

Co-ordination compound

Complex compound or co-ordination compound —

The complex in which the central metal atom directly bonded to ligand through co-ordination bond is called complex or co-ordination compound.

Central metal atom —

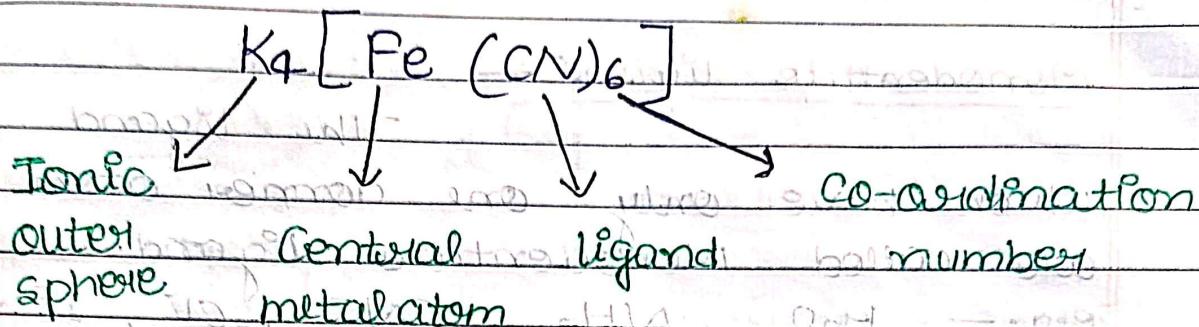
The transition metal atom in complex compound which is surrounded by ligand and bonded to these through co-ordination bond is called central metal atom.

Co-ordination number —

The total number of co-ordination bond in complex compound is called co-ordination number.

OR

The total number of monodentate ligand in complex compound is called co-ordination number.



Ligands —

The ions, groups or molecule which are attached to the central metal ion are through co-ordination number are called ligand.

Ligand donate a pair of electron to central metal atom in complex compound.

Types of Ligands —

On the basis of number of atom which donate a pair of electron to central metal atom in complex compound. Ligands may be following type—

- i - Monodentate or Unidentate
- ii - Bidentate
- iii - Tridentate
- iv - Tetradentate
- v - Polydentate

Monodentate ligand

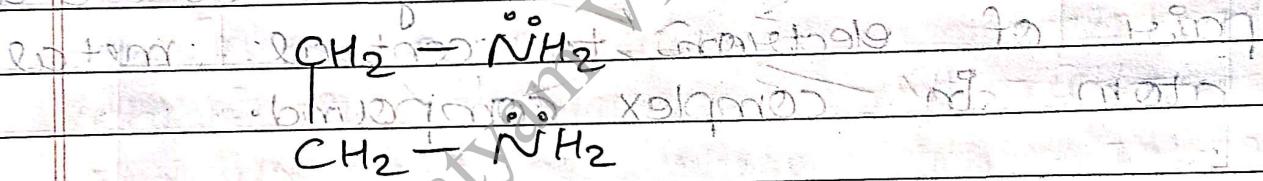
The ligand which have only one donor atom are called Monodentate ligand.

e.g. — H_2O , NH_3 , CN^- , Cl^- ; I^- etc.

Bidentate ligand

The ligand which have two donor atom are called bidentate ligand.

e.g. — ethylene diamine



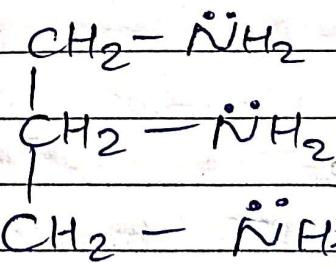
Oxylate ion



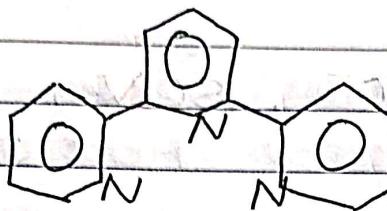
Tridentate ligand

The ligand which have three donor atom are called tridentate ligand.

e.g. —



Tri amine propane



Tri pyridine

stabilizes the metal cation

Tetra dentate ligand —

The ligand which have four donor atom.

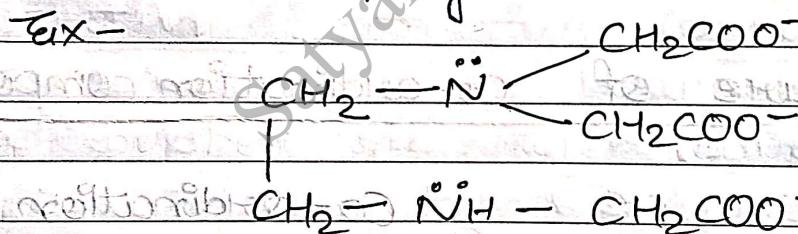
Ex — $(\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}$ — triethylenetriamine

TETRA (2-aminoethyl) amine

Polydentate ligand —

The ligand which have more than four donor atom is called polydentate ligand.

Ex —



Ethylenediamine tetraacetate ion

(EDTA⁴⁻)

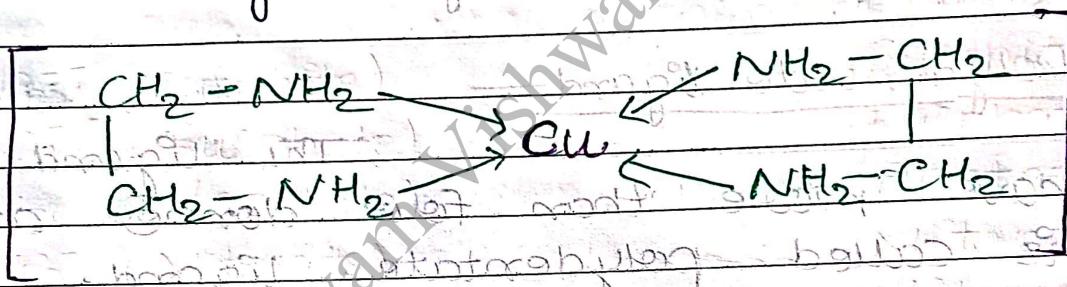
Ambidentate ligand —

The ligand which may be co-ordinate to the central metal ion through more than one donor atom are called ambidentate ligand.

Ex- NO_2^- , ONO^- , SCN , NCS

Chelate compound—

The cyclic complex formed when a multidentate ligand attach through two or more atom to the same central metal atom are called chelate compound. The multidentate ligand chelating dentate.



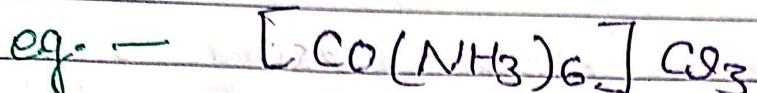
Nomenclature of co-ordination compound—

Co-ordination compound are name I.U.P.A.C system. In this system of nomenclature the following rules are observed.

Order of naming Pn.—

In ionic complex

the cation is named first followed by the anion.



Hexammine cobalt (III) chloride

Naming of co-ordination sphere

In naming of co-ordination sphere, the ligand are named first and then central metal ion.

Order of naming ligand

The order of naming ligand is negative, neutral, positive with separations of hyphens.

Naming of negative ligand

In general, if anion names end in -ide, it is replaced by (o)xyanion.

Name of Negative ligand (Replace of 'ide')

Negative ligand

Name

F^-

fluoro

Cl^-

chloro

Br^-

bromo

OH^-

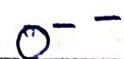
hydroxo

CN^-

cyanato

NO_2^-

Nitro



Oxo



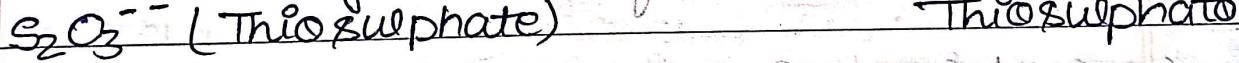
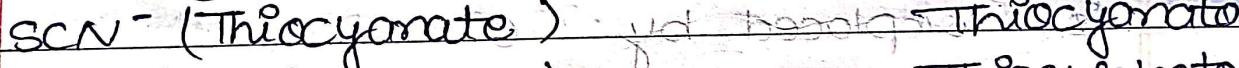
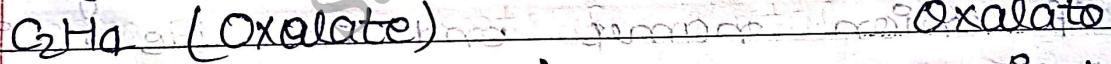
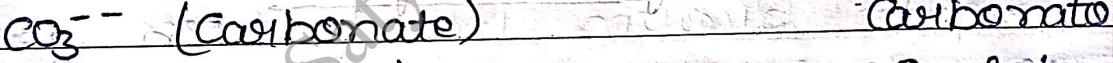
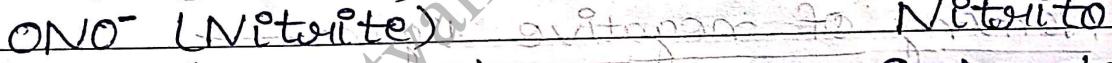
Peroxo

Name of negative ligand (Replace of 'ate')

In general if anion names end in 'ite' or 'ate' it is the final 'e' which is replaced by 'o'

Negative ligand

Name



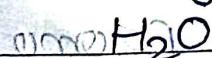
Naming of Neutral ligand

Neutral ligand

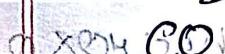
Name



Amine



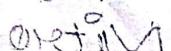
Aqua



Carbonyl



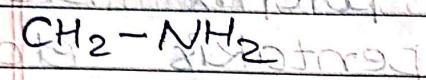
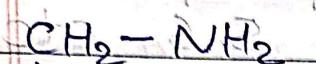
Nitrosyl



