By SHAILENDRA SHUKLA SIR

COORDINATION CHEMISTRY

Difference between Double salt and Complex salt

Double Salt	Complex Salt
(1) In these salts, the two simple salts remain intact only in solid phase. In aqueous solution they get separated and ionise to give their constituent ions.	(1) In these salts, the ions of two simple salts remain intact both in solid phase as well as in their aqueous solutions.
(2) During formation of these salts none of the ions lose its identity no new ion is formed. For example, carnelite ($KCl.MgCl_2.6H_2O$), Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$, Potash alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$. etc.	(2) During formation of these salts, some of the ions lose their identity and some new ions get formed. For example, Potassium ferrocyanide, $K_4[Fe(CN)_6]$, Potassium ferricyanide, $K_3[Fe(CN)_6]$ etc.

Terminology

(1) Central Metal Ion (CMI) and Ligands-

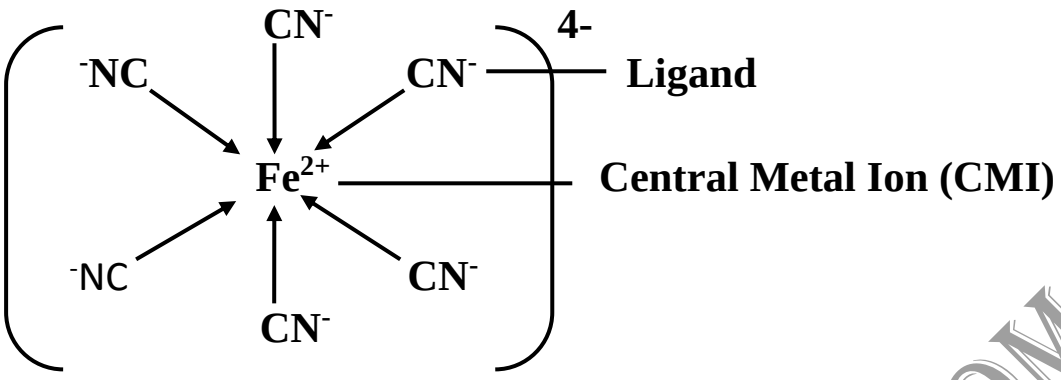
In complexes, a number of ions or groups remain coordinated to a metal ion which is called central metal ion (CMI).

CMI acts like electron pair acceptor and availables the sufficient number of vacant orbitals for the formation of coordinate bonds.

The ions or groups which coordinate to the CMI are called ligands. Ligands act like electron pair donor for the formation of ligand-metal ion coordinate bonds. Thus, they must contain one or more lone pair of electrons that can be donated to the CMI for the formation of ligand-metal ion coordinate bonds.

For example, in ferrocyanide ion $[Fe(CN)_6]^{4-}$, Fe^{2+} ion acts like CMI while, CN^- ions act like ligands.

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Ferrocyanide ion, $[Fe(CN)_6]^{4-}$

Classification of ligands

Depending upon the number of effective donor atoms present, ligands may be of following types-

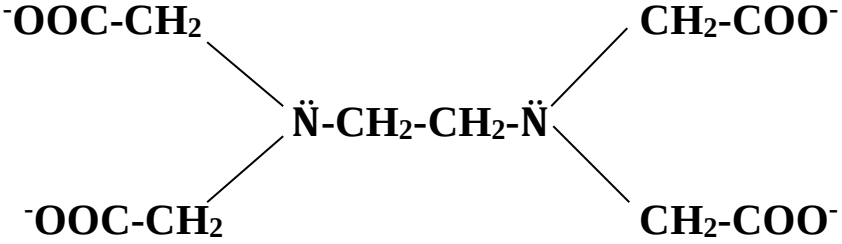
(1) Monodentate ligands- Such ligands which contain only one effective donor atom and therefore, can form only one coordinate bond to the CMI are called Monodentate ligands. For example, Cl^-, Br^-, I^-, OH^-, CN^-, NO_2^-, H_2O, NH_3 etc.

(2) Didentate ligands- Such ligands which contain two effective donor atoms and therefore, can form two coordinate bonds simultaneously to the CMI are called Didentate ligands. For example,



Ethylenediamine or Ethane-1,2-diamine (en) **oxalate ion (ox)**

(3) Polydentate ligands- Such ligands which contain more than two effective donor atoms and therefore, can form more than two coordinate bonds simultaneously to the CMI are called Polydentate ligands. For example, Ethylenediaminetetraacetate (EDTA) ion is a Hexadentate ligand.



Ethylenediaminetetraacetate (EDTA) ion

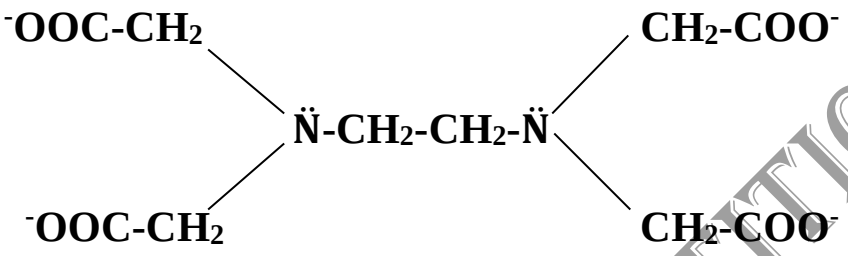
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- **Chelating Ligands- Bidentate and polydentate ligands coordinate to the CMI to form cyclic structures called chelates. Hence, these ligands are termed as chelating ligands. For example,**



Ethylenediamine or Ethane-1,2-diamine (en)

oxalate ion (ox)



Ethylenediaminetetraacetate (EDTA) ion

Chelating ligands form more stable complexes as compared to ordinary ligands.

- **Ambidentate ligands-**

Such Monodentate ligands, which contain two donor atoms but only one of them acts like effective donor are called Ambidentate ligands. These ligands coordinate to the CMI either through one donor atom or through another donor atom but never coordinate simultaneously through both the donor atoms. For example,

(1) 

Nitro-N or nitro

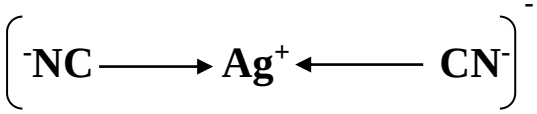
Nitro-O or nitrite

(2) 

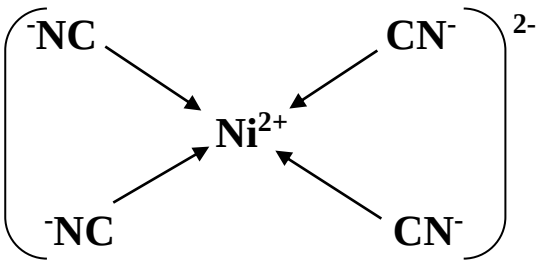
Thiocyanate-S or thiocyanate

Thiocyanate-N or isothiocyanate

(2) Coordination number (CN Number)- The total number of coordinate bonds formed between CMI and ligands in a complex ion is called coordination number (CN Number) of CMI in respective complex ion. For example,

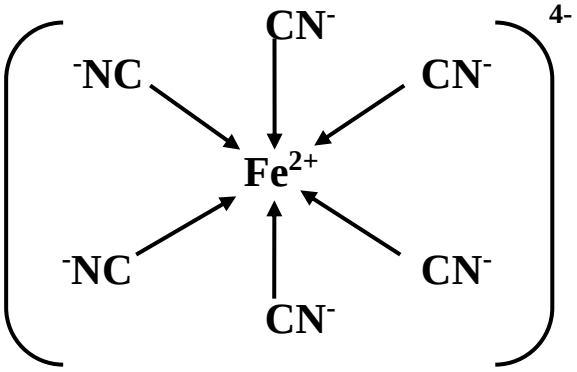


CN No. of Ag^+ = 2



CN No. of Ni^{2+} = 4

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CN No. of Fe^{2+} = 6

If all the ligands attached to the CMI are Monodentate then, the coordination number of CMI corresponds to the number of ligands in the complex ion. However, if the complex ion contains Didentate or Polydentate ligands then, the CN Number of CMI is calculated accordingly. For example, CN No. of Co^{3+} ion in $[Co(en)_3]^{3+}$ ion is 6.

(3) Coordination sphere and ionization sphere- According to modern convention, during expression of the complexes, the CMI and ligands are always written in a square bracket and this part is called coordination sphere of the compound. The ions present inside the coordination sphere are non-ionizable.

On the other hand, the ionisable ions are written out side the coordination sphere and this part is called ionization sphere of the compound. For example,

$\underbrace{K_4}_{\text{Ionization Sphere}}\ \underbrace{[\ \underbrace{Fe}_{\text{CMI}}\ \underbrace{(CN)_6}_{\text{Ligands}}\ ]}_{\text{Coordination Sphere}}$ $\qquad$ $\underbrace{[\ \underbrace{Co}_{\text{CMI}}\ \underbrace{(NH_3)_6}_{\text{Ligands}}\ ]}_{\text{Coordination Sphere}}\ \underbrace{Cl_3}_{\text{Ionization Sphere}}$

(4) Homoleptic and Heteroleptic complexes- Such complexes in which only one type of ligands remain coordinated to the CMI are called Homoleptic complexes. For example, $[Fe\ (CN)_6\ ]^{4-}$ ion, $[Co\ (NH_3)_6\ ]^{3+}$ ion etc.

