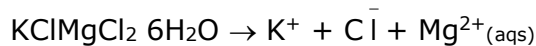


## COORDINATION COMPOUNDS- II PUC

### DOUBLE SALTS:

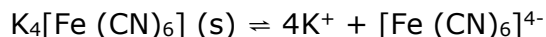
The addition compounds which retain their identity in solid form only and not in solution are known as double salts eg carnallite.



In aqueous solution carnallite shows the properties of  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  ions

### COORDINATION COMPOUNDS:

The addition compounds which retain their identity in solid as well as in solution. Such compounds contain a complex ion formed by the combination of a metal atom and other species having lewis base character eg.



Since the complex ion contains a number of coordinate bonds they are also known as coordination compounds.

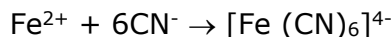
Coordination compounds contain at least one complex ion.

Example:  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  contains  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion which is a complex ion.

Complex ion contains one central metal ion surrounded by definite number of ligands.

Example: Ferrocyanide ion ( $[\text{Fe}(\text{CN})_6]^{4-}$  contains one  $\text{Fe}^{2+}$  (Ferrous ion) surrounded by 6  $\text{CN}^-$  ions.

$\text{Fe}^{2+}$  (Ferrous ion) is surrounded by 6  $\text{CN}^-$  ions.



A ligand is a neutral molecule or a charged particle containing at least one lone pair of electrons.

(a) Cationic ligands:

$\text{NH}_2 - \text{NH}_3^+$ : Hydrazinium ion       $\text{NO}_2^+$ : Nitronium ion.

(b) Anionic ligands:

$\leftarrow \text{CN}^-$ : cyano ligand

$\text{COO}^-$ : oxalato ligand

|

$\text{COO}^-$

(c) neutral ligands:

$\text{H}_2\text{O} \rightarrow :$  aqua ligand

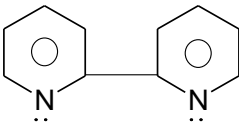
$\leftarrow \text{NH}_3$ : Ammine ligand

**Denticity of a ligand.** The number of donor atoms or ligating groups from a given ligand attached to the same central metal atom is called the denticity of the ligand.

### Types of ligands:

Depending on the no. of binding sites, the ligands have been classified as follows

Type of ligand	Name of ligand	Structure
1) Monodentate		

a) Neutral	H <sub>2</sub> O, NH <sub>3</sub> , CO	H- $\ddot{\text{O}}$ -H, $\ddot{\text{N}}\text{H}_3$ , $\text{C}\equiv\text{O}^{\ominus}$
b) Negative	CN <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NH <sub>2</sub> <sup>-</sup>	$\ominus$ : $\text{C}\equiv\text{N}$ , $\text{:N}\begin{matrix} \diagup \ddot{\text{O}}\text{:} \\ \diagdown \text{O}\text{:} \end{matrix}$ , $\text{:}\ddot{\text{N}}\begin{matrix} \diagup \text{H} \\ \diagdown \text{H} \end{matrix}$
c) Positive	NO <sup>+</sup> , N <sub>2</sub> H <sub>5</sub> <sup>+</sup>	$\text{N}\equiv\text{O}^+$ , $\ddot{\text{N}}\text{H}_2 - \text{NH}_3^+$
<b>2) Bidentate:</b>		
a) Neutral	Ethylene diamine (en)	$\text{CH}_2 - \ddot{\text{N}}\text{H}_2$   $\text{CH}_2 - \ddot{\text{N}}\text{H}_2$
	2, 2 dipyridyl (dipy)	
b) Negative	Oxalate ion	$\text{COO}^-$   $\text{COO}^-$
	Glycinate ion	$\text{CH}_2 - \text{COO}^-$   $\ddot{\text{N}}\text{H}_2$
<b>3) Tridentate:</b>		
	Diethylene triamine (dien)	$\text{CH}_2 - \text{CH}_2 - \ddot{\text{N}}\text{H}_2$   $\text{NH}$   $\text{CH}_2 - \text{CH}_2 - \ddot{\text{N}}\text{H}_2$
<b>4) Tetra or Quadri dentate:</b>		
	Triethylene tetramine (Trien)	$\text{CH}_2 - \ddot{\text{N}}\text{H} - \text{CH}_2 - \text{CH}_2 - \ddot{\text{N}}\text{H}_2$   $\text{CH}_2 - \ddot{\text{N}}\text{H} - \text{CH}_2 - \text{CH}_2 - \ddot{\text{N}}\text{H}_2$
<b>5) Penta dentate:</b>		
	Ethylene diamine triacetate	$\text{CH}_2 - \ddot{\text{N}} \begin{matrix} \diagup \text{CH}_2\text{COO}^- \\ \diagdown \text{CH}_2\text{COO}^- \end{matrix}$   $\text{CH}_2 - \text{NH} \text{CH}_2\text{COO}^-$
<b>6) Hexa dentate:</b>		
	Ethylene diamine tetraacetate (EDTA)	$\text{CH}_2 - \ddot{\text{N}} \begin{matrix} \diagup \text{CH}_2\text{COO}^- \\ \diagdown \text{CH}_2\text{COO}^- \end{matrix}$   $\text{CH}_2 - \ddot{\text{N}} \begin{matrix} \diagup \text{CH}_2\text{COO}^- \\ \diagdown \text{CH}_2\text{COO}^- \end{matrix}$