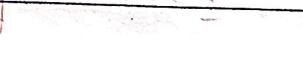
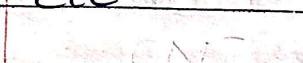
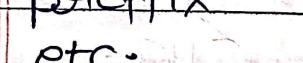
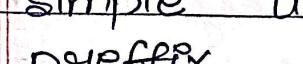
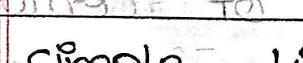
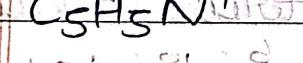
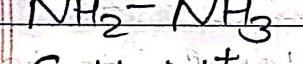
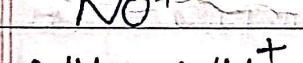
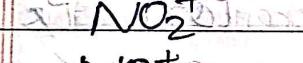
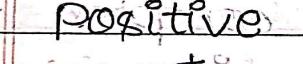
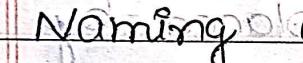
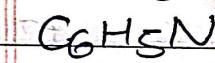
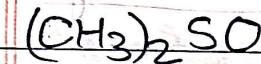
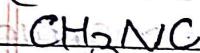
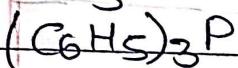
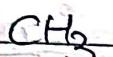
OH

CS

(also NS dipyridyl, diphenyl)



C_6H_5



Thiocarbonyl

Thio Nitosyl

Magnesium Rides

Ethylen diamine (en)

phenyl

methyl

Tri phenyl phosphine

Methyl isocyanate

Iothioeyanate

urea

Dimethyl sulphoxide

pyridine

Naming of positive ligand

positive ligand its name

NO_2^+ Nitronium

NO^+ Nitrosonium

$\text{NH}_2 - \text{NH}_3^+$ Hydrazinium

$\text{C}_5\text{H}_5\text{N}^+$ Pyridinium

hydrazine

Number of ligand

The number of

simple ligand is indicated by greek

prefix di, tri, tetra, penta, Hexa

etc.

If the ligand have complex name such as (en, trialkyl phosphine etc) & their numbers 2, 3, 4, 5, 6 etc.

a) are indicated by prefix bis, tris, tetrakis, pentakis etc.

Naming of the central metal ion —

It is named after naming all the ligands different rules are observed the naming of different complex —

i - For anionic complex the name of central metal ion 'ium' is replaced by 'ate'

ii - For neutral and cationic complex the names of central metal ions is written as usual.

Oxidation state of the central metal ion —

It is indicated by

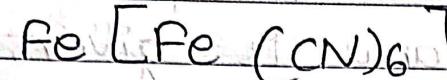
roman number like as = 0, I, II, III

IV etc after naming of central

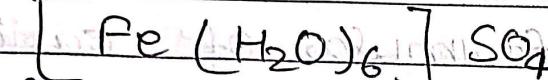
metal atom in its name

oxoH : oxon, metat, metath, metath

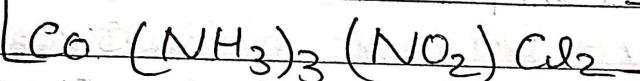
Example —



Tetraammine hexacyanoferrate (III)



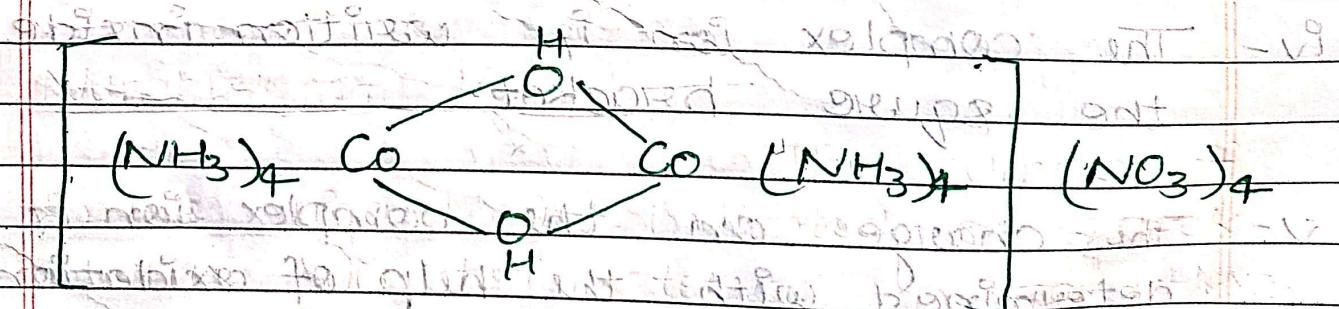
hexaaqua ferri(II) sulphate



tri-amine dichloro nitro cobalt (III)

Naming of bridge complex compound —

If the complex containing two or more metal ion is called polynuclear complex. The ligand which link the two metal atoms are called bridge group and are separated from rest of the complex by hyphens and denoted by greek letter 'μ'.



Octa amine-μ-dihydroxo dicobalt (III) nitrate.

Written formula of complex compound →

The formula of compound if its name is given, the following points are given below—

- i- First write the formula of cation followed by anion present in the complex compound.
- ii- Simple cation or anion are written as the anion obtained from the simple salt.
- iii- Write the formula of complex ion or molecule, ligand and metal ion are in reverse order i.e. first write symbol of metal and then ligand. The ligand are written in the order positive, neutral, negative.
- iv- The complex ion is written inside the square bracket.
- v- The charge on the complex ion is determined with the help of oxidation number of the metal and charge of the ligand.

vi- Cation and anion are multiplied by such a whole number so that positive and negative charge become equal.

Example -

Sodium pentacyanomethyl ferrate (II)
 $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$

Pentaamminenitrocobalt (III) sulphate
 $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$

Isomerism in co-ordination compound

The compound having same molecular formula but different structures and properties are called isomers and this phenomenon is called isomerism.

It is two type -

i- Structural isomerism

ii- Stereoisomerism

Structural isomerism

The isomers which have same molecular formula but different structural arrangement

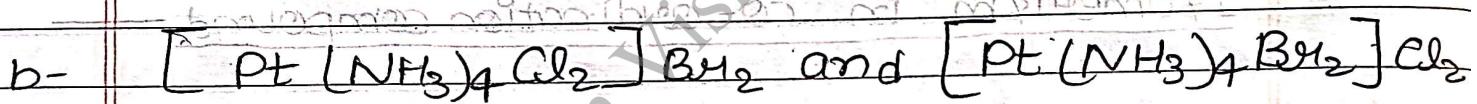
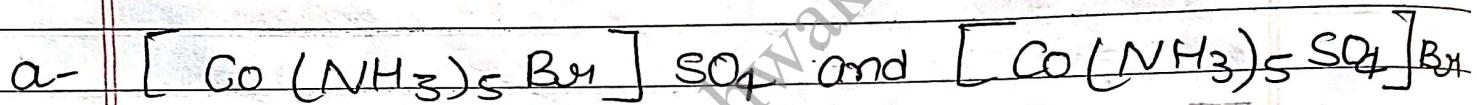
of atom are called structural isomerism.

i- Ionisation isomerism-

The complex

which have same molecular formula

but gives different ion in solution are called ionization isomerism and this phenomenon is called ionization isomerism.

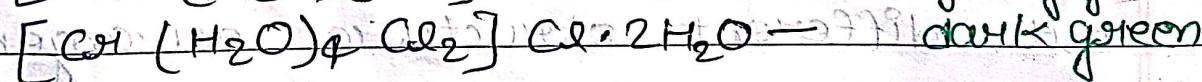
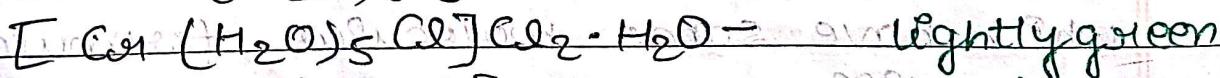
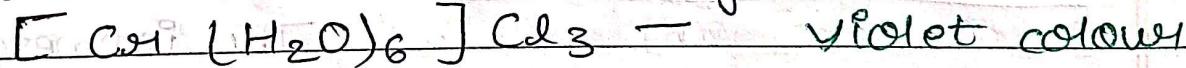


ii- Hydrated isomerism

The isomers obtained by replacing a co-ordinated group by water of hydration are called hydrated isomers and this phenomenon is known as hydrated isomerism.

Example-

Three isomers of $\text{Cr}\cdot\text{Cl}_3(\text{H}_2\text{O})_6$ are known which is given below-

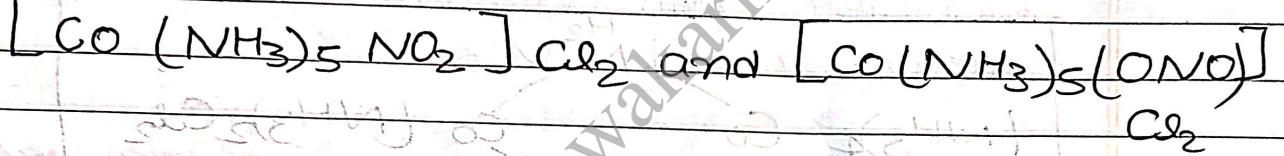


iii-

Linkage Isomerism

This type of isomerism occurs when more than one single atom or a co-ordinated group may act as donor. This type of isomerism is called linkage isomerism.

Example -

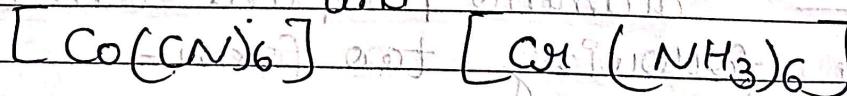


iv-

Co-ordination Isomerism

When both cation and anion are complex isomerism is possible due to the interchange of the ligand between the two complex ion this type of isomerism is called co-ordination isomerism.

