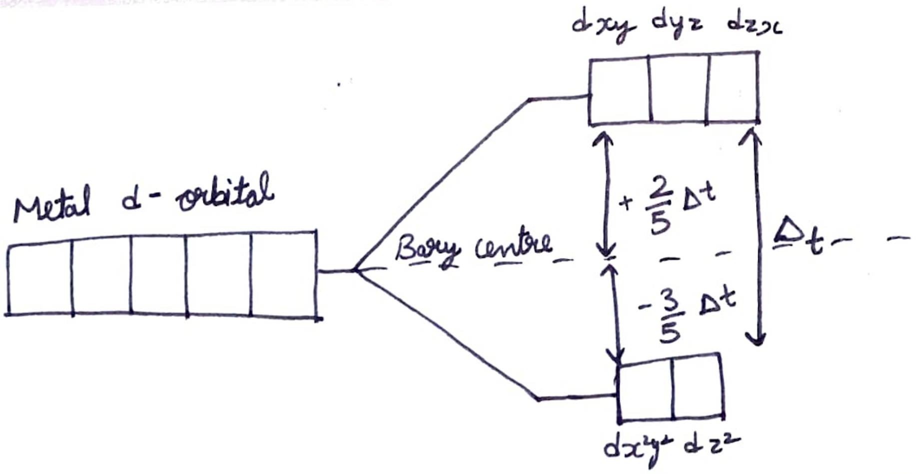
=> Splitting is different for tetrahedral and octahedral complexes.

In octahedral



(d- orbital splitting in a octahedral crystal field).

In Tetrahedral



(d- orbital Splitting in a tetrahedral crystal field).

=> octahedral complexes e_g set $[d_{x^2-y^2}, d_{z^2}]$ is of higher energy while in case of tetrahedral complexes t_{2g} set $[d_{xy}, d_{yz}, d_{zx}]$ has higher energy.

- Factors affecting the magnitude of CFSE :-

=> Spectrochemical Series :-

The arrangement of ligands in order of their increasing crystal field splitting energy [CFSE] values is called spectrochemical series.

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O <$
$NCS^- < EDTA^{4-} < NH_3 < en < NO_2^- < CN^- < CO$.

In case of d^4 ions, two possible pattern of electron distribution arise.
These are explained below.

[P = It is energy required for e- pairing in a single orbital.
Δ_o = crystal field splitting.]

1> If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_2^3 e_g^1$. Ligands for which $\Delta_o < P$, are weak ~~lig~~ field ligands and they form high spin complexes.

2> If $\Delta_o > P$, the fourth electron enters t_{2g} orbital giving the configuration $t_2^4 e_g^0$. Ligands for which $\Delta_o > P$, are strong field ligands and they form low spin complexes.