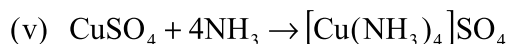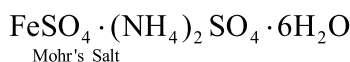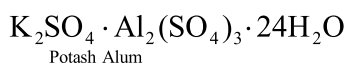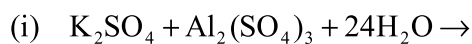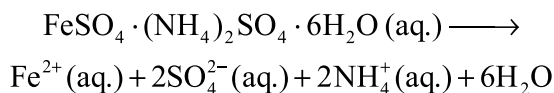# 9
Coordination Compounds

9.1 Addition Compounds

When two or more stable compounds are allowed to combine together in stoichiometric proportions these result in the formation of crystalline substances called addition compounds.

Examples :

(i) $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow$

   $\underset{\text{Potash Alum}}{K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O}$

(ii) $FeSO_4 + (NH_4)_2SO_4 + 6H_2O \rightarrow$

   $\underset{\text{Mohr's Salt}}{FeSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O}$

(iii) $KCl + MgCl_2 + 6H_2O \rightarrow$

   $\underset{\text{Crnallite}}{KCl \cdot MgCl_2 \cdot 6H_2O}$

(iv) $4KCN + Fe(CN)_2 \rightarrow K_4\left[Fe(CN)_6\right]$

(v) $CuSO_4 + 4NH_3 \rightarrow \left[Cu(NH_3)_4\right]SO_4$

(vi) $KCN + AgCN \rightarrow K\left[Ag(CN)_2\right]$

Addition compounds are of two types:

(i) Double Salts- These are stable in solid state but break up into its constituents when dissolved in water. For example, an aqueous solution of Mohr's salt shows the properties of Fe^{+2}, NH_4^+ and SO_4^{2-} ions.

$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \text{ (aq.)} \longrightarrow$

$Fe^{2+}\text{(aq.)} + 2SO_4^{2-}\text{(aq.)} + 2NH_4^+\text{(aq.)} + 6H_2O$

(ii) Complex compounds- These are also known as coordination compounds which retain their identity in the solid as well as in the dissolved state. In such compounds the individual properties of the constituents are usually lost. For example on mixing aqueous solutions of KCN & $Fe(CN)_2$, $K_4[Fe(CN)_6]$

is formed does not shows the properties of Fe^{+2} and CN^- ions.

Thus the coordination compounds contain a central metal atom or ions surrounded by a number of oppositely charged ions or neutral molecules more than its normal valency.

9.2 Important Terms in Coordination Compounds

(1) Central metal ion or atom– The metal atom or ion to which two or more anions or neutral molecules are attached by coordination bond is called central atom or central metal ion.

(2) Ligands– The molecular or ionic species which can donate lone pair of electron to central metal ion or atom during the formation of a coordination compound is called ligands

For Example–

In $[Ag(NH_3)_2]^+$ or

$[H_3N \rightarrow Ag^+ \leftarrow NH_3]$ Ag^+ is cetnral ion,

$\ddot{N}H_3$ is the ligard
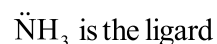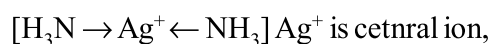
and N is the donor atom

9.3 Types of Ligands

The ligards may contain one or more than one donor atoms for coordination with the central atom. The ligands are classified as follows :

9.3.1 Unidentate or monodentate ligands–

Ligands which can coordinate to the central ion through only one donor atom are known as unidentate or monodentate ligands.

Some common unidentate ligards and their donor atoms are listed in table 1.

Unidentate ligand	Name	Donor atom	Charge
$H_2\ddot{O}:$	aqua	O	O
$\ddot{N}H_3$	ammine	N	O
CO	carbonyl	O	O
$\ddot{P}H_3$	phosphene	P	O
$C_5H_5\ddot{N}$ or Py	pyridine	N	O
$(C_6H_5)_3P$ or Ph_3P	Triphenyl phosphene	P	O
NO	nitrosyl	N	O
X^-	helo	X	-1
$O\overline{H}$	Hydroxo	O	-1
$\overline{C}N$	Cyano	C	-1
$\overline{N}C$	Isocyano	N	
NO_2^-	Nitro	N	-1
$ON\overline{O}$	Nitrito	O	-1
H^-	Hydrido	H	-1
NH_2^-	Amido	N	-1
O_2^{2-}	Peroxò	O	-1
O^{-2}	Oxo	O	-2
CO_3^{2-}	Carbonato	O	-2
SO_4^{2-}	Sulphato	O	-2
NH^{-2}	Imido	N	-2
S^{-2}	Sulphido	S	-2
N^{-3}	Azido or nitrido	N	-3
P^{-3}	Phosphido	P	-3

9.3.2 Bidentate lignads–

Ligands which have two donor atoms

Bidentate ligands	name	Donor Atom	Charge
	ethylene di amine	N	O
	oxalato	O	2
	glycinato	N and O	-1

9.3.3 Tridentate ligands–

Ligands which have three donor atoms

Tridentate ligands	name	Donor atom	charge
	diethylene triamine	N	O
	iminodi acetato	N and O	2

9.3.4 Tetra dentate ligands–

Ligands which have four donor atoms

Tetra dentate	name	Donor atom	charge
	Triethylene tetramine	N	O
	Nitrilo triacetato	N and O	-3

9.3.5 Penta dentate ligands–

Ligands which have five donor atoms

ethylene diamine triacetatao   N and O   3
(EDTA)$^{-3}$
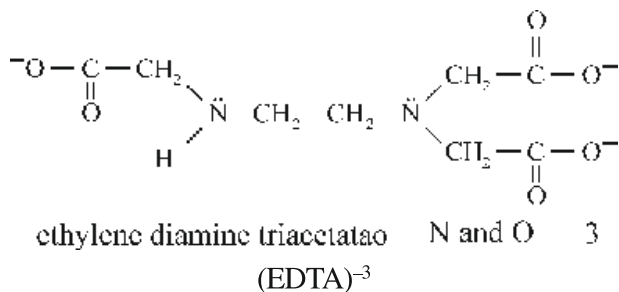
9.3.6 hexadentate ligands–

Ligan which have six donor atoms

ethylene diamine tetra acetato   N and O   4
(EDTA)$^{-4}$
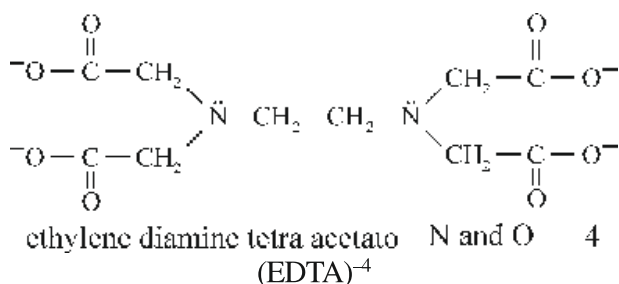
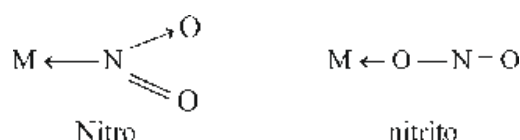## 9.4 Terminology

(i) Ambidentate Ligands– Some unidentate ligands have more than one donor atoms through which they can coordinate to the central atom
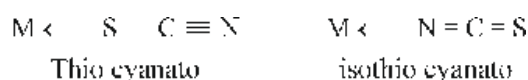
For example– NO_2 can coordinate to the metal atom through N or O as

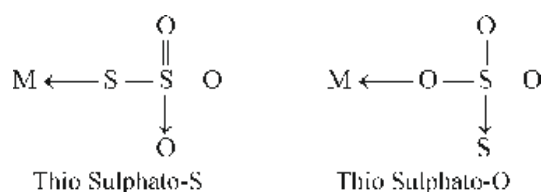Similarly –CN can coordinate through C or N as
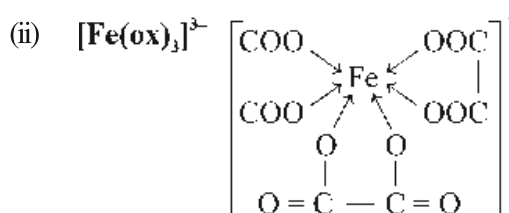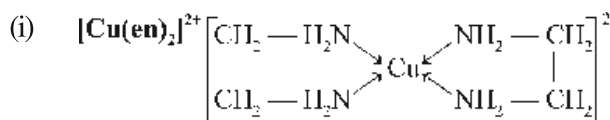

Thiocyanato can coordinate through S or N as

Thisuphato can coordinate through S or O as

(ii) Chelating Ligands– When a bidentate or polydentate ligand is attached by two or more donor atoms to the same central metal ion forming a ring structure, the ligands is called chelating ligand.