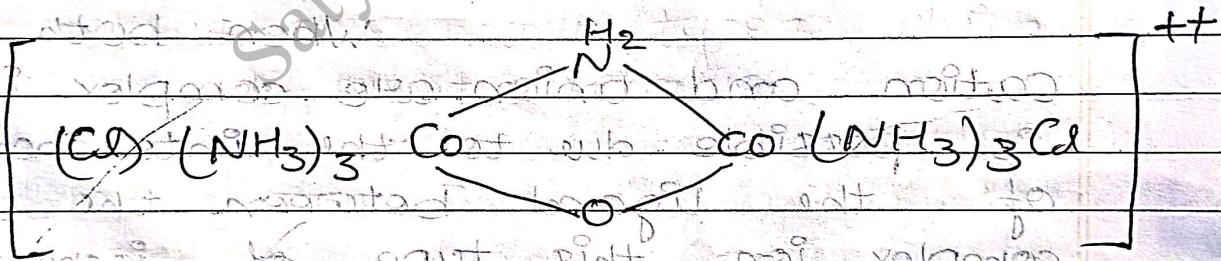
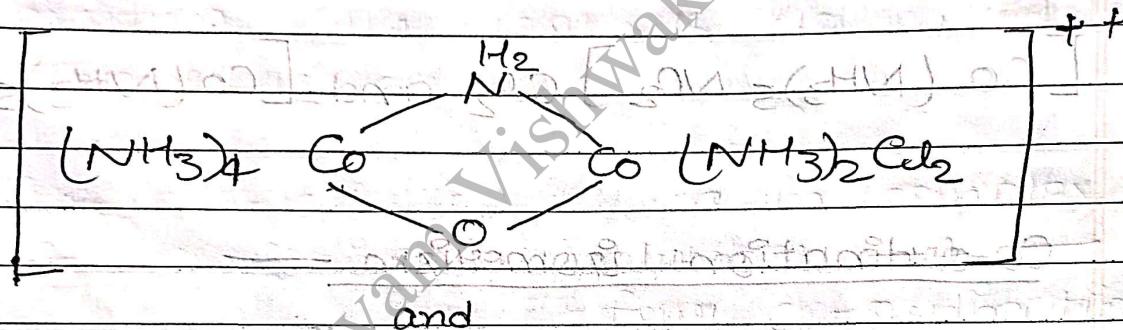
Example -



Co-ordination position isomerism

This isomerism occurs in polynuclear complex in which ligand may be to exchange their position between the different metal nuclei.

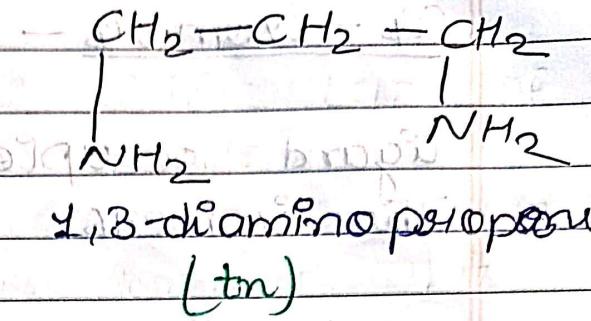
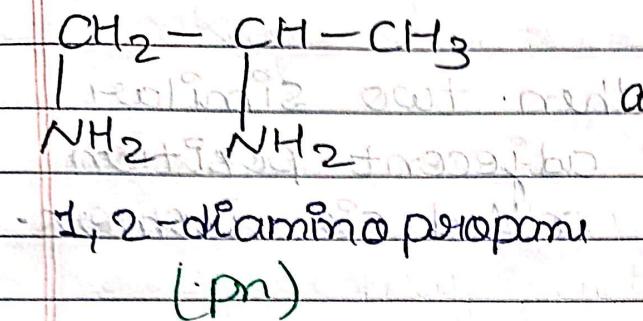
Example —



Ligand isomerism —

This type of isomerism is found in complex in which ligand themselves exist as isomers.

Example — diamino propane can exist in the following two forms —



Stereo Isomerism

This isomerism is due to the difference in the arrangement of ligand in space in a molecule.

The different arrangement are known as stereo isomers and this phenomenon is called stereo isomerism. It is two type —

i- Geometrical Isomerism

ii- Optical Isomerism

i- Geometrical Isomerism

The compound having empirical formula but different physical and chemical properties due to the different arrangement of ligand are called geometrical isomers and the isomerism is called geometrical isomerism.

geometrical isomerism are two form —

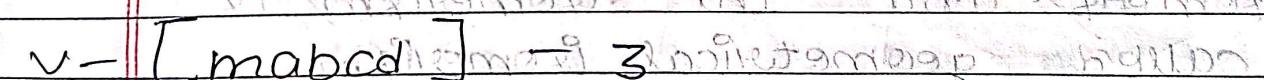
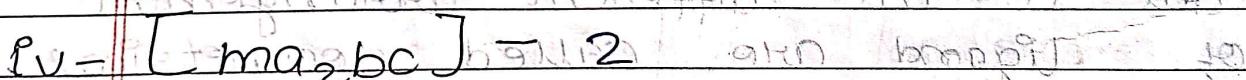
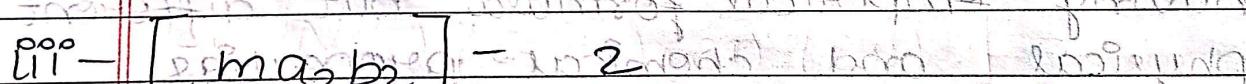
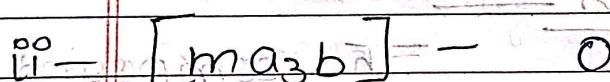
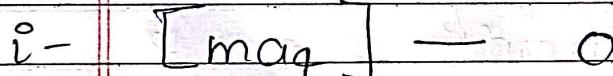
Cis - Isomers -

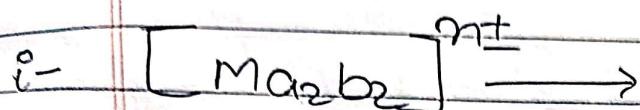
When two similar ligand occupied adjacent position The isomers is called cis - Isomers.

Trans - Isomers -

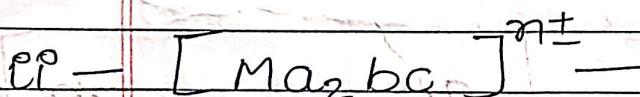
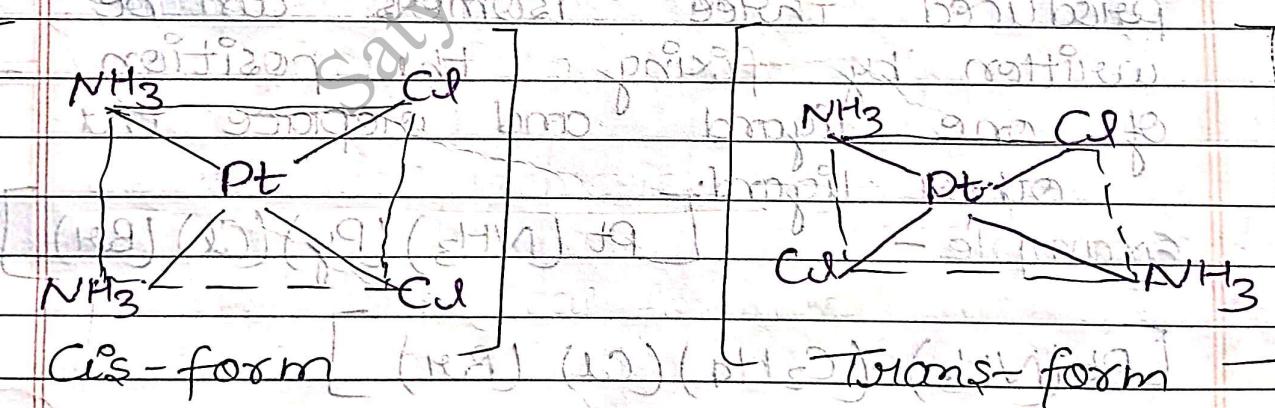
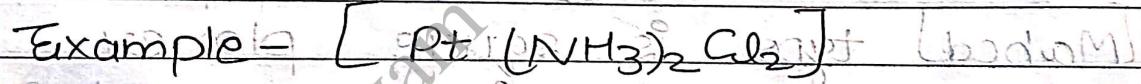
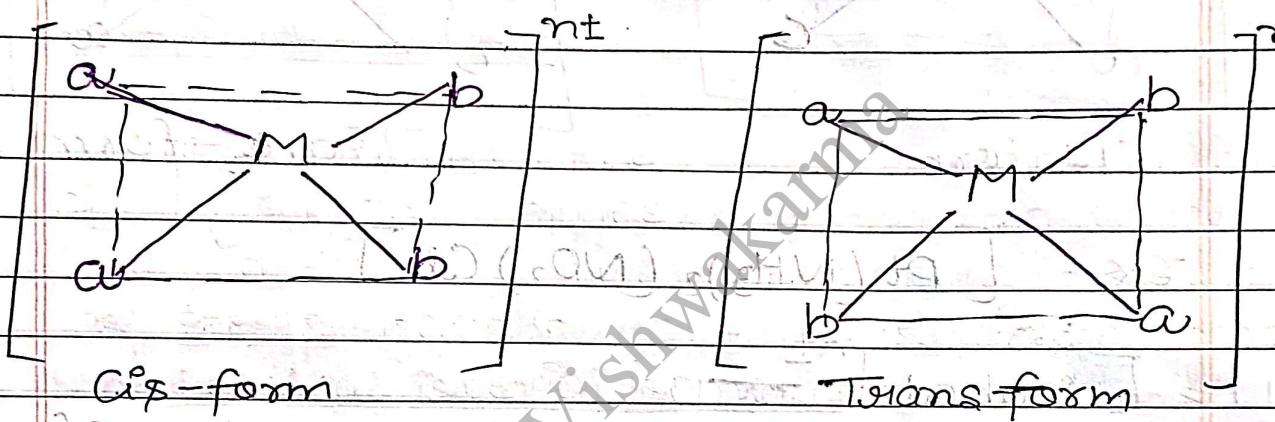
When two similar ligand occupied diagonally opposite position The isomers is called Trans - Isomers.

Geometrical isomerism in complex of co-ordination number = 4
four co-ordination numbers are many types which gives different isomers.