**Bridging ligand:** A bridging ligand is one ligand which because of presence of more than 1 e<sup>-</sup> pair can bind with more than one metal atom at the same time.

e.g., NH<sub>2</sub>-NH<sub>2</sub>, NH<sub>2</sub>, OH<sup>-</sup>, NO<sub>2</sub><sup>-</sup> etc

**Ambidentate ligand:** A ligand which has more than one donor atoms, but at a time only either of them is used for complexation, is ambidentate ligand. e.g., -CN, -SCN, -NO<sub>2</sub>.

**Note:** Polydentate ligands have flexidentate character i.e., they are free either to use all of their available donor sites or only some of them.

e.g., EDTA through uses all the six donor sites while complexation but in some cases, it uses less than six also.

**Homoleptic ligand** – Metal bound to only one type of donor group

**Heteroleptic ligand** – Metal bound to more than one type donor group

**Chelating ligands.** When a multidentate ligand simultaneously coordinates of a metal ion through more than one sigma electron pair donor site or group, a ring like structure is obtained. It is called a chelate and the ligand is known as chelating ligand. The process of formation of rings is called chelation.

**Chelate effect.** The stability of complexes is greatly increased by chelation. This is known as the chelate effect. The more the number of rings present in a complex, the more the stability it acquires. For example,  $[\text{Cu}(\text{en})_2]^{2+}$  is less stable as it has only two rings in the structure. On the other hand  $[\text{Fe}(\text{edta})^-]$  is more stable as it contains five rings in the structure.

**Characteristics of chelates.** (i) Chelates are more stable than the simple type of complexes (formed by unidentate ligands). This is because when chelation occurs, entropy of the system increases and the process becomes more favourable.

(ii) Chelates having five membered rings are more stable if the chelating ligands which form them do not contain double bonds, i.e., if the chelating ligands are saturated, e.g., ethylene diamine complexes. On the other hand, chelates having six membered rings are more stable if the chelating ligands which form them contain conjugate double bonds, e.g., acetylacetonato complexes.

(iii) Chelates formed with chelating ligands having more than six donor groups or larger groups are unstable than those formed with ligands having smaller groups. This is attributed to the steric hindrance produced by a larger group.

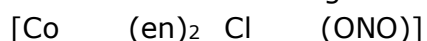
**Importance of Chelates.** Chelates are widely used in the (i) softening of hard water (ii) separation of lanthanoids and actinoids (iii) detection of some metal ions in qualitative analysis and (iv) estimation of  $\text{Ni}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$  ions quantitatively.

**Charge on the complex ion.** The charge carried by a complex ion is the algebraic sum of the charges carried by the central metal ion and the ligands surrounded to the central metal ion.

If the complex is neutral, the sum of the charges of the central metal ion and the ligands is equal to zero. For an anionic or cationic complex, the sum of charges of the constituents (central metal ion and the ligands) is equal to the charge on the coordination sphere.

**Oxidation number of oxidation state or charge on the central metal ion.** It is the charge which a central metal ion actually has or appears to have when present in the combined state with ligands or when all the ligands are removed along with the electron pairs that are shared with the central atom.

For example, in the complex  $[\text{Co}(\text{en})_2\text{Cl}(\text{ONO})]$ , the charge on the complex is zero whereas the charge on the central metal ion may be calculated as under:



$$x + 2 \times 0 + 1 \times -1 + 1 \times -1 = 0 \quad \text{or } x - 2 = 0 \quad \text{or } x = +2.$$

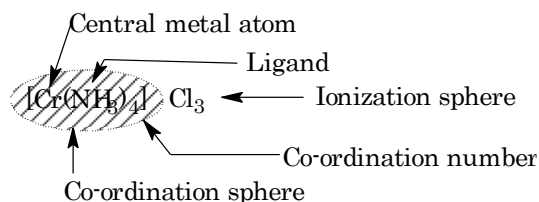
**Coordination polyhedron.** The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a **coordination polyhedron** about the central atom. In coordination compounds tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal coordination polyhedron are more common.

## Co-ordination Sphere

Complex ion enclosed in square bracket, it behaves as a single unit.

## Ionization Sphere

Part of compound present outside co-ordination sphere, e.g



## Types of complexes

**a) Cationic complex:** A complex in which complex ion carries a net positive charge e.g:  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

**b) Anionic complex:** A complex in which complex ion carries a net negative charge

e.g:  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ,  $[\text{Ag}(\text{CN})_2]\text{Cl}$

**c) Neutral complex:** A complex carrying no net charge is called neutral complex. e.g  $[\text{Ni}(\text{CO})_4]$ ,  $(\text{Pt}(\text{NH}_3)_2\text{Cl}_2)$

**d) Homoleptic and heteroleptic complexes.** Complexes in which the central metal atom or ion is linked to only one type of ligands are called homoleptic complexes. Complexes in which the central metal atom or ion is linked to more than one type of ligands are called heteroleptic complexes.

