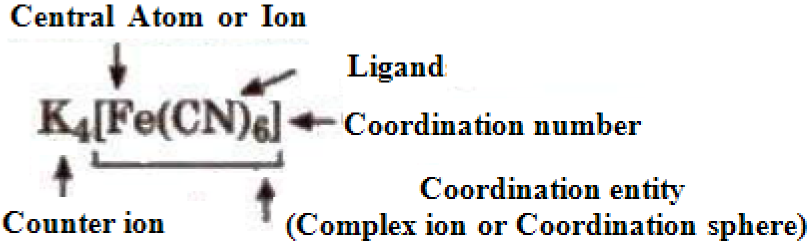
Chapter 9- Coordination Compound

1. Double Salts: These are the addition molecular compounds which are stable in solid state but dissociate into constituent ions in the solution. e.g., Mohr'S salt, [$FeSO_4 \cdot (NH_4)_2SO_4.6H_2O$] get dissociated into Fe^{2+}, NH_4^+ and SO_4^{2-} ions, Potash alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$ etc

2. Coordination Compound: Coordination Compounds are the compounds which contain complex ions like [$Co(NH_3)_6$], [$Fe(CN)_6$]$^{4-}$etc. These compounds contain a central metal atom or cation which is attached with a fixed number of anions or molecules (ligands) through coordinate bonds.



3. Coordination entity (Complex ion): A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. Example: in $K_4[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{4-}$ represents coordination entity.

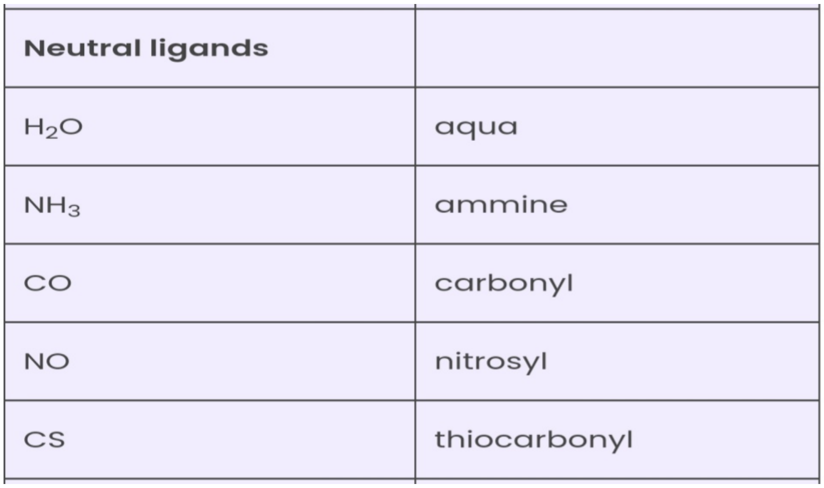
4. Central Atom or Ion: The atom or ion to which a fixed number of ions or molecules are bound in a definite geometrical arrangement. It is also referred as Lewis acid. e.g., in $K_4[Fe(CN)_6]^{4-}$, Fe is central metal atom. It is generally transition element or inner-transition element.

5. Ligands: A molecule, ion or group that is bonded to the metal atom or ion in a complex or coordination compound by a coordinate bond is called ligand.

Classification of Ligands:

A) On the basis of Charge: It can be further classified in following three categories i.e.

i) Neutral Ligands:



Neutral ligands	
H_2O	aqua
NH_3	ammine
CO	carbonyl
NO	nitrosyl
CS	thiocarbonyl

ii) Cationic Ligands:

Positive ligands	
NO_2^+	nitonium
$H_2NNH_3^+$	hydrazinium
NO^+	nitrosonium

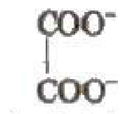
iii) Anionic Ligands:

Negative ligands	Name as ligand
F^-	Fluorido (fluoro)
I^-	Iodide (iodo)
Cl^-	Chlorido (chloro)
OH^-	hydroxo
O_2^{2-}	peroxo
O_2^-	superoxo
CH_3COO^-	acetato
CO_3^{2-}	carbonato
SO_4^{2-}	sulphato
SO_3^{2-}	sulphito
SCN^-	thiosulphato-S
NCS^-	isothiocyanato-N