On the other hand, those complexes in which two or more types of ligands remain coordinated to the CMI are called Heteroleptic complexes. For example, $[Co\ (NH_3)_5\ NO_2]^{2+}$ ion.

(5) Effective Atomic Number (EAN)- The total number of electrons present in CMI of a complex ion is called effective atomic number (EAN) of the CMI in respective complex ion.

Mathematically,

EAN = [At. No. of CMI – Oxidation No. of CMI] +2×(CN No. of CMI)

For example, for $[Co\ (NH_3)_6\ ]^{3+}$ ion,

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EAN of Co^{3+} ion = [27 – 3] + (2 × 6)
= 24 + 12
= 36

Similarly, for $[Fe(CN)_6]^{4-}$ ion,

EAN of Fe^{2+} ion = [26 – 2] + (2 × 6)
= 24 + 12
= 36

EAN of CMI is usually equal to the atomic number of the inert gases.

IUPAC nomenclature of complexes

Following are the important rules for IUPAC naming of the complexes-

(1) First cations then anions are named.

(2) During naming of complex ion, first ligands then CMI is named.

(3) If two or more types of the ligands are present, then they are always named in alphabetical order.

(4) If the name of ligand does not involve numeric prefixes such as di, tri, tetra etc. then their numbers are represented by simply prefixing di, tri, tetra etc. with their names.

However, if the name of ligand itself involves di, tri, tetra etc. For example, Ethylenediamine or Ethane-1,2-diamine (en), Ethylenediaminetetraacetate (EDTA) etc. then its number is given as under-

Bis	**for**	**two**
Tris	**for**	**three**
Tetrakis	**for**	**four**
Pentakis	**for**	**five**
Hexatis	**for**	**six**

(5) During naming of anionic ligands, if the name of ligand ends as -ite, -ide or -ate then last alphabet -e is usually replaced by -o. For example,

Cl^-	**(chloride changes to chlorido)**
Br^-	**(bromide changes to bromido)**
I^-	**(iodide changes to iodido)**
SO_3^{2-}	**(sulphite changes to sulphito)**
CO_3^{2-}	**(carbonate changes to carbonato)**
CH_3COO^-	**(acetate changes to acetato)**
SO_4^{2-}	**(sulphate changes to sulphato)**
$C_2O_4^{2-}$	**(oxalate changes to oxalato)**
S^{2-}	**(sulphide changes to sulphido)**

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Following are some exceptions of this rule-

OH^-	**(hydroxide changes to hydroxo)**
O^{2-}	**(oxide changes to oxo)**
CN^-	**(cyanide changes to cyano)**

(6) The names of cationic ligands usually ends as -ium. For example,

NH_2-NH_3^+	**(hydrazinium)**
$C_5H_5NH^+$	**(pyridinium)**
NO^+	**(nitrosylinium)**

(7) Neutral ligands are usually given their common names. However, following neutral ligands have been assigned special names-

H_2O	**(aquo or aqua)**
NH_3	**(ammine)**
CO	**(carbonyl)**
NO	**(Nitrocyl)**

(8) During naming of CMI, if it is present in cationic complexes, then its common name is given. For example,

$[Ag(NH_3)_2]^+$

Diamminesilver(I) ion

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

Hexaamminecobalt(III) ion

On the other hand, if it is present in anionic complexes, then -ate is added to its Latin name. For example,

$K[Ag(CN)_2]$

Potassium dicyanoargentate (I)

$K_4[Fe(CN)_6]$

Potassium hexacyanoferrate (II)

(9) The oxidation number of the CMI is also expressed in parentheses after the name of CMI.

(10) Naming of Ambidentate ligands-

Such Monodentate ligands, which contain two donor atoms but only one of them acts like effective donor are called Ambidentate ligands.

For example,

(3)	**$-NO_2^-$**	**$-ONO^-$**
	Nitro-N or nitro	**Nitro-O or nitrito**
(4)	**$-SCN^-$**	**$-NCS^-$**
	Thiocyanato-S or thiocyanato	**Thiocyanato-N or isothiocyanato**

During naming of Ambidentate ligands, the donor atom is also represented. For example,

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$[Co(NH_3)_5(NO_2)]Cl_2$

Pentaaminenitro-N cobalt(III) chloride

or

Pentaaminenitrocobalt(III) chloride

$[Co(NH_3)_5(ONO)]Cl_2$

Pentaaminenitro-O cobalt(III) chloride

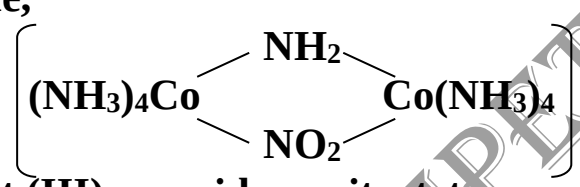
or

Pentaaminenitritocobalt(III) chloride

(11) Naming of bridging ligands-

Such ligands which act like bridge between two metal ions are called bridging ligands.

During naming of bridging ligands the prefix μ- is placed before their names. For example,



Tetraamminecobalt (III)-μ-amido-μ-nitrotetraamminecobalt (III) ion

Q. Give the IUPAC Name of the following-

Ans. (1) $[Ag(NH_3)_2]Cl$

Diamminesilver (I)chloride

(2) $[Co(NH_3)_6]Cl_3$

Hexaamminecobalt (III)chloride

(3) $K[Ag(CN)_2]$

Potassium dicyanoargentate (I)

(4) $K_4[Fe(CN)_6]$

Potassium hexacyanoferrate (II)

(5) $K_3[Fe(CN)_6]$

Potassium hexacyanoferrate (III)

(6) $[Co(NH_3)_5(NO_2)]Cl_2$

Pentaamminenitro-N cobalt(III) chloride

or

Pentaamminenitrocobalt(III) chloride

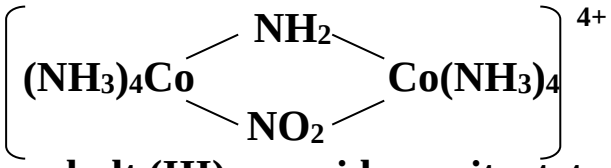
(7) $[Co(NH_3)_5(ONO)]Cl_2$

Pentaaminenitro-O cobalt(III) chloride

or

Pentaamminenitritocobalt(III) chloride

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(8) 

Tetraamminecobalt (III)-μ-amido-μ-nitrotetraaminecobalt (III) ion

Werner's coordination theory

or

Werner's theory of secondary or auxiliary valencies-

In order to explain bonding in complexes, Werner has proposed his coordination theory, which is also called Werner's theory of secondary or auxiliary valencies. The main postulates of this theory are as under-

(1) In complexes, CMI exhibits two types of valencies-

(a) Principal or primary valency

(b) Secondary or auxiliary valency

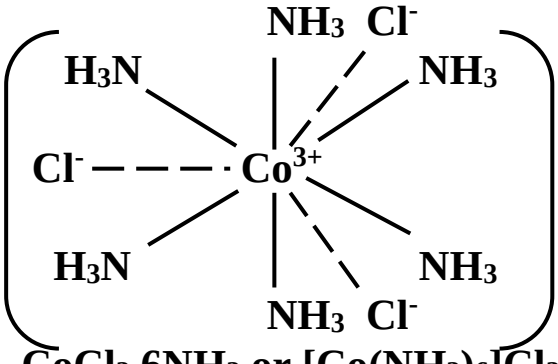
(2) Primary valencies are ionic (electrovslent) in nature and are satisfied by anions. It corresponds to the oxidation number of the CMI in respective complex ion.

(3) Secondary valencies are non-ionic (covalent) in nature and are satisfied by ligands. It corresponds to the coordination number of the CMI in respective complex ion.

(4) CMI tends to satisfy both of its two valencies. For doing so, some times the anions attached to the primary valencies play double role and satisfy both primary and secondary valencies simultaneously. In such case they lose their ionizable nature.

(5) Secondary valencies remain directed in some specified directions in space and provide a definite geometry to the complex ion. Thus, secondary valencies decide the geometry of the complexe ions.