**e) Homonuclear and polynuclear complexes.** Complexes in which only one metal atom is present are known as homonuclear complexes. On the other hand, the complexes in which more than one metal atom is present are known as polynuclear complexes.

## Nomenclature of coordination compounds:

(a) Positive ion is named first and negative ion is named next.

(b) A positive complex ion is named in the order of ligands – metal ion (charge)

(c) A negative complex ion is named as ligands – metal – ate (charge)

(d) A neutral complex is named as ligands – metal (charge)

(e) Two or more identical ligands are named by prefixes like di, tri, tetra, penta etc

(f) Two or more different ligands are named in the alphabetical order of their names.

(g) The formula of a complex is written from its name [metal (ligands)] (charge).

Ligands are placed in the order of negative, neutral and positive ligands.

Example:  $[\text{Pt}(\text{Br})(\text{Cl})(\text{I})(\text{NO}_2)(\text{NH}_3)(\text{NH}_2\text{OH})]$

## Werner's theory:

a) A metal ion possesses primary valency and secondary valency.

b) Primary valency is the charge on metal ion. A secondary valency is its coordination number.

c) Primary valency is satisfied by negative ions and secondary valency is satisfied by ligands.

d) Geometrical shape of the complex ion depends on number of ligands.

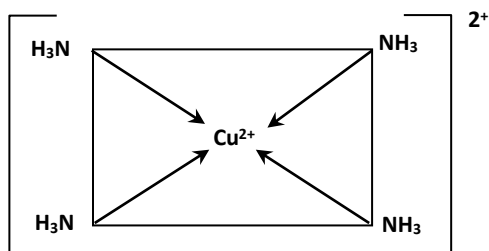
## Examples:

Complex ion	Metal ion	Primary valency	Secondary valency	Geometrical shape
$[\text{Cu}(\text{NH}_3)]^{2+}$	$\text{Cu}^{2+}$	+2	4	Square planar
$[\text{Fe}(\text{CN})_6]^{4-}$	$\text{Fe}^{2+}$	+2	6	Octahedral
$[\text{Ni}(\text{CO})_4]$	Ni	0	4	Tetrahedral

### Sidwick's theory:

a) Ligands form coordinate bonds with metal ions to form complex ions.

Example:  $\text{Cu}^{2+}$  reacts with  $4\text{NH}_3$  molecules to form 4 coordinate bonds



### EAN rule:

Metal ions form complex ions with a definite number of ligands so that the number of electrons around a metal ion should be the atomic number of the next rare gas.

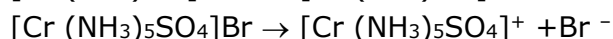
Metal ion	Complex ion	$\text{EAN} = Z - X + Y$
$\text{Fe}^{2+}$	$[\text{Fe}(\text{CN})_6]^{4-}$	$\text{EAN} = 26 - 2 + 12 = 36$
Ni	$[\text{Ni}(\text{CO})_4]$	$\text{EAN} = 28 - 0 + 8 = 36$
$\text{Cu}^{2+}$	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	$\text{EAN} = 29 - 2 + 8 = 35$
$\text{Fe}^{3+}$	$[\text{Fe}(\text{CN})_6]^{3-}$	$\text{EAN} = 26 - 3 + 12 = 35$
$\text{Zn}^{2+}$	$[\text{Zn}(\text{NH}_3)_4]^{2+}$	$\text{EAN} = 30 - 2 + 8 = 36$

$[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  obey EAN rule.

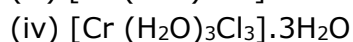
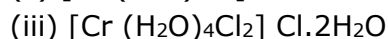
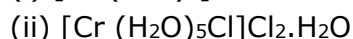
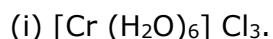
**Isomerism:** Coordinate bond is directional. Hence coordination compounds exhibit isomerism.

#### Structural isomerism

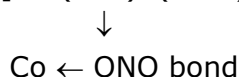
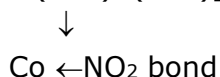
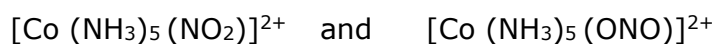
(a) **Ionisation isomerism** – Difference in the ions produced.



(b) **Hydrate isomerism:** Difference in the number of water molecules of coordination as well as the number of water molecules of hydration



(c) **Linkage isomerism:** Difference in the atom of a ligand linked to the central metal ion.



