

AUGUST 17, 2021

[COORDINATION CHEMISTRY]

[B.Sc – II(HONS)]

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Coordination Chemistry:-

Nomenclature of complex compounds:-

Nomenclature of complex compounds is done with the help of following rules:-

- (1) At first cation is named and then anion. But neutral complex is named as such.
- (2) For the nomenclature of complex ion at first ligands are named and then central metal ion.
- (3) Names of ligands are arranged alphabetically.
- (4) There are three types of ligands – anionic ligands, neutral ligands and cationic ligands (rare).
- (5) "O" letter is added in the names of anionic ligands and "ium" is added in the names of cationic ligands and neutral ligands are named as such.

Anionic ligands		Negative ligands	
Ligands	Name	Ligands	Name
Cl ⁻	Chloro	SCN ⁻	Thiocyanato
Br ⁻	Bromo	CN ⁻	Cyano
F ⁻	Fluoro	SO ₄ ²⁻	Sulphato
CH ₃ COO ⁻	Acetato	CO ₃ ²⁻	Carbonato
$\begin{array}{c} \text{COO}^- \\ \\ \text{COO}^- \end{array}$	Oxalato	ONO ⁻	Nitrito
NO ₂ ⁻	Nitro	OH ⁻	Hydroxo
NO ₃ ⁻	Nitrato	NH ⁻	Imido
NH ₂ ⁻	Amido	H ⁻	Hydrido
		O ₂ ²⁻	Peroxo

Positive ligands	Names	Neutral ligand	Names
NO^+	Nitrosonium	$\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$	Ethylene diamine
NH_2NH_3^+	Hydrazinium	$\text{C}_5\text{H}_5\text{N}$	Pyridine
NO_2^+	nitronium	$(\text{C}_6\text{H}_5)_3\text{P}$	Triphenyl phosphine

Exceptions for Neutral ligand:-

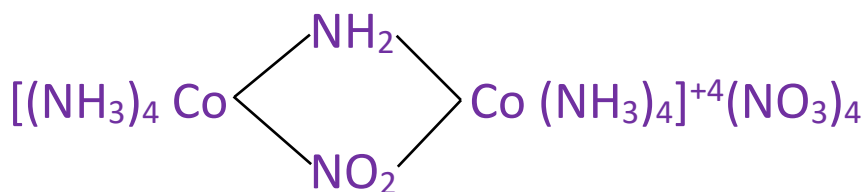
Ligands	Names	Ligands	Names
H_2O	Aqua or aquo	O_2	Dioxygen
NH_3	Ammine	N_2	Dinitrogen
NO	Nitrosyl	CO	Carbonyl

- (6) For the number of ligands di, tri, tetra, penta, etc. prefixes are used for two, three, four, five, etc. ligands respectively.
- (7) For chelating ligands or complex ligands bis, tris, tetrakis etc. prefixes are used for two, three, four etc. ligands and names of ligands are put in a parentheses.
- (8) The name of complex ion ends with the name of central metal ions.
 - (a) If complex ion is cation, the name of central metal ion is written as such followed by O.N in parentheses O.N is written in Roman number.
 - (b) If complex ion is anion at the end of the name of central metal ion 'ate' is added. In this case latin name is written for central metal ion. The O.N of C.M.I is written in parentheses as roman digit.
 - (i) Ex:- Cuperate for Cu.

- (ii) Ferrate for Fe.
- (iii) Alginate for Ag.
- (iv) Stannate for Sn.
- (v) Aurate for Au.
- (c) If the complex ion is neutral the name of central metal ion is written as such followed by its O.N.

Examples of some complexes:-

- (a) $K^+[Pt^{+4}(NH_3)Cl_5]^-$
Potassium ammine pentachloro platinate(iv).
- (b) If bridging groups or ligands are present Greek letter " μ " is used before the name of the group, μ – prefix is repeated before name of each bridging ligand.



Tetra ammine μ – amido μ – Nitro tetra ammine cobalt (III) Nitrate. Or M – amido – M – Nitro bis [tetraaminocobalt(iii)] nitrate.

Or, Octa ammine μ – amido μ – nitro dicobalt (III) nitrate.

(9) Some complex ligands have certain abbreviation.

Ex:- (a) $H_2N - CH_2 - CH_2 - NH_2$

Ethylene diamine = en.

(b). C_6H_5N Pyridine = py.

(10) It should be noted that the names of cation and anion are separated by a space and the no. of each type of ion is not mentioned.

- (11) The name of complex ion should be one word name.
- (12) While writing the formula of complex the coordinated groups are listed in the order of – negative ligands, neutral ligands, positive ligands and alphabetically within each negative or neutral or positive ligands.

(13) Point of attachment of ligands:-

Ligands	Names
– NO ₂	Nitro
– ONO	Nitrito
– SCN	Thiocyanato
– NCS	Isothiocyanato
– CN	Cyano
– NC	Isocyano

(14) When ligands are organic compounds then common names of organic compounds are used.

(15) Sometimes a ligand may be attached through different atoms. These may be named systematically.

(a) For SCN⁻ ligand:-

- (i) Thiocyanato – ligand is attached with C.M.I (central metal ion). through S – atom.
- (ii) Isothiocyanato – ligand is attached with C.M.I. through N – atom.

(b) For ONO⁻ ligand:-

- (i) Nitro – the ligand is attached with N – atom.
- (ii) Nitrito – the ligand is attached with O – atom.

Coordination chemistry:-

Salts may be classified into two groups.

- (1) Simple salts.
- (2) Molecular compounds or salts or addition compounds.

(1) Simple salts:-

Those salts are called as simple salts which are formed by the chemical combination of acids and bases.



Simple salts may be acidic salts, basic salts and neutral salts.

(2) Molecular compounds or salts:-

When two or more than two salts are mixed in stoichiometric proportion (molecular proportion) and subjected to crystallisation or chemical reaction the new compound formed is called as molecular compound or Addition compound.

Again there are two types of molecular compounds:-

- (1) Double salts.
- (2) Complex salts or complex compounds or coordination compounds.

(1) Double salts:-

Those molecular salts are called as double salts in which constituent salts are present in it as such.

Thus, double salts have following characteristics.

- (a) The constituent salts are present in it as such.
- (b) Double salts give the same ions as constituent salts.
- (c) The chemical properties of double salts are the same as its constituent salts.

Ex:- (i) Mohar's salt $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$

(ii) All alums $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ [Potash alum].

(2) Complex salts:-

“Those molecular compounds are called as complex salts in which at least one ion must be complex ion”.

Thus, in complex compounds following characteristics are found.

(a) In complex compounds, the properties of constituent salts are not found.

(b) Thus, in complex compound the nature of ions is not the same as constituent salts.

(c) A complex compound is formed by a chemical reaction.



Pot. ferrocyanide

(d) In a complex compound, either cation or anion or both must be complex ion.

➤ Complex ion:-

That ion is called as complex ion in which at least one central metal ion must be present which is surrounded by many ligands.

Ligands, form coordinate covalent bonds with central metal ion.

➤ Ligands:-

The atom or groups of atoms which surround central metal ion and also form coordinate covalent bonds with the central metal ion are called as ligands.

➤ Coordination polyhedron:-

It is defined as the spatial arrangement of ligand atoms which are directly attached to the central atom or ion. This shows the shape of the complex.

Ex:- (i) $[\text{Co}(\text{NH}_3)_6]^{3+}$ Has octahedral geometry.

(ii) $[\text{PtCl}_4]^{2-}$ Has square planar geometry.

(iii) $[\text{Ni}(\text{CO})_4]$ Has tetrahedral geometry.

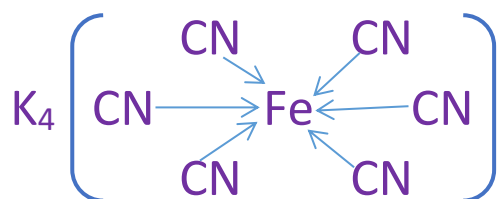
➤ Oxidation number of central metal atom:-

The oxidation number of central metal atom is defined as the charge it would carry if all the ligands are removed along with electron pairs that are shared with the central metal atom.

❖ Coordination Number (CN):-

“It is the total number of atoms of ligands or total no. of Coordinate bonds formed between central metal ion and ligands”.

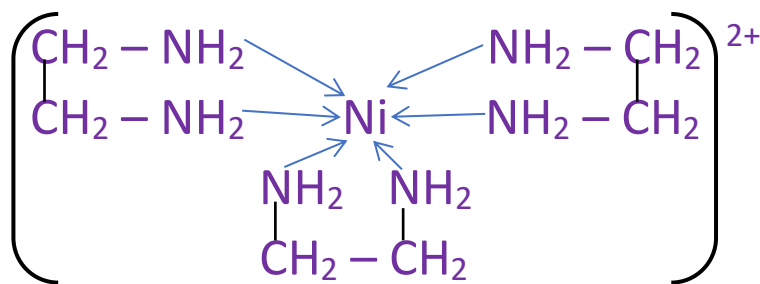
Ex:- (i) In pot. Ferrocyanide CN is equal to six.



(ii) In $[\text{Ni}(\text{NH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2)_3]^{2+}$

Complex ion C.N. is equal to = 6

Because one ethylenediamine ligand forms two Coordinate bonds with central metal ion.