For example– Ethylene diamine (en), oxalato (ox) ion

(i)   **[Cu(en)$_2$]$^{2+}$**

(ii)   **[Fe(ox)$_3$]$^{3-}$**

(iii) Coordination number– The total number of ligands attached to the central metal atom in the coordination sphere is called the coordination number of the metal atom. **For example–** $[Cu(NH_3)_4]^{2+}$ the coordination number of Cu is 4.

$[Ag(CN)_2]^-$ the coordination number of Ag is 2.

Similarly ethylene dimine (en) and oxalato (ox) are bidentate ligands therefore. In the complexes $[Fe(ox)_3]^{3-}$, and $[Co(en)_3]^{3+}$ the coordination number of Fe an Co is 6, 6.

9.5 Coordination Sphere and Ionic Sphere

Central metal atom and thel ligand bonded to it is collectively known as the coordination sphere. This part of the complex behaves as one unit ad is non ionizable. It is generally written in square bracket [ ].

The portion outside the square bracket is ionizable and is known as ionic sphere.

Example :-

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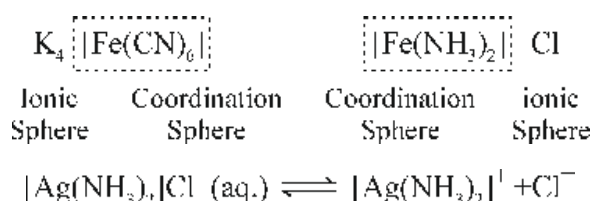
9.6 Coordination Polyhedron–
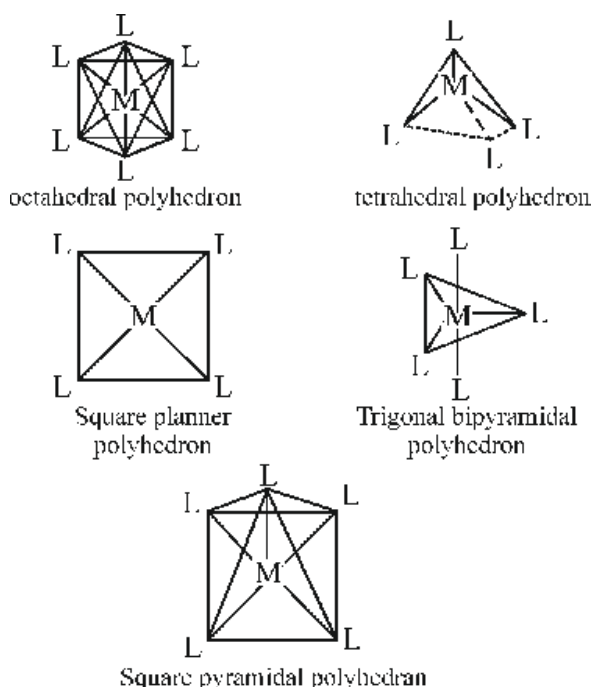
Space location system in which central metal atom/ion is bonded to ligands group is known as coordination polyhedron. The geometry of these are as follows :

octahedral polyhedron   tetrahedral polyhedron

Square planner polyhedron   Trigonal bipyramidal polyhedron

Square pyramidal polyhedran

9.7 Homoleptic and Heteroleptic Complexes

Complexes in which central metal atom bonded with one type of ligands are known as Homoleptic complexes.

For Example– $[Co(NH_3)_6]^{3+}$, $[Cu(en)_2]^{2+}$, $[Fe(CN)_6]^{4-}$ etc.

Complexes in which central metal atom bonded with different ligands are known as heteroleptic complexes.

Example– $[Cr(en)_2Cl_2]$, $[Pt(NH_3)_2Cl_4]$, $[Co(NH_3)_4Cl(NO_2)]$ etc.

9.8 Oxidation number of the central metal atom

It is the number which represents the charge which an atoms actually has or appears to have when combined with other ions or molecules. It must be noted that

(i) The sum of charges of the constituents is euqal to zero if the complex is neutral and

(ii) For an anionic or cationic complex, the sum of charges of the constituents is equal to the charge on the coordination sphere.

Example –

(i) Oxidation state of Pt in $[Pt(NH_3)_3Cl_3]$ can be determined as

Oxidation state of $NH_3 = 0$

Oxidation state of $Cl = -1$

Oxidation state of $Pt = x$

$x + 3(0) + 3(-1) = 0$, $x + 0 - 3 = 0$, $x = +3$

(ii) Oxidation state of Fe in $K_4[Fe(CN)_6]$ can be determined as

Oxidation state of $K = +1$

Oxidation state of $CN = -1$

Oxidation state of $Fe = x$

$4(+1) + x + 6(-1) = 0$, $+4 + x - 2 = 0$, $x = +2$

9.9 IUPAC Nomenclature of Coordination Compounds

1. In ionic complexes the positive ion (cation) is named first followed by the negative ion (anion)

2. Non ionic complexes are given a single word name.

3. **Naming the coordination sphere**

Name of ligands are written first followed by the name of the central metal ion. The oxidation number of the central metal atom is expressed by Roman numeral in parenthese just after the name of the central metal atom.

4. **Naming of Ligands**

(i) Names of the negative ligands end with the letter O

Example– $\overline{CN}$ cyano, CO_3^{2-} Carbonato Cl^- chloro etc.

(ii) For neutral ligands no charactersitic ending is used.

Example– H_2O, aqua, NH_3, ammine, CO Carbonyl

(iii)   Name of the positive ligands and with ium.

Example– NO^+ nitrosonium, $NH_2NH_3^+$ Hydrazinium etc.

(iv)   When there are several ligands of the same kind in the complex then prifixes di, tri, tetra, penta, hexa etc. are used to indicate the number of ligands in the complex.

(v)   When the name of the ligand itself includes a numerical prefix (such as di, tri, tetra etc.) then the terms bis, tris, tetrakis are used for describing two, three or four ligands repectively.

(vi)   A ligands which is attached directly to two metal atom/ions there by acting as a bridge between the two is called a briding ligand.
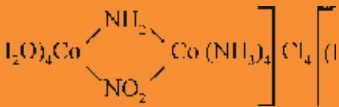
A Bridging ligand is indicated by adding the prefix μ before the name of the ligand.

5.   Ending of name of the central atom

(i)   In anionic complexes the name of the metal is ended with the suffix ate

(ii)   In cationic and neutral complexes the metal is ended with usual name and have no distinguishing termination.

(iii)   The oxidation state of the central metal atom is designated by Roman numera (I, II, III) in th bracket at the end of the name complex.

S.No.	Complex	IUPAC Name
1.	$K_4[Fe(CN)_6]$	Potassium hexa cyano ferrate (II)
2.	$Na[Ag(CN)_2]$	Sodium dicyano argentate (I)
3.	$[Ni(CN)_4]^{2-}$	Tetra cyano nicklate (II) ion
4.	$[CrF_6]^{3-}$	Hexa fluoro chromate (III) ion
5.	$K[PtCl_3(NH_3)]$	Potassium ammine trichloro platinate (II)
6.	$Hg[Co(CNS)_4]$	Mercury tetra thiocyanato cobaltate (II)
7.	$[Pt(Py)_4][PtCl_4]$	Tetra Pyridine platinum (II) tetra chloro platinate (II)
8.	$[Co(CO)_6]$	Hexa carbonyl cobalt (O)
9.	$[Mn_3(CO)_{12}]$	Doedeca carbonyl tri magnezes(O)
10.	$[Fe(C_5H_5)_2]$	bis (cyclo penta dienyl) iron (II)
11.	$[CoCl(ONO)(en)_2]^+$	Chloro bis (ethylene diamine) nitrito cobalt (III) ion
12.	$[Cr(NH_3)_4SO_4]ClO_4$	Tetra ammine sulphato chromium (III) perchlorate
13.	$[Cr(PPh_3)(CO)_5]^{+2}$	Penta carbonyl triphenyl phosphine chromium (II)
14.	$Fe_4[Fe(CN)_6]_3$	Ferric hexa cyano ferate (II)
15.	$Na[PtBrCl(NO_2)(NH_3)]$	Sodium ammine bromo chloro nitro platinate (II)
16.	$[Cu(H_2O)_2(NH_3)_4]SO_4$	Tetra ammine diaqua copper (II) sulphate
17.	$[Cu(Gly)_2]$	Diglycinato copper (II)
18.		Tetra aqua cobalt (III) -μ- amido-μ- nitro tetra ammine cobalt (III) chloride
19.	$[PtCl_2(en)_2](NO_3)_2$	Dichloro bis (ethylene diamine) platinum (IV) nitrate
20.	$K_3[Fe(C_2O_4)_3]$	Potassium trioxalato Ferrate (III)

9.10 Isomerism in Coordination Compounds

The two or more chemical compounds with identical chemical formula but different structures are called isomers and the phenomenon is known as isomerism.

Isomers can be broadly classified into two major categories :

(i) Structural Isomers

(ii) Stereo Isomers

9.11 Structural isomers

These are the isomers which have different arrangement of ligands around the central metal atom. The various types of structural isomers are being discussed as follows:
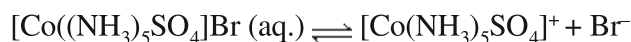
9.11.1 Ionization Isomers–

The coordination compounds which have the same molecular formula but give different ions in the solution are called ionization isomers.

For example, there are two distinct compounds of the formula, $Co(NH_3)_5BrSO_4$

$[Co((NH_3)_5Br]SO_4(aq) \rightleftharpoons [Co(NH_3)_5Br]^{2+} + SO_4^{2-}$
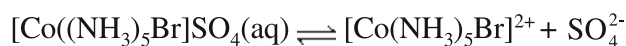
It gives white precipitate with $BaCl_2$ solution

$[Co((NH_3)_5SO_4]Br\ (aq.) \rightleftharpoons [Co(NH_3)_5SO_4]^+ + Br^-$

It gives light-yellow precipitate with $AgNO_3$ solution other compounds showing ionization iosmerism are:

(i) $[Pt(NH_3)_4Cl_2]Br_2$ or $[Pt(NH_3)_4Br_2]Cl_2$

(ii) $[Co(NO_3)(NH_3)_5]SO_4$ or $[Co(SO_4)(NH_3)_5]NO_3$

(iii) $[Co(en)_2Cl_2]NO_2$ and $[Co(en)_2ClNO_2]Cl$

9.11.2 Hydrate Isomers–

This type isomerism arises because of capability of water molecules to appear in a variety of ways, inside and outside the coordination sphere to give a number of hydrate isomers.

Example– There are three hydrate isomers of the formula $CrCl_3.6H_2O$ as shown below

(i) $[Cr(H_2O)_6]Cl_3$ violet

(ii) $[Cr(H_2O)_5]Cl_2.H_2O$ blue green

(iii) $[Cr(H_2O)_4Cl_2]Cl.(H_2O)_2$ dark green

9.11.3 Linkage isomers–

The compounds which have the same molecular formula, but differ in the mode of attachment of a ligand to the central atom/ion are called linkage isomers.

Example–

(i) $[Cr(H_2O)_5CN]Cl_2$
Penta aqua cyano chromium (III) chloride

and

$[Cr(H_2O)_5NC]Cl_2$
Penta aqua iso cyano chromium (III) chloride

(ii) $[Co(NH_3)_5NO_2]Cl_2$
Penta ammine nitro cobalt (III) chloride

and

$[Co(NH_3)_5ONO]Cl_2$
Penta ammine nitrito cobalt (III) chloride
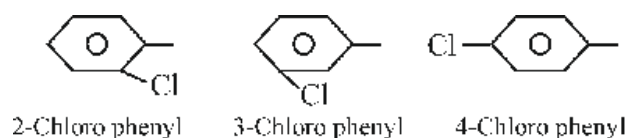
9.11.4 Co-ordination Isomers–

This type of isomerism is shown by the compounds which contain complex cation and comples anion. It is caused by the interchange of ligands between the complex cation and complex anion.

Example–

(i) $[Co(NH_3)_6]\ [CrCl_6]$ and $[Cr(NH_3)_6]\ [CoCl_6]$

(ii) $[Pt(NH_3)_4]\ [PtCl_4]$ and $[PtCl(NH_3)_3]$ $[PtCl_3NH_3]$

9.11.5 Ligand Isomers–

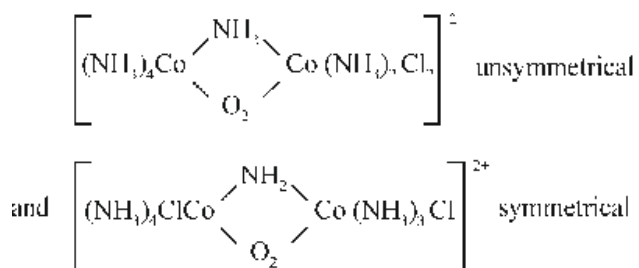In this type of complexes ligands it self shows isomerism.

2-Chloro phenyl   3-Chloro phenyl   4-Chloro phenyl

Example–

(i) $[Cr(NH_3)_5\{C_6H_4Cl(2)\}]Cl_3$

(ii) $[Cr(NH_3)_5\{C_6H_4Cl(3)\}]Cl_3$

(iii) $[Cr(NH_3)_5\{C_6H_4Cl(4)\}]Cl_3$

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9.11.6 Coordination Position Isomersim–

This type of isomerism is exhibited by bridging complexes and results from different attachment of ligands.

Example–

$$\left[(NH_3)_4Co \overset{NH_3}{\underset{O_2}{\diamond}} Co\,(NH_3)_2\,Cl_2 \right]^{2} \quad \text{unsymmetrical}$$

$$\text{and} \left[(NH_3)_4ClCo \overset{NH_2}{\underset{O_2}{\diamond}} Co\,(NH_3)_3\,Cl \right]^{2+} \quad \text{symmetrical}$$

9.12 Stereoisomers

These isomers contain same atoms and the same atom to atom bonding but differ only in the spatial arrangement of atoms or groups about the central metal atom. It is possible only in the complexes with a coordination number four or greater than four. The two important types of stereoisomers are being described as follows.
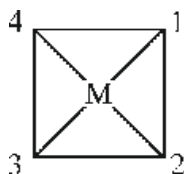
9.12.1 Geometrical isomers–
The geometrial isomers is due to the ligands occupying different geometrical positions arround the central metal ion.

When the similar ligands occupy the adjacent positions. This arrangement give rise to **cis-Isomer.**

When the similar ligands occupy positions opposite to each other. This arrangement give rise to **trans-Isomer.**

(i) **Geometrical isomerism** in square planner complexes with coordination number 4

It may be noted than in square planar complexes the positions 1-2, 2-3, 3-4 and 1-4 are cis with respect to each other while the position 1-3 and 2-4 are trans to each other.
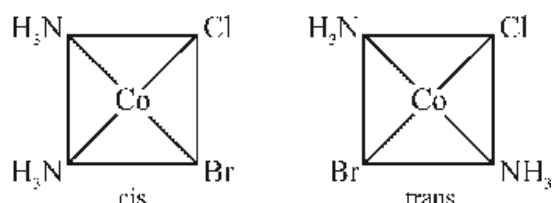

Square planner complexes of the type MA_2X_2, MA_2XY, $MABX_2$ can exist as geometrical isomers

(Here A and B are neutral ligands whereas X and Y are anionic ligands)

★ **MA_2X_2 type–** Diammine dichloro platinum (II) $[Pt(NH_3)_2Cl_2]$
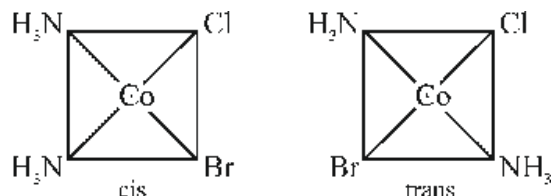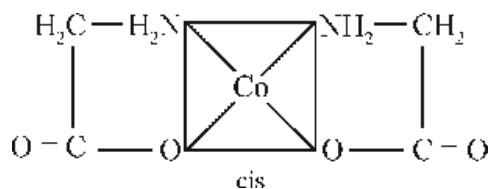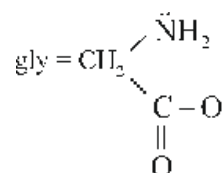

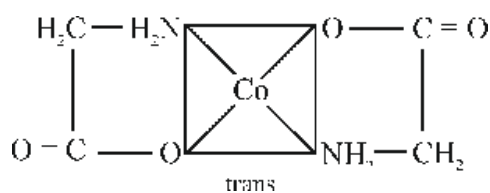★ **MA_2XY type–** diammine bromochloro cobalt (II) $[Co(NH_3)_2ClBr]$

★ **$MABX_2$ type–** These complexes have same cis-trans isomers like MA_2XY type.

★ The square planar complexes containing unsymmetrical bidentate ligands such as $[M(AB)_2]$ also show geometrical isomerism.

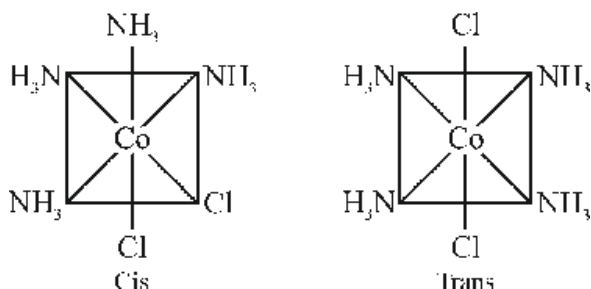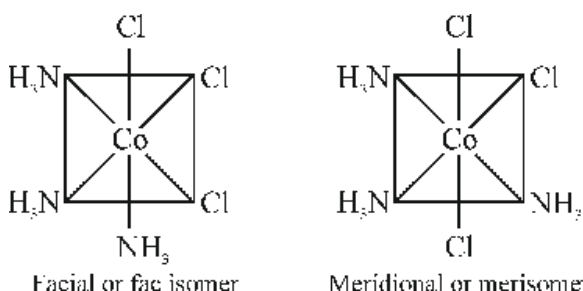**Example–** Di (glycenato) Platinum (II) $[Pt(gly)_2]$

and

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(ii) Geometrical Isomerism in octahedral complexes with coordination umber 6

★ **MA$_4$X$_2$ type**– tetraammine dichloro cobalt (II) [Co(NH$_3$)$_4$Cl$_2$]

Cis   Trans

★ **MA$_3$X$_3$ type**– Triammine trichloro cobalt (III) [Co(NH$_3$)Cl$_3$]

Facial or fac isomer   Meridional or merisomer

Octahedral complexes having bidentate ligands of the type [M(AA)$_2$X$_2$] can also as cis and trans isomers, where AA represents a symmetrical bidentate ligand.

Example– dichloro bis (ethylene diamine) cobalt (III) ion

Cis   Trans
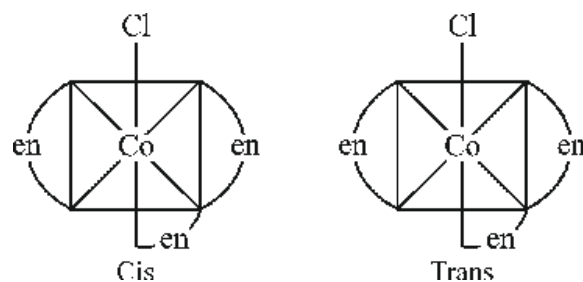
9.12.2 Optical Isomers–

This type of isomerism is exhibited by the chiral molecules i.e., molecules which do not have plane of symmetry. These isomers are non superimposable mirror image of each other. They are optically active and rotate the plane of polarised light equally but in opposite directions. The isomer which rotate the plane of polarised light towards left is called laevorotatory (–) while that which rotate plane towards right is called dextro rotatory (+).

Complexes with a co-ordination number of 4 and 6 shows this kind of isomerism.

(i) Tetrahedral Complex– Tetrahedral ligands with symmetrical bidentate ligands such as [Ni(CH$_2$NH$_2$COO)$_2$] i.e. bis (glycinato) nickel (II) show optical isomerism as:
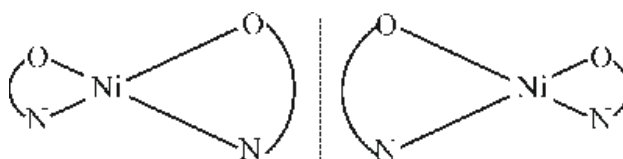
(ii) Octahedral complex– Complexes of the type M(AA)$_3$ (where AA is symmetrical bidentate ligands) exist as optical isomers.

Example–
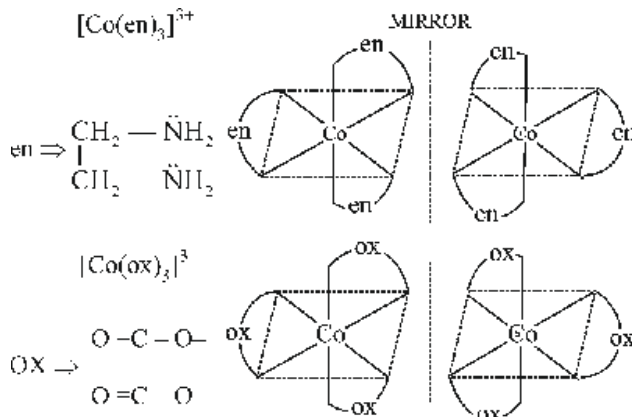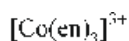
Complexes of the type [M(AA)$_2$XY] (where AA is symmetrical bidentate and X, Y are monodentate ligands) also exhibit optical activity.

Example– [Co(en)$_2$Cl$_2$]$^{+1}$

trans isomer optically inactive

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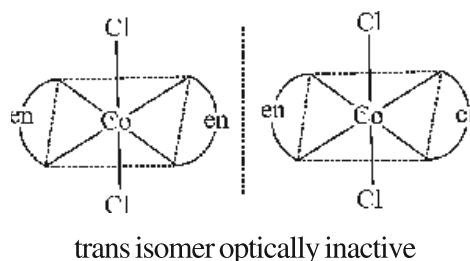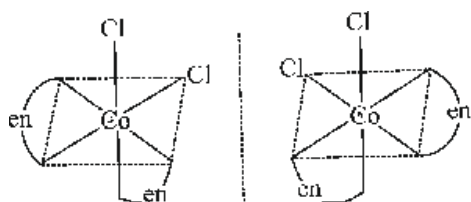
cis isomer optically active

Complexes of the type $[M(AA)X_2Y_2]$ containing one symmetrical bidentate ligand show optical isomerism and d– and l– forms

$[Co(en)(NH_3)_2Cl_2]^+$

d-form   l-form
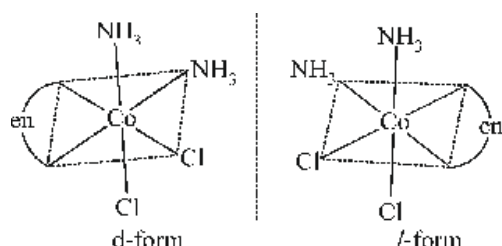
9.13 Bonding in coordination compouds

Valence bond theory– It is given by Pauling. The main assumption of this theory are listed below:

(i) The central metal ion in the complex makes available a number of empty orbitals for the formation of coordination bonds with suitable ligands. The number of empty orbitals made available for this purpose is equal to coordination number of the central metal ion.

(ii) The appropriate atomic orbitals (s, p and d) of the metal hybridise to give a set of equivalent orbitals of definite geometry.

(iii) The hybridised orbitals are then allowed to overlap with those ligand orbitals that can donote an electron pair for bonding.

(iv) The outer orbital (high spin) or inner orbital (low spin) complexes are formed depending upon whether nd orbitals or (n–1)d orbitals of the inner shell are used in hybridization scheme.

(v) Square planner, Tetrahedral, Octahedral complexes are obtained from dsp^2, sp^3, d^2sp^3 or sp^3d^2 hybridisation respectively.

(i) $[Ni(CN)_4]^{2-}$ Tetracyano nickelate (II) ion

It is a square planar complex in which nickel is in +2 oxidation state and has the electronic configuration $3d^8$. In this case the two unpaired electrons of the 3d orbitals are forced to be pair in the presence of strong ligand, $\overline{CN}$ ion. Since four ligands are to be accommodated, therefore, nickel (II) ion undergoes dsp^2 hybridisation forming four equivalent dsp^2 hybrid orbitals. These accomodate the four pair of electrons from the ligands.

dsp^2 hybridisation
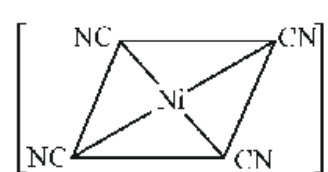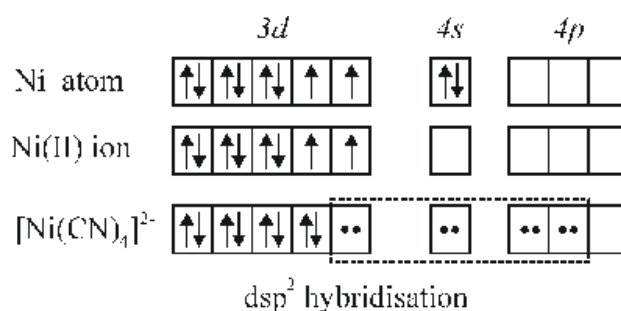
geometry – square planar bond angle – 90°;
nature – dimagnetic

(ii) $[Ni Cl_4]^{2-}$ Tetra chloro nickelate (II) ion

The nickel (II) has two unpaired electrons as shown below. The magnetic measurements of the complex $[NiCl_4]^{2-}$ show that it is paramagnetic and has two unpaired electrons. Therefor, in this case the 3d-orbitals remain undisturbed and sp^3 hybridisation occurs resulting in tetrahadral structure of the complex.

sp^3 hybridisation

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geometry → Tetrahedral
bond angle 109°28'
nature - paramagnetic
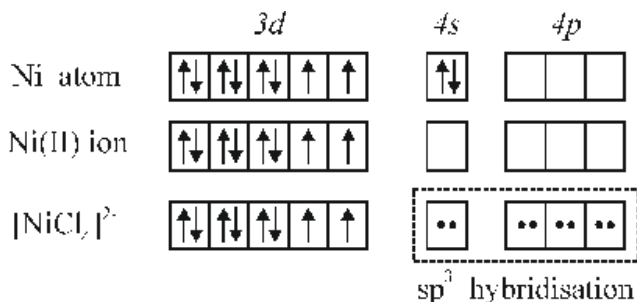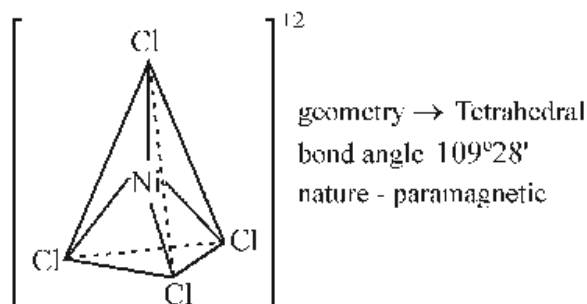
(iii) $[Co(NH_3)_6]^{3+}$ Hexa ammine Cobalt (III)

In this complex the cobalt ion is in +3 oxidation state and has an electronic configuration of $3d^6$, as shown below

d^2sp^3 hybridisation

geometry = octahedral
Nature - dimagnetic
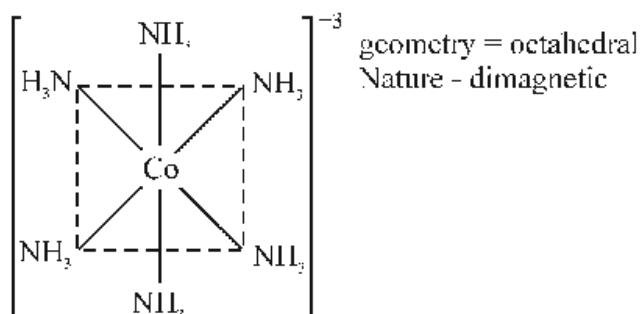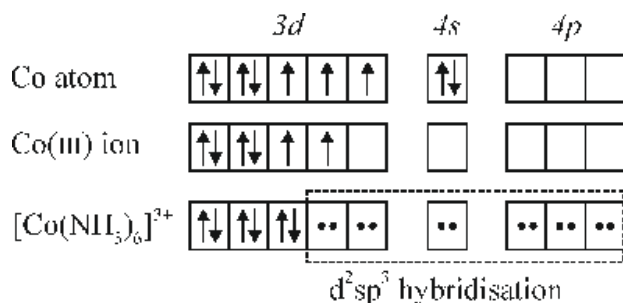
The two 3d, one 4s and three 4p orbitals then hybridise to yield six d^2sp^3 hybrid orbitals pointing towards the six ends of an octahedron. The absence of unpaired electron in the remaining orbitals of Co(III) makes the complex diamagnetic.

(iv) $[CoF_6]^{3-}$ Hexa Fluoro Cobalt (III)

In this complex the outer electronic configuration of Co in excited state is $3d^6$. Since F^- ion provides a weak ligand field therefore one 4s, three 4p and two 4d orbitals hybridise to yied six sp^3d^2 hybrid orbitals pointing towards the six ends of an octahedron. The presence of unpaired electrons in 3d orbitals makes the complex paramagnetic.

sp^3d^2


geometry − octahedral
Nature - paramagnetic
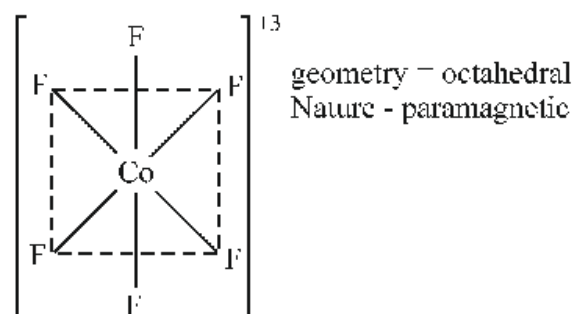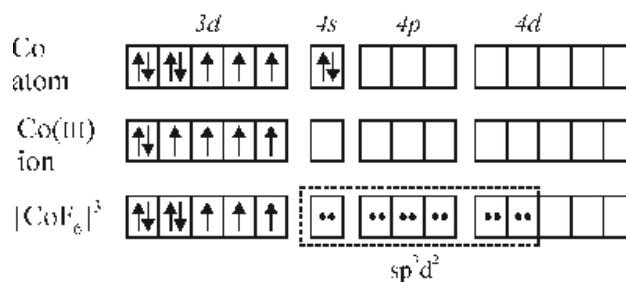
Limitations of Valence Bond Theory

(i)   It gives only the qualitative explanations for complexes.

(ii)   It does not explain the detailed magnetic properties of the complexes.

(iii) This theory does not explain the absorption spectra of complexes.

(iv)   It does not explain the relative stability of different complexes.

9.13.1 Crystal Field Theory–

Crystal field theory was proposed by *Bethe and van Vleck*. This theory can explain the electronic spectra and magnetism of transition metal complexes more celarly.

The crystal field theory considers that the metal ion is situated in an electrical field caused by the surrounding ligands.

The crystal field theory is based on the following assumptions.

1.   The transition metal atom/ion is considered as a positive ion of charge equal to the oxidation state.

2.   The transition metal atom/ion is surrounded by a definite number of ligands. The ligands may be negative ions or neutral molecules having lone-pair of electrons.

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3. The attraction between the central metal ion and the logands in a complex is purely electrostatic or ionic. The negative end of the dipole of the neutral molecule ligand is directed towards the metal ion.

4. The ligands are considered as point charges and produce an electric field. This electric field changes the energy of the orbitals on the metal atom/ion.

5. There is no interaction between the metal orbital and ligand orbitals.

1. Crystal Field Splitting in Octahedral Co-ordination Entities– When ligands approach the central metal ion from particular direction they create negative field around the central metal ion. Inittially the central metal atom/ion is surrounded by a spherically symmetrical field of negative charges; the d-orbitals remain degenerate. However, the energy of the orbitals is symmetically raised due to the repulsion between the negative field and electrons of d-orbitals in the metal atom/ion. In most transition metal complexes, the field produced by ligands is not spherically symmetrical. Thus

the d-orbitals are affected differently and their degeneracy gets lost.

In an octahedral complex, the metal ion is at the centre of the octahedron and the six ligands are at its six corners. From the shapes of the d-orbtials, it is seen that :-

The lobes of eg orbitals, dx^2-y^2 and dz^2 are directed along the axes x, y and z.

The lobes of t_{2g} orbitals, d_{xy}, d_{yz} and d_{zx} are situated in between the axes.

Thus, if six ligands approach the metal ion along the $-x$, $-y$ and $-z$ directions, the dx^2-y^2, dz^2 orbitals get affected more than dxy, dyz and dzx orbitals due to greater interaction in the former case. As a result, energy of the dx^2-y^2 and dz^2 orbitals increases much more than the energy of dxy, dyz and dzx orbitals. Thus, the octahedral field of the ligands disturbs the degeneracy of the d-orbitals and the d-orbitals split into two groups t_{2g} and e_g of different energies. The difference in energy between the groups of d-levels is denoted by Δ_o or 10 Δq.

Splitting of d-orbitals in octahedral field
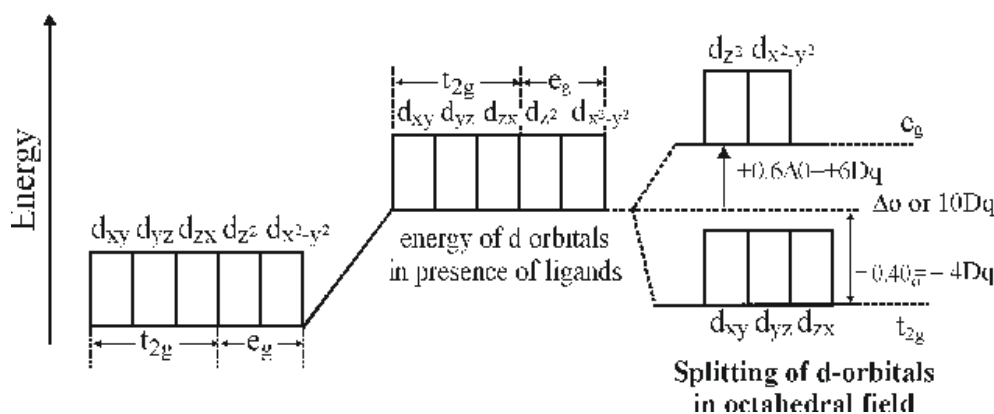
Spectrochemical Series– The crysal field splitting depends upon the nature of ligands. The ligands which cause only a small crystal field splitting are called weak field ligands.

The ligands which cause a large crystal field splitting are called strong field ligands. The arrangement of common ligands in the ascending order of crystal field splitting (Δ_o) is called spectrochemical series.

The spectrochemical series is determined experimentally.

$I^- <$ $Br^- <$ $SCN^- <$ $Cl^- <$ $N^{3-} <$ $NO_3^- <$ $F^- <$ $OH^- <$ $C_2O_4^{2-} <$ $H_2O <$ $NC\overline{S} <$ $EDTA^{-4} <$ $H^- <$ $NH_3 <$ en $<$ $CN^- <$ $NO_2^- <$ CO
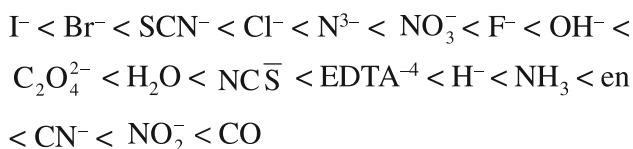
Distribution of electrons in octahedral co-ordination Entities

Distribution of d-electrons depends on two following types of energy-

(i) Crystal field splititting energy Δ_o.

(ii)   Pairing energy P-it is defied as the necessary energy for the pairing of electrons in an orbital.

(iii) For strong field ligands $\Delta_o > P$ so pairing of electrons occurs and low spin complex is formed.

(vi) For weak field licands $\Delta_O < P$ so electrons gets places in eg set and high spin comple is formed

$de^{(\cdot)}$	Strong field ligand t_{2g}, e_g configuration	n value	$\mu = \sqrt{n(n+2)}$	Weak field ligand t_{2g}, e_g configuration	n value	$\mu = \sqrt{n(n+2)}$
d^1	$t_{2g}^{1} e_g^{0}$	1	1.73 BM	$t_{2g}^{1} e_g^{0}$	1	1.73 BM
d^2	$t_{2g}^{2} e_g^{0}$	2	2.82 BM	$t_{2g}^{2} e_g^{0}$	2	2.82 BM
d^3	$t_{2g}^{3} e_g^{0}$	3	3.87 BM	$t_{2g}^{3} e_g^{0}$	3	3.87 BM
d^4	$t_{2g}^{4} e_g^{0}$	2	2.82 BM	$t_{2g}^{3} e_g^{1}$	4	4.89 BM
d^5	$t_{2g}^{5} e_g^{0}$	1	1.73 BM	$t_{2g}^{3} e_g^{2}$	5	5.91 BM
d^6	$t_{2g}^{6} e_g^{0}$	0	0	$t_{2g}^{4} e_g^{2}$	4	4.89 BM
d^7	$t_{2g}^{6} e_g^{1}$	1	1.73 BM	$t_{2g}^{5} e_g^{2}$	3	3.87 BM
d^8	$t_{2g}^{6} e_g^{2}$	2	2.82 BM	$t_{2g}^{6} e_g^{2}$	2	2.82 BM
d^9	$t_{2g}^{6} e_g^{3}$	1	1.73 BM	$t_{2g}^{6} e_g^{3}$	1	1.73 BM
d^{10}	$t_{2g}^{6} e_g^{4}$	0	0	$t_{2g}^{6} e_g^{4}$	0	0

2.   Crystal Field splitting in tetrahedral co-ordination Entities

In a regular tetrahedral geometry, the central metal ion is at the centre of the cube and the four ligands occupy four corners of a cube.

The directions x, y and z point to the centres of the faces of the cube.

The orbitals $dx^2–y^2$ and dz^2 (belonging to the eg group) and the orbitals d_{xy}, d_{yz} and d_{zx} (belong to the t_{2g} group) are oriented between the x, y and z directions.

Thus, in tetrahedral complexes the directions of approach of ligands does not coincide with either the e_g or t_{2g} orbitals.

Splitting of d-orbitals in tetrahedral field

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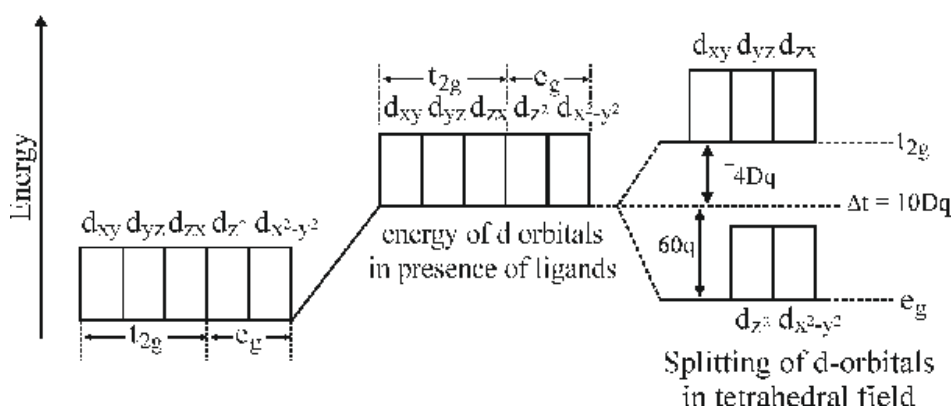
From the geometry, it can be seen that t_{2g} orbitals are closer to the direction of the ligands than the eg orbitals. Therefore, the approach of ligands raises the energy of both the groups of the orbitals. The energy of t_{2g} orbitals is raised the most.

For Tetrahedral complex $\Delta_t < P$ therefore pairing of electron is not possible. So low spin complex is not found.

Relation between Δ_t and Δ_o is $\Delta_t = \dfrac{4}{9}\Delta_O$ (for same metal ion)

Crystal field stabilization energy (CFSE)

for octahedral complex

$(CFSE) = [-4\, n(t_{2g}) + 6\, n(e_g)]D_q$

for tetrahedral complex

$(CFSE) = [+6\, n(t_{2g}) - 4\, n(e_g)]D_q$

Where n = number of electrons in orbitals.

Colour in Coordination Compounds–

We have already discussed that crystal field splitting of the d-energy levels produce the energy difference, Δ. This value of enery difference is usually small. thus promotion of electrons from lower to higher d-level results from the absorption of an appropriate wavelength of white light.

Colour of absorbed light	Complementary Colour
Red	Blue
Ultra violet	Pale yellow
Yellow	Purple
Greenish blue	Reddish blue
Blue	Yellow-orange

9.14 Stability of Co-ordination Compounds

The formation of a co-ordination compound involves reaction between a metal ion an ligands. If the force of attraction of the metal ion with ligand is strong a stable complex may result. Mostly the complex ions are highly stable. A chemical equilibrium may be established between the dissociated ions and the undissociated complex.

$$M^{a+} + nL^{x-} \rightleftharpoons [ML_n]^{b+}$$
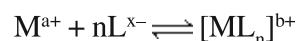
Here a^+, $x-$, $b+$ are the charges on metal atom, ligand and complex respectively and $b+ = a^+ + x^-$

The equilibrium constant for the above reaction is given by the expression

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

Here K_s is the stability complex for the comple

$$K_s \text{ value} \propto \text{ stability}$$

Example–

For $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$ $K_s = 1.6 \times 10^7$

For $Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$ $K_s = 5.4 \times 10^{18}$

For $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$ $K_s = 4.5 \times 10^{21}$

For $Cu^{2+} + 4C\overline{N} \rightleftharpoons [Cu(CN)_4]^{2-}$ $K_s = 2 \times 10^{27}$
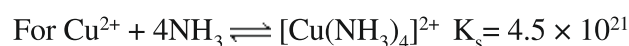
On the basis of K_s value the stability of a complex depend upon–

(1) **Nature of central ion–** The term nature means the charge density on the central ion i.e. greater is the charge density or larger the charge/radius ratio more is the stability of a complex

for $Fe^{3+} + 6C\overline{N} \rightleftharpoons [Fe(CN)_6]^{3-}$ $K_s = 1.2 \times 10^{31}$ high

for $Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]$ $K_s = 1.8 \times 10^6$ less
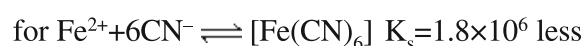
For the ions which carry the same charge the one with a smaller size gives the more stable complexes.

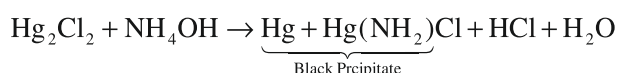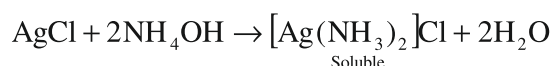e.g. $Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$

(2) **Nature of ligands–** More basic is a ligands, greater is the ease with which it can donate its electrons and therefore more is the stability of complex.

(3) **Chelatilization–** The ring structure complex formed by the bidentate or polydentate ligands are more stable than complexes formed from monodentate ligands.
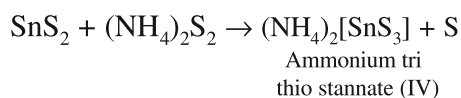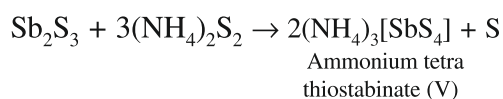
## 9.15 Importance of coordination compounds

(A) Qualitative Analysis

(i) The complex formation method is used in qualitative scheme of group I for the separation of silver ion and mercuras ion from the precipitate of AgCl and Hg_2Cl_2. We add aqueous ammonia solution to the precipitation when silver chloride and mercuras chloride dissolves due to the formation of the complex ion

$$AgCl + 2NH_4OH \rightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

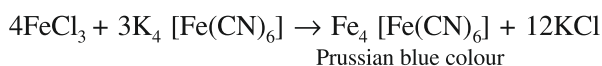$$Hg_2Cl_2 + NH_4OH \rightarrow \underbrace{Hg + Hg(NH_2)Cl}_{\text{Black Prcipitate}} + HCl + H_2O$$

(ii) In the group II, IIA and IIB group metal sulphides ion are seperated by using yellow Ammonium sulphide solution wher IIA group metal sulphides remains unsoluble while IIB group metal sulphides formed soluble complex.

$$Sb_2S_3 + 3(NH_4)_2S_2 \rightarrow 2(NH_4)_3[SbS_4] + S$$
$$\underset{\substack{\text{Ammonium tetra} \\ \text{thiostabinate (V)}}}{}$$

$$SnS_2 + (NH_4)_2S_2 \rightarrow (NH_4)_2[SnS_3] + S$$
$$\underset{\substack{\text{Ammonium tri} \\ \text{thio stannate (IV)}}}{}$$

In the II group Cu^{2+} ion are estimated by forming complex with pottassium ferro cyanide solution.

$$2CuSO_4 + K_4[Fe(CN)_6] \rightarrow \underset{\text{Dark brown precipitate}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$$
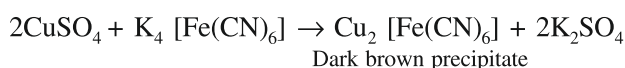
(iii) In the III group Fe^{+3} are estimated by forming complex with pottassium ferro cyanie solution.

$$4FeCl_3 + 3K_4[Fe(CN)_6] \rightarrow \underset{\text{Prussian blue colour}}{Fe_4[Fe(CN)_6]} + 12KCl$$

(iv) In the IV group Zn^{2+} are estimated by forming complex with pottassium ferro cyanide solution.

$$2ZnCl_2 + K_4[Fe(CN)_6] \rightarrow \underset{\text{Blue colour}}{Zn_2[Fe(CN)_6]} + 4KCl$$
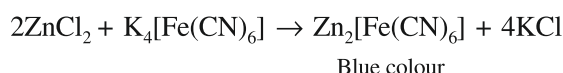
Also Ni^{+2} ion are estimated by forming complex with dimethyl glyoxime (DMG)

Pink colour

$$+ 2NH_4Cl + 2H_2O$$
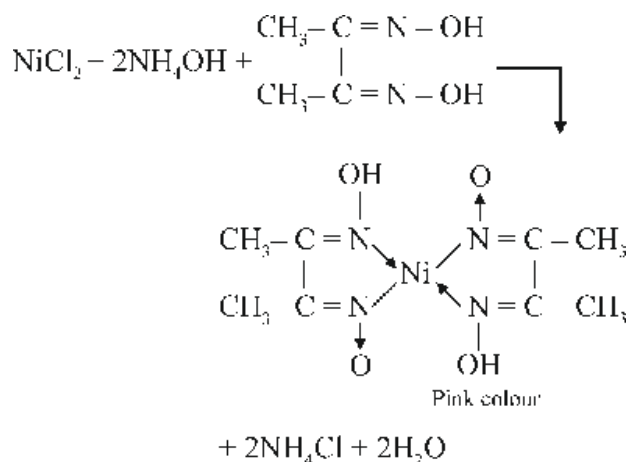
(B) Extraction of Metals–
Silver and gold are extracted from their respective are by treatment with sodium cyanide solution. This also involves complex formation.

$$\begin{bmatrix} Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S \\ 2Na[Ag(CN)_2] + Zn \rightarrow Na[Zn(CN)_4] + 2Ag \end{bmatrix}$$

$$\begin{bmatrix} 4Au + 8NaCN + 2H_2O + O_2 \rightarrow 4Na[Au(CN)_2] + 4NaOH \\ 2Na[Au(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Au \end{bmatrix}$$
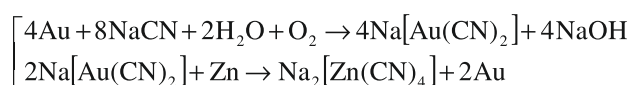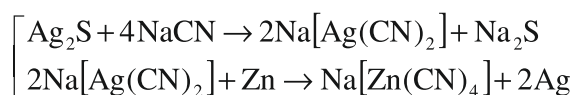
(C) Biological Uses–
Many biological important natural compounds exist as a coordinated complexes.

For example–

(i) **Haemoglobin** a complex of Iron i.e. of Fe^{2+}

(ii) **A platinum complex cis**$[Pt(NH_3)_2Cl_2]$ known as cis platin has found use in cancer chemotherapy.

(iii) **Chlorophyll is the main factor of phtoshynthesis–** is a complex of magnesium.

(iv) **Vitam B_{12}–**i.e. cyanocobalamin is complex of cobalt.

(v) **British Anti-Lewisite (BAL)** its a medication used to treat acute poisoing by arsenic, mercury gold, and lead. May also be used for antimony, thallium, or bismuth poisoing.

EXERCISE QUESTIONS

Multiple choice questions

1. Oxidation number of Fe in $K_3[Fe(CN)_6]$ is :
   - (a) 2
   - (b) 3
   - (c) 0
   - (d) non of above

2. Complex which has tetrahedral geomertry is
   - (a) $[Ni(CN)_2]^{2-}$
   - (b) $[NiCl_4]^{2-}$
   - (c) $[PdCl_4]^{2-}$
   - (d) $[Ni(CN)_4]^{2-}$

3. Coordination number of $(EDTA)^{-4}$ is
   - (a) 3
   - (b) 6
   - (c) 4
   - (d) 5

4. Number of geometrical isomer of $[Pt(NH_3)Cl_2]$.
   - (a) 3
   - (b) 2
   - (c) 4
   - (d) 1

5. A complex formed from nitrato and chloro ligands gives precipitate of two moles of AgCl with $AgNO_3$. The formula of complex is :
   - (a) $[Co(NH_3)_5NO_3]Cl_2$
   - (b) $[Co(NH_3)_5Cl]NO_3Cl$
   - (c) $[Co(NH_3)_5Cl]NO_2$
   - (d)

6. Which of the following complex shows optical isomerism.
   - (a) $[Co(CN)_6]^{3+}$
   - (b) $[ZnCl_4]^{2-}$
   - (c) $[Co(en)_2Cl_2]$
   - (d) $[Cu(NH_3)_4]^{2+}$

7. Hybridisation in $[Ni(CO)_4]$ is
   - (a) sp
   - (b) sp^2
   - (c) dsp^2
   - (d) sp^3

8. Element present in chlorophyll is
   - (a) Cobalt
   - (b) Magnesium
   - (c) Iron
   - (d) Nickel

Short answer Questions

1. Write oxidation number and coordination number of central metal atom in complex.
$$K_3[Fe(C_2O_4)_3]$$

2. What will be the name of necessary ligand required for the estimation of hardness of water.

3. Write IUPAC name of $Li[AlH_4]$

4. Draw both mirror images of complex
$$cis[Co\,(en)_2\,Cl_2]$$

5. Determine magnetic moment of Ni^{+2} ion.

6. Write IUPAC name of $[Mn_2(CO)_{12}]$

7. Give an example of ambidentate ligand. Explain why it is ambidentate ligand.

8. Classify following ligands in monodentate, bidentate.... etc. ligands
   - (i) en
   - (ii) CN^-
   - (iii) acac
   - (iv) dmg

Very short answer question

1. What is chelation effect ? give an example.

2. Two bottles A and B filled with complexes of the molecular formula $Co(NH_3)_5SO_4Br$. Out of these one complex give white precipitate with $BaCl_2$ while other gives pale yellow precipitate with $AgNO_3$. Write the formula of complex present in A and B.

3. Determine oxidation state of central metal atom in comples.
   - (i) $K_3[Fe(C_2O_4)_3]$
   - (ii) $[Fe(CN)_6]^{3-}$

4. What will be the geometry of sp^3 and dsp^2 hybridisation. Give an example of each.

5. Explain the importance of complex compounds in the extraction of Metals.

Descriptive questions

1. Give the Geometry of $[Ni(CN)_4]^{2-}$ and explain the hybridisation state of central atom.

2. Differenciate $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ on the basis of crystal field theory.

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3. Define ionisation isomerism. Write IUPAC names of $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$.

   Prove that both above complexes are ionisation isomers.

4. Write IUPAC name of the following coordination compounds.

   (a) $[Pt(NH_3)_2Cl(NO_2)]$

   (b) $Na[BH_4]$

   (c) $[Co(NH_3)_5(CO_3)]Cl$

   (d) $Zn_2[Fe(CN)_6]$

Answers of multiple choice questions

1. (b),   2. (b),   3. (b),   4. (b),

5. (a),   6. (c),   7. (c),   8. (b)

❑❑❑