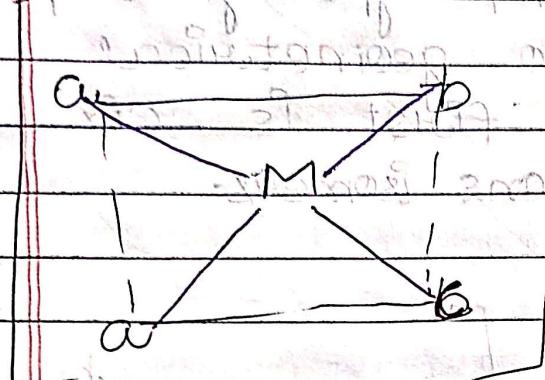


This type of complex compound shows two geometrical isomerism which is first is cis and second is trans isomers.

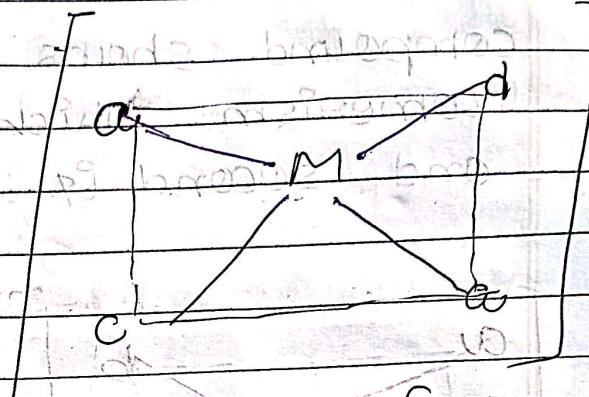


In a complex of the $M_{2}bc$ type there, cis and trans isomers depend upon the two similar groups are adjacent or opposite

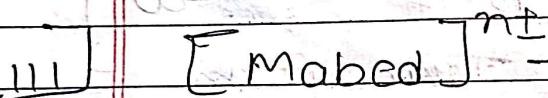
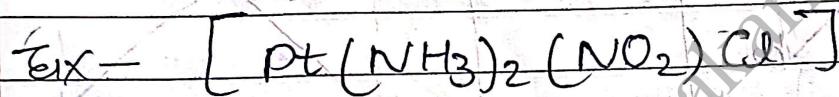
to another.



Cis-form

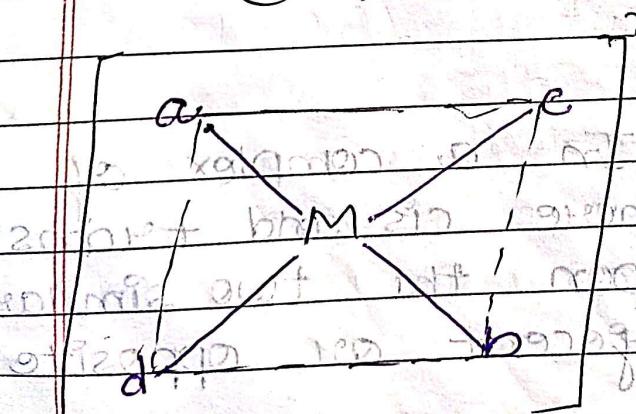
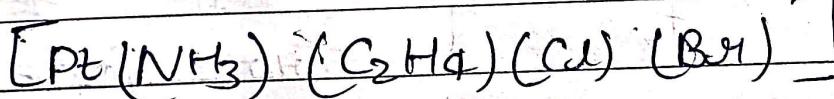
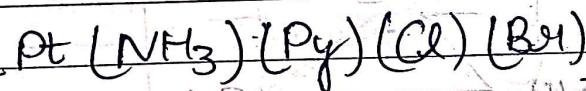


Trans-form

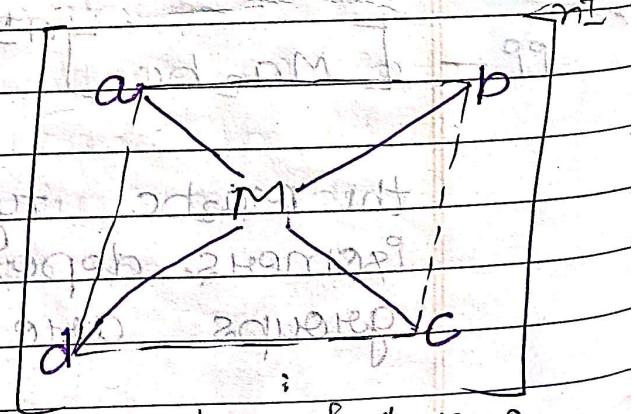


In the complex of $[\text{Mabcd}]$ type is square planar produced three isomers can be written by fixing the position of one ligand and replace the other ligand.

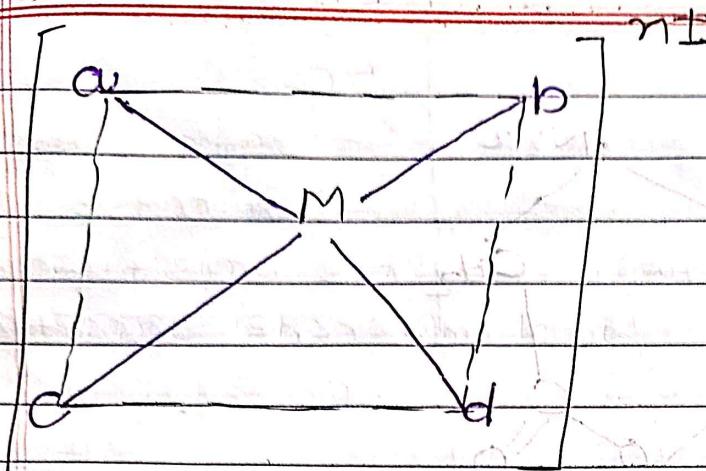
Example -



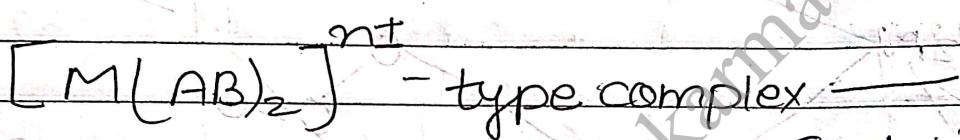
(a-b) trans



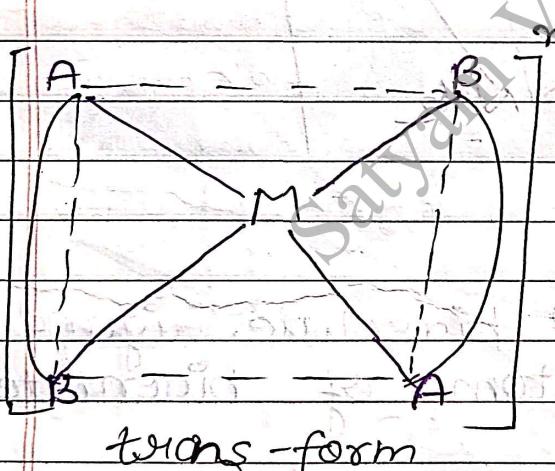
(a-c) trans



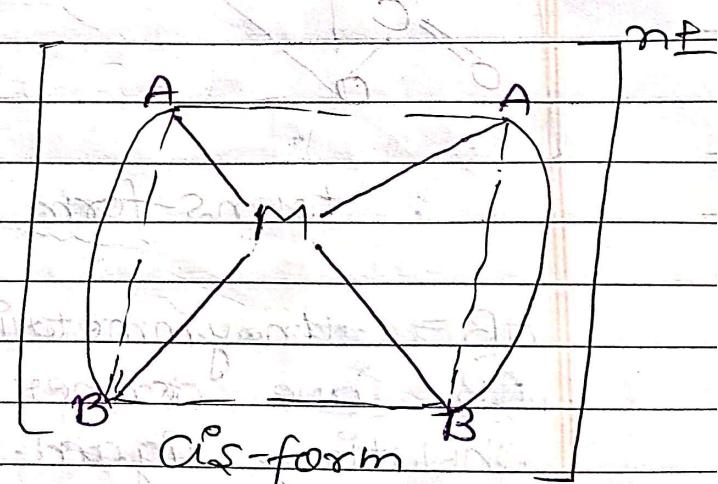
(a-d) trans



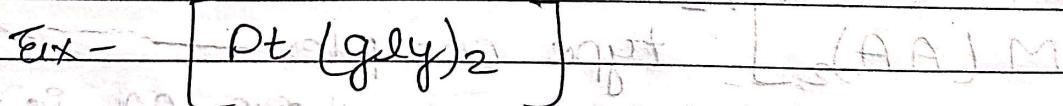
Such type
of complex shows that cis and
trans isomerism which is —