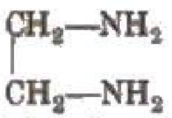
B) On the basis of number of Donor Site:

i) Unidentate: Ligands which has one donor site so that bound to a metal ion through a single donor site. Examples H_2O, NH_3 etc.

ii) Didentate: Ligands which have two donor sites like oxalate ion , ethylene diamine(en) etc

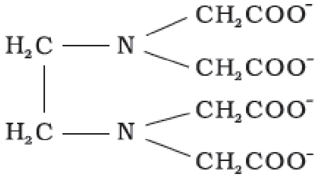


(oxalate ion)



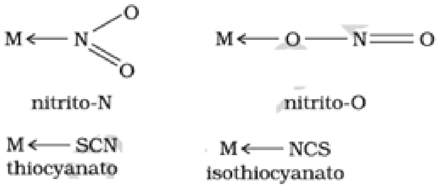
(ethylene diammine)

iii) Polydentate: Ligand which have several donor sites like ethylenediamine tetraacetate ion, $[EDTA]^{4-}$ is hexadentate ligand.



C) On the basis of Bonding:

i) Ambidentate ligands: Ligands which have two donor atoms or sites but at a time only one form coordinate bond with central atom / ion is called ambidentate ligand. Example are NO_2^-, SCN^- etc.



ii) Chelating ligands: When a bidentate or a poly dentate ligand uses its two or more donor atoms to bind a single metal ion, then a ring like structure is obtained. It is called chelate and ligand is known as chelating ligands.

The chelating ligands form more stable complexes than the unidentate ligand this is b/c when chelation occurs entropy increases and the process becomes more favourable.

More the number of chelate rings more is the stability of complex. The stabilization of coordination compounds due to chelation is known as **chelate effect**.

D) On the basis of nature of bonding between central metal atom and ligand:

i) Normal or Classical ligands or sigma bonded ligands:

ii) Non-Classical or pi acid or pi acceptor ligands or sigma pi ligands (Synergic bonding:

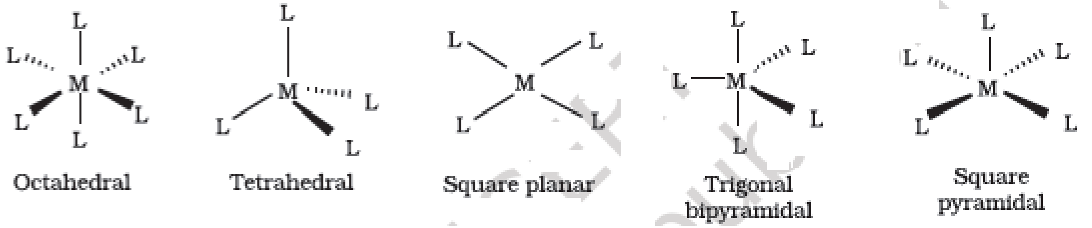
6. The coordination number (CN): The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded.

For example, in the complex ions, $[PtCl_6]^{2-}$ and $[Ni(NH_3)_4]^{2+}$, the coordination number of Pt and Ni are 6 and 4 respectively but in the complex ions, $[Fe(C_2O_4)_3]^{3-}$ and $[Co(en)_3]^{3+}$, the coordination number of both, Fe and Co, is 6 because $C_2O_4^{2-}$ and en (ethane-1,2-diamine) are didentate ligands.

7. Coordination sphere and Counter ions: The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the **coordination sphere**.

The ionisable groups are written outside the bracket and are called counter ions.
For example, in the complex $K_4[Fe(CN)_6]^{4-}$, the coordination sphere is $[Fe(CN)_6]^{4-}$ and the counter ion is K^+.