Coordination sphere or first sphere of attraction:-

This term was given by Werner which is as follows.

“The central metal ion (S) and ligands enclosed in a square bracket is called as Coordination sphere or first sphere of attraction”.

The ion outside the Coordination sphere is called as “second sphere of attraction”.

Werner's coordination compounds Theory Historical

Background:-

Hexamine cobalt chloride $[\text{Co}^{3+}(\text{NH}_3)_6]^{3+}\text{Cl}_3$, was the first complex compound discovered by Tassaert in 1799. Tassaert obtained it by mixing CoCl_3 and aq 4NH_3 . He was unable to understand how NH_3 and CoCl_3 each of which is a stable compounds, could combine to give yet another very stable compound $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. No satisfactory answer could be given by chemist to explain the Tassaert's experimental observations, until approximately 100 years later. In this period many Co(iii) complexes were prepared and their properties were also studied. These studies are given in the table below.

Colour	Ammine Complexes	No. of Cl^- Precipitated as AgCl by AgNO_3	Molar Conductivity (Ohm^{-1})	Total No. of Ions given by complexes	Charge type On ions	Ionic formulation
Yellow	$\text{CoCl}_3 \cdot 6\text{NH}_3$	3	430	4	$3^+ \text{ } 1^-$	$[\text{Co}^{3+}(\text{NH}_3)_6]^{3+} \text{Cl}_3^-$
Purple	$\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$	3	430	4	$3^+ \text{ } 1^-$	$[\text{Co}^{3+}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} \text{Cl}_3^-$
	$\text{CoCl}_3 \cdot 5\text{NH}_3$	2	250	3	$2^+ \text{ } 1^-$	$[\text{Co}^{3+}(\text{NH}_3)_5\text{Cl}]^{2+} \text{Cl}_2^-$
Green	$\text{CoCl}_3 \cdot 4\text{NH}_3$	1	100	2	$1^+ \text{ } 1^-$	$[\text{Co}^{3+}(\text{NH}_3)_4\text{Cl}_2]^{+} \text{Cl}^-$
	$\text{CoCl}_3 \cdot 3\text{NH}_3$	0	0	—	—	$[\text{Co}^{3+}(\text{NH}_3)_3 \text{Cl}_3]$ Non - electrolyte

Note:- Alfred werner won Nobel prize in 1913.

❖ **Werner's Theory:-**

In 1893 Alfred werner presented a theory known as **werner's coordination Theory** which could explain all the observed properties of complex compounds.

Postulates of this theory are:-

(1) In complexes most elements exhibit two types of Valencies-

- (a) Primary valency.
- (b) Secondary valency.

(a) Primary valency:-

This corresponds to oxidation state of the metal ion. This is also called as principal, ionizable or ionic valency. It is satisfied by -ve sign.

(b) Secondary or Auxiliary valency:-

Total coordination number or total coordinate bonds formed by ligands and central metal ion is called as secondary valency.

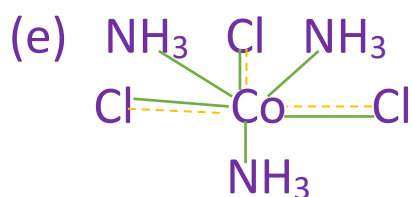
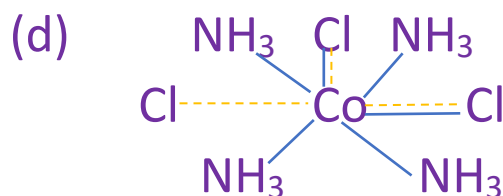
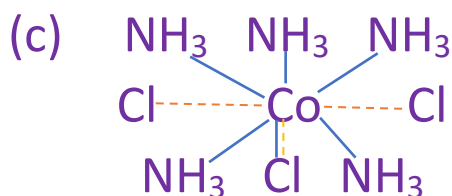
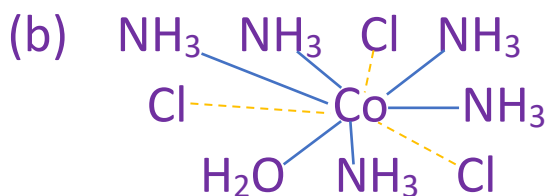
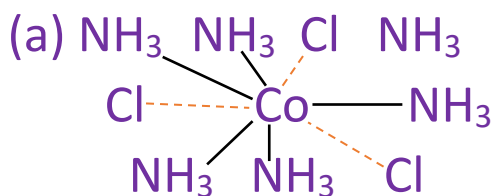
Secondary valencies are shown by deep lines and central metal ion, ligands and deep lines are shown within a square bracket called Co - ordination sphere.

This postulate predicted the existence of different types of isomerism in coordination complexes and after 19 years werner actually succeeded in resolving various Co - ordination example into optically active isomers.

(2) Every complex element tends to satisfy both its primary and secondary valencies. In order to meet this requirement a -ve ion may often show a dual character, i.e it may satisfy both

primary and secondary valency. Since in every case the fulfilment of Co – ordinate number of the central metal ion appears essential.

➤ **Designation and formation of Co (III) amines complexes:-**



The above structures of complexes given by werner gives following suggestions which resembles with the earlier studies;

- In all complexes of cobalt given above the oxidation number of Co is always +3.
- The anion satisfying only primary valency gives precipitate of AgCl when AgNO₃ solution is added.
- The central metal ion, ligands and ions satisfying secondary valence are represented in Co – ordination sphere.
- The ions satisfying only primary valency are represented out of Co – ordination sphere.

- (e) The above structure of werner regarding Co^{+3} complexes resemble the conductivity measurement.
- (f) The above structures give idea of total number of ions is s complex.

➤ **Sidwick's concept of effective atomic number (EAN Concept of Noble gas rule):-**

This EAN rule was given by Sidgwick which is as follows;
"After the ligands have donated a certain number of electrons to the central metal ion through Co – ordinate bond, the total number of electrons on the central atom including those gained from the ligands in the bonding is called as Effective atomic number of the central metal ion (EAN)".

In many case EAN is equal to the atomic number of Noble gas or Inert gas but not in all case.

Ex:- $\text{K}_4 [\text{Fe}(\text{CN})_6]$

Complex ion = $[\text{Fe}^{2+}(\text{CN})_6]^{4-}$

Electron no. $\text{Fe}^{2+} = 24$

Electron denoted by

$6 \text{CN}^- \text{ ligands} = 6 \times 2 = 12$

$\therefore \text{EAN of Fe(ii) in } [\text{Fe}(\text{CN})_6]^{4-} \text{ ion is} = 24 + 12 = 36$

36 is the atomic number of Kr.

Exception of EAN rule:-

Although in many cases the EAN is the same as the atomic number of the next inert gases, yet it is not always so. The EAN may be a few units more or less than the atomic number of next inert gases. So, these cases are called as exception to EAN rule.

Ex:- (i) $[\text{Fe}^{+3}\text{Cl}_4]^-$

No. of electrons in $\text{Fe}^{3+} = 23$

No. of electrons in 4 Co – ordinate bonds of 4 ligands = $4 \times 2 = 8$

\therefore EAN of Fe^{3+} ion = $23 + 8 = 31$

So, here EAN rule is not followed.

Thus, the EAN rule correctly predicts the number of ligands in many complexes. There are, however a significant number of exceptions where EAN is not quite that of a Noble gas.

(ii) $[\text{Fe}^{3+}(\text{CN})_6]^{3-}$

Total number of electrons in Fe^{3+} ion = 23

Total no. of electrons in 6, Co – ordinate bonds by 6 – ligands = $6 \times 2 = 12$

\therefore EAN of $\text{Fe}^{3+} = 23 + 12 = 35$

So, here also the EAN rule is not followed.

If the original metal ion has an odd number of electrons, for example the adding of electron pairs cannot result in a noble gas configuration is a significant factor but not a necessary condition for complex formation. It is also necessary to produce a symmetrical structure (tetrahedral, square planar, octahedral) irrespective of the number of electrons involved.

➤ Shape of d – orbitals:-

There are five d – orbitals in d – subshell.

There five d – orbitals are divided into two sets-

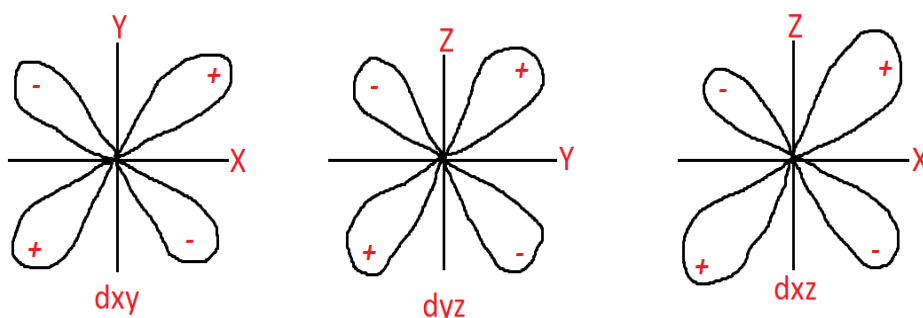
(i) t_{2g} or dE set:- t_{2g} is a symbol according to group theory were t refers to triple degenerate set.

(ii) **eg set or dY:-** eg set is also a symbol of group theory in which 'e' refers to doubly degenerate set.