Werner's theory can be explained by taking the example of chlorocobalt amine complexes where, primary valency of CMI is +3 and secondary valency is 6. If primary valencies are represented by dotted lines (-------) and secondary valencies by solid lines (——), then the structure of $CoCl_3.6NH_3$ can be represented as under-



$CoCl_3.6NH_3$ or $[Co(NH_3)_6]Cl_3$

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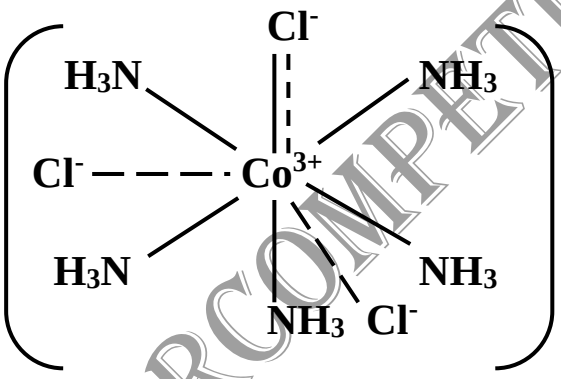
Here, ammonia molecules satisfy all the six secondary valencies of Co^{3+} ion while, chloride ions satisfy its primary valencies.

This compound ionises to give in all four ions and therefore, conducts current equivalent to four ions.

$$[Co(NH_3)_6]Cl_3 \quad \leftrightharpoons \quad [Co(NH_3)_6]^{3+} + 3Cl^-$$

It gives white precipitate of AgCl equivalent to three chloride ions with aqueous solution of $AgNO_3$. All these experimental facts support Werner's coordination theory.

In case of $CoCl_3.5NH_3$ only five ammonia molecules are available to satisfy secondary valencies. Hence, one of the three Cl^- ions plays double role and satisfies both primary and secondary valencies simultaneously (represented by combined line ═══).



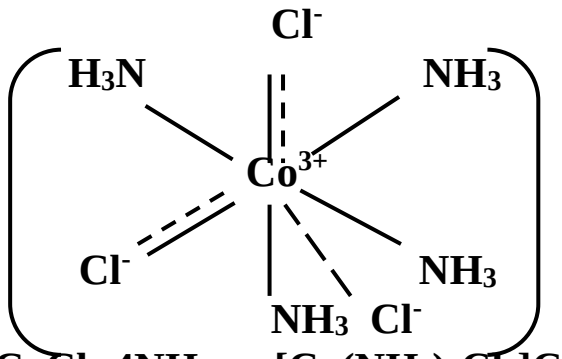
$CoCl_3.5NH_3$ or $[Co(NH_3)_5Cl]Cl_2$

This compound ionises to give only three ions and therefore, conducts current equivalent to three ions.

$$[Co(NH_3)_5Cl]Cl_2 \quad \leftrightharpoons \quad [Co(NH_3)_5Cl]^{2+} + 2Cl^-$$

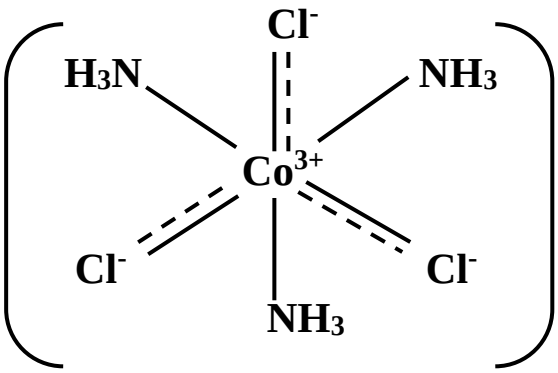
It also gives white precipitate of AgCl equivalent to two chloride ions with aqueous solution of $AgNO_3$. These experimental facts also support Werner's coordination theory.

In the same way, the structure of $CoCl_3.4NH_3$ and $CoCl_3.3NH_3$ can be represented as under-



$CoCl_3.4NH_3$ or $[Co(NH_3)_4Cl_2]Cl$

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$CoCl_3.3NH_3$ or $[Co(NH_3)_3Cl_3]$

Here, $CoCl_3.4NH_3$ or $[Co(NH_3)_4Cl_2]Cl$ ionises to give only two ions and therefore, conducts current equivalent to two ions.

$$[Co(NH_3)_4Cl_2]Cl \leftrightharpoons [Co(NH_3)_4Cl_2]^+ + Cl^-$$

It gives white precipitate of AgCl equivalent to only one chloride ion with aqueous solution of $AgNO_3$.

$CoCl_3.3NH_3$ or $[Co(NH_3)_3Cl_3]$ does not ionise in its aqueous solution and therefore, its aqueous solution does not conduct current and is bad conductor of electricity.

It does not give any precipitate of AgCl with aqueous solution of $AgNO_3$.

These experimental facts also support Werner's coordination theory.

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Valence Bond Theory (VBT)-

In order to explain bonding in complexes, this theory was for the first time proposed by Pauling. The main postulates of this theory are as under-

(1) In complexes, CMI acts like electron pair acceptor and availables the sufficient number of vacant orbitals for bonding.

(2) The number of vacant orbitals made available by CMI is equal to the coordination number of the CMI in respective complex ion.

(3) The vacant orbitals made available by CMI hybridize together to form hybridized orbitals of exactly same energy, same shape and same size in same number.

(4) Hybridized orbitals remain directed in some specified directions in space and provide a definite geometry to the complex ion. Thus, the type of hybridization in CMI decides the geometry of the complex ion.

(5) For hybridization CMI can available either its inner d-orbitals [(n-1)d-orbitals] or outer d-orbitals [nd-orbitals]. On this basis, the complexes are called inner orbital and outer orbital complexes respectively.

(6) In presence of strong field ligands such as NH_3, NO_2^-, CN^-, CO etc., there may occur forced pairing of electrons in inner d-orbitals of CMI against Hunds rule. It leads in the formation of inner orbital, spin paired, low spin complexes.

On the other hand, weak field ligands such as Cl^-, Br^-, I^-, H_2O etc., cannot cause forced pairing of electrons in inner d-orbitals of CMI. Hence, complexes formed by these ligands are usually outer orbital, spin free and high spin complexes.

(7) Ligands act like electron pair donor. Hence, they must contain one or more lone pair of electrons that can be donated to the CMI for the formation of ligand -metal ion coordinate bond.

(8) If a complex ion contains one or more unpaired electrons, then it is attracted in magnetic field and is paramagnetic in nature. On the other hand, if it does not contain any unpaired electron, then it is not attracted in magnetic field and is diamagnetic in nature.

Applications-

(1) Formation of $[Co(NH_3)_6]^{3+}$ ion- In $[Co(NH_3)_6]^{3+}$ ion, CMI is present in +3 oxidation state. Here, NH_3 molecules being strong field ligands cause forced pairing of electrons in inner 3d orbitals of CMI. Two vacant inner d-orbitals thus obtained, undergo d^2sp^3 hybridization with one s and three p-orbitals of outermost shell to

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form six vacant d^2sp^3 orbitals. Completely filled orbital of ligands NH_3 overlap with these vacant orbitals to form $H_3N \rightarrow Co^{3+}$ bonds.

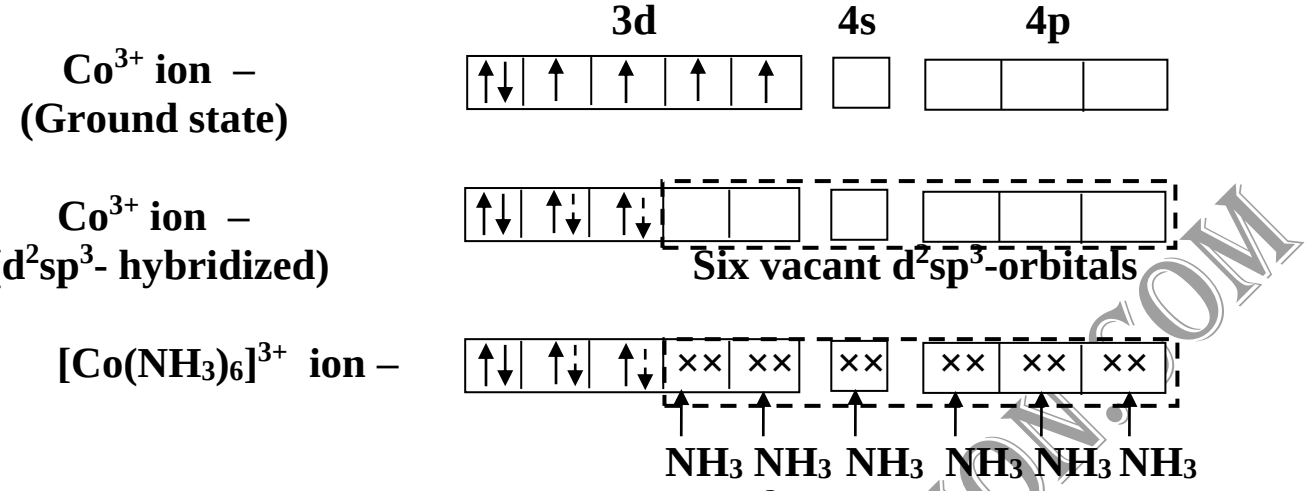


Fig.- Formation of $[Co(NH_3)_6]^{3+}$ ion (schematic)

It is clear that, $[Co(NH_3)_6]^{3+}$ ion is an inner orbital, spin paired, low spin complex. It does not contain any unpaired electron and therefore, it is not attracted in magnetic field and is diamagnetic in nature. Its magnetic moment is zero.