**(d) Coordination isomerism:** Difference in the ligands present around a metal ion.

Examples:  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

$[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{SCN})_6]$  and  $[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]$

$[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{C}_2\text{O}_4)_3]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3]$

$[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{en})_3][\text{Co}(\text{CN})_6]$

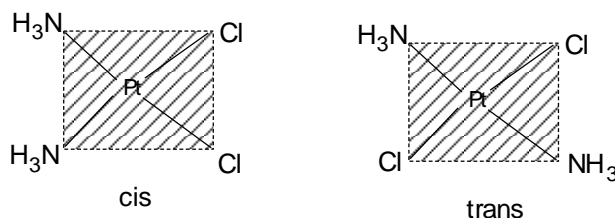
**Stereo isomerism or space isomerism.** Here the isomers differ only in the spatial arrangement (specific orientation in space) of atoms or groups about the central metal atom. It is of two types:

**Geometrical or cis-trans isomerism.** This isomerism arises in heteroleptic complexes due to the difference in geometrical arrangement of the ligands around the central atom. When two identical ligands (groups) occupy adjacent positions, it is called cis-isomer and when these are in the opposite position, it is called trans-isomer. Thus, this kind of isomerism is also referred to a cis-trans isomerism.

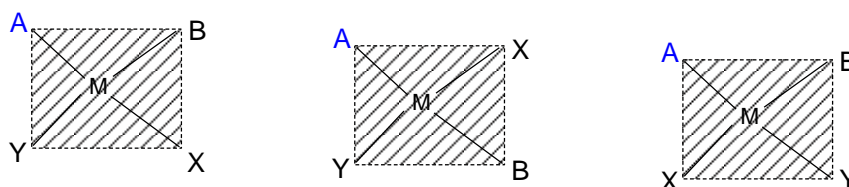
It is very common in disubstituted complexes with coordination number of 4 and 6 i.e., square planar and octahedral coordination entities, respectively. Complexes with coordination number 2, 3 and 4 (tetrahedral) do not show this type of isomerism.

**Isomerism in complexes with coordination number 4.** Tetrahedral complexes do not show geometrical isomerism because the relative position of the atoms with respect to each other will be the same. The square planar complexes on the other hand, show this kind of isomerism as discussed below: square planar complexes of the type

(i)  $\text{MA}_2\text{X}_2$ ,  $\text{MA}_2\text{XY}$ ,  $\text{MABX}_2$  and  $\text{MABXY}$  (where A and B are unidentate neutral ligands and X and Y are anionic ligands) show cis-trans isomerism. Some common examples are:  $[\text{Co}(\text{NH}_3)_2\text{Cl}_2]$ ,  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ ,  $[\text{Co}(\text{NH}_3)_2\text{BrCl}]$ .

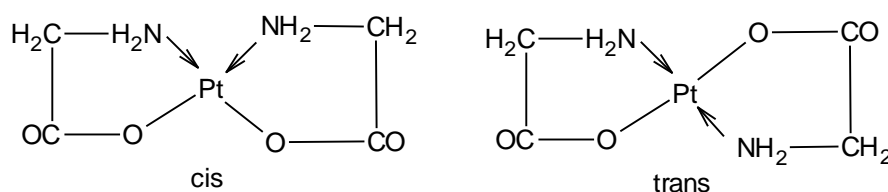


Common example of the type  $\text{MABXY}$  is  $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})\text{NO}_2(\text{py})]^+$  which will have three isomers as shown below:



These isomers are obtained by fixing the position of the ligand say A while the other ligands B, X and Y are placed trans to it.

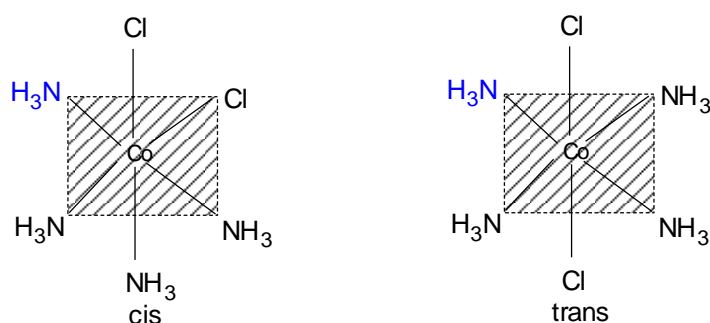
Square planar complexes of the type (ii)  $[\text{M}(\text{AB})_2]$  where AB is unsymmetrical bidentate ligand also show cis-trans isomerism. For example, bis(glycinato) platinum (II), i.e.,  $[\text{Pt}(\text{gly})_2]$  where  $\text{gly} = \text{H}_2\text{NCH}_2\text{COO}^-$ .



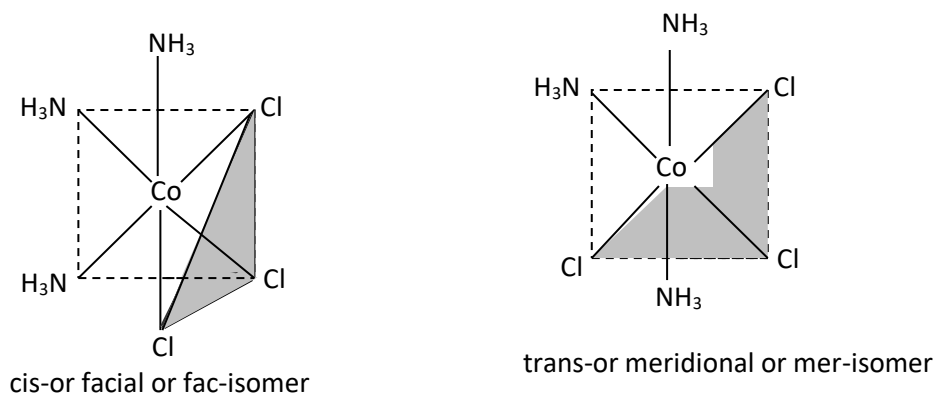
On the other hand, square planar complexes of the type (iii)  $MA_3X$  and  $MAX_3$  will not show geometrical isomerism because the spatial arrangements for all these complexes will be equivalent.