(i) **t_{2g} set:-**

In this t_{2g} set there are three orbitals,

Such as dxy, dy², dxz, all these three orbitals taken in t_{2g} set because these orbitals lie between x, y and z axis.

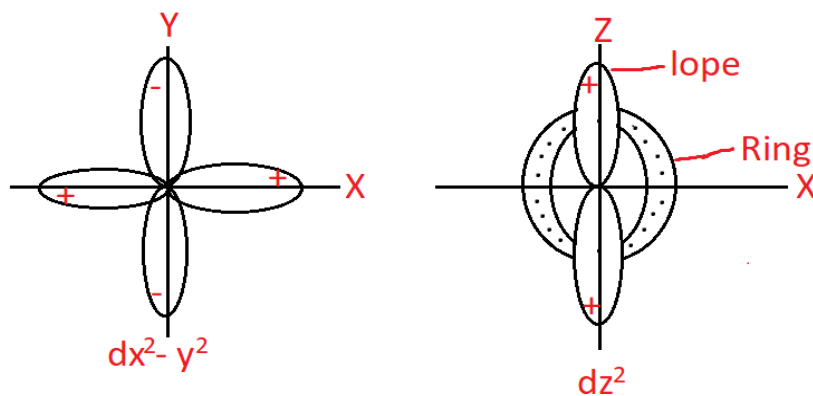


Those orbitals are taken in t_{2g} set whose lobes lie between axes.

(ii) **eg set:-**

Those d – orbitals are taken in eg whose lobes lie on the axes.

There are two orbitals in eg set, i.e dx² – y² and dz².



➤ **Theories of bonding in complexes:-**

To discuss bonding in complexes four theories have been come into light. All these theories have been given after 1930's.

Those four theories are-

(i) Valence bond theory.

- (ii) Crystal field theory.
- (iii) Molecular orbital theory.
- (iv) Ligand field theory.

(i) Valence bond theory of bonding in complexes:-

This theory was given by Pauling in 1931 which is as follows-

- (a) There are central metal ions in complexes.
- (b) There are ligands around central metal ion.
- (c) Central metal ion must have empty orbital having suitable energies.
- (d) Ligands must have lone pair of electrons for donation.
- (e) Thus Co – ordinate bond must be formed between central metal ion and ligands.
- (f) This theory can explain magnetic properties of complexes but not for coloration.
- (g) The empty orbitals of central metal ion hybridise to give hybridised orbitals.
- (h) V.B theory also predicts about the shape of the complex ions.

➤ Explanation of Co^{3+} or $Co(III)$ complexes with the help of V.B theory:-

Co(27) : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7, 4s^2$, V.E = 9

$Co^{3+}(24)$: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6$

So, Ground state of Co^{3+}



Co^{3+} ion forms two types of complexes.

- (i) Outer orbital complexes.
- (ii) Inner orbital complexes.

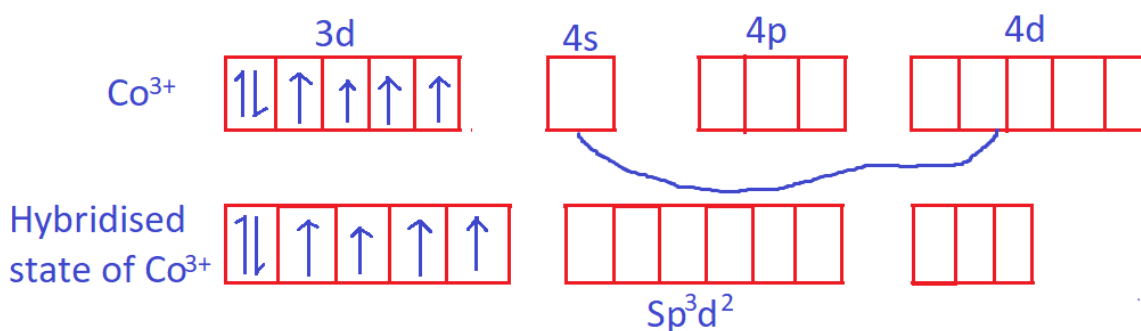
(i) Outer orbital complexes:-

Generally, Co^{3+} ion forms complex ion with six ligands.

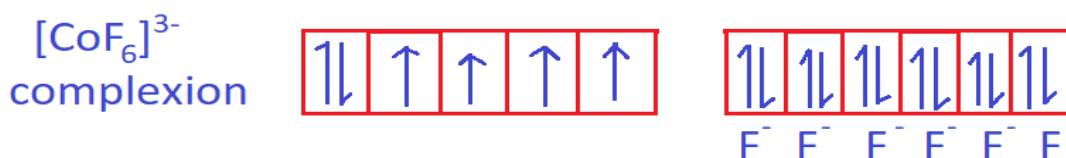
So, if ligands are weak one 'S' three '4p' and two '4d' orbitals (empty) are engaged in the formation of Co – ordinate bonds.

These orbitals hybridise to give Sp^3d^2 hybridised orbitals.

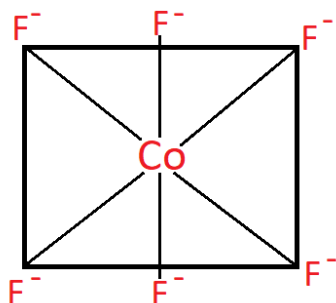
Thus, when ns, np, and nd orbitals (here n = outer most orbit) participate in hybridisation and hence in bonding it is called as **outer orbital complexes or high spin complexes.**



Formation of 6 Co – ordinate bonds with 6 F ligands:-



\therefore shape of $[\text{CoF}_6]^{3-}$ is octahedral bond angle all 90° .



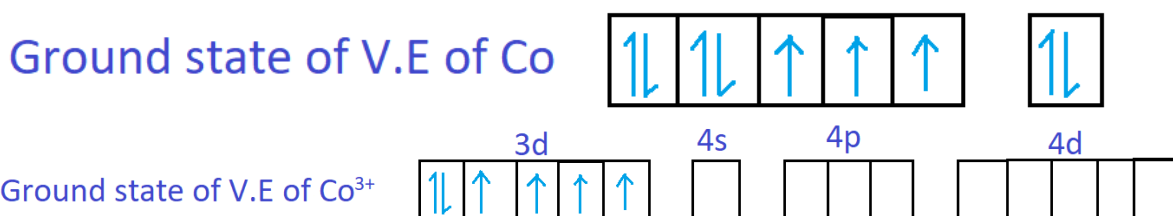
Since in outer orbital complexes the no. of unpaired electrons is larger it is called as High spin complexes. So, these complexes are paramagnetic.

With the help of experiment, it has been observed that the above complex is paramagnetic. So, it will be outer – orbital complex but not inner orbital complex.

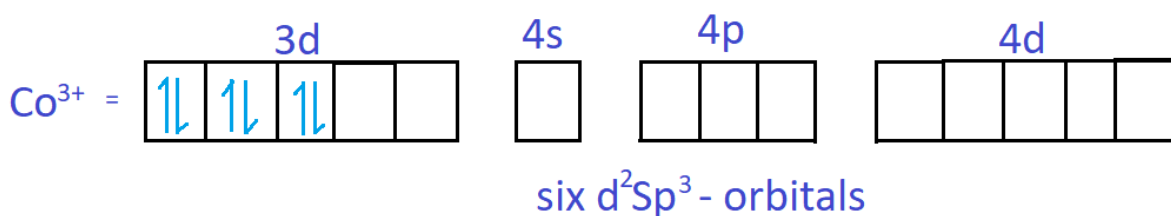
(ii) Inner orbital complex of Co^{3+} ion-

$[\text{Co}(\text{NH}_3)_6]^{3+}$ - example.

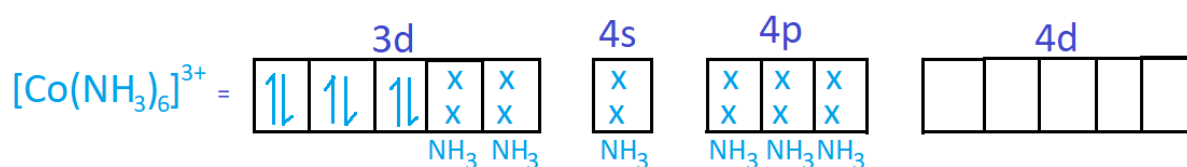
$\text{Co}(27): 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7, 4s^2$



Now, when NH_3 ligands approach to the central metal ion $[\text{Co}^{3+}]$ two unpaired electrons pair up. So, the no. of unpaired electrons become zero. Hence new configuration of Co^{3+} ion will be.



Now, six NH_3 ligands form Co – ordinate covalent bond with Co^{3+} ion.



Structure – Octahedral.

Thus, $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion will be inner orbital complex or Low – spin complex. Hence this complex has been found Diamagnetic.