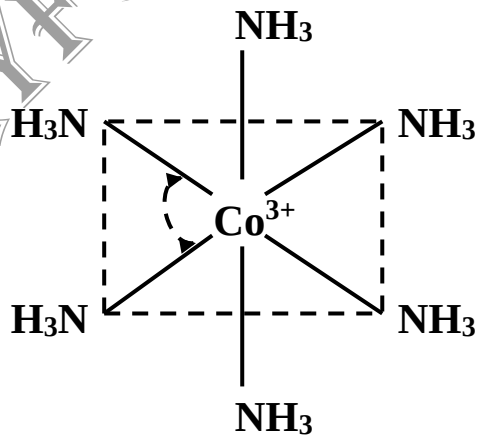
$$\mu = \sqrt{n(n+2)}\ B.M.$$

Where, n= number of unpaired electrons

$$\therefore \quad \mu = \sqrt{0(0+2)}\ B.M.$$

$$= 0 \text{ B.M.}$$

Since, $[Co(NH_3)_6]^{3+}$ ion involves d^2sp^3 hybridization, it is octahedral in shape with a bond angle of 90^0.



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

(2) Formation of $[CoF_6]^{3-}$ ion- In $[CoF_6]^{3-}$ ion, CMI is present in +3 oxidation state. Here, F^- ions being weak field ligands cannot cause forced pairing of electrons in inner 3d orbitals of CMI. Hence, CMI undergo sp^3d^2 hybridization to form six vacant sp^3d^2 orbitals. Completely filled orbital of ligands F^- ions overlap with these vacant orbitals to form $F^- \rightarrow Co^{3+}$ bonds.

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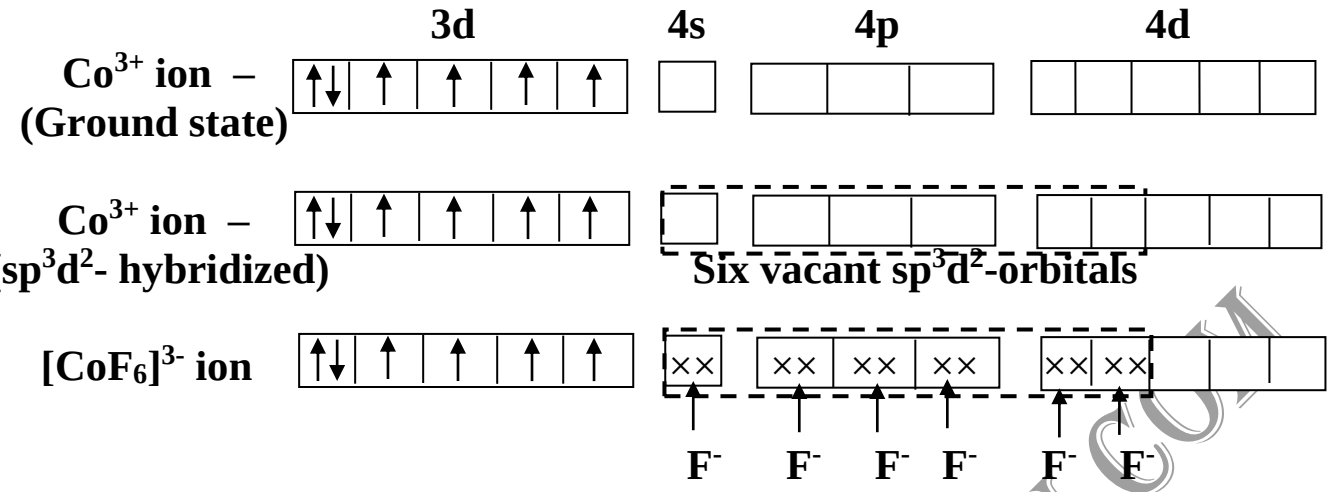


Fig.- Formation of $[CoF_6]^{3-}$ ion (schematic)

It is clear that, $[CoF_6]^{3-}$ ion is an outer orbital, spin free, high spin complex. It contains four unpaired electrons and therefore, it is attracted in magnetic field and is paramagnetic in nature. Its magnetic moment is $\sqrt{24}$ B.M.

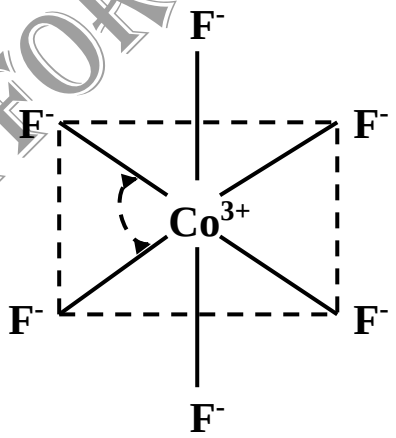
$$\mu = \sqrt{n(n+2)}\ B.M.$$

Where, n= number of unpaired electrons

$$\therefore \quad \mu = \sqrt{4(4+2)}\ B.M.$$

$$= \sqrt{24}\ \text{B.M.}$$

Since, $[CoF_6]^{3-}$ ion involves sp^3d^2 hybridization, it is octahedral in shape with a bond angle of 90^0.



$[CoF_6]^{3-}$ ion (Octahedral)

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Crystal Field Theory

This theory was for the first time proposed by Orgel to explain nature of bonding in complexes. It is an electrostatic model where ligand-metal bond is considered to be ionic arising purely from electrostatic interactions between metal ion and ligands. Here, ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. In an isolated gaseous metal atom or ion all the five d-orbitals have same energy i.e. they are degenerate. This degeneracy is maintained even in a spherically symmetrical magnetic field of negative charges surrounding the metal atom or ion. However, if the magnetic field is due to ligands (anions or negative ends of polar molecules), it is asymmetrical and penta-degeneracy of five d-orbitals gets vanished and they get splitted into two or more sets of orbitals having different energy. This phenomenon is called Crystal Field Splitting of d- orbitals. Here, the pattern of splitting depends upon the nature of crystal field and is different in different types of crystal fields.

Crystal Field Splitting in Octahedral Magnetic Field

When ligands approach octahedrally to the CMI, the penta-degeneracy of its five d-orbitals gets vanished and they get splitted into two sets of orbitals, namely t_{2g} set (d_{xy}, d_{yz} and d_{xz}) having lower energy and e_g set ($d_x2\text{-}_y2$ and d_z2) having higher energy. Here, the difference of the energy of the orbitals of e_g and t_{2g} set is called crystal field splitting energy (CFSE) and is represented by Δ_o.

In fact, axial d-orbitals ($d_x2\text{-}_y2$ and d_z2) lie in direct path of the ligands and therefore, they feel relatively more repulsion as compared to the non-axial d-orbitals (d_{xy}, d_{yz} and d_{xz}) which do not lie in direct path of the ligands. Thus, energy of axial d-orbitals ($d_x2\text{-}_y2$ and d_z2) gets increased more as compared to the average energy in spherical crystal field (barycentre) while, increase in energy of non-axial d-orbitals (d_{xy}, d_{yz} and d_{xz}) is relatively lesser as compared to that in spherically symmetrical crystal field.

Here, any electron entering in t_{2g} orbitals lower the energy of the complex ion by 2/5 Δ_o, while those entering in e_g orbitals increase the energy of complex ion by 3/5 Δ_o.

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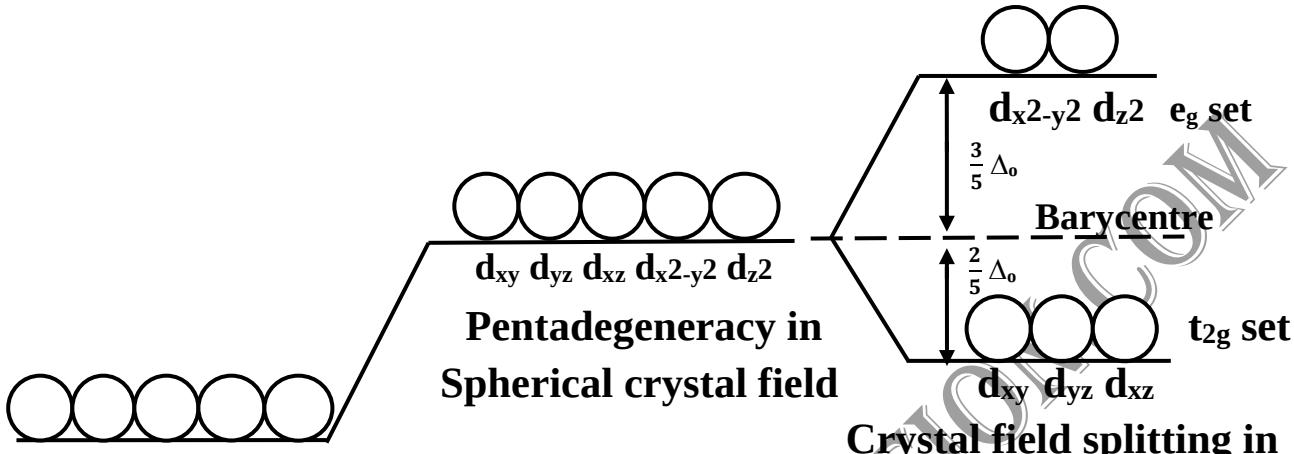


Fig.- Crystal Field Splitting of d-orbitals in octahedral magnetic field

Crystal field splitting energy Δ_o depends upon the nature of crystal field produced by ligands and charge on the metal ion.