### Isomerism in complexes with coordination number 6.

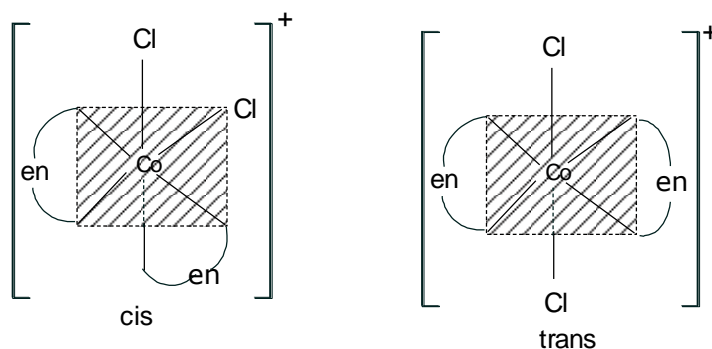
Octahedral complexes of the type (i)  $MA_4X_2$ ,  $MA_3X_3$ ,  $MA_4XY$  exist as cis and trans isomers. Common examples are:  $[Co(NH_3)_4Cl_2]$ ,  $[Co(NH_3)_4Cl(NO_2)]$



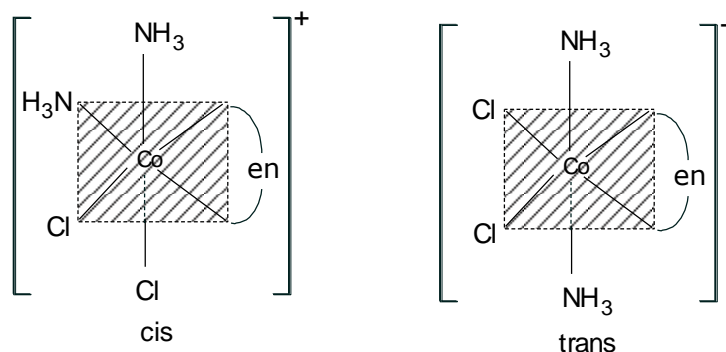
For the complexes of the type  $MA_3B_3$  e.g.,  $[Co(NH_3)_3Cl_3]$ ,  $[RhCl_3(py)_3]$ , the geometric isomer is called cis-or facial (fac) when each trio of donor atoms of the similar ligands occupy adjacent positions at the corners of the same face of an octahedron as shown below. The other geometric isomer of the compound is called trans-or meridional (mer) if the positions occupied are around the meridian of the octahedron.



Complexes of the type (ii)  $M(AA)_2X_2$  and  $M(AA)_2XY$  can also show cis-trans isomerism (Here (AA) refers to symmetrical bidentate ligands and X and Y refer to unidentate anionic ligands. Common examples are:  $[CoCl_2(en)_2]^+$ ,  $[NiCl_2(ox)_2]^{4-}$  etc.



Complexes of the type (iii)  $[M(AA)X_2Y_2]$  can show geometrical (cis and trans) isomerism. For examples,  $[Co(NH_3)_2Cl_2(en)]^+$  exhibits cis and trans isomerism as shown below:



Octahedral complexes of the type (iv)  $MABCDEF$  where all the six unidentate ligands are different exist in 15 theoretical isomers.

**Inner and outer orbital octahedral complexes.** The complexes involving inner  $(n - 1)$  d orbitals in the hybridization i.e. all cases of  $d^2sp^3$  hybridization mentioned above are called inner orbital or hyperligated complexes. These are generally diamagnetic or have reduced paramagnetism. They are therefore, also called low spin or spin paired complexes. The complexes involving outer nd orbitals in the hybridization i.e., all cases of  $sp^3d^2$  hybridization are called outer orbital or hypoligated complexes. These complexes are paramagnetic and are therefore, also called high spin or spin free complexes.

**Predicting the type hybridization form magnetic behaviour of the complexes.**

The magnetic moments of the coordination compounds can be determined by measuring their magnetic susceptibilities experimentally. This helps us to know the number of unpaired electron present from the spin only formula  $\mu = \sqrt{n(n+2)}$  BM

For metal ions having  $d^{1-3}$  configuration ( $Ti^{3+} = d^1$ ,  $V^{3+} = d^2$ ,  $Cr^{3+} = d^3$ ), two vacant d-orbitals are always available for  $d^2 sp^3$  hybridization. Their magnetic moments are found to be corresponding to 1, 2, and 3 unpaired electrons, respectively. For metal ions containing more than 3 unpaired electrons, respectively. for metal ions containing more than 3 unpaired electrons in the d-orbitals, two empty d-orbitals can be make available only if 3d electrons pair up.