➤ **V.B theory explanation for Ni – complexes:-**

Ni – ion or Ni – atom forms complexes with Co – ordination number four. CN = 4

$[\text{Ni}^{2+}(\text{CN})_4]^{2-}$ complex-

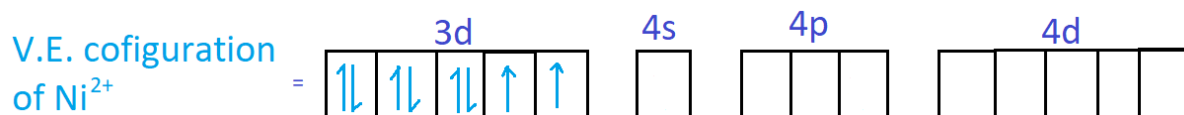
Here, CN = 4

Ni (28): $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8, 4s^2$

Here O.N of Ni is +2

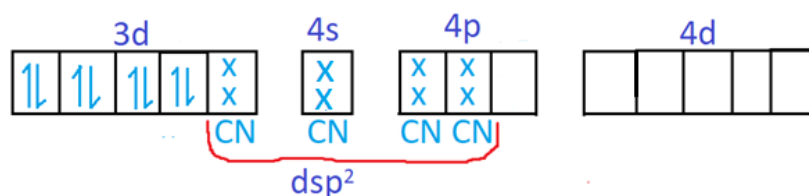
So, Ni^{2+} ion is present here

Ni^{2+} (26): $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^8$

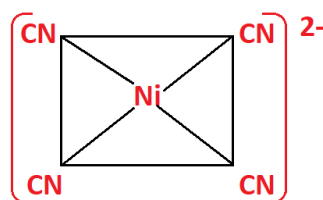


Now, from experiment it is found that $[\text{Ni}(\text{CN})_4]^{2-}$ complex is Diamagnetic.

Then the V.E. configuration will be-



Here, in the above complex the hybridisation is dsp^2 and hence the structure of complex will be square planar.



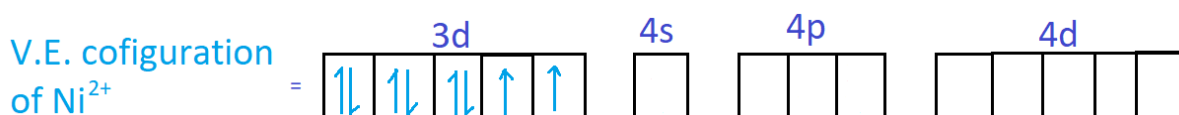
- In dsp^2 hybridization d – orbital involved is $dx^2 - y^2$.
- In sp^3d^2 hybridization d – orbital involved are $dx^2 - y^2$.
- (Inner orbital – Low energy - stable) and dz^2 (outer orbital – High energy - reactive).

(Q) Comment on the magnetic properties of the following complex ion with the help of V.B. theory-

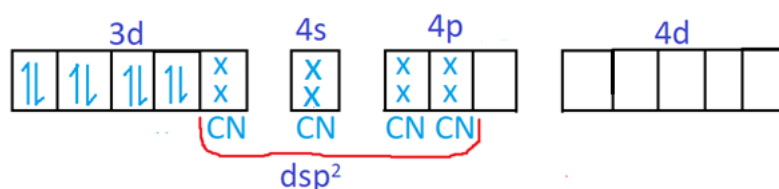


Ans- (i) In $[\text{Ni}(\text{CN})_4]^{2-}$ complex ion Ni is found in +2 oxidation state.

So, its (Ni^{2+}) electronic configuration will be-



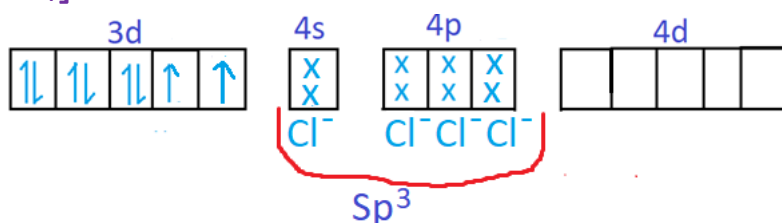
And electronic configuration of $[\text{Ni}(\text{CN})_4]^{2-}$ ion will be-



Since, from experiment it has been observed the $[\text{Ni}(\text{CN})_4]^{2-}$ complex ion is diamagnetic. So, it shows dsp^2 hybridization in which there is not any unpaired electron as shown above. That is why $[\text{Ni}(\text{CN})_4]^{2-}$ complex is diamagnetic and the shape of the ion is "square planer".

(ii). For $[\text{NiCl}_4]^{2-}$ complex ion:-

From experiment it has been found that $[\text{NiCl}_4]^{2-}$ complex is paramagnetic. So, electronic configuration is this complex will be $[\text{NiCl}_4]^{2-}$.



Since in $[\text{NiCl}_4]^{2-}$ complex ion, there are two unpaired electrons in 3d – orbitals as shown above, this complex is paramagnetic.

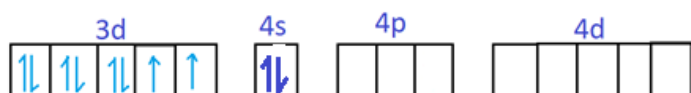
Also, since here hybridization is Sp^3 this complex ion is of tetrahedral structure.

(Q) Show that $[Ni(Co)_4]$ complex is diamagnetic:-

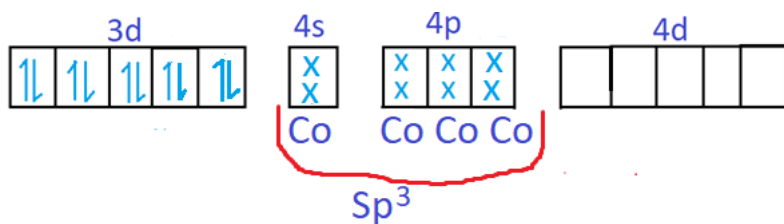
Ans:- Here O.N. of Ni is zero.



In box model-



Here since $[Ni(Co)_4]$ complex is diamagnetic. So, two electrons of 4s sub – shell will pair up the un – paired electrons in 3d sub – shell.



Since in this complex there is not any unpaired electrons it is diamagnetic.

Again, since here the hybridization is Sp^3 it is tetrahedral in structure.

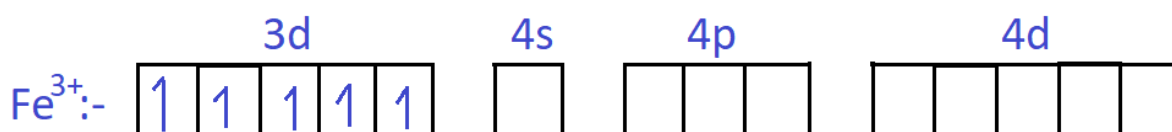
(Q) Determine the hybridization in following complex ions

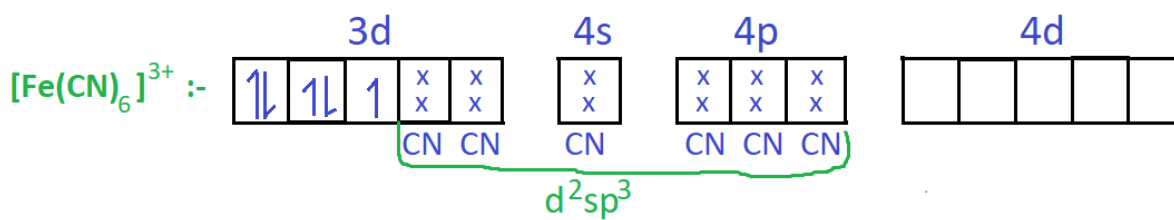
$[Fe(CN)_6]^{3-}$ and $[FeF_6]^{3-}$:-

Ans:- (i) $[Fe(CN)_6]^{3-}$

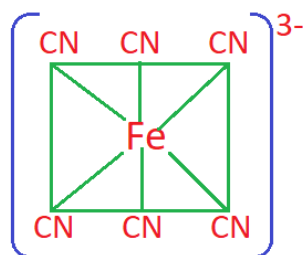


In box model-



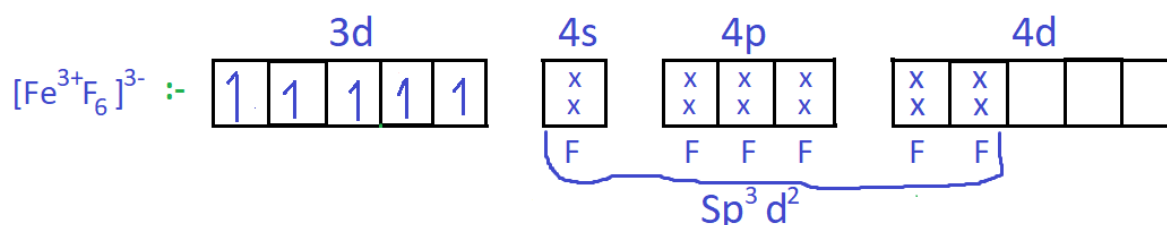


- Thus, in this complex hybridization is d^2sp^3 .
- It is a paramagnetic complex (unpaired $e^- = 1$).



- C.N = 6
- Octahedral shape.
- Inner orbital complex.
- Low spin complex.