8. Coordination polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral.



9. Types of Complexes

1) **Homoleptic complexes:** Complexes in which the metal atom or ion is linked to only one kind of donor atoms, are called homoleptic complexes e.g., $[Co(NH_3)_6]^{3+}$

2) **Heteroleptic complexes:** Complexes in which the metal atom or ion is linked to more than one kind of donor atoms are called heteroleptic complexes e.g., $[Co(NH_3)_4Cl_2]^+$

10. Nomenclature of Coordination Compounds: Nomenclature is based on set of rules given by IUPAC.

- Name of the compound is written in two parts, first write down the name of cation after than name of anion.
- During the naming of complex sphere, first write down the name of ligands in alphabetically order after than name of central metal atom or ion.
- Use prefixes like di, tri, tetra, etc are before naming of ligands if they are two, three or four respectively.
- If the complex part is a cation, the metal name is same as the element. For example, Co in a cation complex is called cobalt and Pt is called platinum.
- If ligands name already have di, tri, tetra etc then bis, tris, tetrakis are used as a prefix.
- Names of the anionic ligands end in 'o' (like OH^- hydroxido, $C_2O_4^-$ oxalato, NO_2^- nitrito, CO_3^- carbonato, SCN^- thiocyanato etc). Names of positive ligands end with 'ium'. Names of neutral ligands remains as such but exception are there as we use aqua for H2O, ammine for NH3, carbonyl for CO and nitrosyl for NO.

$[Co(NH_3)_4(H_2O)Cl]Cl_2$ Tetraammineaquachloridocobalt(III) chloride
$[CoCl_2(en)_2]^+$ Dichloridobis(ethane-1,2-diamine)cobalt(III)
$[Co(en)_3]_2(SO_4)_3$ tris (ethane-1,2-diamine) cobalt (III) sulphate

$[Co(NH_3)_4(H_2O)Cl]Cl_2$ Tetraammineaquachloridocobalt(III) chloride

- If the complex part is anion, use suffix ‘ate’ after the naming of central metal atom or ion For example, Co in a complex anion is called cobaltate, Zn called zincate, aluminum called aluminate, ferrate for Fe, aurate for Au, argintate for Ag etc

$K_2[Zn(OH)_4]$ Potassium tetrahydroxidozincate(II)
$K_3[Al(C_2O_4)_3]$ Potassium trioxalatoaluminate(III)

- If the complex part is neutral, molecule is named similar to that of the complex cation.

$[Ni(CO)_4]$ Tetracarbonylnickel(0)

- Oxidation state for the metal in cation, anion or neutral coordination compounds is indicated by Roman numeral in parentheses like cobalt (III), nickel (0) etc.

- The name of the complex part is written as one word.

 # Nomenclature of Bridging Coordination Compounds:

 # Nomenclature of Double Complex Sphere Coordination Compounds:

Effective Atomic Number (EAN):

EAN = [Total No of electron in central metal atom or ion + (2 x No. of coordination Bond)]

Que, Find out EAN in following

Significance of EAN:

12. Bonding in Coordination compounds:

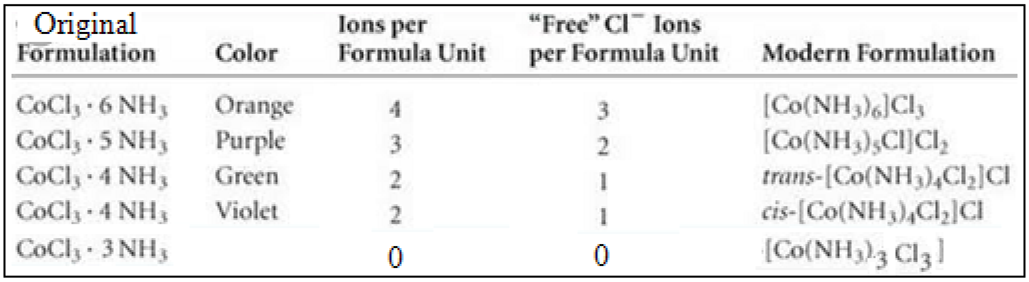
A) Werner's Theory of Coordination Compounds: The main postulates of this theory are:

1. In coordination compds metals show two types of linkages (valences)- primary and secondary.

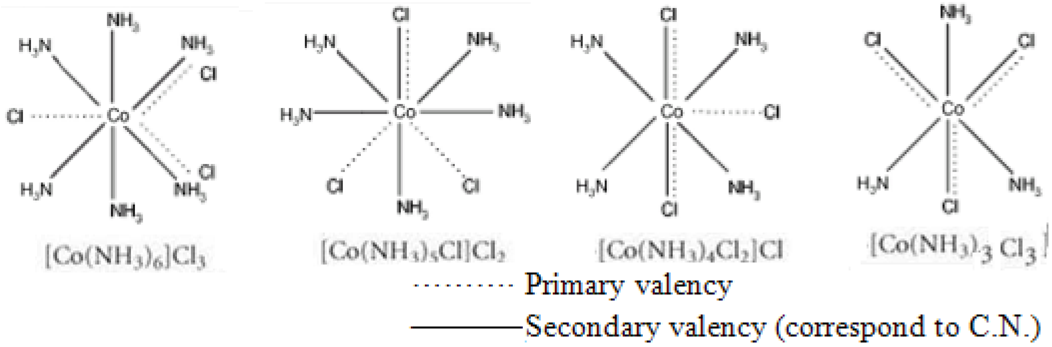
2. The primary valences are normally ionisable and are satisfied by negative ions.

3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.

4. The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.



Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$CoCl_3 \cdot 6\,NH_3$	Orange	4	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5\,NH_3$	Purple	3	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4\,NH_3$	Green	2	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4\,NH_3$	Violet	2	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 3\,NH_3$		0	0	$[Co(NH_3)_3\,Cl_3]$



1) Valence bond theory (VBT): This theory was proposed by L. Pauling in 1930 s. According to this theory:

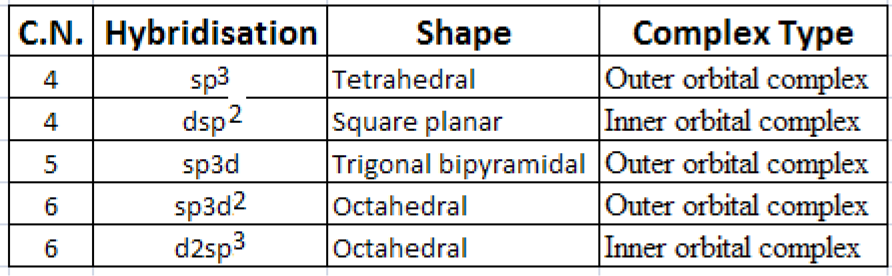
(i) The metal atom or ion under the influence of ligands can use its (n-1)*d*, n*s*, n*p* or n*s*, n*p*, n*d* orbitals for hybridisation to form a set of equivalent energy hybrid orbitals of definite geometry.

(ii) These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

(iii) Hybridisation of empty orbitals are depends on the nature of metal and on the nature of approaching ligand.

(iv) When d-orbitals of (n – 1) shell are used, these are known as ***inner orbital complex***, they are formed due to strong field ligands or low spin ligands and hybridisation such as d^2sp^3, dsp^2 as so on.

(v) When outer d-orbital are used in bonding, the complexes are called **outer orbital complexes**. They are formed due to weak field ligands or high spin ligands and hybridisation such as sp^3d^2, sp^3d, sp^3 as so on.



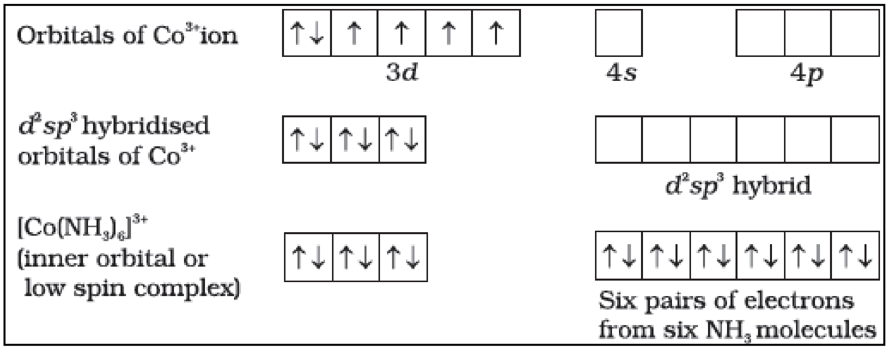
C.N.	Hybridisation	Shape	Complex Type
4	sp^3	Tetrahedral	Outer orbital complex
4	dsp^2	Square planar	Inner orbital complex
5	sp3d	Trigonal bipyramidal	Outer orbital complex
6	$sp3d^2$	Octahedral	Outer orbital complex
6	$d2sp^3$	Octahedral	Inner orbital complex