For example, in  $d^4$  ( $Cr^{2+}$ ,  $Mn^{3+}$ ),  $d^5$  ( $Mn^{2+}$ ,  $Fe^{3+}$ ) and  $d^6$  ( $Fe^{2+}$ ,  $Co^{3+}$ ) cases. The magnetic moment data shown that maximum spin pairing occurs in many cases especially in compounds with  $d^6$  ions but there are complications with species having  $d^4$  and  $d^5$  ions.

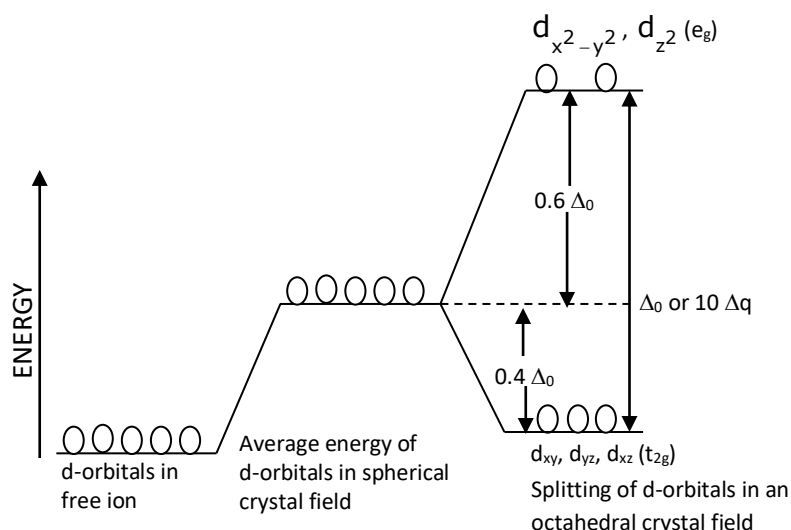
(i) Complexes with stronger field ligands such as  $[Mn(CN)_6]^{3-}$ ,  $[Fe(CN)_6]^{3-}$  and  $[Co(C_2O_4)_3]^{3-}$  have magnetic moments corresponding to two, one and zero unpaired electrons and are inner orbital complexes involving  $d^2sp^3$  hybridization.

(ii) Complexes with weaker field ligands such as  $[MnCl_6]^{3-}$ ,  $[FeF_6]^{3-}$  and  $[CoF_6]^{3-}$  have magnetic moments corresponding to four, five and four unpaired electrons and are outer orbital complexes involving  $sp^3 d^2$  hybridization.



**Crystal Field Theory (CFT).** Crystal field theory [developed by H. Bethe (1929) and John V. Vleck (1932)] is based on the assumption that the metal ion and the ligands act as point charges and the interaction between them is purely electrostatic, i.e., metal-ligand bonds are 100% ionic. The five d-orbitals in an isolated gaseous metal atom/ion are degenerate. This degeneracy is maintained in a spherically symmetrical field of negative charges. However, when this negative field is due to real ligands in a complex, the degeneracy of the d-orbitals is lifted due to asymmetrical field. This results in splitting of the d-orbital energies. The pattern of splitting depends upon (a) nature of the crystal field such as octahedral, tetrahedral or square planar and (b) basic strength of ligands.

**Crystal field theory for octahedral coordination entities (complexes).** In an octahedral complex, the six ligands approach the central metal atom lying at the origin symmetrically along the Cartesian axes. Initially, there is an increase in the energy of d-orbitals relative to that of the free ion (just like that in spherical field). Next, the orbitals lying along the axes ( $d_{z^2}$  and  $d_{x^2-y^2}$ ) get repelled more strongly by the negative ligands and are raised in energy than the orbitals which have lobes directed between the axes ( $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$ ) which are lowered in energy relative to the average energy in the spherical crystal field (which is taken as zero and sometimes called as Bary Centre) as shown below:



**Splitting of five d-orbitals in an octahedral crystal field**

The energy sequence of d-orbitals after splitting in an octahedral field is

$$t_{2g} (d_{xy} = d_{yz} = d_{xz}) < e_g (d_{x^2-y^2} = d_{z^2})$$

This splitting of five degenerate d-orbitals of the metal ion into two sets of d-orbitals with different energies is called crystal field splitting. The two sets of d-orbitals,

i.e.,  $d_{x^2-y^2}$  and  $d_{z^2}$  and  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  are commonly called  $e_g$  (or  $d_{\gamma}$ ) and

$t_{2g}$  (or  $d_{\epsilon}$ ) orbitals respectively. The crystal field splitting is the energy difference between  $t_{2g}$  and  $e_g$  orbitals and is frequently measured in terms of a parameter  $\Delta_0$  where the subscript (0) stands for octahedral. (This is also measured in terms of another parameter called  $D_q$ . The magnitude of splitting is arbitrarily fixed at  $10 D_q$  so that  $\Delta_0 = 10 D_q$ ).