(ii) $[\text{Fe}^{3+}\text{F}_6]^{3-}$



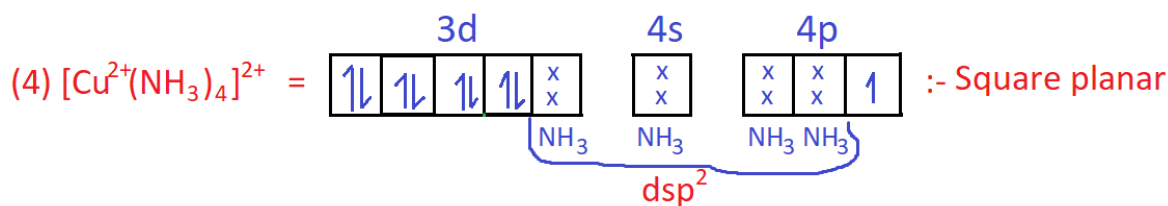
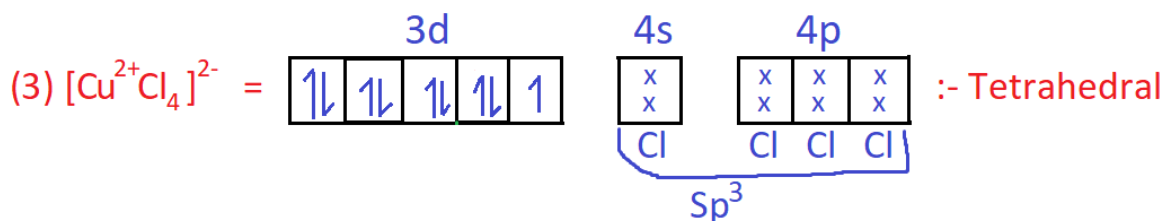
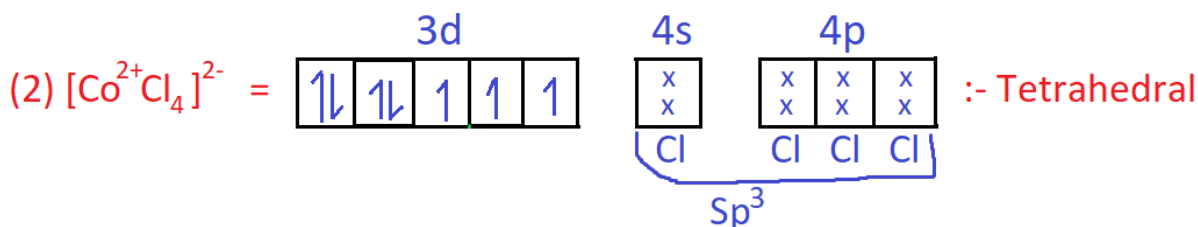
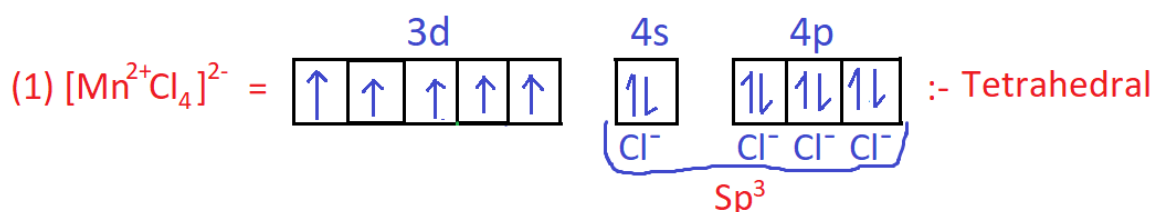
- Hybridization = Sp^3d^2 .
- No. of unpaired $e^- = 5$.
- High spin complex.
- Paramagnetic.
- Outer orbital complex.
- Octahedral.

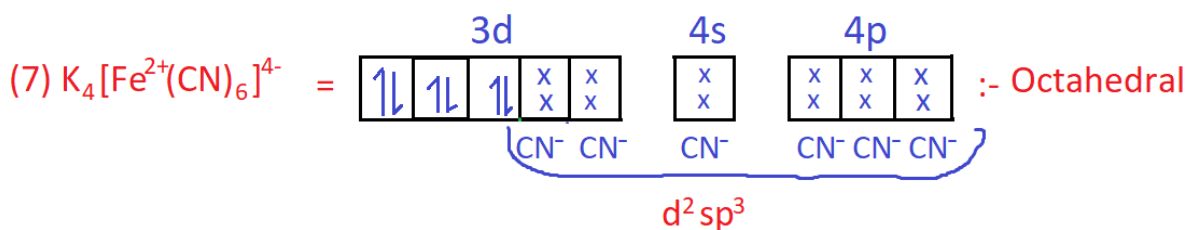
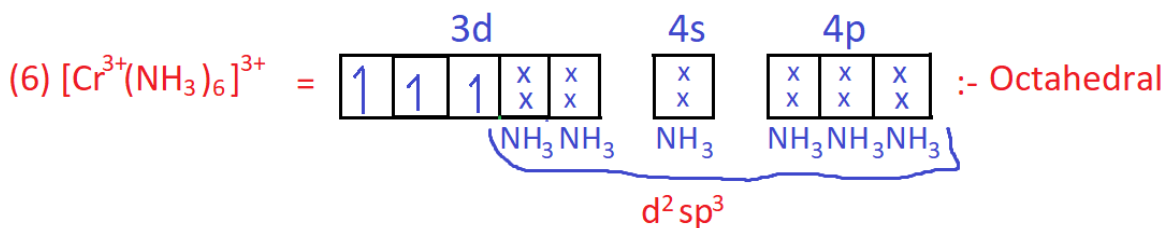
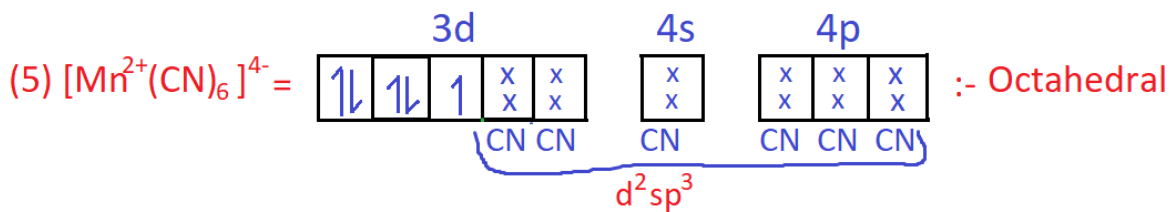
(Q) Explain why in $[Pt^{4+}(NH_3)_4]^{4-}Cl_4$ all the four chloride ions get precipitated with $AgNO_3$ while in $[Pt(NH_3)Cl_3]Cl$ only one chloride ion is precipitated ?

Ans:- Since, in $[Pt^{4+}(NH_3)_4]^{4-}Cl_4$ four Cl^- ions are out of Co – ordination sphere. So, it gives four molecules of $AgCl$ as precipitate. When $AgNO_3$ solution is added.

And in $[Pt(NH_3)Cl_3]Cl^-$ complex only one Cl^- ion is out of Co – ordination sphere. So, it can precipitate only one Cl^- ion as $AgCl$ when $AgNO_3$ solution is added.

Some more complexes:-





Isomerism:-

Definition:- When two or more than two compounds have same molecular formula but having different physical and chemical properties due to difference in structure the phenomenon is called as isomerism.

And the compounds are called as isomerism.

Types of isomerism:-

Isomerism is of two types-

- (i) Structural isomerism.
- (ii) Stereo isomerism.

Again, structural isomerism is of following types-

- (a) Ionic isomerism.
- (b) Hydrate isomerism.
- (c) Co – ordination isomerism.
- (d) Linkage isomerism.

(e) Co – ordination position isomerism.

And stereoisomerism is of two types-

(i) Geometrical isomerism.

(ii) Optical isomerism.

(1) Structural isomerism:-

Those, isomerism are called as structural isomerism which arise due to different arrangement of atoms or group.

(i) Ionic isomerism or ionization isomerism:-

When two or more than two compounds have same molecular formula but different arrangement of groups in the Co – ordination sphere and outside the Co – ordination sphere.

Due to this isomerism different types of ions are formed.

Ex:-[1]. $\text{Co}(\text{NH}_3)_5\text{Br SO}_4$:- Molecular formula.

This compound shows following two types of isomers-

(a) $[\text{Co}(\text{NH}_3)_5 \text{Br}]\text{SO}_4$:- This complex has got red violet colour.

And also it gives precipitate of BaSO_4 with BaCl_2 solution.

(b) $[\text{Co}(\text{NH}_3)_5 \text{SO}_4]\text{Br}^-$:- This complex is red colour. Also, it gives precipitate of AgBr with AgNO_3 solution.

Ex:- [2]. $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2] \text{NO}_2^-$ and $[\text{Co}(\text{NH}_3)_4 \text{Cl} (\text{NO}_2)] \text{Cl}$.

Ex:- [3]. $[\text{Pt}^{4+}(\text{NH}_3)_4 \text{Cl}_2]^{2+}$ and $[\text{Pt}(\text{NH}_3)_4 \text{Br}_2] \text{Cl}_2$.

(2) Hydrate isomerism:-

When two or more than two compounds have same molecular formula but having different arrangement of H_2O molecules in the Co – ordination sphere the phenomenon is called as Hydrate isomerism.