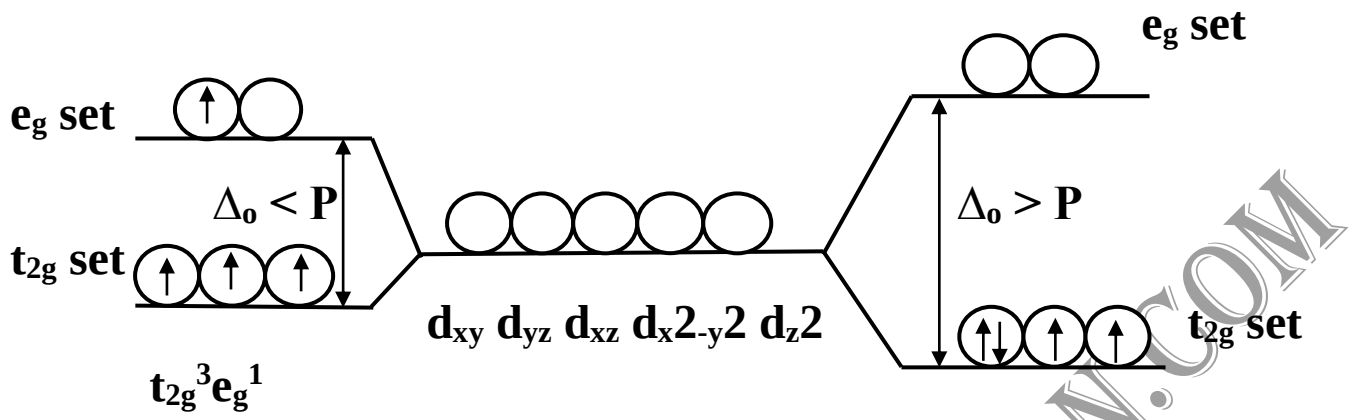
Electronic configuration of complexes-

For strong field ligands, the value of CFSE is more than pairing energy, P (energy required for pairing of electron in orbital of lower energy). Hence, the electrons prefer to pair up in t_{2g} orbitals instead of entering in e_g orbitals having higher energy.

On the other hand, for weak field ligands, the value of CFSE is lesser than the pairing energy, P. Hence, the electrons prefer to enter in e_g orbitals instead of being paired in t_{2g} orbitals of lower energy.

For example, the electronic configuration of CMI having d^4 configuration in a complex ion with weak and strong field ligands can be expressed as under-

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Spectro-Chemical Series-

If different ligands are arranged in increasing order of their crystal field splitting energy i.e. field strength, a series is obtained which is called Spectro-Chemical Series.

An Spectro-Chemical Series of some most common ligands is as under-

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} <$$
$$< H_2O < NCS^- < edta^{4-} < NH_3 < EN < CN^- < CO$$

This series has been determined experimentally by absorption of light by complexes containing different ligands.

Crystal Field Splitting in Tetrahedral Magnetic Field

When ligands approach tetrahedrally to the CMI, the penta-degeneracy of its five d-orbitals gets vanished and they get splitted into two sets of orbitals, namely t_2 set (d_{xy}, d_{yz} and d_{xz}) having higher energy and e-set ($d_{x^2-y^2}$ and d_{z^2}) having lower energy. Here, the difference of the energy of the orbitals of t_2 and e set is called crystal field splitting energy (CFSE) and is represented by Δ_t.

Here, none of the d-orbitals lie in direct path of the ligands, but non-axial d-orbitals (d_{xy}, d_{yz} and d_{xz}) are more closure to the ligands and

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therefore, they feel relatively more repulsion as compared to the axial d-orbitals (d_x2-$_y2$ and d_z2). Thus, energy of non-axial d-orbitals (d_{xy}, d_{yz} and d_{xz}) gets increased more as compared to the average energy in spherical crystal field (barycentre) while, increase in energy of axial d-orbitals (d_x2-$_y2$ and d_z2) is relatively lesser as compared to that in spherically symmetrical crystal field. Thus, pattern of crystal field splitting in tetrahedral crystal field gets inverted as compared to that in octahedral crystal field.

Here, any electron entering in e-orbitals lower the energy of the complex ion by 3/5 Δ_t, while, those entering in t_2 orbitals increase the energy of complex ion by 2/5 Δ_t.

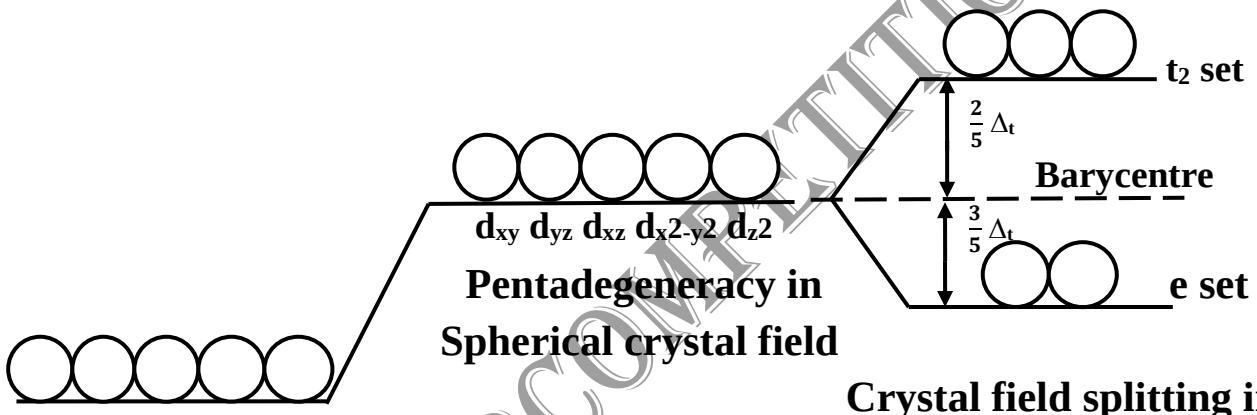


Fig.- Crystal Field Splitting of d-orbitals in tetrahedral magnetic field

Crystal field splitting energy, Δ_t for tetrahedral complexes is relatively lesser as compared to that of octahedral complexes. For same metal ion, same ligands and same distance of ligands from the metal ion, Δ_t is related to Δ_o as under-

$$\Delta_t = \frac{4}{9}\Delta_o$$

Here, the crystal field splitting energy is not sufficiently large for forced pairing of electrons in orbitals of lower energy. It is the reason why, low spin configurations are rarely observed in tetrahedral complexes.

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Isomerism-

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

Complexes show following two types of isomerism-

Structural Isomerism- The compounds having same molecular formula but different structural formula and therefore, different properties are called structural isomers and this phenomenon is called structural isomerism.

In complexes, structural isomerism may be of following types-

(1) Ionisation isomerism- It arises due to interchange of anions present inside and outside the coordination sphere. Here, different isomer ionise to give different ions. For example,

$[Co(NH_3)_5(SO_4)]Cl$ and $[Co(NH_3)_5Cl]SO_4$

These two isomers ionise as under-

$$[Co(NH_3)_5(SO_4)]Cl \leftrightharpoons [Co(NH_3)_5(SO_4)]^+ + Cl^-$$

$$[Co(NH_3)_5Cl]SO_4 \leftrightharpoons [Co(NH_3)_5Cl]^{2+} + SO_4^{2-}$$

Here, first isomer gives white precipitate of AgCl with aqueous solution of $AgNO_3$, but does not give any precipitate with aqueous $BaCl_2$. On the other hand, second isomer gives white precipitate of $BaSO_4$ with aqueous solution of $BaCl_2$, but does not give any precipitate with aqueous $AgNO_3$.

(2) Solvate isomerism- It arises due to interchange of anions present inside the coordination sphere with solvent molecules present outside the coordination sphere as crystallisation molecules. Here, if solvent is water, then solvate isomerism is also called hydrate isomerism. For example, $CrCl_3.6H_2O$ has following three hydrate isomers-

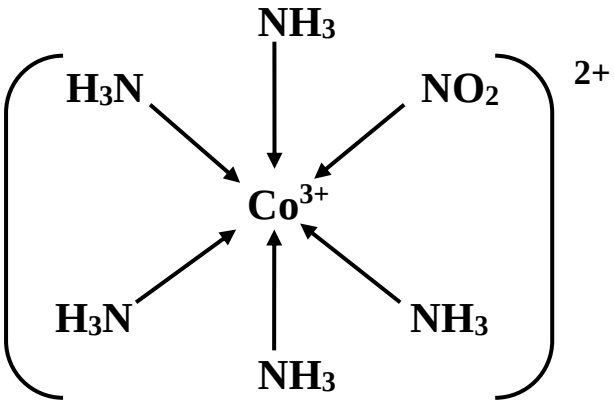
$[Cr(H_2O)_6)]Cl_3$	$[Cr(H_2O)_5Cl)]Cl_2.H_2O$	$[Cr(H_2O)_4Cl_2)]Cl.2H_2O$
Violet	**Grey-green**	**Green**

Here, first isomer gives white precipitate of AgCl with aqueous solution of $AgNO_3$ equivalent to three chloride ions but does release any water molecule with conc. H_2SO_4. second isomer gives white precipitate of AgCl with aqueous solution of $AgNO_3$ equivalent to two chloride ions and releases a water molecule with conc. H_2SO_4. Third isomer gives white precipitate of

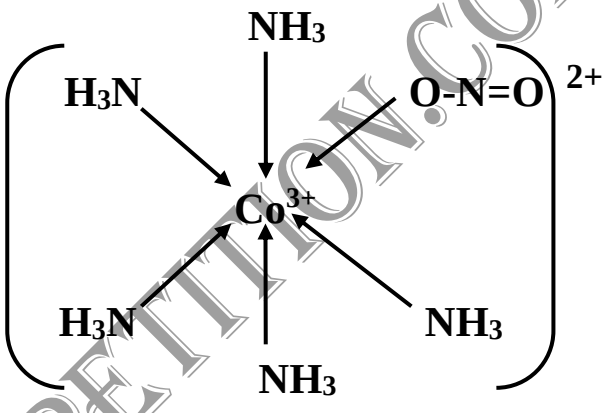
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AgCl with aqueous solution of $AgNO_3$ equivalent to only one chloride ion and releases two water molecules with conc. H_2SO_4.

(3) Linkage or Salt isomerism- It is especially exhibited by those complexes which contain ambidentate ligands which co-ordinate through one donor atom in one isomer and through another donor atom in another isomer. For example, $[Co(NH_3)_5NO_2]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$ ions are linkage isomers of each other.



$[Co(NH_3)_5NO_2]^{2+}$



$[Co(NH_3)_5(ONO)]^{2+}$

Similarly, $[Co(NH_3)_5(SCN)]^{2+}$ and $[Co(NH_3)_5(NCS)]^{2+}$ ions are linkage isomers of each other.

(4) Coordination isomerism- It is especially exhibited by those complexes in which both cation and anion are complex ions. It arises due to inter-change of one or more ligands present in cationic entity to that present in anionic entity. For example,

(i) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

(ii) $[Cr(NH_3)_6][Cr(SCN)_6]$ and $[Cr(NH_3)_4(SCN)_2][Cr(NH_3)_2(SCN)_4]$

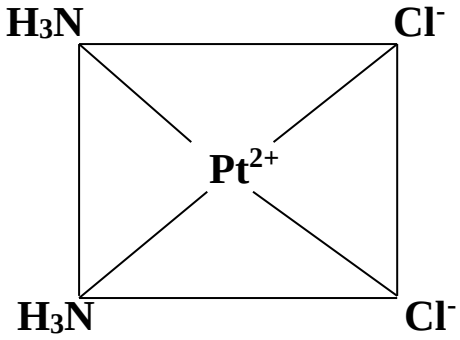
Stereo Isomerism-

It may be of following two types-

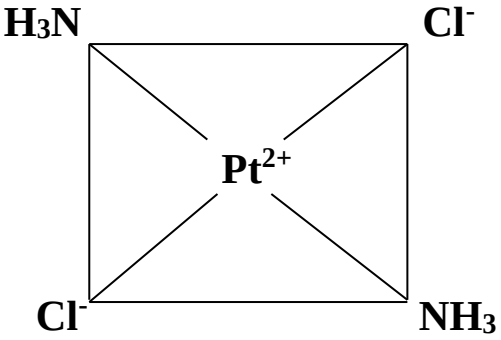
(1) Geometrical Isomerism- Amongst tetra coordinated complexes, tetrahedral complexes do not show geometrical isomerism. It is because in tetrahedral complexes all the ligands are adjacent to one another.

Tetra coordinated square planar complexes of type $[Ma_2b_2]$ and $[Ma_2bc]$ show geometrical isomerism and exist in cis and trans forms. Here, in cis form similar ligands lie at an angle of 90^0 they while in trans form lie at an angle of 180^0. For example, $[Pt(NH_3)_2Cl_2]$ exists in cis and trans forms.

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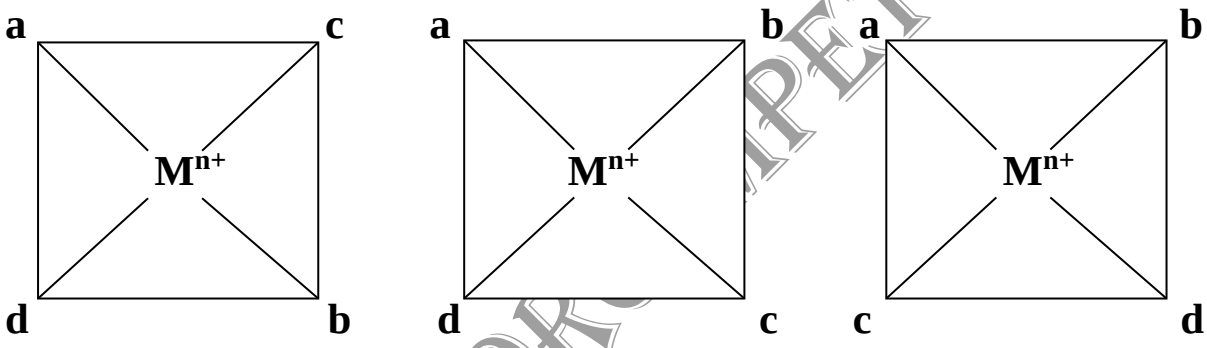
Cis isomer



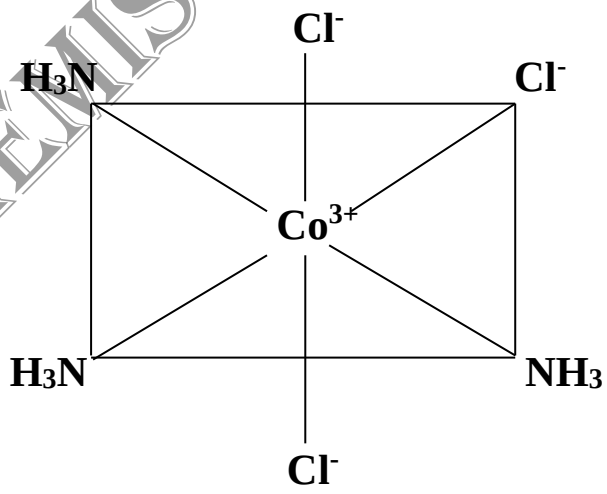
Trans isomer

- **Cis Platin i.e. cis $[Pt(NH_3)_2Cl_2]$ is used in treatment of cancer.**

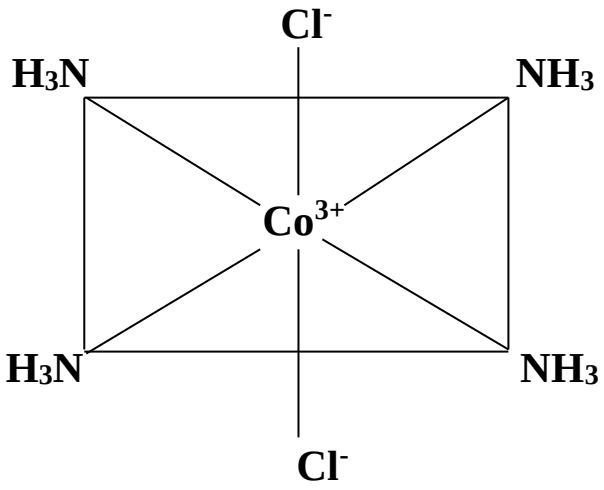
Similarly, for tetra coordinated square planar complexes of type [Mabcd] such as $[Pt(NH_3)(Py)(Cl)(Br)]$, $[Pt(NH_3)(C_2H_4)(Cl)(Br)]$, $[Pt(NH_3)(Py)(NO_2)(NH_2OH)]$ etc. following three geometrical isomers are possible.



Hexa coordinated octahedral complexes of type $[Ma_4b_2]$, $[Ma_4bc]$, $[M(aa)_2b_2]$ and $[M(aa)_2bc]$ show geometrical isomerism and exist in cis and trans forms. For example, $[Co(NH_3)_4Cl_2]^+$ shows geometrical isomerism and exist in cis and trans forms.