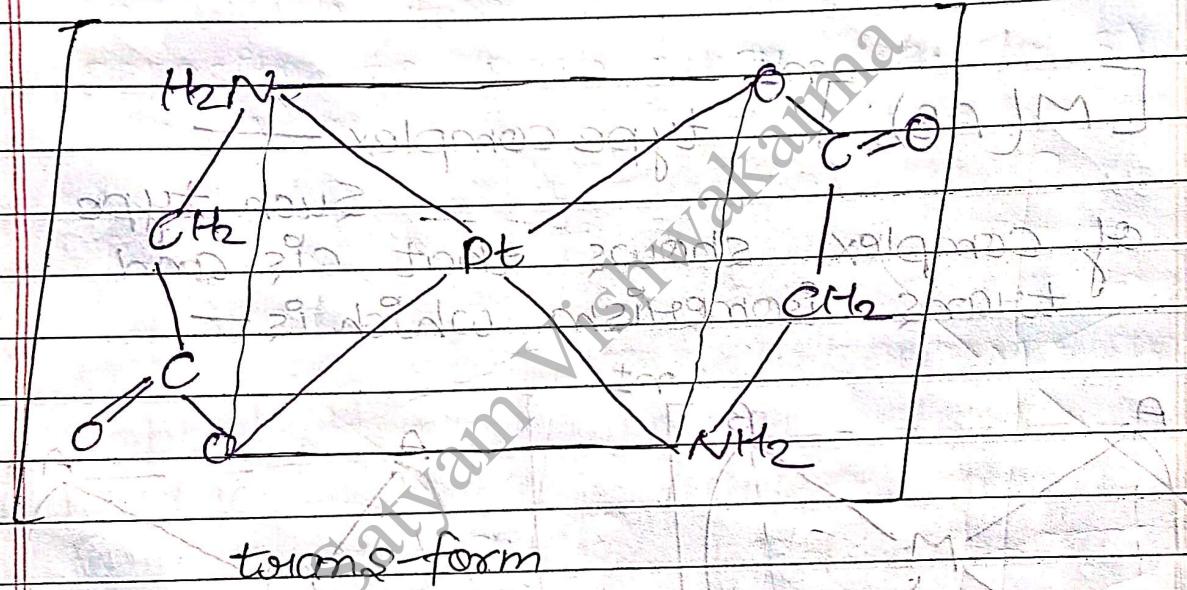
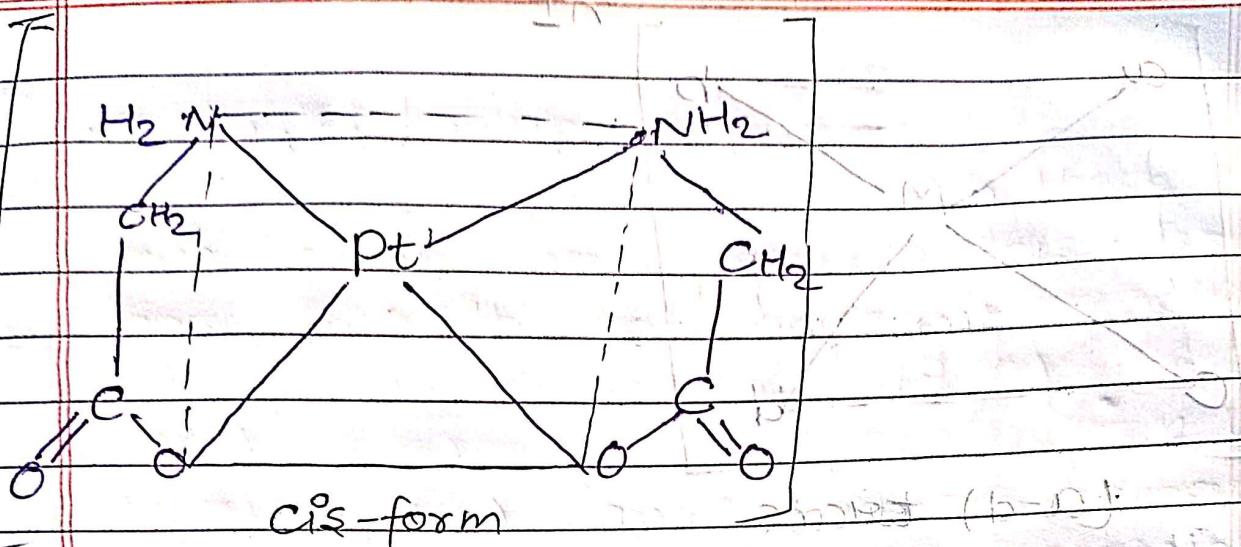
trans-form



cis-form



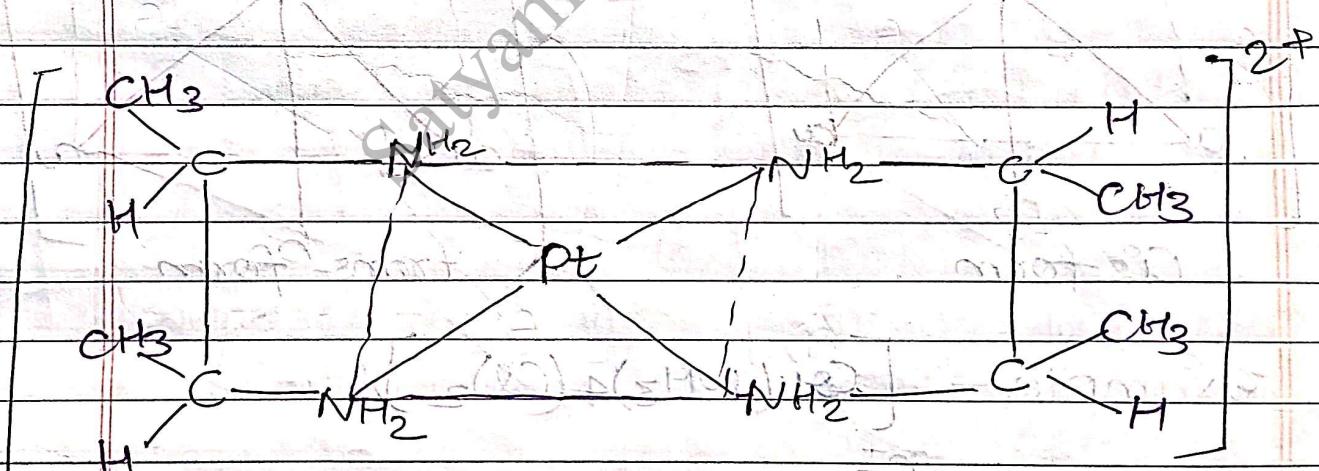
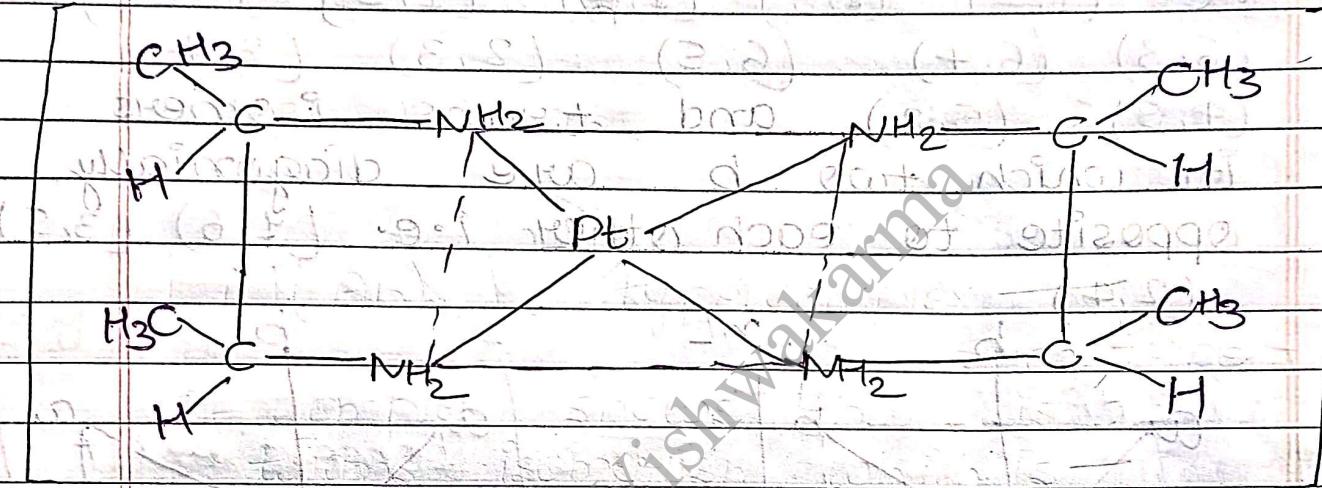
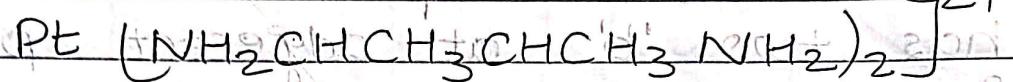
reaction of homolytic substitution
for aromatic halogen with nitro group
leads to homolytic substitution - nitrosubstitution



$AB =$ unsymmetrical bidentate ligand
 AB are donor atom of bidentate chelating ligand.

$[M(AA)_2]$ type complex — where AA is the symmetrical bidentate ligand in which A and A are donor atom of bidentate chelating ligand.

Such type of complex also shows cis and trans isomers.

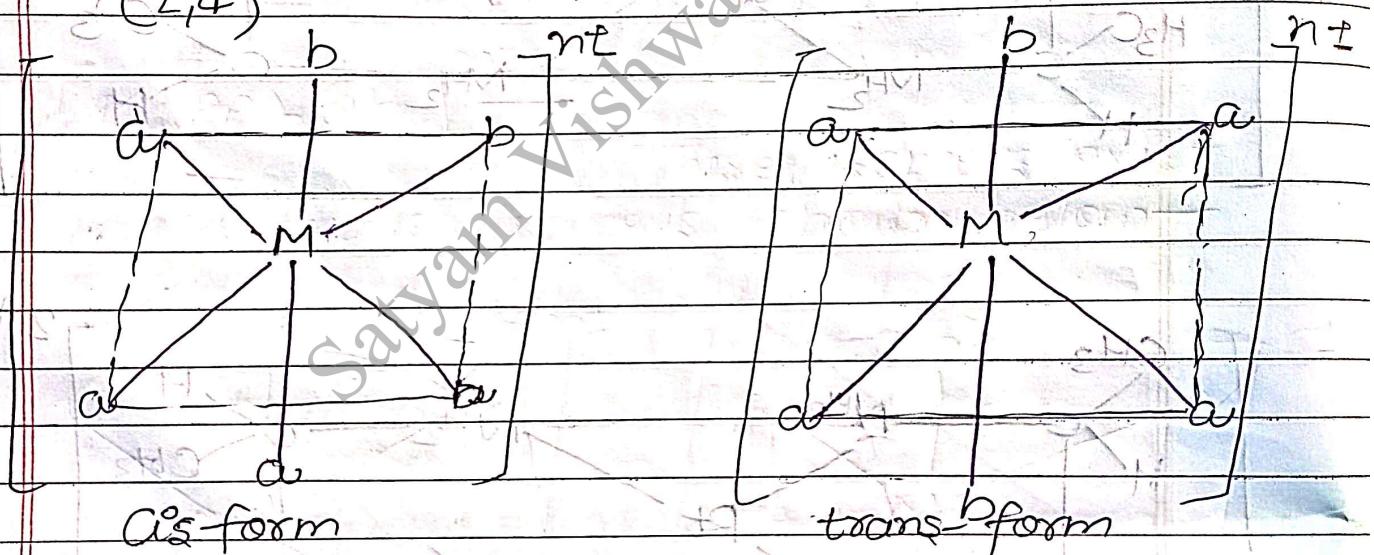


Co-ordination Number - 6 —

The following of octahedral complex shows geometrical isomerism.