Note:

- Generally carbonyl, cyano ligands are act as strong field ligand.
- Ammonia act as a weak field ligand with iron, nickel and manganese but with cobalt it act as strong field ligand.
- In case of 4d and 5d series of transition metals, all ligands are act as Strong field ligands
- When cobalt is in its +3 oxidation state, water, ammonia and oxalate ligands act as strong field ligands. This causes pairing of electrons in the d-orbital, which forms an inner orbital complex with d2sp3 hybridization.

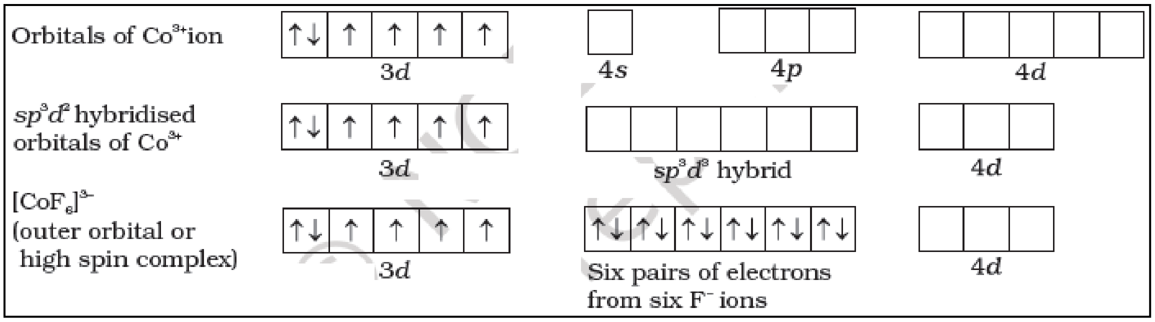
Application of valence bond theory (VBT): It is generally applicable to predict the geometry of a complex and also knowing the magnetic behaviour of the complexes.

a) Six coordinated complexes (strong field unidentate ligands): like $[Fe(NH_3)_6]^{2+}$ $[Co(NH_3)_6]^{3+}$:



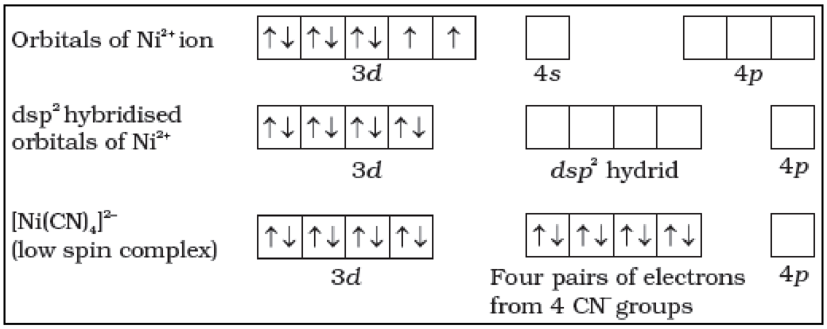
- Due to presence strong ligand electrons get paired up so metal ion provides vacant '3d' orbitals for hybridisation
- As inner'd' orbitals are involved in hybridisation, hence it is an inner orbital complex.
- All electrons are paired; therefore complex will be diamagnetic in nature.
- It is a low spin complex.

b) Six coordinated complexes (weak field unidentate ligands): like $[Fe(H_2O)_6]^{2+}$, $[CoF_6]^{3-}$:



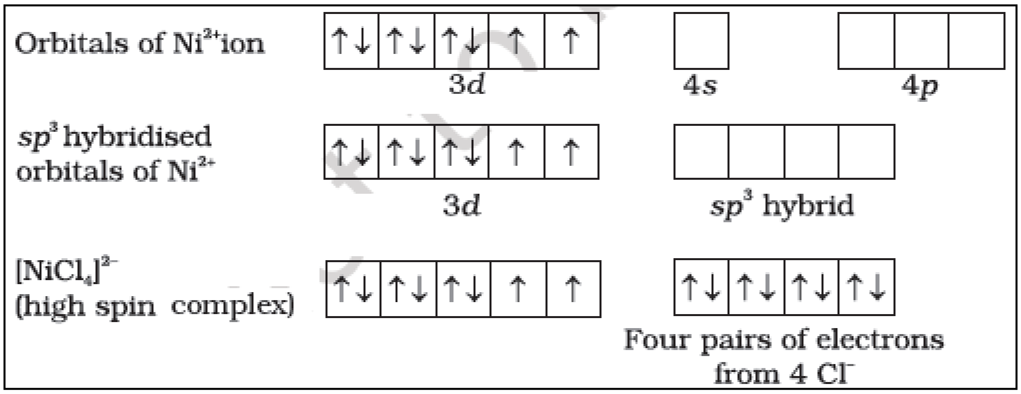
- The unpaired electrons remain as such b/c F$^-$ is a weak ligand as it is a paramagnetic complex.
- As outer‘d’ orbitals are involved in hybridisation, hence it is an outer orbital complex.
- It is a high spin complex.

c) Four coordinated complexes (strong field unidentate ligands): like [Ni(CN)$_4$]$^{2-}$:



- CN$^-$ is strong field ligand. Thus the complex has square planar geometry.
- It is an inner orbital complex and a low spin complex.
- All electrons are paired; therefore complex will be diamagnetic in nature.

d) Four coordinated complexes (weak field unidentate ligands):: like [Ni(Cl)$_4$]$^{2-}$:



- The unpaired electrons remain as such b/c Cl$^-$ is a weak ligand as it is a paramagnetic complex.
- The complex has tetrahedral geometry.
- It is an inner orbital complex and a high spin complex.

Limitations of VBT:

- This theory could not explain the quantisation of the magnetic data.
- It could not explain the existence of inner orbital and outer orbital complex,
- It could not explain the change of magnetic moment with temperature and colour of complexes.

Que. *Why $[Fe(NH_3)_6]^{2+}$ is diamagnetic but $[Fe(H_2O)_6]^{2+}$ is paramagnetic?*

Crystal Field Theory (CFT): This theory was proposed by H. Bethe and van Vleck. Orgel. in 1952, applied this theory to coordination compounds. In this theory, ligands are treated as point charges in case of anions and dipoles in case of neutral molecules.

The five d-orbitals are classified as

(i) Three d-orbitals i.e., dxy, dyz and dzx are oriented in between the coordinate axes and are called t2g – orbitals.

(ii) The other two d-orbitals, i.e., d x
2 - y
2 and d z
2 oriented along the x – y % axes are called eg –
orbitals.

Due to approach of ligands, the five degenerate d-orbitals split. Splitting of d-orbitals depends on the nature of the crystal field.

[The energy difference between t2g and eg level is designated by Δ and is called **crystal field splitting energy.**]

By using spectroscopic data for a number of coordination compounds, having the same metal ions but different ligand, the crystal field splitting for each ligand has been calculated. A series in which ligand are arranged in order of increasing magnitude of crystal field splitting, is called **spectrochemical series**.

Spectrochemical series

C) Crystal field splitting in octahedral complexes(CFSE):

In case of octahedral complexes, energy separation is denoted by Δo (where subscript 0 is for octahedral).

In octahedral complexes, the six-ligands approach the central metal ion along the axis of d x
2 -
y
2 and d z
2orbitals.

Energy of eg set of orbitals > energy of t2g set of orbitals.

The energy of eg orbitals will increase by (3/5) Δo and t2g will decrease by (2/5) Δo.

If Δo < P, the fourth electron enters one of the eg orbitals giving the configuration t3
2g e1

g.
Ligands for which Δo < P are known as weak field ligands and form high spin complexes.
If Δo > P, it becomes more energetically favourable for the fourth electron to occupy a t2g orbital with configuration t4
2g eo
g. (where, P = energy required for e- pairing in an orbital).
Ligands which produce this effect are known as strong field ligands and form low spin complexes.