For any given metal cation, the magnitude of  $\Delta_0$  depends upon the nature of the ligands.

**Spectrochemical series.** Ligands can be arranged in increasing order of their strength (ability to cause crystal field splitting) and the series so obtained is called as spectrochemical series  $I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < O^{2-} < H_2O < NCS^- < py < NH_3 < en < NO_2^- < CN^- < CO$ . Ligands arranged left to  $NH_3$  are generally regarded as weaker ligands which can not cause forcible pairing of electrons within 3d level and thus form outer orbital (or high spin) octahedral complexes. On the other hand  $NH_3$  and all ligands lying right to it are stronger ligands which form inner orbital (or low spin) octahedral complexes after forcible pairing of electrons within 3d level. Spectrochemical series has been obtained by calculating crystal field splitting for each ligand by taking the same metal ion but different ligands for a number of coordination compounds and using spectroscopic data.

### Valence Bond theory

- Metal ions provide vacant orbitals to overlap with ligand orbitals.
- Metal orbitals undergo hybridization to provide a definite geometry to the complex ion.
- The hybrid orbitals overlap with ligand orbitals to form coordinate bonds.
- Geometrical shape, magnetic property and stability of a complex can be explained using this theory

### Examples:

Metal ion	Complex ion	Hybridisation	Geometrical shape	Magnetic property
$Fe^{2+}$	$[Fe(CN)_6]^{4-}$	$d^2sp^3$	octahedral	Diamagnetic
$Fe^{3+}$	$[Fe(CN)_6]^{3-}$	$d^2sp^3$	octahedral	Paramagnetic
Ni	$[Ni(CO)_4]$	$sp^3$	tetrahedral	Diamagnetic
$Cu^{2+}$	$[Cu(NH_3)_4]^{2+}$	$dsp^2$	Square planar	Paramagnetic
$Ni^{2+}$	$[Ni(CN)_4]^{2-}$	$dsp^2$	Square planar	Diamagnetic

### Complexes in different coordination states and their stereochemistry.

Coordination No.	Hybridization	Example	Stereochemistry
2	$sp$	$[Ag(NH_3)_2]^+$ , $[CuCl_2]^-$	Linear
3	$sp^2$	$[HgI_3]^-$	Trigonal planar
4	$sp^3$	$[CoCl_4]^{2-}$ , $[Ni(CO)_4]$	Tetrahedral
4	$dsp^2$	$[Ni(CN)_4]^{2-}$ , $[Cu(en)_2]^{2+}$	Square planar
5	$sp^3d$	$[Cu(dipy)_2]$	Trigonal bipyramidal
6	$sp^3d^2$	$[Ni(NH_3)_6]^{2+}$ , $[Ni(en)_3]^{2+}$	Octahedral
7.	$sp^3d^3$	$[ZrF_7]^{3-}$ , $[HgF_7]^{3-}$	Pentagonal pyramidal

**Factors affecting the stability of a complex.** (i) Greater the charge on the central metal ion, greater is the stability.

a) For divalent ions of 3d-transition series, the stabilities of their complexes with any type of ligand vary in the **Irving – Williams Order**:  $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$ .

b) Metal ions of groups 1, 2, inner transition elements and transition elements belonging to groups 3 to 6 are classified as '**class a' acceptors**. These form their most stable coordination entities with ligands containing N, O or F donor atoms.

c) Metal ions of transition elements such as Rh, Pd, Ag, Ir, Au and Hg having relatively full d-orbitals are classified as '**class b' acceptors**. These form their most stable complexes with ligands whose donor atoms are the heavier members of N, O and F groups i.e., P, S and Cl etc.

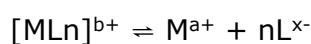
(ii) Greater the **basic strength** (i.e. power of donation of electron pairs) of the ligand, greater is the stability

(iii) Formation of **chelate rings** increases the stability due to chelate effect.

(iv) If a multidentate ligand happens to be cyclic, a further increase in stability occurs due to **macrocyclic effect** provided there are no unfavourable steric effects.

## STABILITY OF COORDINATION COMPOUNDS IN SOLUTION:

Consider the following equilibrium between undissociated complex ion and dissociated ion.



The equilibrium constant  $K_c = \frac{[M^{a+}][L^{x-}]^n}{[ML_n]^{b+}}$

The smaller the value of  $K_c$ , the greater is the stability of complex ion and vice versa. The reciprocal of equilibrium constant is called stability constant.

$$K_s = \frac{1}{K_c} = \frac{[ML_n]^{b+}}{[M^{a+}][L^{x-}]^n}$$

The higher the value of  $K_s$ , the more is the stability of complex ion. The value of  $K_s$  depends on.

**1. Nature of central metal atom** – The more the polarizing power of the central metal ion the more is the stability of complex ion.