i) $[M a_4 b_2]^{n+}$ type complex —

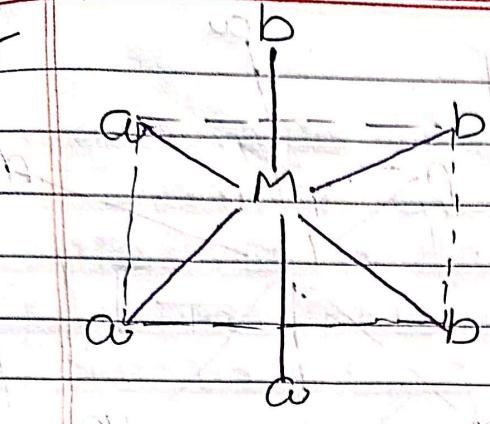
In these complex two isomers are possible cis - isomers has two 'b' at adjacent position.
i.e. (4,2) (4,3) (4,4) (4,5) (6,2)
(6,3) (6,4) (6,5) (2,3) (3,4)
(4,5) (5,2) and trans isomers
in which two 'b' are diagonally opposite to each other i.e. (4,6) (3,5)
(2,4)



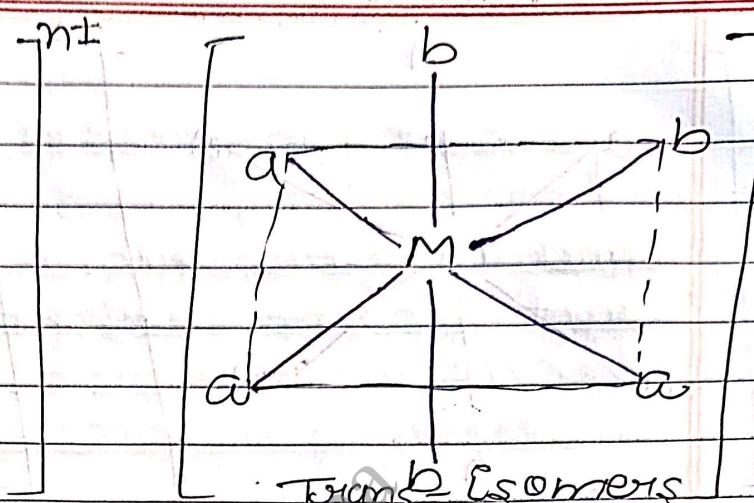
Example — $[Co \cdot (NH_3)_4 \cdot Cl)_2]$

ii) $[Ma_4 b_3]^{n+}$ type complex —

In these complex two isomers are possible cis - isomers occupied in (1,2,3) and trans isomers - (1,2,6)

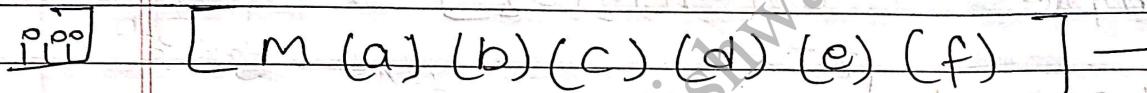


cis - Isomers



Trans Isomers

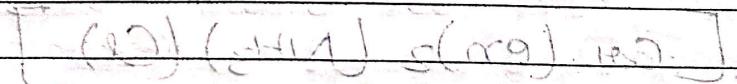
Example -

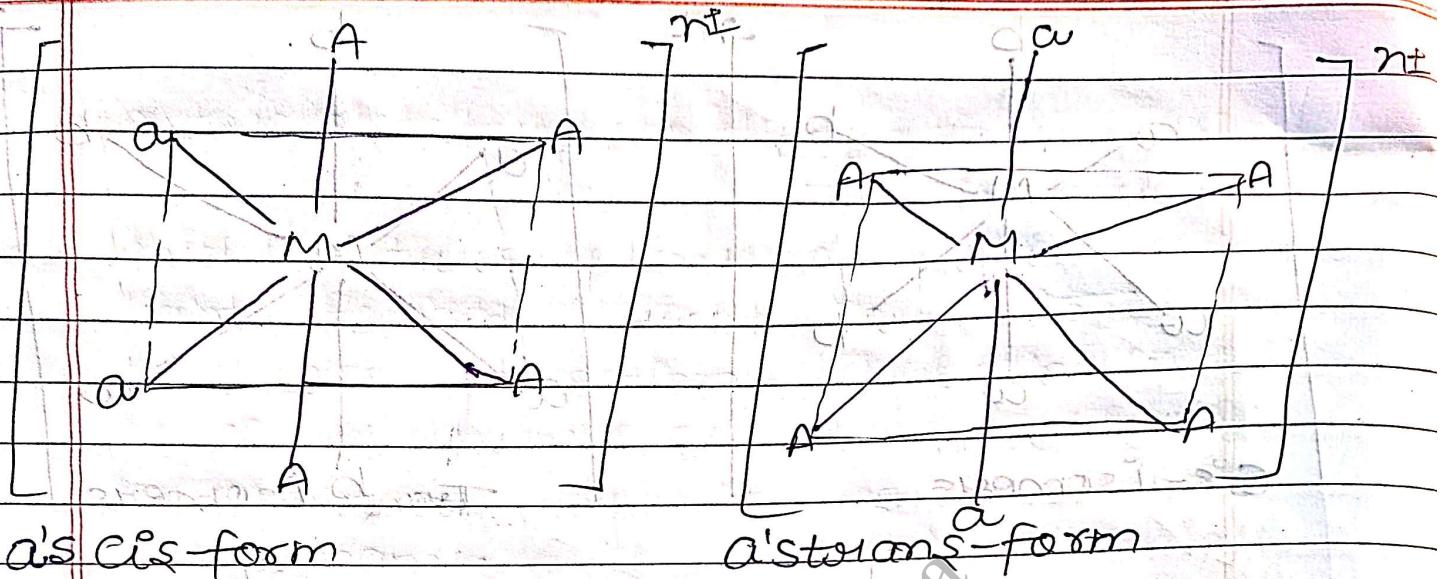


such type of complex exist in 15 different geometrical forms however the only one compound of this type is $[Pt(py)(NH_3)(NO_2)(Cl)(Br)(I)]$. The geometrical isomers are 15 type.

Octahedral complex containing monodentate and symmetrical bidentate chelating ligand -

These complex exist in cis and trans isomers.

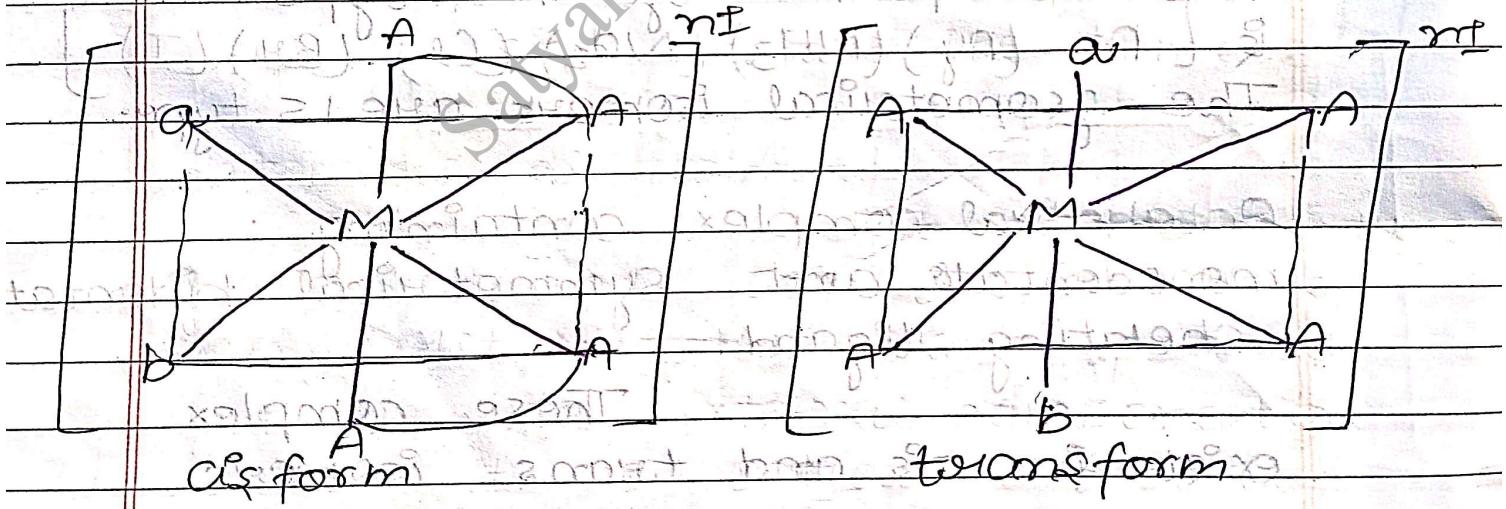




Example - $[Co(en)_2Cl_2]^+$

ii) $[M(AA)_2ab]$ —

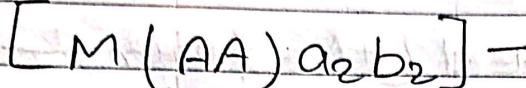
These isomers exist
in a's trans isomers shown below —