Ex:- [1]. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ complex forms following three types of isomers-

- (a) $[\text{Cr}^{3+}(\text{H}_2\text{O})_6]^{3+}\text{Cl}_3$ (**Violet**) :- It does not lose water of crystallisation with H_2SO_4 . It also gives 3AgCl with AgNO_3 .
- (b) $[\text{Cr}^{3+}(\text{H}_2\text{O})_5\text{Cl}]^{2+}\text{Cl}_2\cdot\text{H}_2\text{O}$ (**Green**) :- It loses 1 water molecule with conc. H_2SO_4 . Also, it gives 2AgCl molecules with AgNO_3 .
- (c) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$. It loses two H_2O molecules with H_2SO_4 . Also, it gives one AgCl molecule with AgNO_3 .

Ex:- [2]. $[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ and $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}(\text{H}_2\text{O})$.

(3) Co – ordination isomerism:-

This isomerism is shown by only those compounds in which both cation and anion are complex ion.

When two or more than two complex compounds have same molecular formula but having different arrangement of central metal ions or ligands in two cationic and anionic complexes. Here, there is exchange of central metal ion or ligands between complex cation and anion.

Ex:- [1](a). $[\text{Co}^{3+}(\text{NH}_3)_6]^{3+} [\text{Cr}^{3+}(\text{CN})_6]^{3-}$

(b). $[\text{Cr}^{3+}(\text{NH}_3)_6]^{3+} [\text{Co}^{3+}(\text{CN})_6]^{3-}$

[2](a). $[\text{Cu}(\text{NH}_3)_4]^{2+} [\text{PtCl}_4]^{2-}$

(b). $[\text{Pt}^{2+}(\text{NH}_3)_4]^{2+} [\text{Cu}^{2+}\text{Cl}_4]^{2-}$

[3](a). $[\text{Cr}^{3+}(\text{NH}_3)_4]^{3+} [\text{Cr}^{3+}(\text{CN})_6]^{3-}$

(b). $[\text{Cr}^{3+}(\text{NH}_3)_4(\text{CN})_2]^{1+} [\text{Cr}^{3+}(\text{NH}_3)_2(\text{CN})_4]^{1-}$

[4](a). $[\text{Pt}^{2+}(\text{NH}_3)_4]^{2+} [\text{Pt}^{2+}\text{Cl}_4]^{2-}$

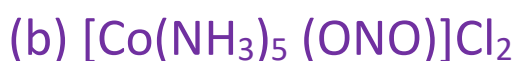
(b). $[\text{Pt}^{2+}\text{Cl}(\text{NH}_3)_3]^{+1} [\text{Pt}^{2+}\text{Cl}_3(\text{NH}_3)]^{-1}$

(4) Linkage isomerism:-

If two or more than two complex compounds have same molecular formula but having linkage with different atoms of same functional group the phenomenon is called as linkage isomerism.



Pentaamine nitro cobalt (iii) chloride.



Pentaamine nitrito cobalt (iii) chloride.

Other ligands which can show this isomerism are-

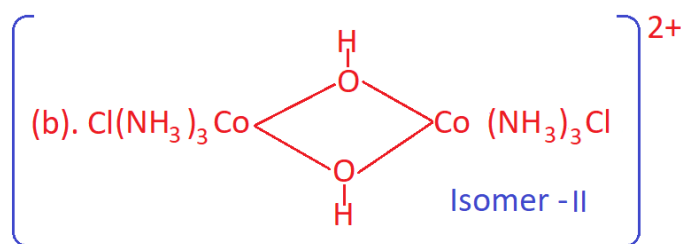
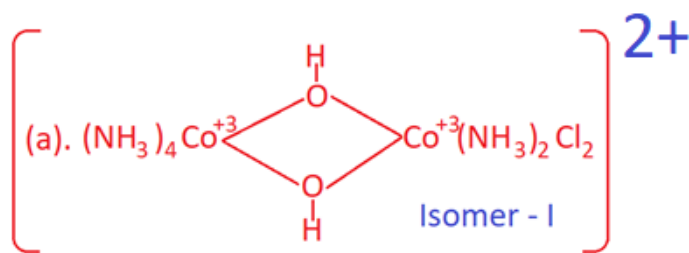
- (a). $-\text{CN}$ and $-\text{NC}$ (b) $-\text{SCN}$, $-\text{NCS}$
 Cyano isocyano thiocynato isothiocyanato

(5) Co – ordination position isomerism:-

This types, of isomerism arises in bridged complexes.

It is that isomerism in which there is different arrangement of ligands around central metal ion.

Example:-



Stereoisomerism:-

Stereo = space

Definition:- When two or more than two compounds have same molecular formula and structural formula but having different arrangement of ligands around central metal ion in space.

Again, stereoisomerism is of two types-

(i) Geometrical isomerism.

(ii) Optical isomerism.

(1) Geometrical isomerism:-

When two or more than two Co – ordination compounds have same molecular formula but having different special arrangement of ligands around central metal ion. The phenomenon is called as geometrical isomerism.

When the same ligands are arranged at the same adjacent side it is called as Cis – isomer and when they are arranged at opposite side, it is called as trans – isomer.

No. of geometrical isomers in Co – ordination compound is much larger than organic compounds due to exhibition of geometrical isomerism up to 9. C.N.

In C.N. 2 and 3 geometrical isomerism is not exhibited.

In C.N = 4 and 6 maximum geometrical isomerism is shown.

Geometrical isomerism in Co – ordination number = 4:-

In C.N = 4 tetrahedral (Sp^3) and square planar (dsp^2) structures are possible. But in tetrahedral complexes geometrical isomerism is not possible because each ligand is adjacent to each other.

So, geometrical isomerism is possible in case of square planar complexes.

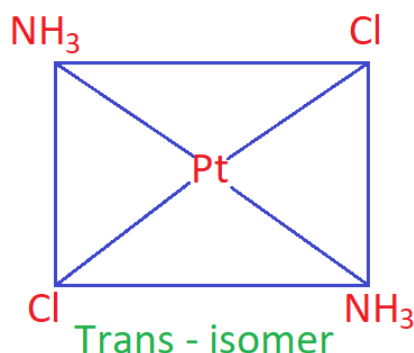
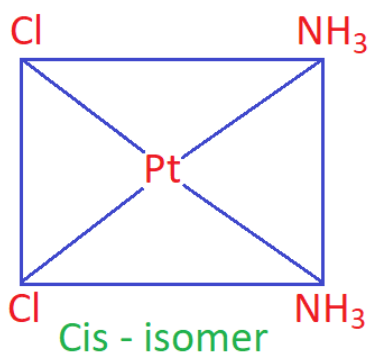
Again, in square planar complexes following types of geometrical isomerism are exhibited Ma_2b_2 , Ma_2bc , $Mabcd$.

But geometrical isomerism is not possible in case of Ma_4 , Ma_3b , Mab_3 .

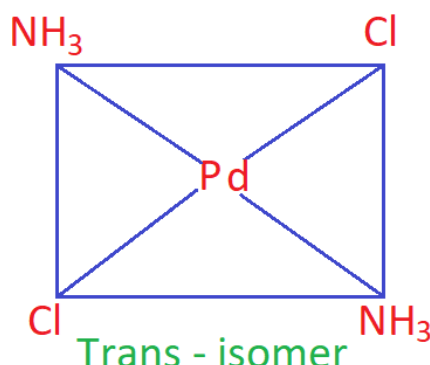
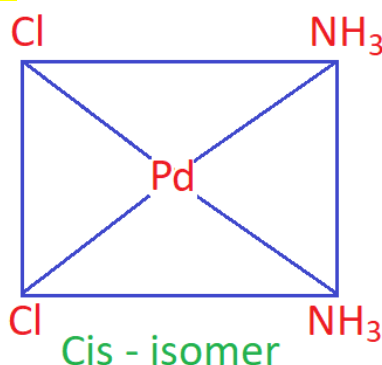
Case 1:- In Ma_2b_2 type of complexes:-

In this, types when two same ligands are present at the same adjacent side, it is called as Cis – isomer and when two same ligands are present at the opposite side, it is called as Trans – isomer.

Ex (i):- $[Pt^{2+}(NH_3)_2 Cl_2]^0$



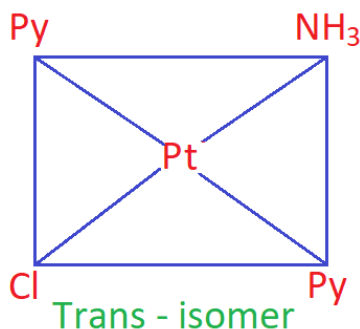
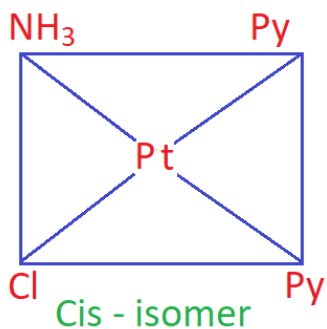
Ex (ii):- $[Pd(NH_3)_2 Cl_2]$



Case 2:- Ma_2bc type of complex:-

When two same ligands (a) are found the same adjacent side, it is called same ligands are found at the opposite side it is called as Trans – isomer.

Ex:- $[\text{Pt}(\text{Py})_2 \text{NH}_3\text{Cl}]$

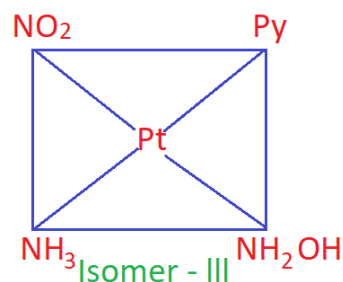
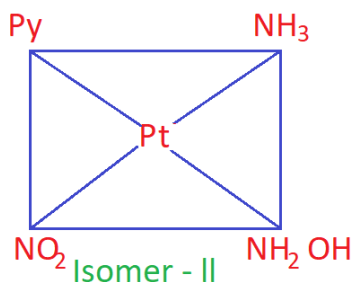
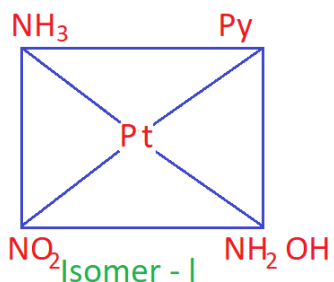


Case 3:- Mabcd type of complex:-

In this type of complex one ligand is fixed and rest three ligands are placed one by one opposite to the fixed ligand. In this way three isomers are exhibited here.

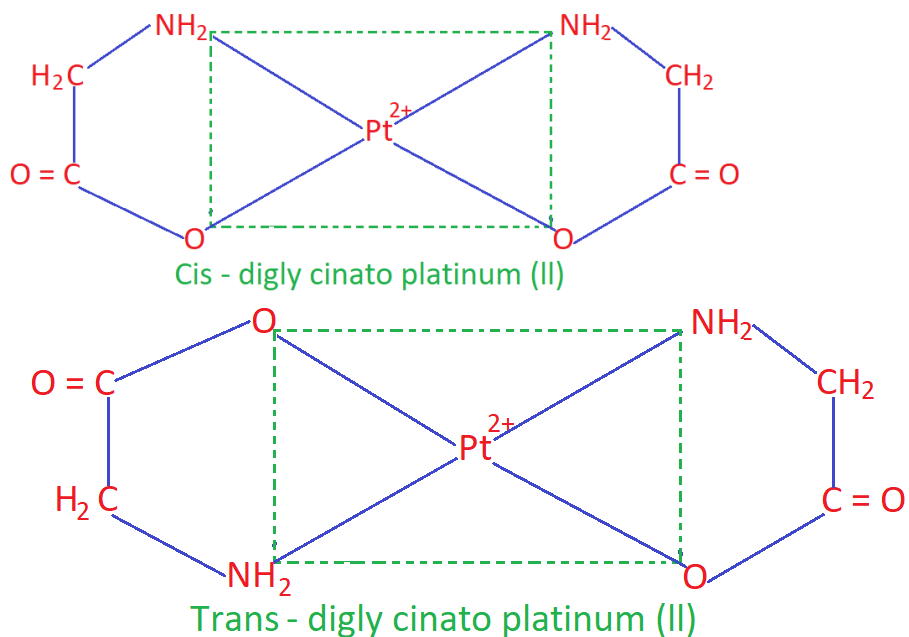
Here, in this type of geometrical isomerism, one ligand is kept at a fixed position while rest three ligands are kept at Trans – position to the first ligand one by one. In this way there are altogether three geometrical isomerism.

Ex:- $[\text{Pt}(\text{NH}_3) (\text{NH}_2\text{OH}) \text{Py} (\text{NO}_2)]^+$



Case 4:- If bidentate ligands are present in square – planar complexes, it can show geometrical isomerism.

Ex:- $[\text{Pt}(\text{gly})_2]^0$ gly = $\text{NH}_2\text{CH}_2\text{COO}^-$



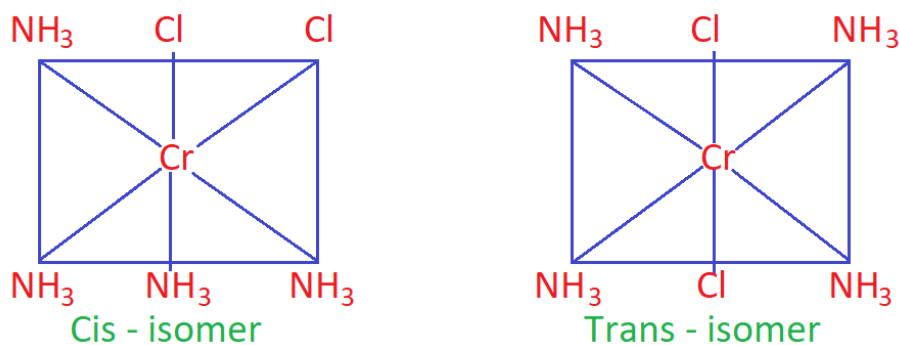
Geometrical isomerism in Co – ordination compounds having $C.N = 6$:-

Ma_6 , Ma_5b , types of Co – ordination compounds do not show geometrical isomerism.

But Ma_4b_2 , Ma_2b_4 , Ma_4bc etc. types of Co – ordination compounds can show geometrical isomerism.

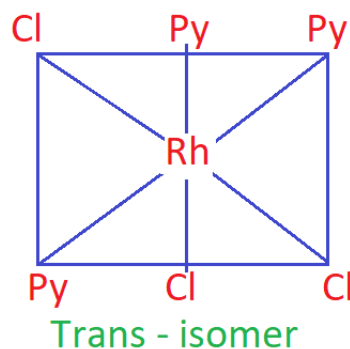
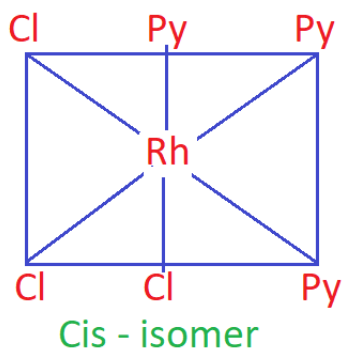
(1) Geometrical isomerism of Ma_4b_2 type:-

Ex:- $[Cr(NH_3)_4 Cl_2]^+ Cl^-$



(2) Geometrical isomerism in Ma_3b_3 types :-

Ex:- $[Rh(Py)_3 Cl_3]^0$



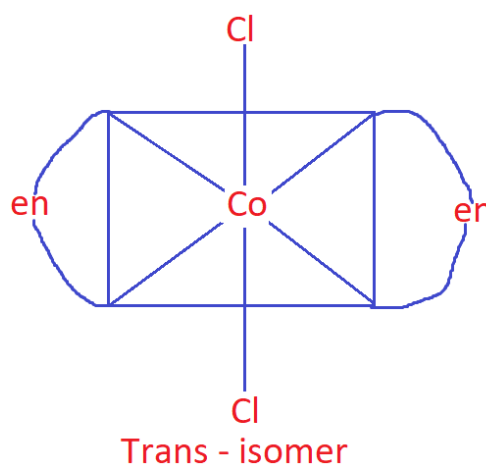
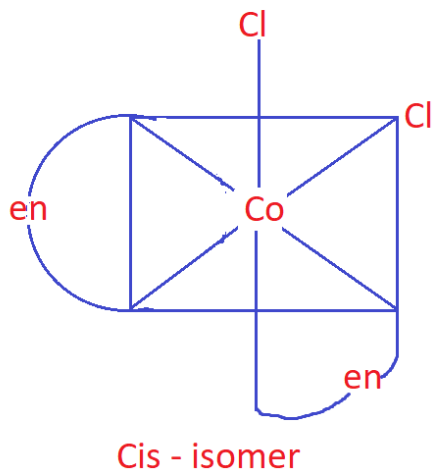
(3) Geometrical isomerism of Mabcdef type:-

In this, types 15 geometrical isomerism is possible.

However the only compound of this type has been prepared so far is – $[\text{Pt}(\text{Py})(\text{NH}_3)(\text{NO}_2)(\text{Cl})(\text{Br})(\text{I})]$. It has been possible to isolate only three isomerism of this complex.

(4) The complexes of $[\text{M}(\text{aa})_2\text{b}_2$ or $[\text{M}(\text{aa})_2\text{bc}]$ type:-

Ex:- $[\text{Co}^{3+}(\text{en})_2\text{Cl}_2]^+$



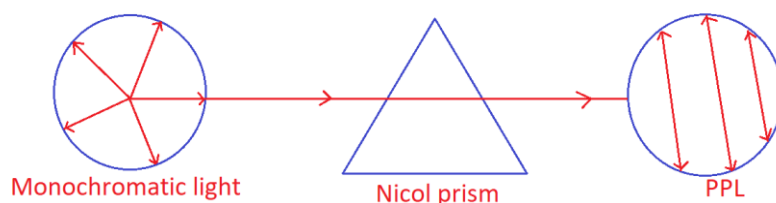
Optical isomerism:-

Definition:- When two or more than two compounds have same molecular and structural formula and also having same physical and chemical properties but having different optical activity. The phenomenon is called as optical isomerism.

Those compounds which show optical isomerism are called as optical isomers.

Plane polarised light (PPL):-

When monochromatic light (light having only one wave length) is passed through Nicol prism, we get a light travelling in perpendicular to the horizontal plane, is called as PPL.



Condition of optical isomerism:-

Molecular dissymmetry is the sufficient condition for optical isomerism.

Thus, if a molecule has got molecular dissymmetry, it will show optical isomerism otherwise not.

Dextro and Laevo forms:-

Dextro form:- When a molecule rotates the PPL in right direction, it is called as d – form isomer.

Laevo form:- When a molecule rotates PPL to the left direction, it is called as l – form isomer.

Enantiomers:- A pair of optically active isomers are called as enantiomers when they are mirror image to each other and also are non – super imposable to each other.

Optical isomerism in tetrahedral and square planar complexes:-

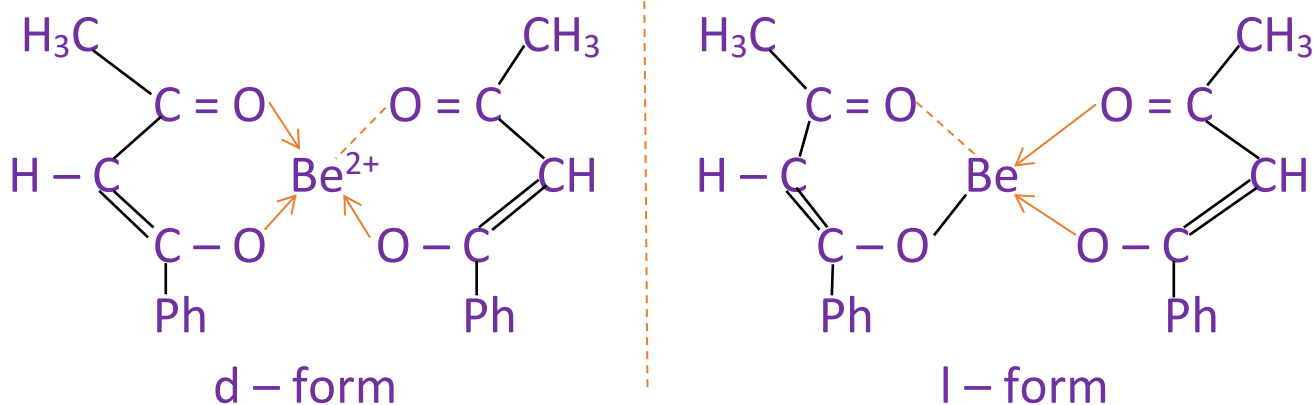
In C.N = 4 two type of structures are possible-

- (1) Tetrahedral.
- (2) Square planar.

(1) Optical isomerism in tetrahedral complexes:-

Since, all four groups (ligands) in tetrahedral complexes are in four planes. So, it has got molecular dissymmetry. That is why this type of molecules can show optical isomerism. But unfortunately, optically active tetrahedral complexes have not been resolved very much into d and l – forms.

However, following optically active compounds in tetrahedral complexes has been detected.



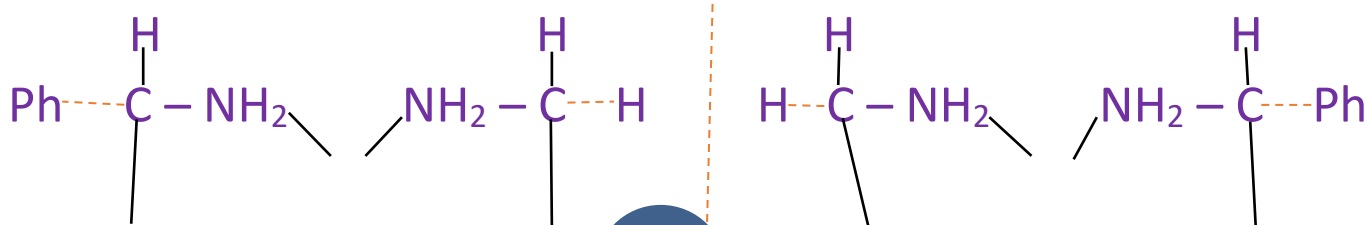
bis (benzoylacetato) beryllium.

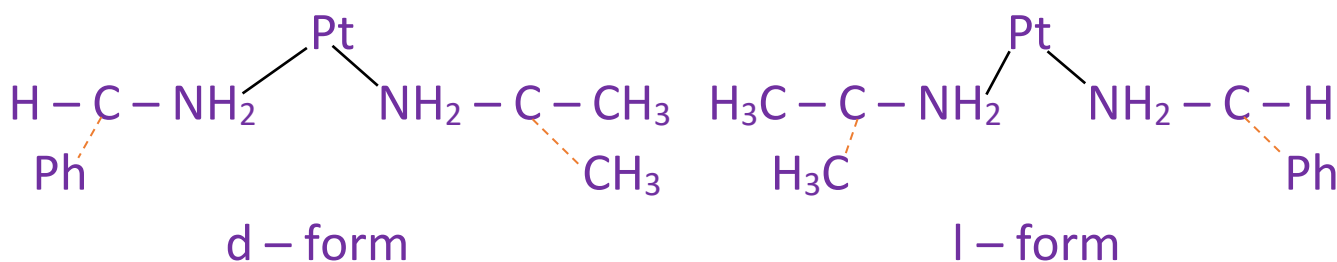
Above two optically active isomers are enantiomers, because they are non – superimposable and also mirror image to each other.

Optical isomers in square planar complexes:-

In general square planar complexes do not show optical isomerism because these complexes have not molecular dissymmetry (i.e they have plane of symmetry).

However, a square planar complex has been detected optically active which is given below. Actually, any how in this complex there is molecular dissymmetry.





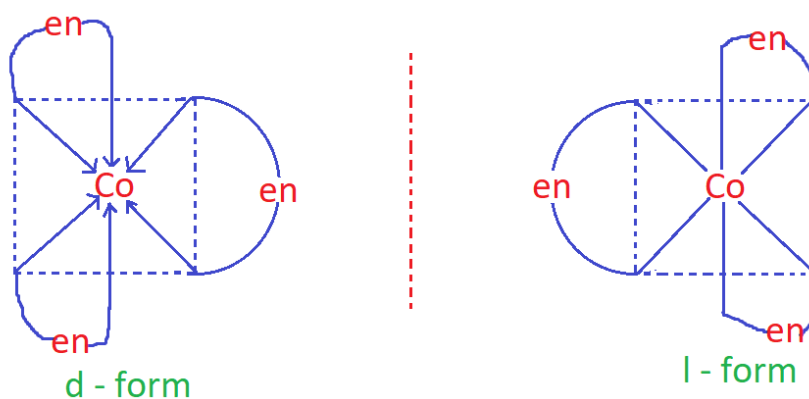
Optical isomerism in octahedral complex:-

Mostly in octahedral complexes optical isomerism is exhibited. Generally, in octahedral complexes optical isomerism is exhibited in the presence of bidentate ligands.

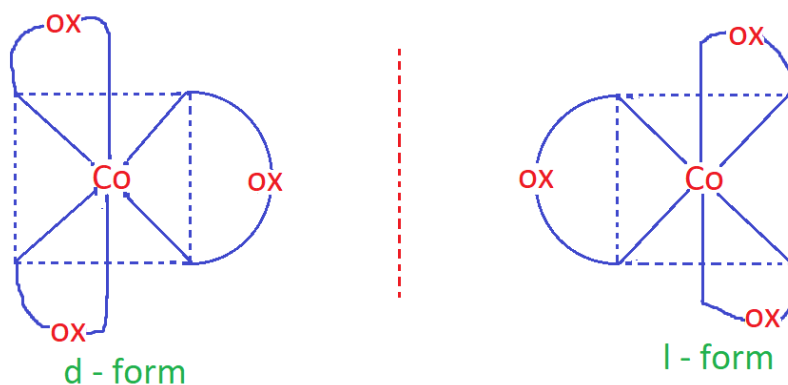
Case 1:- Complexes of the type $[M(aa)_3]$

Here, aa = bidentate ligand.

Ex:- (a). $[\text{Co}(\text{en})_3]\text{Cl}_2$



(b). $[\text{Cr}(\text{OX})_3]^{3-}$

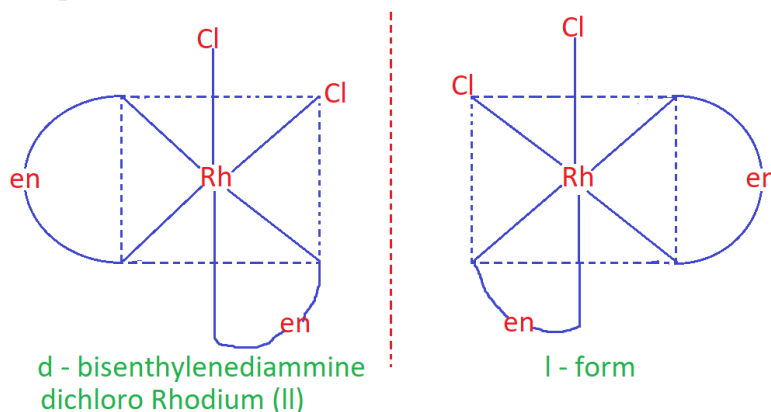


Case 2:- optical isomerism in $[M(aa)_2 b_2]$ type complex:-

This type of complexes show two types of geometrical isomerism i, e Cis and Trans.

Here trans form can't show optical isomerism but Cis form shows optical isomerism because trans form has got molecular symmetry, but Cis form has got molecular dissymmetry.

Ex:- $[Rh^{2+}(en)_2 Cl_2]$



Case 3:- Optical isomerism in $[M(aa)b_2c_2]$ type complex:-

Ex:- $[Co^{3+}(en) (NH_3)_2 Cl_2]^{+1}$