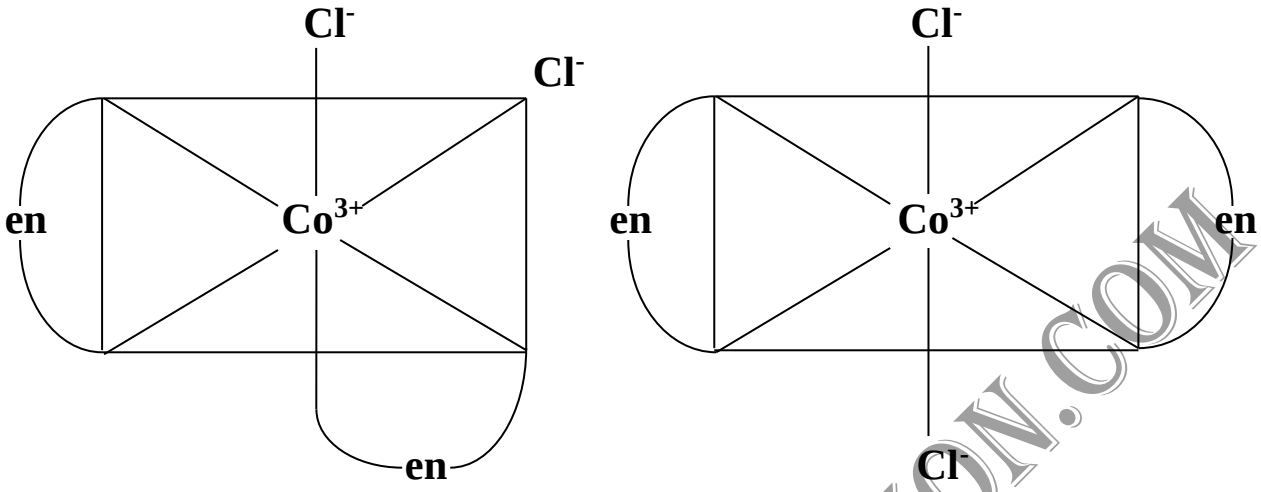
Cis isomer



Trans isomer

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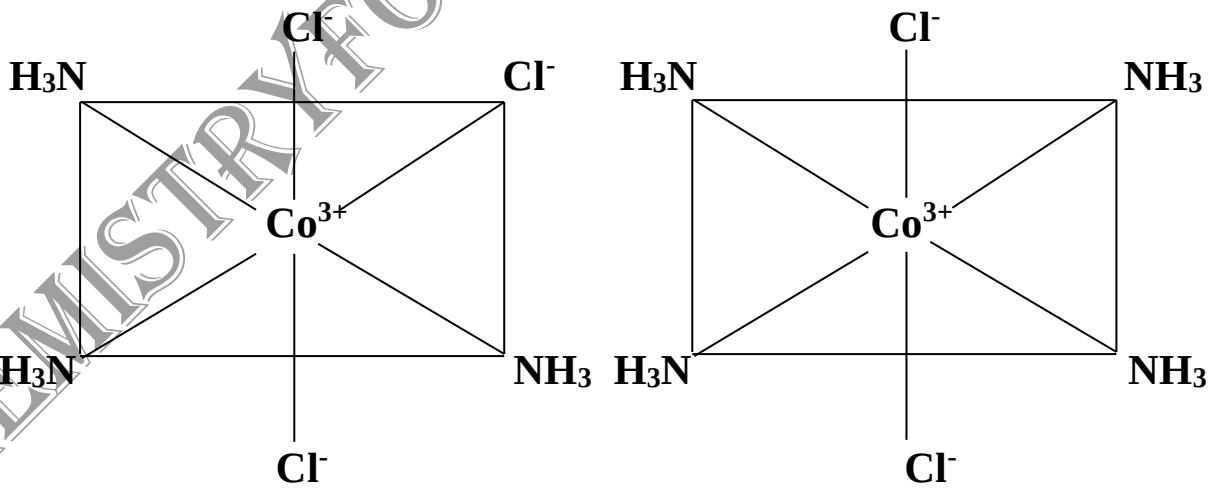
Similarly, cis and trans forms of $[Co(en)_2Cl_2]^+$ ion can be represented as under-



Cis isomer **Trans isomer**

Similarly, $[Co(en)_2(NO_2)_2]^+$, $[Ir(C_2O_4)_2Cl_2]^{2-}$, $[Rh(C_2O_4)_2Cl_2]^{2-}$ and $[Cr(C_2O_4)_2(H_2O)_2]^-$ ions also exist in cis and trans forms.

Hexa coordinated octahedral complexes of type $[Ma_3b_3]$ also show geometrical isomerism and exist in facial (fac) and peripheral or meridional (mer) forms. In fac form similar ligands lie on same face while, in mer form they lie in meridional positions. For example, $[Co(NH_3)_3Cl_3]$, $[Cr(NH_3)_3Cl_3]$, $[Co(NH_3)_3(NO_2)_3]$, $[Cr(NH_3)_3Cl_3]$, $[Rh(Py)_3Cl_3]$ etc. exist in fac and mer forms.



Fac isomer (1,2,3 isomer) **Mer- isomer (1,2,6 isomer)**

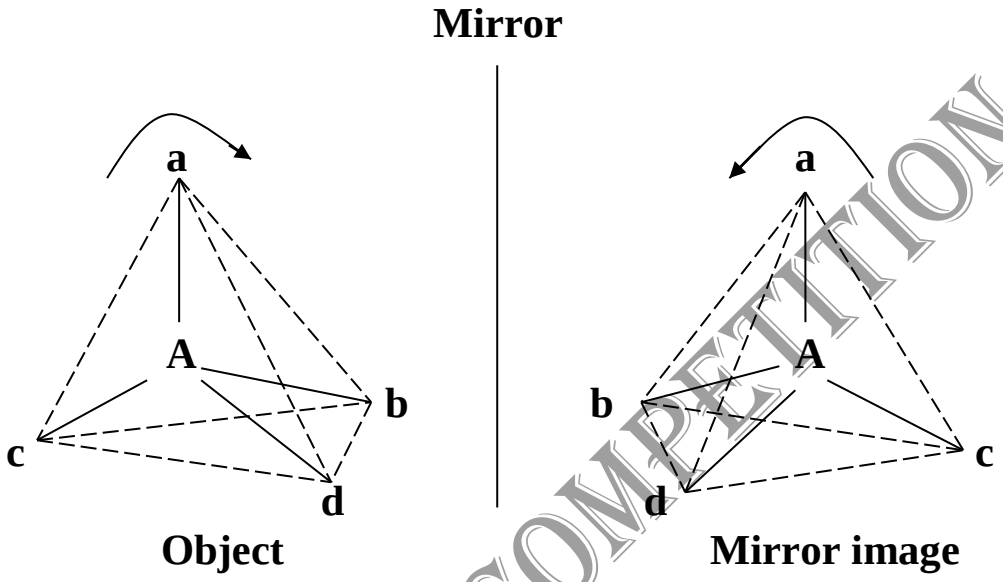
Fig.- Fac and Mer forms of $[Co(NH_3)_3Cl_3]$

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(2) Optical Isomerism-

Amongst tetra coordinated complexes, square planar complexes do not show geometrical isomerism. It is because in these complexes central metal ion and all the ligands are co-planar so that, they have a plane of symmetry.

Tetra coordinated tetrahedral complexes of only type [Mabcd] show optical isomerism and exist in dextrorotatory (d-form) and laevo rotatory (l-form). These two forms are related with each other as object and its mirror image, but do not super-impose on each other.



For example, $[As(CH_3)(C_2H_5)(S)(C_6H_5COO)]^{2+}$ ion shows optical isomer and exists in d- and l - forms.

Amongst hexa-coordinated octahedral complexes, the complexes of type [Mabcdef] such as $[Pt(NO_2)(NH_3)(Py)(Cl)(Br)(I)]$, do not contain plane of symmetry and show optical isomerism and exist in d and l forms.