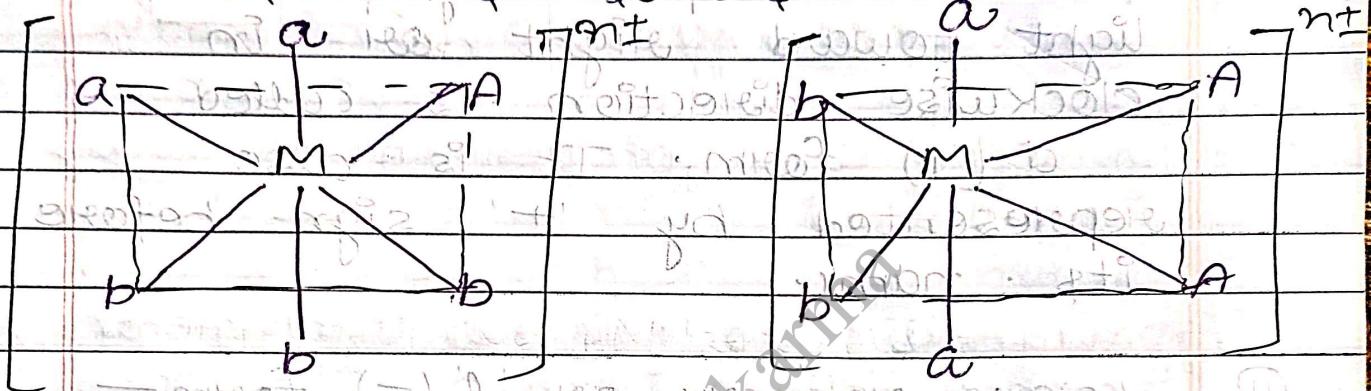
Example - $[Co(C_2O_4)_2(Py)(NO)]$

$[Co(en)_2(NH_3)(Cl)]$

100



These complex exist in cis and trans isomers.



cis - isomers

trans - isomers

Optical Isomerism

The compound which both have similar but different behaviour of ligand on mirror is different called optical isomers and this phenomenon is known as optical isomerism.

The compound which rotate rapidly in plane polarised light called optical active compound.

Optical active compound exist in the following type-

optically active
enantiomers
meso
racemic pair
chiral
achiral

① Dextro rotatory or 'd' (+) form —

The isomers

which rotates plane of polarise light toward right or in clockwise direction is called d (+) form. It is also represented by '+' sign before its name.

② Laevo rotatory or 'l' (-) form —

The isomers

which rotates the plane polarise light towards left or anticlock wise direction is called laevo rotatory or 'l' form. It is represented by '-' sign before its name.

③ Racemic or 'dl' form —

It is the mixture of 50% 'd' and 50% 'l'. It does not rotate the plane polarise light due to external compensation hence it is optically inactive.

④ Meso form —

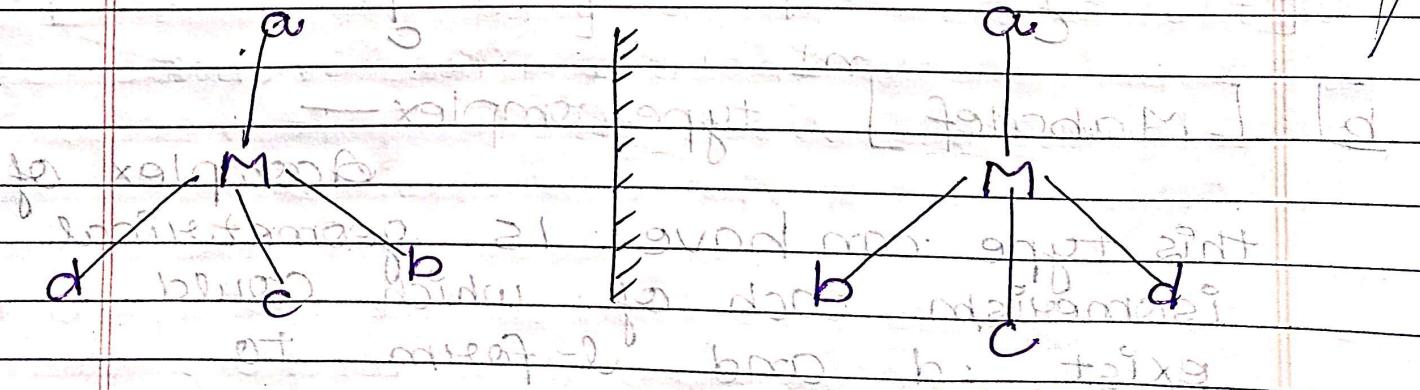
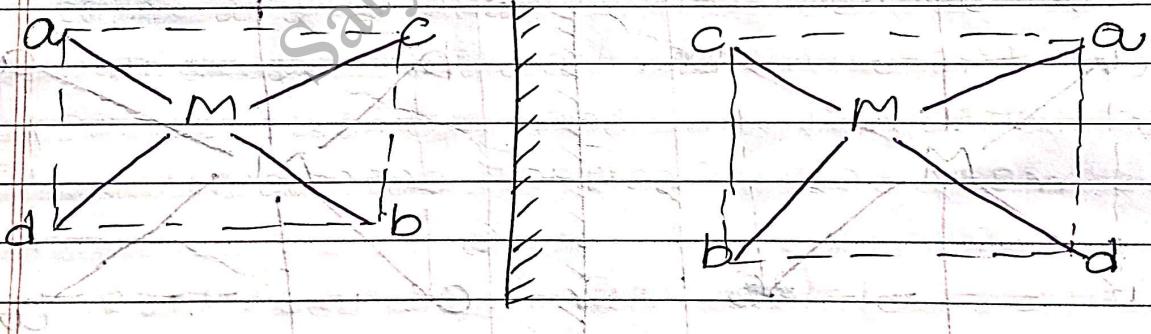
In meso form the half molecules rotates plane polarise light towards right while other

half rotates towards left. It does not rotates the plane polarise light due to internal compensation hence it is optically inactive.

Optical Isomerism in co-ordination No-4 →

Optical isomerism is not possible with square planar and tetrahedral complex of type - $[ma_2]^{n \neq}$, $[ma_3b]^{n \neq}$ and $[ma_3b_2]^{n \neq}$ but $[mab_2]^{n=}$ shows the 2 optical isomers.

$[mab_2]$ type complex -



2+

Ex - $[As(CH_3)(C_2H_5)(S)(C_6H_4COO)]$

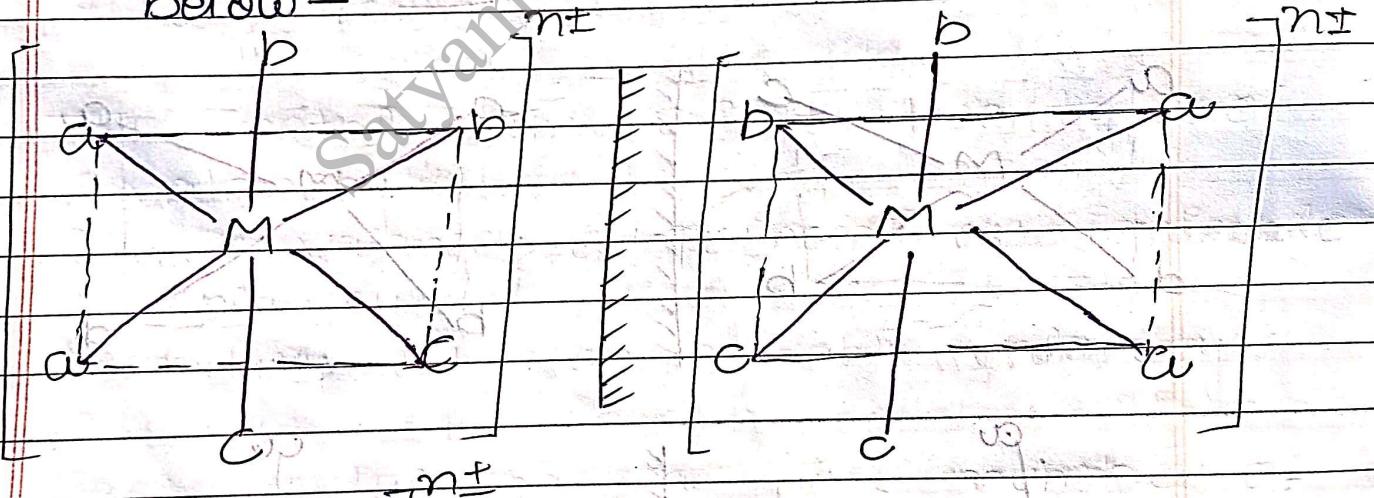
Optical isomerism in complex with six co-ordination number —

optical isomerism in octahedral complex is following types —

a) Octahedral complex containing only monodentate ligand

a) $[ma_2b_2c_2]$ type complex

such complex having two optical isomerism shown below —



b) $[abcdef]$ type complex —

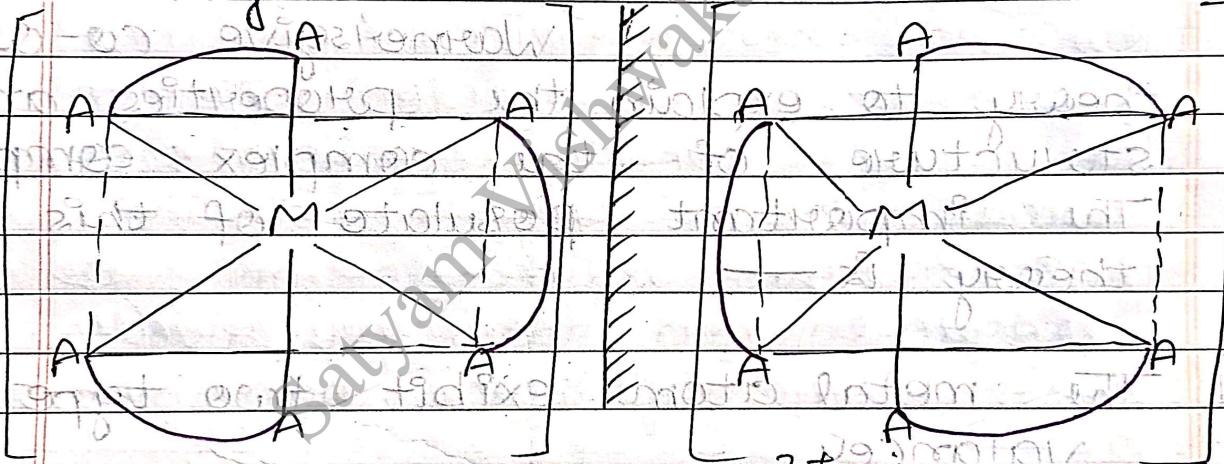
A complex of this type can have 15 geometrical isomerism each of which could exist d and l-form to

give a total 30 optical isomers.

Octahedral complex containing b.
symmetrical bidentate chelating
ligand -

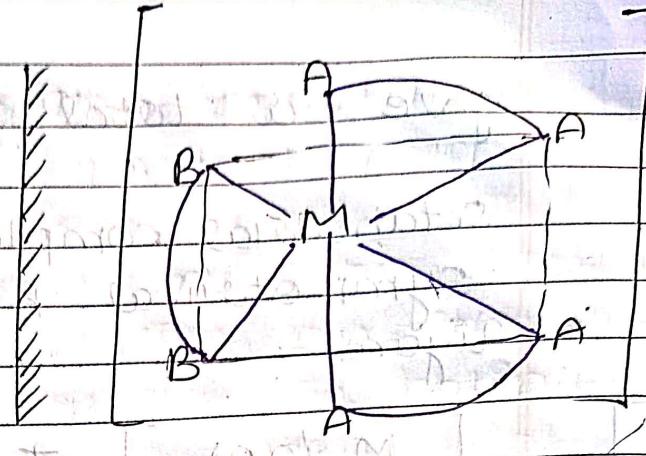
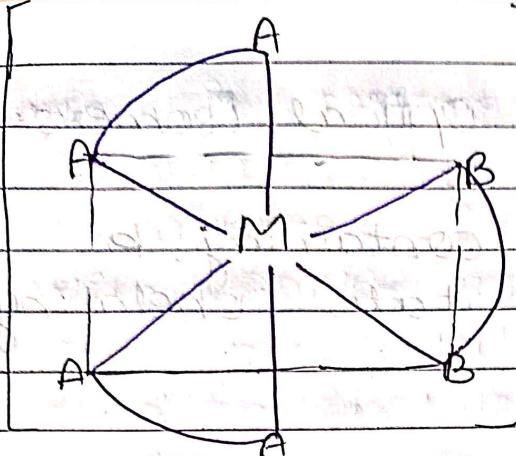
i) $[M(AA)_3]$ type complex -

AA - symmetrical bidentate chelating ligand.



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

ii) $[M(AA)_2(BB)]$ type complex
where AA and BB
are two different unsymmetrical bidentate
chelating ligand.



Werner co-ordination theory

Werner gave co-ordination theory to explain the properties and structure of the complex compound. The important postulate of this theory is —

- i] The metal atom exhibit two type of valency.
 - a] Primary valency or principle or ionisable valency.
 - b] Secondary or non-ionisable valency.
- ii] Each metal has a fixed number of secondary valency i.e. it has a fixed co-ordination number.
- iii] The primary valency are satisfied by negative ion whereas secondary valency

are satisfied by negative or neutral ligand.

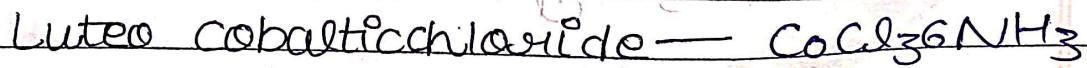
vi Primary valencies of metal are represented by solid line and secondary valencies are represented by dotted line.

iv The secondary valencies are directed towards fixed position in space around the central metal atom.

v The net charge on the complex is the algebraic sum of charge born by the central metal ion and the ligand.

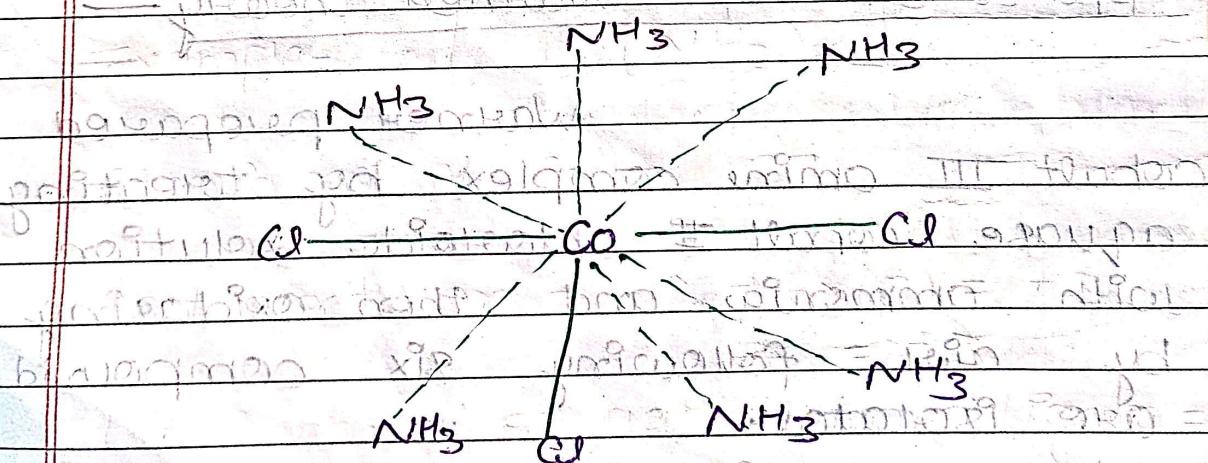
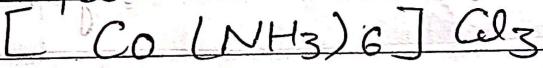
Application of Werner theory —

Werner prepared cobalt III amine complex by treating aqueous cobalt II chloride solution with ammonia and then oxidising by air, following six compound are isolated.



This is orange-yellow crystalline compound. Its important properties are -

- i) with AgNO_3 solution all the chlorine are precipitated AgCl from the solution of this complex, indicating that the bonding between Co and Cl are purely ionic.
- ii) with HCl ammonia is not removed even at 100°C showing that all the 6 NH_3 molecule are unremovable from the above consideration it follows that NH_3 molecule are secondary valency and Cl molecules are primary valency. Thus, Werner formula are written as -

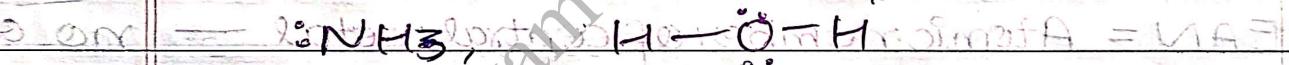


Sidgwick Electronic Interpretation of Co-ordination

Sidgwick suggested that

i - Warner's primary valency have similar to electrovalency and his secondary valency was similar to co-ordination valency.

ii - The ligand attached with the central metal ion have atoms with atleast one lone pair of electron in their balance shell.



+ no. terminal end孤对 lone pair

iii - The lone pair of electron is donated to the central metal ion by each ligand. The atoms who donate the electron pair are called donor and central metal ion which accept the electron pair is called acceptor. The bonds of this type are called co-ordinate or dative or semi-polar bond. These bonds are represented as $\text{L} \rightarrow \text{M}$



Valence bond theory

Pauling suggested a theory to explain the nature of metal ligand bonding to complex. This theory known as VBT or pauling theory.

This theory is based on the following assumptions—

- i- Central metal atom provides a number of empty s, p-d- atomic orbital equal to its co-ordination number for the formation of co-ordinate bond with ligand orbital.
- ii- The empty orbital of metal ion hybridised together to form hybrid orbital which are equal in number as the atomic orbital taking part in hybridisation. These are valent equivalent in energy and have definite geometry.

Co-ordination No.	Hybridisation	Geometry	Example
2	sp	Linear or diagonal	$[Ag(NH_3)_2]^+$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$[Ni(CO)_4]$
4	dsp^2	Square planar	$[Ni(CN)_4]^{10-}$
5	dSp^3	Trigonal bipyramidal	$[Fe(CO)_5]$
5	sp^3d	Square pyramidal	$[SbF_5]$
6	d^2sp^3	Octahedral	$[Fe(CN)_6]^{4-}$
6	sp^3d^2	Octahedral	$[Fe(F_6)]^-$

iii) Each ligand has at least one orbital containing a lone pair of electron

iv) Empty hybrid orbital of the metal ion overlap with the filled lone pair of e^- of the ligand to form ligand \rightarrow metal σ bond.

v - Inner orbital t_e i.e. $(n-1)d$ known as low spin complex and outer orbital t_d and d complex are known as high spin complex.

vi - If the complex has paired electron it is called diamagnetic while the complex containing one or more unpaired electron called paramagnetic.

vii - In complex formation Hund rule of maximum multiplicity is strictly followed.

viii - Limitation of VBT - This theory fails to explain the following fact -

i) Octahedral, tetrahedral and square planar of d^1 , d^2 , d^3 and d^9 ion have the same number of unpaired electron and hence cannot be distinguished from each other.

ii) Complex formation of certain metal ions is not totally unsatisfactory for example in dsp^2 -hybridisation in Cu^{+2} ion obtained by promoting one p

3d-electron to form d-orbital hence,
cuff ion should gradually oxidised
to cuff ion which occurs very
rarely.

- iii) This theory fails to explain that why a particular structure is preferred i.e. d⁸ ion form square planar complex d⁸-sp²-hybridisation after maximum pairing. These ion may also form tetrahedral complex (sp³-hybridisation)
- iv) This theory does not predict magnetic behaviour quantitatively except the number of unpaired electron in the complex.
- v) This theory does not explain state of reaction and mechanism of reaction
- vi) It does not explain thermodynamic property of the complex.
- vii) It does not explain spectra of complex.
- viii) This theory fails to explain the temperature dependent paramagnetism of complex.
- ix) It does not consider the splitting of d-block energy level.