The polarizing power  $\phi = \frac{\text{charge}}{\text{radius}}$

Thus complex of  $Fe^{3+}$  is more stable than  $Fe^{2+}$

**2. Nature of ligand** – Since ligand is a Lewis base the more the basic character of ligand the more is the stability of complex ion. Thus complex ion of  $\bar{F}$  is more stable than that of  $\bar{Cl}$  or  $\bar{Br}$

Chelating ligands give much larger values of stability constant.

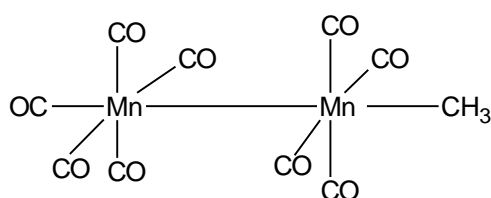


**Perfect or penetrating complexes:** They are fairly stable and dissociate negligibly or not at all e.g.  $\text{K}_4[\text{Fe}(\text{CN})_6] \rightleftharpoons 4\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-}$

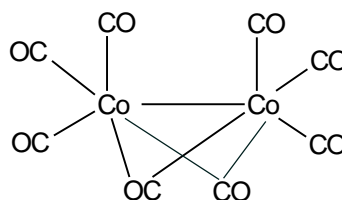
**Imperfect or normal complexes:** The complex ion is reversibly dissociated



**Structure and bonding in metal carbonyls.** Homoleptic binary metal carbonyls have simple well defined structures. The metal atom in them is in zero oxidation state.  $\text{Ni}(\text{CO})_4$  is tetrahedral,  $\text{Fe}(\text{CO})_5$  is trigonal bipyramidal,  $\text{M}(\text{CO})_6$  where  $\text{M} = \text{V}, \text{Cr}, \text{Mo}, \text{W}$  are octahedral,  $[\text{Mn}_2(\text{CO})_{10}]$  is made up of two square pyramidal  $\text{Mn}(\text{CO})_5$  units joined by a  $\text{Mn} - \text{Mn}$  bond whereas  $[\text{Co}_2(\text{CO})_8]$  has a  $\text{Co} - \text{Co}$  bond bridged by two  $\text{CO}$  groups.



Structure of  $[\text{Mn}_2(\text{CO})_{10}]$

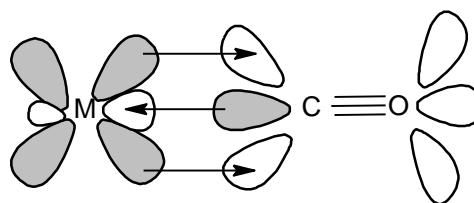


Structure of  $[\text{Co}_2(\text{CO})_8]$

The bonding in metal-carbonyls is best explained by molecular orbital theory (MOT).  $\text{CO}$  as a ligand binds itself to metal atom through carbon atom. It is weak donor (a weak base) and forms a weak  $\sigma$  bond to the central atom by donating a lone pair of electrons from  $\sigma_{2p_z}$  highest occupied molecular orbital (HOMO) of  $\text{CO}$  to empty  $d$ -orbital of the metal ( $\text{M} \leftarrow \text{C} \equiv \text{O}$ ).  $\text{CO}$  also acts as an acceptor ligand and forms a  $\pi$  bond to the metal by accepting electrons from filled metal  $d$ -orbitals having  $\pi$  symmetry to lowest unoccupied molecular orbitals (LUMO) which are the  $\pi^*$  ( $\pi_{2p_x}^*$  or  $\pi_{2p_y}^*$ ) orbitals of  $\text{CO}$  ( $\pi \text{M} \rightarrow \text{C} \equiv \text{O}$ ). This is called **synergic effect** (i.e., working together towards the same goal). As a result of synergic effect, the bond between  $\text{CO}$  and metal is strengthened. The total bonding is thus  $\text{M} = \text{C} = \text{O}$ . The bond order of  $\text{C} - \text{O}$  bond is reduced from triple to double bond. This is supported by fact that  $\text{C} - \text{O}$  bond length in  $\text{C} \equiv \text{O}$  is 112.8 pm and it increases to about 115 pm in many carbonyls. The metal carbon bonds in these carbonyls possess both  $\sigma$  and  $\pi$  character.

**Properties and uses of metal carbonyls.** Mostly

metal carbonyls are solids at room temperature except iron and nickel carbonyls which are liquids. Mononuclear carbonyls are toxic, volatile, colourless but  $[\text{Fe}(\text{CO})_5]$  is light straw coloured. Polynuclear carbonyls are deeply coloured. For example,  $[\text{Fe}_3(\text{CO})_{12}]$  is a deep grass green solid. They are highly reactive due to (a) metal centre of the carbonyl and (b) the  $\text{CO}$  ligands.



$\sigma$ -and  $\pi$ -overlap

They are used as catalysts and precursors in organic synthesis. Ligands such as CO which are capable of accepting an appreciable amount of electron density from the metal atom into empty  $\pi$  or  $\pi^*$  orbital of their own are called  $\pi$ -acceptor or  $\pi$ -acid or  $\pi$ -bonding ligands.