Crystal field splitting in tetrahedral complexes

In tetrahedral complexes, four ligands may be imagined to occupy the alternate comers of the cube and the metal ion at the center of the cube.
Energy of t2g set of orbitals > Energy of eg set of orbitals.
In such complexes d – orbital splitting is inverted and is smaller as compared to the octahedral field splitting.
Orbital splitting energies are so low that pairing of electrons are not possible so these are high spin complexes.

11. Isomerism in Coordination Compounds: Coordination compounds exhibit the following types of isomerism:

1) Structural Isomerism: In this isomerism, isomers have different bonding pattern. Different types of structural isomers are

(i) Linkage isomerism: This type of isomerism is shown by the coordination compounds having ambidentate ligands. e.g.,
$[Co(NH_3)_5(NO_2)]Cl$ and $[Co(NH_3)_5(ONO)]Cl$;
$[Mn(CO)_5SCN]$ and $[Mn(CO)_5NCS]$

(ii) Coordination isomerism: This type of isomerism arises from the interchange of ligands between cationic and anionic complexes of different metal ions present in a complex, e.g.
$[Cr(NH_3)_6)$ $[Co(CN)_6]$ and $[Co(NH_3)_6]$ $[Cr(CN)_6]$;
$[Pt(NH_3)_4]$ $[PtCl_4]$ and $[PtCl(NH_3)_3]$ $[PtCl_3(NH_3)]$

(iii) Ionisation isomerism: This isomerism arise due to exchange of ionisable anion with anionic ligand. e.g..
$[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$
$[Pt(NH_3)_4]Cl_2]Br_2$ and $[Pt(NH_3)_4]Br_2]Cl_2$

(iv) Solvate isomerism: This is also known as hydrate isomerism. In this isomerism, water is taken as solvent. It has different number of water molecules in the coordination sphere and outside it. e.g..

$[Co(H_2O)_6]CI_3$, $[Co(H_2O)_4C1_2]Cl\cdot 2H_2O$, $[Co(H_2O)_3Cl_3]. 3H_2O$

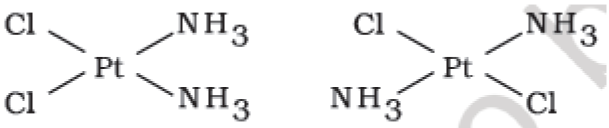
2) Stereoisomerism: Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. These are of two types:

(i) Geometrical isomerism: Geometrical isomers are of two types i.e., cis and trans isomers. This isomensm is common in complexes with coordination number 4 and 6.

a) Geometrical isomerism in complexes with coordination number 4:

- Tetrahedral complexes do not show geometrical isomerism. Reason: (from NCERT intex)

- Square planar complexes like $[MA_2X_2]$, $MA_2XY]$, [MABXY], (X and are unidentate ligand) etc show geometrical isomerism.

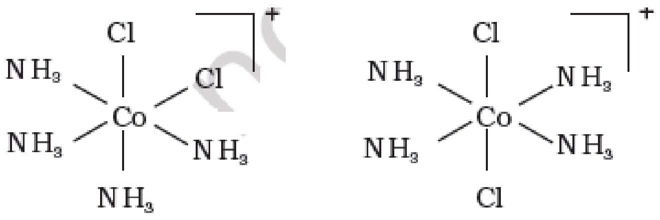


cis trans

Geometrical isomers (cis and trans) of Pt$[NH_3)_2Cl_2]$

b) Geometrical isomerism in complexes with coordination number 6:

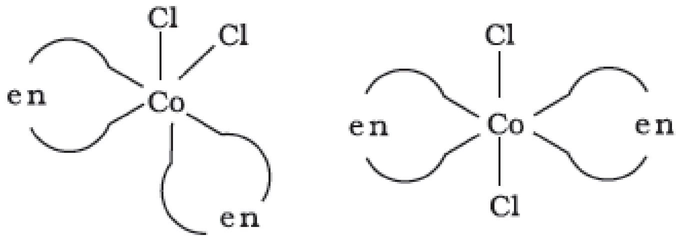
Octahedral complexes of formula $[MX_2L_4]$, in which the two X ligands may be oriented cis or trans to each other, e.g., $[Co(NH_3)_4Cl_2)]^+$.