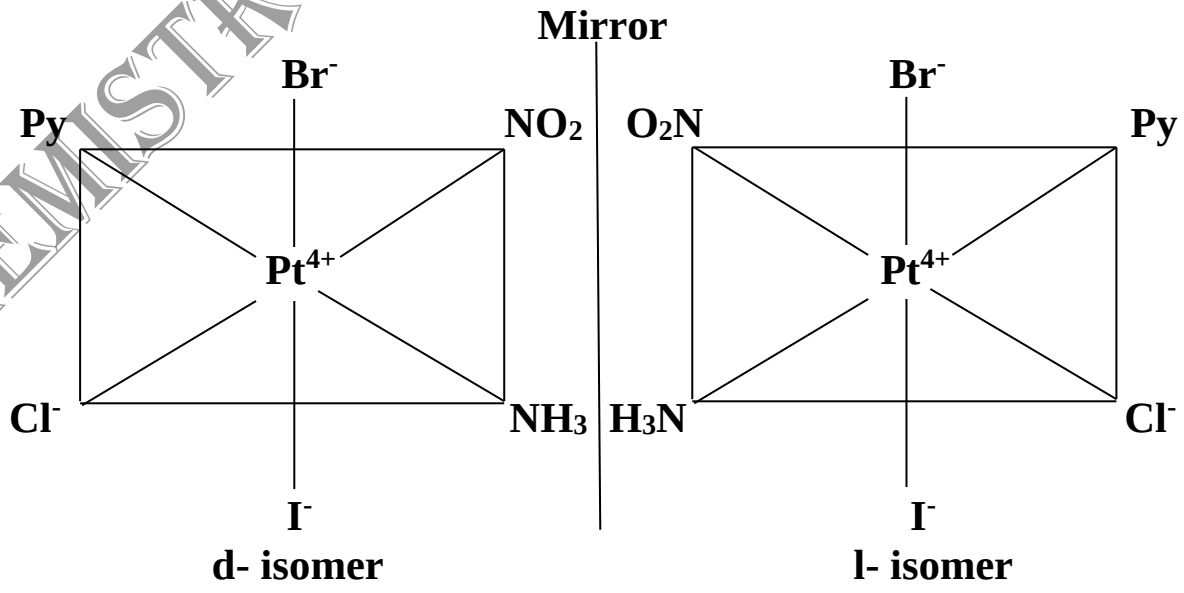


Fig.- Optical isomers of $[Pt(NO_2)(NH_3)(Py)(Cl)(Br)(I)]$

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Optical isomerism arises due to dissymmetry in the complexes. For example, cis form of the complexes of type $[M(aa)_2b_2]$ do not contain plane of symmetry and show optical isomerism. For example, cis form of $[Co(en)_2Cl_2]^+$, $[Co(ox)_2Cl_2]^{3-}$ shows optical isomerism and exists in d and l-forms.

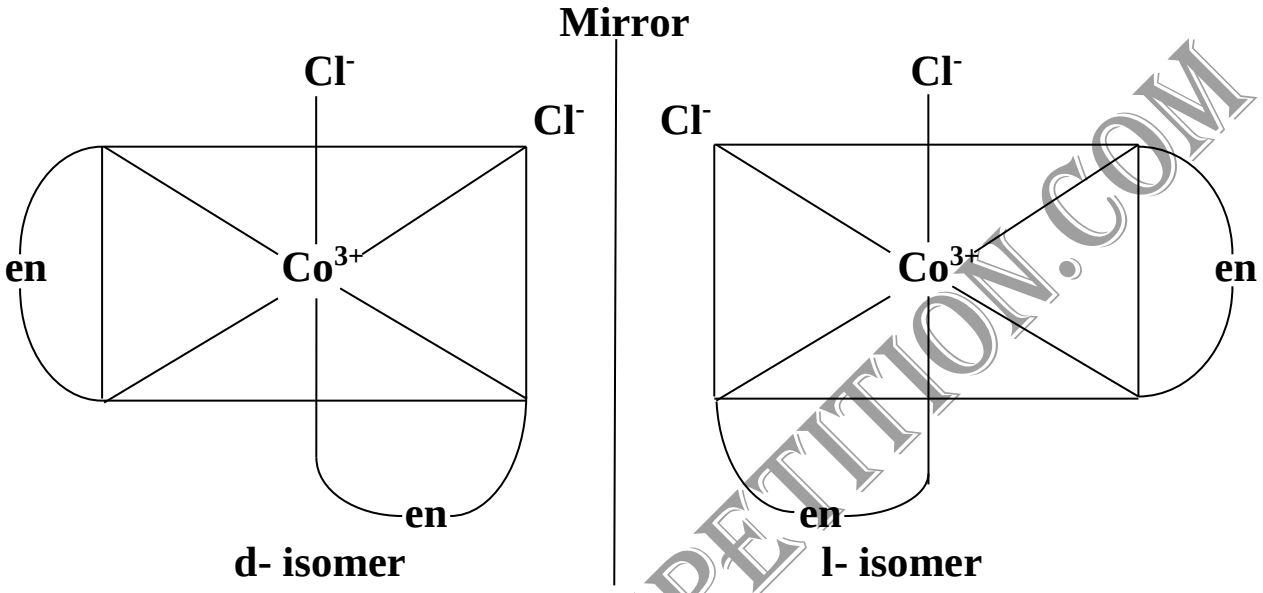


Fig.- d and l-forms of $[Co(en)_2Cl_2]^+$ ion

On the other hand, trans forms of these ions contains plane of symmetry and therefore does not show optical isomerism.

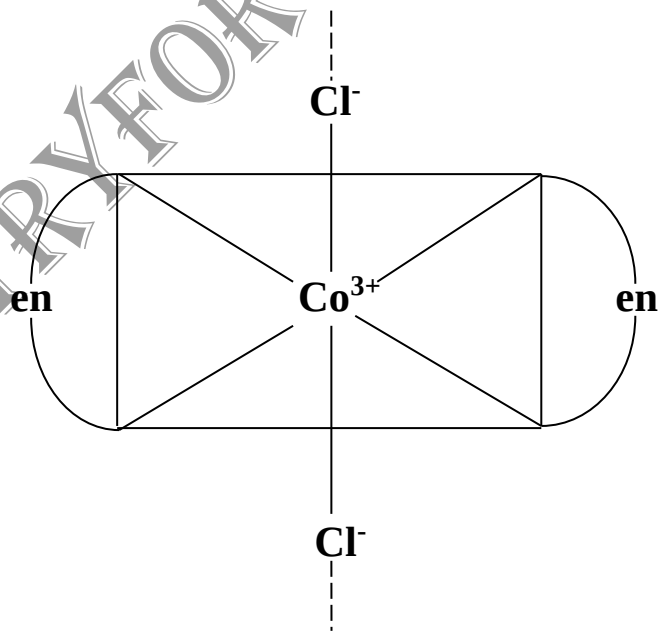


Fig.- Trans $[Co(en)_2Cl_2]^+$ having plane of symmetry

Octahedral complexes of type $[M(aa)_3]$ such as $[Co(en)_3]^{3+}$, $[Pt(en)_3]^{4+}$, $[Rh(en)_3]^{4+}$, $[Co(ox)_3]^{3-}$, $[Cr(ox)_3]^{3-}$ etc. also do not contains plane of symmetry and therefore, show optical isomerism.

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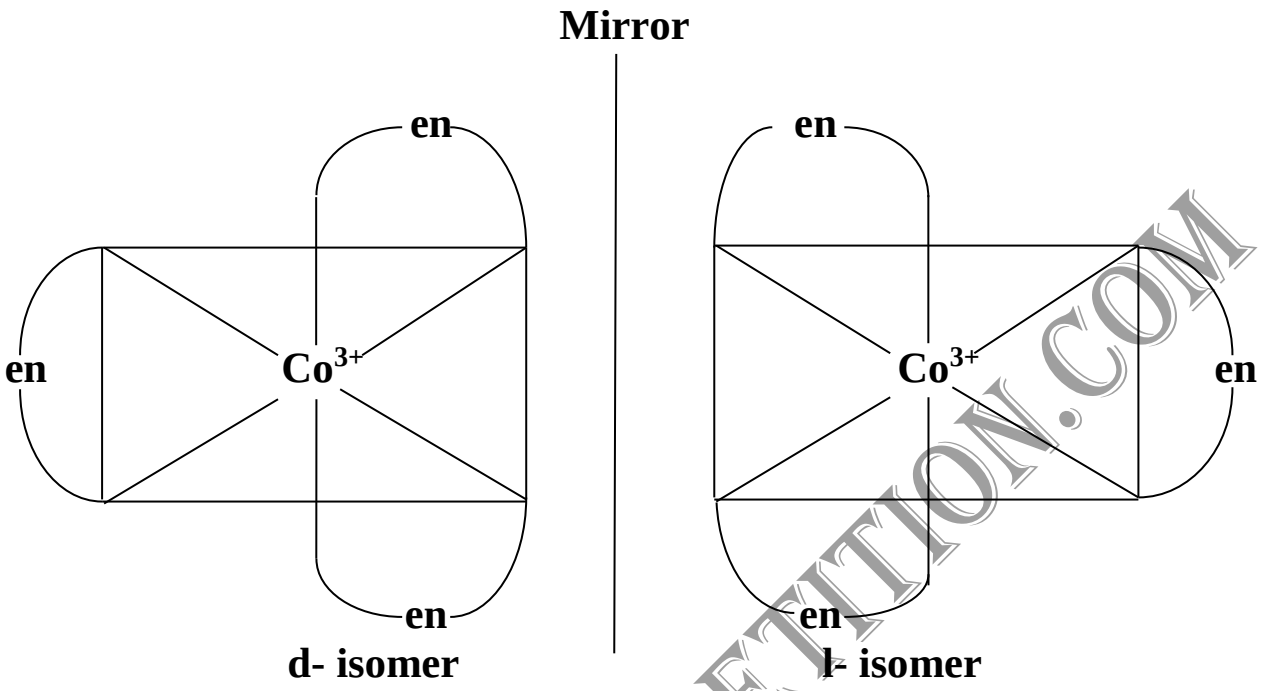


Fig.- d and l-forms of $[Co(en)_3]^{3+}$ ion

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