cis trans

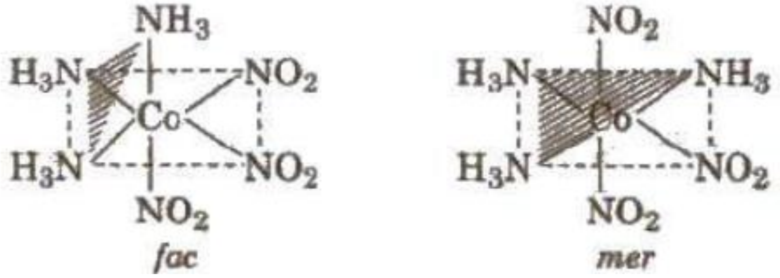
Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]^+$

Octahedral complexes of formula $[MX_2A_2]$, where X are unidentate ligands and A are bidentate ligand form cis and trans isomers, e.g., $[CoC1_2(en)_2]$’



Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$

In octahedral complexes of formula $[MA_3X_3]$, if three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face. It is known as facial (fae) isomer, when the positions are around the meridian of the octahedron, it is known as meridional (mer) isomer. e.g., [Co(NH_3)$_3$(NO_2)$_3$]

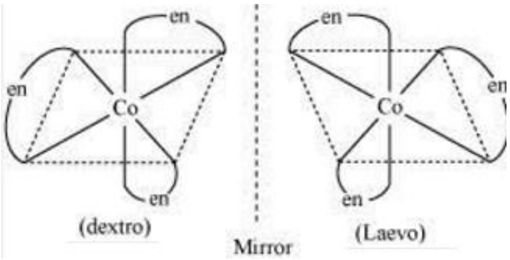


Facial (fac) and meridional (mer) isomer of [Co(NH_3)$_3$(NO_2)$_3$]

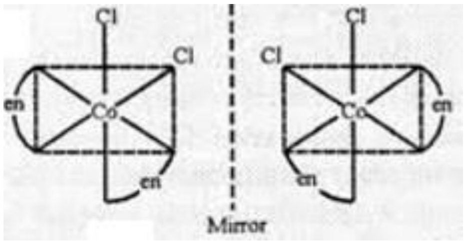
(ii) Optical Isomerism: The mirror images of a chiral molecule or ion are called Enantiomers or optical isomers and this phenomenon is called Optical Isomerism. The two forms are called dextro (d) and laevo (l) forms.

(a) Optical isomerism in complexes with coordination number 4:
Both tetrahedral and square planar complex does not show optical isomerism due to following reason,
In square complex POS is available So it is optically inactive.

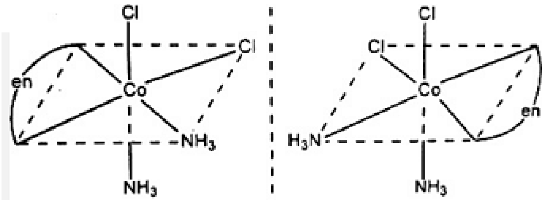
(b) Optical isomerism in complexes with coordination number 6:
Optical isomerism is common in octahedral complexes involving didentate ligands. Some different types of octahedral complexes that showing optical isomerism are as following-
Type [M(AA)$_3$]: Examples are [Co(en)$_3$]$^{3+}$, [Cr(ox)$_3$]$^{3-}$



Type [M(AA)$_2$X$_2$] or [M(AA)$_2$XY]: Only the *cis*-isomer shows that type of optical activity examples are cis-[Pt(en)$_2$Cl$_2$]$^{2+}$, cis-[Co(en)$_2$Cl$_2$]$^+$



Type $[M(AA)X_2Y_2]$: Examples is $[Co(en)_3(NH_3)Cl_2]$



Organometallic Compound

Application of Coordination Chemistry: