COORDINATION CHEMISTRY

Molecular/Addition Compound :

Molecular/Addition compounds are formed when stoichiometric amounts of two or more simple compounds join together. Molecular/Addition compounds are of two types.

To understand coordination compound, we first need to understand about salts.

Salts : A ionic compound that contains a cation and an anion.

There are three type of salts :

1. Simple salts : It is formed by neutralization of an acid and a base.

NaOH + HCl $\rightarrow$ NaCl + H2O

2. Double salts : Those which don't retain their identity in solutions are called double salts. For example.

$KCl + MgCl_2 + 6H_2O \longrightarrow KCl.MgCl_2.6H_2O$

carnallite

$K_2SO_4 + Al_2(SO_4)_3 + 24\ H_2O \longrightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$

potash alum

3. Complex compounds : Those which retain their identity in solution are called complex compounds. For example,

$CuSO_4 + 4\ NH_3 \longrightarrow CuSO_4.4NH_3$ or $[Cu(NH_3)_4]SO_4$

tetraamminecopper(II)sulphate

$Fe(CN)_2 + 4\ KCN \longrightarrow Fe(CN)_2.\ 4KCN$ or $K_4[Fe(CN)_6]$

potassium ferrocyanide

When crystals of carnallite are dissolved in water, the solution shows properties of K^+, Mg^{2+} and Cl^- ions. In a similar way, a solution of potash alum shows the properties of K^+, Al^{3+} and SO_4^{2-} ions. These are the examples of double salts which exist only in the crystalline state. While in the other two examples of coodination compounds / complexes, When they dissolved in water they do not forms simple ions, Cu^{2+}/Fe^{2+} and CN^-, instead their complex ions are formed.

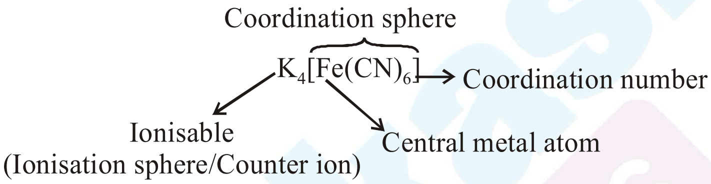
Representation of Complex Ion :

$$[ML_x]^{n\pm}$$

where

M = Central metal atom /ion (usually of d-block)
L = Ligand
x = No. of ligands
$n^{\pm}$ = Charge on coordination entity

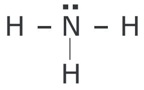
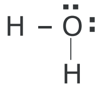
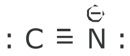
Coordination compound :



The region outside the coordination sphere is the ionisation sphere.

1. **Central metal atom/ion :** Central ion acts as an acceptor (Lewis acid) and accommodate electron pairs donated by the donor atom of the ligand, it must have empty orbitals. This explains why the transition metals having empty d-orbitals forms co-ordination compounds readily. e.g., in complexes $[Ni(NH_3)_6]^{2+}$ and $[Fe(CN)_6]^{3-}$, Ni^{2+} and Fe^{3+} respectively are the central metal ions.

2. **Ligands :** Species which are directly linked with the central metal atom/ ion in a complex ion are called ligands. The ligands are attached to the central metal atom/ion through coordinate or dative bond, free ligands have at least one lone pair.

The ligands are thus Lewis bases and the central metal ions/atoms are Lewis acids.

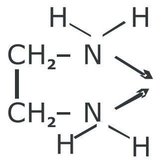
Classification of Ligands should be done on three basis:

1. Based on Charge : Occasionally ligands can be cations (NO^+, $N_2H_5^+$) and electron- pair acceptors, Example for anionic ligands are F^-, Cl^-, Br^-, I^-, S_2^-, CN^-, NCS^-, OH^-, NH^{-2} and neutral ligands are NH_3, H_2O, NO, CO.

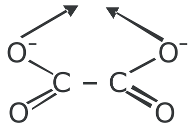
2. Based on Denticity : On the basis of the number binding sites with the central metal atom.

(i) Mono/Unidentate Ligands : They have one donor atom, i.e., they can donate only one electron pair to the central metal atom /ion eg., F^-, Cl^-, Br^-, H_2O, NH_3, CN^-, NO_2^-, OH^-, CO etc.

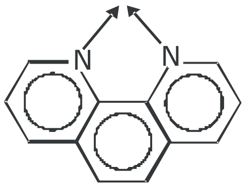
(ii) Bidentate Ligands : Ligands which have two donor atoms and have the ability to link with the central metal atom/ion at two position are called bidentate ligands e.g.



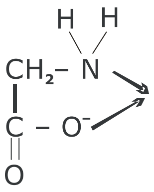
ethylenediamine (en)



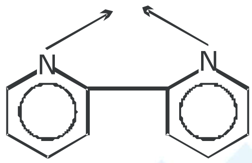
oxalate (ox)



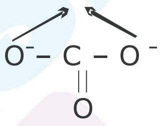
1,10-phenanthroline (phen)



glycinate (Gly)

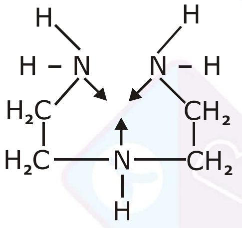


2,2-dipyridine (dipy)

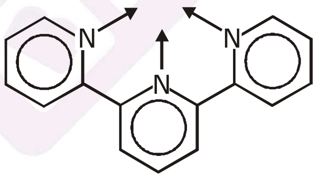


carbonate

(iii) Tridentate Ligands : Ligands having three donor atoms are called tridentate ligands. Examples are

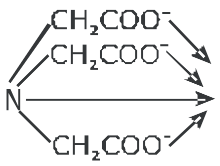


diethylenetriamine (dien)

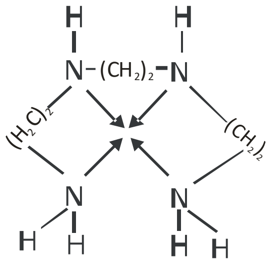


2, 2', 2"-terpyridine (terpy)

(iv) Tetradentate Ligands : These ligands possess four donor atoms. Examples are

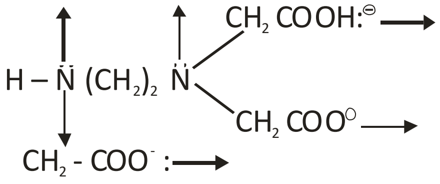


Nitriloacetate

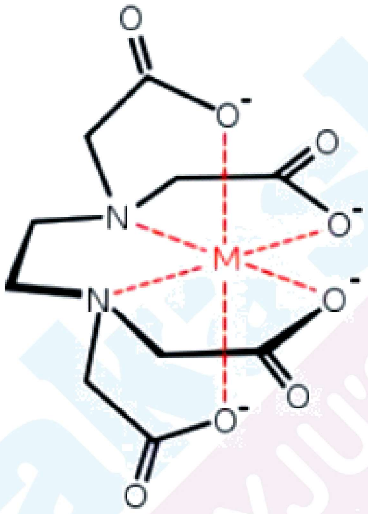


Triethyleneteramine (trien)

(v) Pentadentate Ligands : They have five donor atoms. For example, ethylenediamine triacetate ion.



(vi) Hexadentate Ligands : They have six donor atoms. The most important example is ethylenediamine tetraacetate ion.



Ethylenebiaminetetraacetate ion (EDTA)$^{-4}$

(vii) Ambidentate ligands : There are certain ligands which have two or more donor atoms but in forming complexes, only one donor atom is attached to the metal/ion. Such ligands are called ambidentate ligands. Some examples of such ligands are

$M \longleftarrow NO_2^-$

nitrite – N

$M \longleftarrow ONO^-$

nitrite –O

$M \longleftarrow CN^-$

cyanide

$M \longleftarrow NC^-$

isocyanide

$M \longleftarrow SCN^-$

thiocyanide

$M \longleftarrow NCS^-$

isothiocyanide

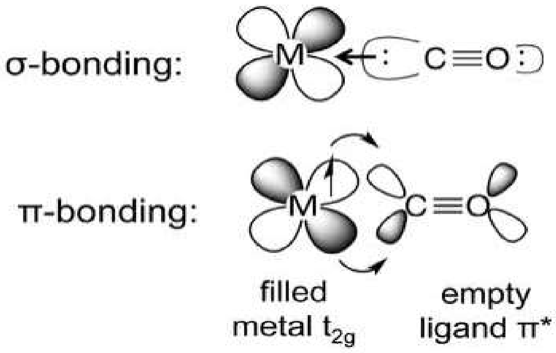
Chelate ligand

Ligands having more than two donor atoms are called polydentate or multidentate ligands. Multidentate ligands are also known as a chelating ligands, it results in the formation of a stable cyclic ring thus the complexes formed are called chelates. Chelating ligands are usually organic compounds.

3. **Based on bonding interaction between metals and ligands :**

(i) pi-acceptor ligand - ligand that donates a pair of electrons from a lone pair to the metal centre but also has the ability to accept electron density from the metal d orbitals into either d-orbitals or pi-antibonding orbitals.

(ii) sigma-donor ligand - a ligand that acts as a Lewis base donating electrons from a lone pair to the metal centre.



3. **Coordination sphere :** The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere. Coordination sphere is written inside square brackets, for examples, $[Co(NH_3)_6]^{3+}$. Remember that the central metal atom and the ligands inside the square brackets behave as a single entity.
4. **Ionisation sphere** constitutes of the ions which may satisfying the primary valency.
5. **Coordination number (C.N.) :** The coordination number (C.N.) of a metal atom/ion in a complex is the total number of e^- pairs accepted by central metal atom/ion from ligands through coordinate bond. Some common coordination numbers of metal ions are summarised in the following Table (1) and examples of complexes of various coordination number are given in Table (2).

Table (1) Coordination number of metal ion

Metal ion	Coordinaton number
Ag^{+}	2,4
Cu^{+}	2,4
Cu^{2+}	4,6
Au^{+}	2,4
Ca^{2+}	4,6
Fe^{2+}	4,6
Fe^{3+}	6
Co^{2+}	4,6
Co^{3+}	6
Ni^{2+}	4,6
Zn^{2+}	4
Al^{3+}	4,6
Sc^{3+}	6
Cr^{3+}	6
Pd^{2+},Pt^{2+}	4
Pd^{4+}, Pt^{4+}	6

Table (2) Examples of complexes of various coordination numbers

Complex	Coordinaton number
$[Ag(NH_3)_2]^{+}$	2
$[HgI_3]^{-}$	3
$[PtCl_4]^{2-}$, $[Ni(CO)_4]$	4
$[Fe(CO)_5]$, $[Ni(CN)_5]^{3-}$	5
$[Co(NH_3)_6]^{3+}$, $[W(CO)_6]$	6
$[Mo(CN)_7]^{3-}$	7
$[Mo(CN)_8]^{4-}$	8

6. **Oxidation number/oxidation state (O.S.) of central metal ion :** The oxidation number of the central atom in a complex is defined as the charge is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. For example the oxidation number of Fe, CO and Ni in $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$ and $[Ni(CO)_4]$ are +2, +3 and zero, respectively. Let us take few examples to illustrate this.

(i) **Potassium Ferrocyanide, $K_4[Fe(CN)_6]$** Since the complex has four monovalent cations outside the coordination sphere, the complex ion must carry four negative charges, i.e., it is

$[Fe(CN)_6]^{4-}$. The number of CN^- ions (univalent ions), that is 6 represents the coordination number of Fe cation. The oxidation state of iron can be determined easily as below, knowing that cyanide ions are unidentate and the complex on the whole carries a -4 charge.

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

$$x + (-6) = -4$$

$$\therefore \quad x = +2$$

Thus, here iron is present as Fe^{2+} or Fe(II).

(ii) $\mathbf{[Cr(C_2O_4)_3]^{3-}}$ Note that here the oxalate ligand is dinegative ion, that is, it is bidentate. Therefore three oxalate ligands carry a total charges of –6 and coordination number of Cr is 6. Now since the complex carries –3 charge, therefore the oxidation state of Cr is +3.

(iii) $\mathbf{[Ni(CO)_4]}$ Here the coordination number of Ni is 4 as carbonyl group is unidentate. Further since the complex as well as the ligands have no charge, nickel atom must also be neutral , that is, it is in zero oxidation state.

18 electron rule :

The 18 electron rule states that, for a transition element to be stable it needs to have 18 electrons in its valence shell so that they have the configuration of an inert gas, and that they form chemical bonds in order to attian this state.

This rule was proposed in order to explain the stability of transition metals and the organometallic compounds which they form.

7. Effective atomic number - EAN (Sidgwick Theory and EAN Rule) : Total no. of electrons present on the central metal atom/ion after accepting electron pairs from donor atom of the ligands through coordinate bond is called E.A.N. of central metal atom/ion.

$$\boxed{\text{E.A.N} = \text{Z} - \text{O.S.} + 2 \times \text{C.N.}}$$

Sidgwick also suggested that the metal ion will continue accepting electron pairs till the totalnumber of electrons in the metal ion and those donated by ligands is equal to that of the nearest noble gas. This total number of electrons is called effective atomic number (EAN) of the metal /ion. This will become clear by taking the example of hexamminecobalt(III)ion $[Co(NH_3)_6]^{3+}$

Atomic number of cobalt = 27

In the present complex, cobalt is present in the oxidation state of +3.

∴ E.A.N. of Co^{3+} = Z – O.S. + 2 × C.N.

= 27 – 3 + 2 × 6 = 36

In the above example since the number 36 corresponds to the atomic number of krypton, according to Sidgwick, the complex will be stable. Though EAN rule (which states that those complexes are stable whose EAN is the same as the atomic number of the next noble gas) is applicable in many metal carbonyl complexes, however there are several examples in which EAN rule is not obeyed.

IUPAC nomenclautre of complexes :

The rules for the systematic naming of coordination compounds are as follows.

(i) The positive part is named first followed by the negative part, whether it is simple or complex.

(ii) In naming of a complex ion, the ligands are named first in alphabetical order, followed by naming of central metal atom /ion.

(iii) When there are several monodentate ligands of the same kind, then we normally use the prefixes di, tri tetra, penta and hexa to show the number of ligands of that type. If ligand's name already contain any of these prefix , then to avoid confusion in such cases, bis, tris and tetrakis are used instead of di, tri and tetra and name of the ligand is placed in parenthesis. For example, bis(ethylene diamine) for two **en**-ligands.

(iv) Negative ligands have suffix-o, positive ligands have suffix -ium, where as neutral ligands have no specific suffix.

The names of negative ligands ending with -ide are changed to 'o'. For example,

F^- (fluoro /fluorido)
Cl^- (chloro /chlorido)
Br^- (bromo / bromido)
I^- (iodo / iodido)

H^- (hydrido)
OH^- (hydroxo/hydroxido)
O^{2-} (oxo/oxido)
O_2^{2-} (peroxo/peroxido)

HS^- (mercapto)
S^{2-} (sulphido)
CN^- (cyano/Cyanido)

Ligands ending with -ate/-ite are changed to -ato/-ito. For example, SO_4^{2-} (sulphato), SO_3^{2-} (sulphito) etc.

Positive groups end with -ium. For example, $NH_2 – NH_3^+$ (hydrazinium), NO^+ (nitrosonium)

(v) Neutral ligands have no special ending and usually common name are provided to neutral ligands except NH_3 (ammine), H_2O (aqua), CO (carbonyl), NO(Nitrosyl).

(vi) The oxidation state of the central metal ion is shown by Roman numbers in brackets immediately following its name.

(vii) Complex positive ions and neutral molecules have no special ending but complex negative ions end with ate suffix in metal.

Table (3) Complex ions

Example	Negative complex	Positive/neutral complex
Ni	nickelate	nickel
Pb	plumbate	lead
Sn	stannate	tin
Fe	ferrate	iron

(viii) If the complex compound contains two or more metal atoms, then it is termed as polynuclear complex compound. The bridging ligand which links the two metal atoms together are indicated by the prefix μ–. If there are two or more bridging groups of the same kind, this is indicated by di– μ–, tri – μ– and so on. If a bridging group bridges more than two metal atoms, it is shown as μ^3, μ^4, μ^5 or μ^6 to indicate how many atoms arebonded.

(ix) Ambidentate ligands may be attached through different atoms. Thus, M–NO_2 is called nitro and M–ONO is called nitrito. Similarly M–SCN (thiocyanato) or M–NCS (Isothiocyanato). These may be named systematically, thiocyanato–S and thiocyanate –N respectively to indicate which atom is bonded to the metal. This convention may be extended to other cases where the mode of linkage is ambiguous.

(x) If any lattice component such as water or solvent of crystallisation are present, these follow their name, and are proceeded by the number of these groups in Arabic numericals. These rules are illustrated by the following examples.

(a) Complex cations	**IUPAC name**
$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride
$[CoCl(NH_3)_5]^{2+}$	Pentaamminechloridocobalt(III) ion
$[CoSO_4(NH_3)_4]NO_3$	Tetraamminesulphatocobalt(III) nitrate
$[Cd(SCN)_4]^{2+}$	Tetrathiocyanato-S-cadmium(II) ion.

(b) Complex anions	
$Li[AlH_4]$	Lithium tetrahydridoaluminate(III)
$Na[ZnCl_4]$	Sodium tetrachloridozincate(II)
$K_4[Fe(CN)_6]$	Potassium hexacyanidoferrate(II)
$Na_2[Fe(CN)_5NO]$	Sodium pentacyanidonitrosyliumferrate(II)
$K_2[OsCl_5N]$	Potassium pentachloridonitridoosmate(VI)
$Na_3[Ag(S_2O_3)_2]$	Sodium bis(thiosulphato)argentate(I)
$K_2[Cr(CN)_2O_2(O_2)NH_3]$	Potassium amminedicyanidodioxidoperoxidochromate(VI)

(c) Organic groups

$[Pt(py)_4]\ [PtCl_4]$	tetrapyridineplatinum(II) tetrachloridoplatinate(II)
$[Cr(en)_3]Cl_3$	Tris(ethylenediamine) chromium(III)chloride
$[CuCl_2(CH_3NH_2)_2]$	Dichloridodimethylaminecopper(II)
$Fe(C_5H_5)_2$	Bis(η^5–cyclopentadienyl)iron(II)
$[Cr(C_6H_6)_2]$	Bis(η^6-benzene)chromium(0)

(d) Bridging groups

$[(NH_3)_5Co.NH_2.Co(NH_3)_5](NO_3)$	μ-amidobis[pentaamminecobalt(III)] nitrate
$[(CO)_3Fe(CO)_3Fe(CO)_3]$	Tri-μ-carbonyl-bis [tricarbonyliron(0)]
$[Be_4O(CH_3COO)_6]$	Hexa-μ-acetato(O,O')-μ^4-oxidotetraberyllium(II) (basic beryllium acetate)

(e) Hydrates

$AlK(SO_4)_2.12H_2O$	Aluminium potassium sulphate 12-water

Writing the formula of a coordination compound :

When writing the formula of complexes, the complex ion should be enclosed by square brackets. The metal is written first, then the coordinated groups are listed in the order : negative ligands, neutral ligands, positive ligands (and alphabetically according to the first symbol within each group).

[M negative ligands, Neutral ligands, positive ligands]n ±

Isomerism in compelxes :

Complex compounds that have the same chemical formula but a different arrangements of atoms and because of this they differ in one or more physical & chemical properties. These are of two types, namely structural and stereoisomers.

Type of isomerism

Structural isomerism
–Ionisation isomerism
–Hydrate isomerism
–Linkage isomerism
–Coordination isomerism
–Coordination position isomerism

Space/stereo isomerism
–Geometrical isomerism
–Optical isomerism

Structural Isomerism

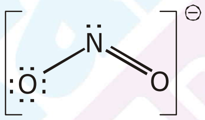
Structural isomers are those isomers in which the atoms are completely arranged in a different order with the same molecular formulas. These are the molecules having the same kind of molecular formula with different connectivities depending upon the order they are put together.

(i) Ionisation Isomerism : This type of isomerism is due to the exchange of groups between the complex ion and ions outside it. $[Co(NH_3)_5Br]SO_4$ is red -violet. An aqueous solution of it gives a white precipitate of $BaSO_4$ with $BaCl_2$ solution, thus confirming the presence of free SO_4^{2-} ions. In contrast $[Co(NH_3)_5SO_4]Br$ is red. A solution of this complex does not give a positive sulphate test with $BaCl_2$. It does give a cream coloured precipitate of AgBr with $AgNO_3$, thus confirming the presence of free Br^- ions. Other examples of ionisation isomerism are $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$
and $[Co(en)_2NO_2.Cl]SCN$, $[Co(en)_2NO_2.SCN]Cl$ and $[Co(en)_2Cl.SCN]NO_2$.

(ii) Hydrate isomerism : These isomers arise by the exchange of groups in the complex ion with water. Three isomers of $CrCl_3.6H_2O$ are known. From conductivity measurements and quantitative precipitation of the ionised Cl^-, they have been given the following structures

$$[Cr(H_2O)_6]Cl_3$$
$$[Cr(H_2O)_5Cl]Cl_2.H_2O$$
$$[Cr(H_2O)_4Cl_2]Cl.2H_2O$$

(iii) Linkage Isomerism : This type of isomerism arises when the ligand attaches to the central metal ion of a complex in different ways. Such ligands are called ambidentate ligands. Nitrite ion has electron pairs available for coordination both on N and O atoms.



Examples :

(a) $[Co(NH_3)_5\ ONO]Cl_2$ pentaamminenitrito-O-cobalt(III) chloride (red)

and

$[Co(NH_3)_5\ NO_2]\ Cl_2$ pentaamminenitrito-N-cobalt-(III) chloride (yellow)

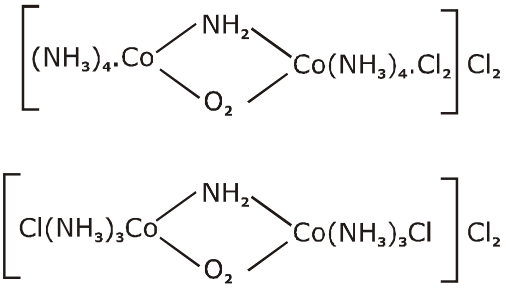
(b) $[Mn(CO)_5.SCN]^+$ pentacarbonylthiocyanto–S-manganese(II) ion

and

$[Mn(CO_5)\ NCS]^+$
pentacarbonylthiocyanato–N-manganese(II) ion

(iv) Coordination Isomerism : When both the cation and anion are complex ions, then isomerism may be caused by the interchange of ligands between the anion and cation. For example $[Pt(NH_3)_4]\ [PtCl_4]$ and $[PtCl(NH_3)_3]\ [PtCl_3(NH_3)]$. These isomers are called coordination isomers.

(v) Coordination Position Isomerism : In polynuclear complexes, an interchange of ligands between the metal nuclei gives rise to coordinaton position isomerism, for example.



Coordination position isomers

Polymerisation Isomerism : This is not a true type of isomerism because it occurs among compounds having the same empirical formula, but different molecular formula. Thus, $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_4][PtCl_4]$, $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$ and $[Pt(NH_3)_3Cl]_2[PtCl_4]$ all have the same empirical formula.

Stereo Isomerism :

These are the isomers in which ligands have different spacial arrangements around central metal atom /ion in 3-D space.

(i) Geometrical Isomerism : Geometrical isomers are the isomers in which the atoms are joined to one another in the same way but differ in space because some ligands occupy different relative positions in space.

Sq. planar complex with symmetrical bidentate ligand – No G.I.

Sq. planar complex can exhibit G.I. only in two types $\begin{bmatrix} M(AB)_2 \\ M(AB)ab \end{bmatrix}$

On increasing number of one type of ligand total number of geometrical isomers decreases. Octahedral $[M(AA)a_4]$ and $[M(AA)_3]$ type of complex can not exhibit G.I. $[M(AA)_2a_2]$ type of complex have two G.I. (cis & trans)

* $[M(AA)_2a_2]$ type of complex gives three stereoisomer :

(1) cis (2) trans (3) mirror image of cis

(a) Geometrical Isomerism (GI)

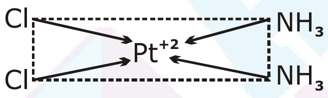
- CN = 4
  - Tetrahedral (No G.I.)
  - Square planar
    - Ma_4 – NO G.I.
    - Ma_3 – NO G.I.
    - Ma_2b_2 – 2 G.I. (cis & trans)
    - Ma_2bc – 2 G.I. (cis & trans)
    - $Mabcd$ – 3 G.I.
- CN = 6 (Octahedral)
  - $Mabcdef$ – 15 G.I.
  - Ma_2bcde – 9 G.I.
  - Ma_2b_2cd – 6 G.I.
  - $Ma_2b_2c_2$ – 5 G.I.
  - Ma_3bcd – 4 G.I.
  - Ma_3b_2c – 3 G.I.
  - Ma_3b_3 – 2(Fac - Mer)
  - Ma_4bc – 2(cis-trans)
  - Ma_4b_2 – 2(cis-trans)
  - Ma_5b – NO G.I.
  - Ma_6 – NO G.I.

Geometrical Isomerism in complex compound having C.N. = 4

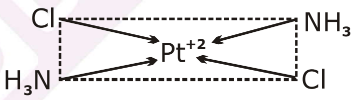
Tetrahedral complexes (sp^3 hydrididation) never exhibit geometrical isomerism, however, it is very common in square planar complexes (dsp^2 hybridisation).

For Example

(a) $[Pt(NH_3)_2Cl_2]$ can exist as two geometrical isomers.

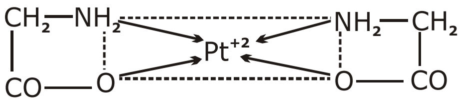


cis form (orange yellow)

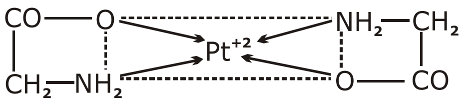


trans form (pale yellow)

(b) $[Pt(Gly)_2]$ also exist in two geometrical isomers.



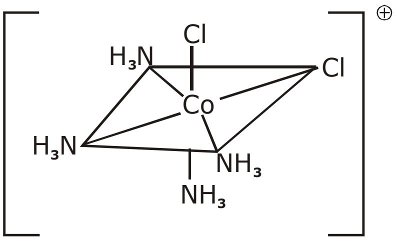
cis form



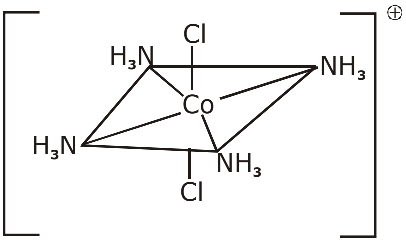
trans form

Geometrical Isomerism in Complex compound having coordination number 6

(a) $[Co(NH_3)_4Cl_2]^+$ can exist as

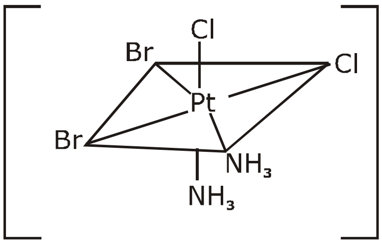


cis form (violet)

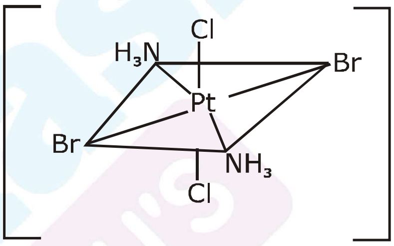


trans form (green)

(b) $[Pt(NH_3)_2Cl_2Br_2]$ can exist as five G.I. because it is kind of $Ma_2b_2c_2$ complex, (aa) (bb) (cc), (aa)(bc)(bc), (bb)(ac)(ac), (cc)(ab)(ab), (ab)(ac)(bc),



cis form

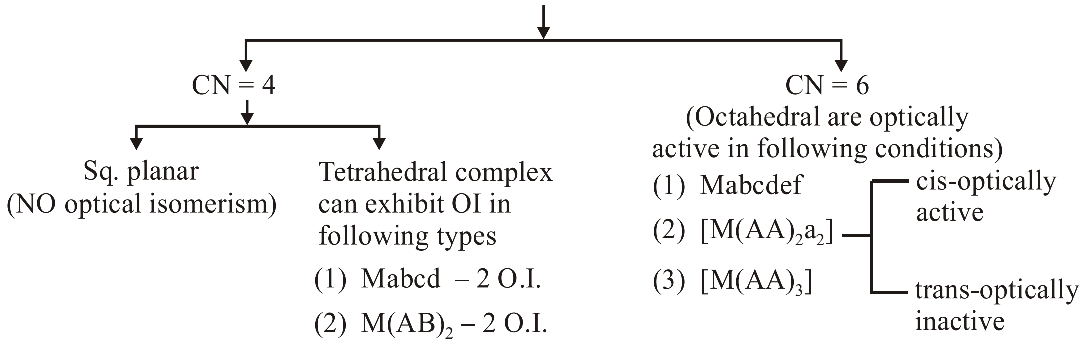


trans form

There are many more trans arrangements.

(ii) **Optical Isomerism :** A coordination compound which can rotate the plane of polarised light is said to be optically active. When the coordination compounds have same formula but differ in their ability to rotate directions of the plane of polarised light are said to exhibit optical isomerism and the molecules are optical isomers. Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. This is due to the absence of elements of symmetry in the complex. The two forms are called dextro(d) and laevo(l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left).

(b) Optical Isomerism (OI)



CN = 4

Sq. planar (NO optical isomerism)

Tetrahedral complex can exhibit OI in following types

(1) Mabcd – 2 O.I.

(2) $M(AB)_2$ – 2 O.I.

CN = 6

(Octahedral are optically active in following conditions)

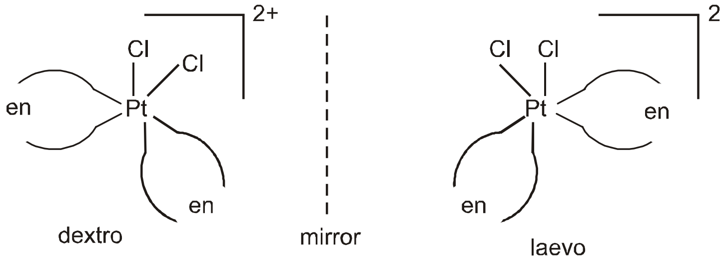
(1) Mabcdef

(2) $[M(AA)_2a_2]$ — cis-optically active; trans-optically inactive

(3) $[M(AA)_3]$

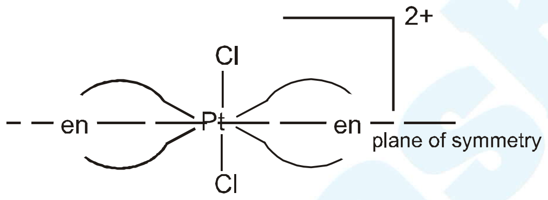
(iii) Optical isomerism is common in octahedral complexes involving bidentate ligand.

(iv) Cis-isomer of $[PtCl_2(en)_2]^{2+}$ show optical isomerism as shown below because of the absence of plane of symmetry as well as centre of symmetry.

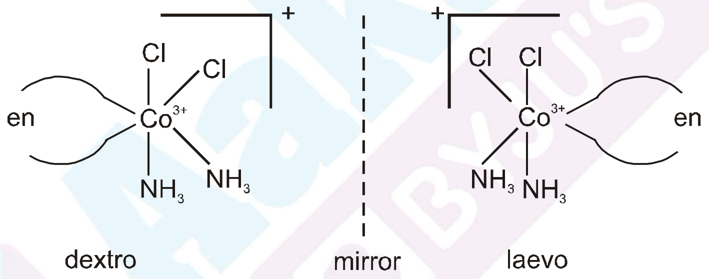


d and ℓ of cis-$[PtCl_2(en)_2]^{2+}$

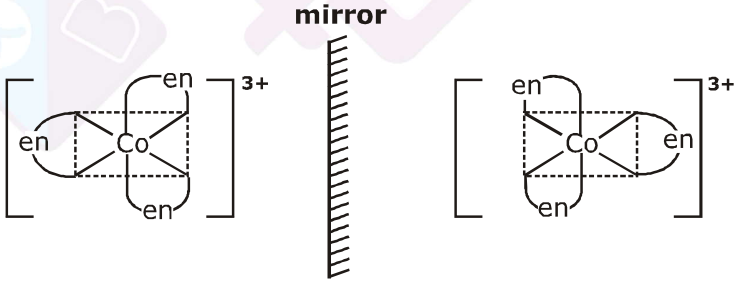
But trans isomer of $[PtCl_2(en)_2]^{2+}$ does not show optical isomerism.



cis-$[Co(NH_3)_2Cl_2(en)]^+$ can show optical isomerism due to the absence of plane of symmetry as well as centre of symmetry.



(v) Optical isomers of $[Co(en)_3]^{3+}$ are



Bonding in complexes

Werner's Coordination Theory :

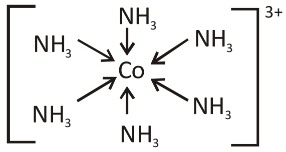
Alfred Werner (1866-1919), a Swiss chemist was the first to formulate his ideas about the structures of coordination compounds. He prepared and characterised a large number of coordination compounds and studied their physical and chemical behaviour by simple experimental techniques.

The fundamental postulates of Werner's theory are as follows:

(i) Metals possess two types of valencies, namely, primary (principle or ionisable) valency and secondary (auxillary or non-ionisable) valency.

In modern terminology, the primary valency corresponds to oxidation number and secondary valency to coordination number. According to Werner, primary valencies are shown by dotted lines and secondary valencies by solid lines.

(ii) Every metal cation in a complex compound has a fixed number of secondary valencies, for example, $CoCl_36NH_3$, Co^{3+} cation has six secondary valencies.



(iii) Primary valency is satisfied by negative ions, whereas secondary valency is satisfied either by negative ions or by neutral molecules.

(iv) Primary valency has non-directional character, whereas secondary valency has directional character, therefore a complex ion has a definite geometry eg. $[Co(NH_3)_6]^{3+}$ – octahedron.

(v) It is the directional nature of secondary valency due to which coordination compounds exhibits the phenomenon of isomerism.

Werner's Representation of Complexes

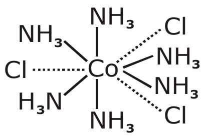
Consider the case of $CoCl_3.xNH_3$ where the primary valency = +3 and the seconary valency = 6.

Various structures are summarised in Table -4.

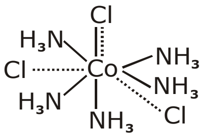
	Werner complexes	*Modern formula*	*Ionisation*	*Secondary valency satisfied by*	*Primary valency satisfied by*
(A)	$CoCl_3.6NH_3$	$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+} + 3Cl^-$	six (NH_3)	three (Cl^-)
(B)	$CoCl_3.5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	$[Co(NH_3)_5Cl]^{2+}+2Cl^-$	five (NH_3) and one (Cl^-)	including one (Cl^-) with dual nature
(C)	$CoCl_3.4NH_3$	$[Co(NH_3)_4Cl_2]Cl$	$[Co(NH_3)_4Cl_2]^++Cl^-$	four (NH_3) and two (Cl^-)	three (Cl^-) including two (Cl^-) with dual nature
(D)	$CoCl_3.3NH_5$	$[Co(NH_3)_3Cl_3]$	$[Co(NH_3)_3]Cl_3$	three (NH_3) and three (Cl^-)	three (Cl^-) all with dual nature

* From Table 4, it is clear that conduction of the complexes will be in the order D < C < B < A.

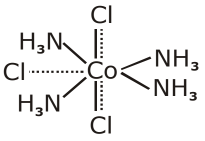
* They are represented as



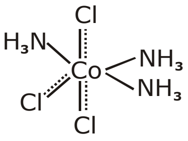
(A)



(B)



(C)



(D)

Valence Bond Theory :

It was developed by Pauling. The salient features of this theory are summerised below :

(i) Under the influence of a strong field ligands, the electrons of central metal ion can be forced to pair up against the Hund's rule of maximum multiplicity.

(ii) Under the influence of weak field ligands, electronic configuration of central metal atom / ion remains same.

(iii) If the complex contains unpaired electrons, it is paramagnetic in nature, whereas if it does not contain unpaired electrons, then it is diamagnetic in nature and magnetic moment is calculated by spin only formula.

$$\text{Magnetic moment } (\mu) = \sqrt{n(n+2)}\,\text{BM}$$

where n is the number of unpaired electrons in the metal ion.

Table 5 Relation between unpaired electrons and magnetic moment

Magnetic moment (Bohr magnetons)	0	1.73	2.83	3.87	4.90	5.92
Number of unpaired electrons	0	1	2	3	4	5

Thus, the knowledge of the magnetic moment can be of great help in ascertaining the type of complex.

(iv) When ligands are arranged in increasing order of their splitting power then an experimentally determined series was obtained named as spectrochemical series.

$$\underbrace{I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < EtOH < CH_3COO^- \approx C_2O_4^{2-} < H_2O}_{\text{Weak field ligands}}$$

$$< \underbrace{EDTA < NH_3 \approx py < en < dipy < phen < NO_2^- < CN^- < CO}_{\text{Strong field ligands}}$$

(v) The central metal ion has a number of empty orbitals for accommodating electrons donated by the ligands.
The number of ligands surrounds the metal ion is the coordination number of metal.

(vi) The atomic orbitals (s, p or d) of the metal ion hybridise to form hybrid orbitals with definite directional properties. These hybrid orbitals now accept e^- pairs from ligands to form coordination bonds.

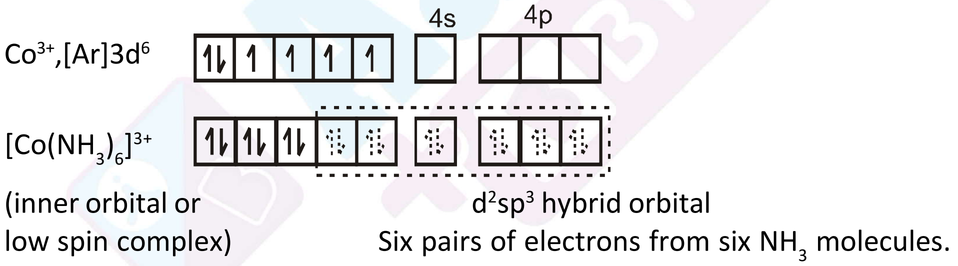
(vii) The d-orbitals involved in the hybridisation may be either inner (n –1) d orbitals or outer n d-orbitals. The complexes formed in these two ways are referred to as inner orbital complexes and outer orbital complexes, respectively.

Following table provides the types of hybridisation with different coordination number.

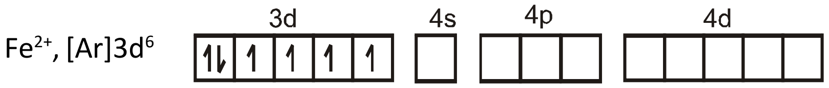
Coordination number of metal	Type of hybridisation	Shape of complex	Types of d-orbitals
2	**sp**	**Linear**	**–**
4	sp^3	Tetrahedral	–
4	dsp^2	Square planer	$d_{x^2-y^2}$
4	d^3s	Tetrahedral	d_{xy}, d_{yz}, d_{xz}
5	sp^3d	Trigonal bipyramidal	d_{z^2}
5	dsp^3	Square pyramidal	$d_{x^2-y^2}$
6	sp^3d^2	Octahedral	$d_{x^2-y^2}$ d_{z^2}
6	d^2sp^3	Octahedral	$d_{x^2-y^2}$ d_{z^2}

It is to be noted that the type of hybridisation of metal and shape of complex involved can be predicted conveniently, if some characteristic of the complex like magnetic nature, geometry or whether exhibits isomerism or not, etc., be known.

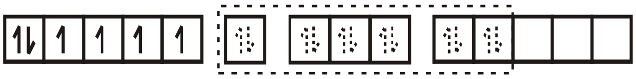
Coordination Number Six.
In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration represented as shown below.



Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. Since in the formation of complex the inner d-orbital (3d) is used in hybridisation, the complex is called an inner orbital or low spin or spin paired complex.
The complex $[FeF_6]^{4-}$ is paramagnetic and uses outer orbital (4d) in hybridisation (sp^3d^2) ; it is thus called as outer orbital or high spin or spin free complex. So,



$[FeF_6]^{4-}$



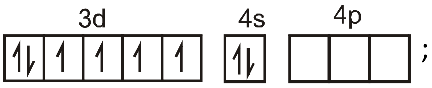
sp^{3}d^2 hybrid orbitals

Six pairs of electrons from six F$^-$ ions.

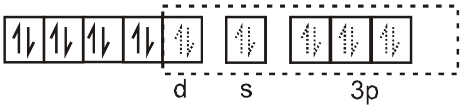
Coordination Number Five :

In the square pyramidal complex $[Fe(CO)_5]$, Iron is in 0 oxidation state

Fe^0 [Ar] 3d^{6}4s^2



$[Fe\ (CO)_5]$

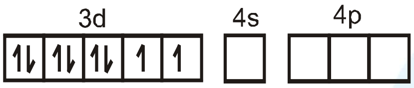


The compound is diamagnetic as it contains 0 unpaired electrons

Coordination Number Four :

In the paramagnetic and tetrahedral complex $[NiCl_4]^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration 3d^8. The hybridisation scheme is as shown in figure.

Ni^{2+}, [Ar]3d^8



$[NiCl_4]^{2-}$

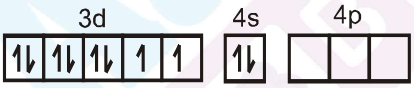
sp^3 hybrid orbitals

Four pairs of electrons from four Cl$^-$ ions.

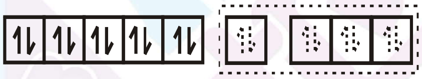
The compound is paramagnetic since it contains two unpaired electrons.

Similarly complex $[Ni(CO)_4]$ has tetrahedral geometry and is diamagnetic as it contains no unpaired electrons. The hybridisation scheme is as shown in figure.

Ni^0, [Ar] 3d^8 4s^2



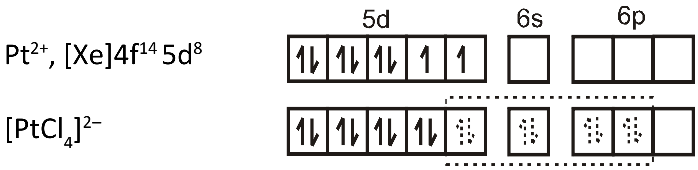
$[Ni(CO)_4]$



sp^3 hybrid orbitals

Four pairs of electrons from four CO molecules.

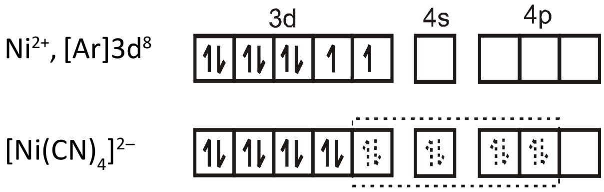
Complexes of Pd(II) and Pt (II) are usually four-coordinate, square planar, and diamagnetic and this arrangement is often found for Ni(II) complexes as well, e.g., in $[Ni(CN)_4]^{2-}$ (here nickel is in +2 oxidation state and has electronic configuration 3d^8). In as much as the free ion is in the ground state each case is paramagnetic, the bonding picture has to include pairing of electrons as well as ligand-metal-ligand bond angles of 90º and this occurs via hybridisation of one (n–1) d, one ns and two np orbitals to form four equivalent dsp^2 hybrid orbitals directed toward the corners of a square. These orbitals then participate in covalent coordinate σ bonds with the ligands, the bonding electron pairs being furnished by the ligands. The hybridisation scheme for $[PtCl_4]^{2-}$ is as shown in figure.



dsp^2 hybrid orbitals

Four pairs of electrons from four Cl$^-$ ions.

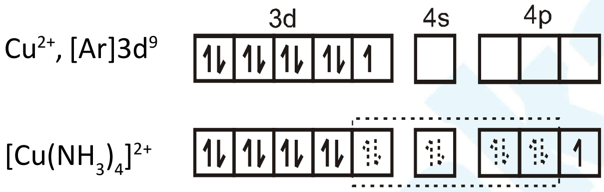
Similarly the hybridisation scheme for [Ni(CN)$_4$]$^{2-}$ is as shown in figure.



dsp^2 hybrid orbitals

Four pairs of electrons from four CN$^-$ ions.

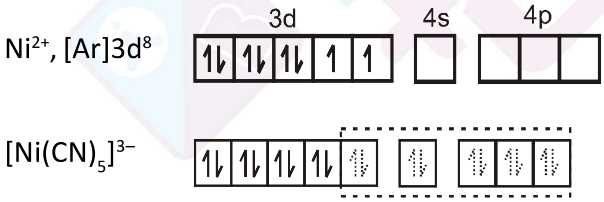
It is found that [Cu(NH$_3$)$_4$]$^{2+}$ is square planar and paramagnetic with one unpaired electron in 4p-orbital. The hybridisation scheme is as follow.



dsp^2 hybrid orbitals

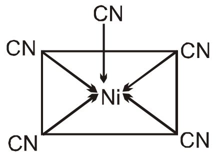
Four pairs of electrons from four NH$_3$ molecules.

Note. [Ni(CN)$_5$]$^{3-}$ is found to be diamagnetic with 2 types of Ni – C bond lengths, out of which four bond lengths are found to be equal and the fifth one is different. The hybridisation scheme for [Ni(CN)$_5$]$^{3-}$ is as shown in figure.



dsp^3 hybrid orbitals

Five lone pairs of electrons from five CN$^-$ ions.



square pyramidal.

While the valence bond theory, to a large extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following **shortcomings** :

1. A number of assumptions are involved.
2. There is no quantitative interpretation of magnetic data.
3. It has nothing to say about the spectral (colour) properties of coordination compounds.
4. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
5. It does not make exact predictions regarding the tetrahedral and square-planar structures of 4-coordinate complexes.
6. It does not distinguish between strong and weak ligands.

Limitations of valence bond theory

(i) Correct magnetic moment of complex compounds cannot be theoritically measured by Valence bond theory.

(ii) The theory does not offer any explanation about the spectra of complex (i.e., why most of the complexes are coloured).

(iii) Theory does not offer any explanation for the existence of inner -orbital and outer -orbital complexes.

(iv) In the formation of $[Cu(NH_3)_4]^{2+}$, one electron is shifted from 3d to 4p orbital. The theory is silent about the energy availability for shifting such an electron.
If such an electron can be easily lost then why $[Cu(NH_3)_4]^{2+}$ complex does not show reducing properties ?

Crystal Field Theory (CFT) :

Crystal field theory is now much more widely accepted than the valence bond theory. It is assumed that the attraction between the central metal and ligands in a complex is purely electrostatic. The transition metal which forms the central atom cation in the complex is regarded as a positive ion of charge equal to its oxidation state. It is surrounded by negative ligands or neutral molecules which have a lone pair of electrons. If the ligand is a neutral molecule such as NH_3, the negative end of the dipole in the moelcule is directed toward the metal cation. The electrons on the central metal are under repulsive forces from those on the ligands. Thus, the electrons occupy the d orbital remains away from the direction of approach of ligands.

In the crystal field theory, the following assumptions are made.

(i) Ligands are treated as point charges.

(ii) There is no interaction between metal orbitals and ligands orbitals.

(iii) All the d orbitals on the metal have the same energy (that, is degenerate) in the free atom. However, when a complex, is formed, the ligands destroy the degeneracy of these orbitals, that is , the orbitals now have different energies. In an isolated gaseous metal ion, all five d orbitals have the same energy and are termed degenerate. If a spherically symmetrical field of ligands surrounds the metal ion, the d orbitals remain degenerate. However, the energy of the orbitals is raised because of repulsion between the field of ligands and electrons on the metal. In most transition metal complexes, either six or four ligands surround the metal, giving octahedral or tetrahedral/square planar structures. In both these cases, the field produced by the ligands is not spherically symmetrical. Thus, the d orbitals are not all affected equally by the ligand field.

In an octahedral complex, the metal is at the centre of the octahedron and the ligands are at the six corners.

The direction x, y and z points to three adjacent corners of the octahedron as shown in the fig.

The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes x,y and z. The lobes of the t_{2g} orbitals (d_{xy}, d_{xz} and d_{yz}) point in betwen the axes. If follows that the approach of six ligands along the x, y, z, –x, –y, and –z directions will increase the energy of the $d_{x^2-y^2}$ and d_{z^2} orbitals while the dxy, dyz and dxz orbitals which are directed between the axes will be lowered in energy relative to the average energy. Thus, under the influence of an octahedral ligand field the d orbitals split into two groups of different energies.

Rather than referring to the energy level of a isolated metal atom. The difference in energy between the two d levels is given by the symbols Δ_0 or 10 Dq.

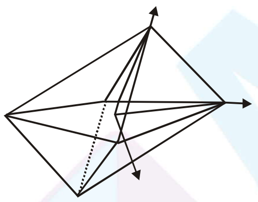


Fig. The directions in an octahedral complex

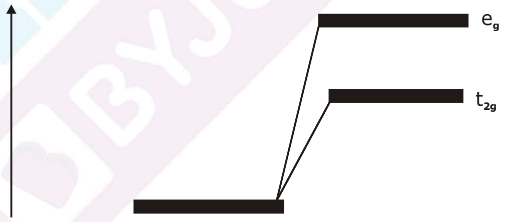


Fig Crystal field spliting of energy levels in an octahedral field

It follows that the e_g orbitals are +0.6 Δ_0 above the average level, and the t_{2g} orbitals –0.4 Δ_0 below the average level.

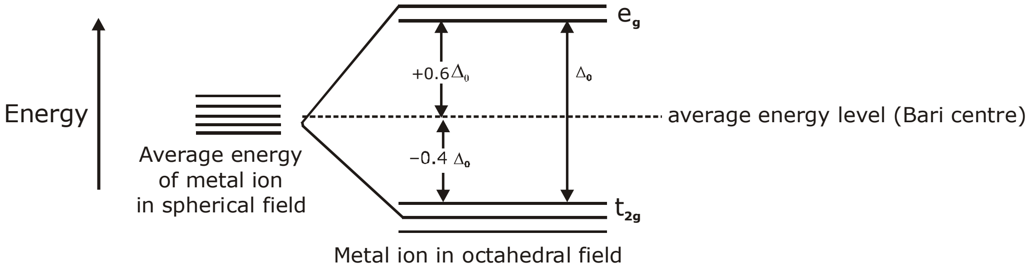
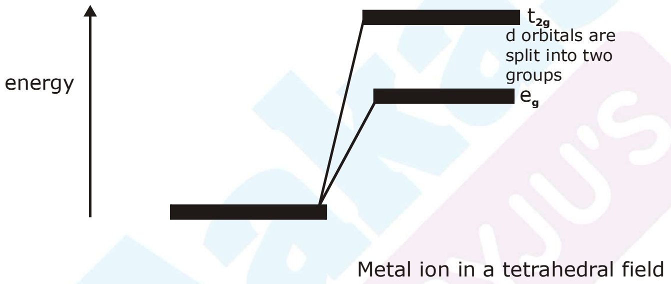


Fig. Diagram of the energy levels of d -orbitals in a octahedral field

Tetrahedral Complexes: A regular tetrahedron is related to a cube. One atom is at the centre of the cube, and alternate four of the eight corners of the cube are occupied by ligands as shown in Fig. The direction x, y and z point to the centres of the faces of the cube. The e_g orbitals point along x, y and z (that is , to centre of the faces.)

Fig. Relation of tetrahedron to a cube

The approach of the ligands raised the energy of both sets of orbitals. The energy of the t_{2g} orbital raised most because they are closest to the ligands. This crystals field splitting is opposite to that in octahedral complexes. The t_{2g} orbitals are 0.4 Δ_t above the average energy of the two groups (Bary centre) and the e_g orbitals are 0.6 Δ_t below the average level.



Free metal ion (five degenerate d orbitals)
Fig Crystal fleld splitting of energy levels in a tetrahedral field

Formula : CFSE = $[-0.4\,(n)\,t_{2g} + 0.6\,(n')\,e_g]\,\Delta_0 + {}^*nP$.

where n & n′ are number of electron(s) in t_{2g} & e_g orbitals respectively and Δ_0 crystal field splitting energy for octahedral complex. *n represents the number of extra electron pairs formed because of the ligands in comparison to normal degenerate configuration.

(b) Crystal field splitting in tetrahedral coordination entities :

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\Delta_0$. This may attributes to the following two reasons.

(i) There are only four ligands instead of six, so the ligand field is only two thirds the size; as the ligand field spliting is also the two thirds the size and (ii) the direction of the orbitals does not concide with the direction of the ligands. This reduces the crystal field spliting by roughly further two third. So $\Delta_t = \frac{2}{3} \times \frac{2}{3} = \frac{4}{9}\Delta_o$.

Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

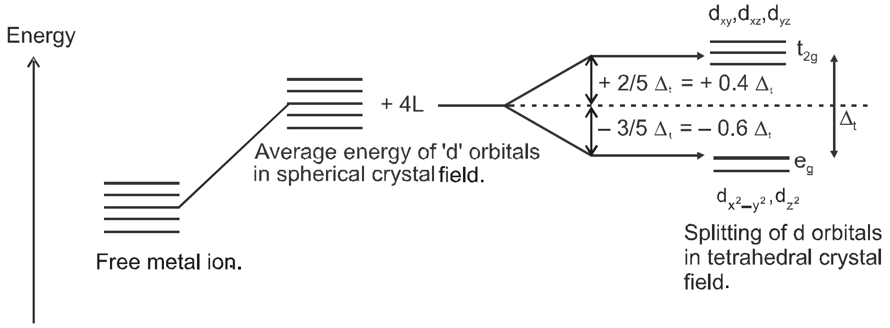


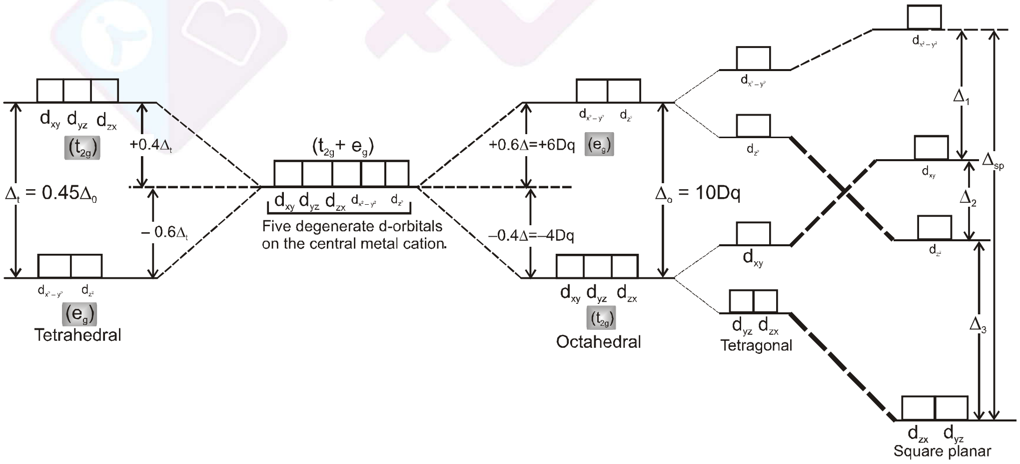
Figure showing crystal field splitting in tetrahedral complex.

Since $\Delta_t < \Delta_o$ crystal field spliting favours the formation of octahedral complexes.

(c) Crystal field splitting in square planar coordination entities :

The square planar arrangement of ligands may be considered to be one derived from the octahedral field by removing two trans-ligands located along the Z-axis. In the process, the e_g and t_{2g} sets of orbitals is lifted i.e., these orbitals will no longer be degenerate.

The four ligands in square planar arrangement around the central metal ion are shown in Fig. As the ligands approach through the axes, they would have greatest influence on $d_{x^2-y^2}$ orbital, so the energy of this orbital, will be raised most. The d_{xy} orbital, lying in the same plane, but between the ligands will also have a greater energy though the effect will be less than that on the $d_{x^2-y^2}$ orbital. On the other hand, due to absence of ligands along Z-axis, the d_{z^2} orbital becomes stable and has energy lower than that of d_{xy} orbital. Similarly d_{yz} and d_{xz} become more stable. The energy level diagram may be represented as Figure along with tetrahedral and octahedral fields.



The value of Δ_{sp} has been found larger than Δ_o because of the reason that d_{xz} and d_{yz} orbitals interact with only two ligands in the square planar complexes, while in octahedral complexes the interaction takes place only with four ligands. Δ_{sp} has been found equal to $1.3\Delta_o$. Thus,

$$\Delta_{sp} = (\Delta_1 + \Delta_2 + \Delta_3) > \Delta_o \qquad \text{and} \qquad \Delta_{sp} = 1.3\,\Delta_o.$$

Colour in Coordination Compounds :

Coordination compounds of transition metals have fascinating colours. According to the crystal field theory the colour is due to the d-d transition of electron under the influence of ligands. We know that the colour of a substance is due to the absorption of light at a specific wavelength in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmission or reflection of the rest of the wavelengths. An object that absorbs all visible light appears black. The mechanism of light absorption in coordination compounds is that photons of appropriate energy can excite the coordination entity from its ground state to an excited state. Consider the Ti(III) ion in solution, that is $[Ti(H_2O)_6]^{3+}$. This is a violet colour octahedral complex, where in the ground state of the complex a single electron is present in t_{2g} level. The next higher state available for the transition is the empty e_g level. If the light corresponding to the energy of yellow-green is absorbed by the complex, it would excite the electron from t_{2g} level to e_g level. Consequently the complex appears violet in colour. In case of copper (II) ions in solution, for example, it can be imagined that one of the d-electrons from the t_{2g} set ($d_{xy,}$ d_{yz}, d_{xz} orbitals) gets excited to the e_g set ($d_{x^2-y^2,}d_{z^2}$ orbitals). In this case since high energy light is transmitted it means that low energy light (red region) is absorbed. For copper (II) ions in aqueous solution, the energy gap Δ_t is relatively small. Table below gives the relationship of the wavelength of light absorbed and the colour observed.

Relationship between the wavelength of light absorbed and the colour observed In some coordination entities

Coordination entity absorbed (nm)	Wavelength of light absorbed	Colour of light	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
$[Co(CN)_6]^{3-}$	310	Ultraviolet	Pale Yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue Green	Purple

Note : (a) In absence of ligand, crystal field splitting does not occur and as a consequence the substance appears colourless. For example ; (i) removal of water from violet coloured complex $[Ti(H_2O)_6]Cl_3$ on heating makes it colourless, (ii) similarly anhydrous copper sulphate ($CuSO_4$) is white, but hydrated copper sulphate ($CuSO_4.5H_2O$) is blue coloured.
(b) The nature of the ligand and the molar ratio of metal : ligands also influence the colour of the complex. For example ; in the pale green complex of $[Ni(H_2O)_6]$, the colour change is observed when ethylenediamine is progressively added to it.

Molar ratio of en : Ni	Coloured observed
1 : 1	Pale blue
2 : 1	Blue/Purple
3 : 1	Violet

Stability of complexes

A coordination compound is formed in solution by the stepwise addition of ligands to a metal ion. Thus, the formation of the complex, ML_n (M = central metal cation, L= monodentate ligand and n = coordination number of metal ion) supposed to take place by the following n consecutive steps.

$$M + L \rightleftharpoons ML;\ K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2;\ K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftharpoons ML_3;\ K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$ML_{n-1} + L \rightleftharpoons ML_n;\ K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

K_1, K_2, K_3........K_n are called stepwise stability constants. With a few exceptions, the values of successive stability constants decrease regularly from K_1 to K_n. The overall stability constant K is given as

$$M + nL \rightleftharpoons ML_n;$$

$$K = K_1K_2K_3....K_n = \frac{[ML_n]}{[M][L]^n}$$

The higher the overall stability constant value of the complex, the more stable it is. Alternatively, 1/K values are called instability constant explains the dissociation of the complex into metal ion and ligands in the solution. The value of the stability constant for some of the complexes are given in the Table.

Table : Stability constant of complexes

Complex	*Stability constant*
$[Cu(NH_3)_4]^{2+}$	4.5×10^{11}
$[Ag(NH_3)_2]^{+}$	1.6×10^{7}
$[Co(NH_3)_6]^{2+}$	1.12×10^{6}
$[Co(NH_3)_6]^{+}$	5.0×10^{33}
$[AgCl_2]^{-}$	1.11×10^{5}
$[AgBr_2]^{-}$	1.28×10^{7}
$[Ag(CN)_2]^{-}$	1.0×10^{22}
$[Cu(CN)_4]^{2-}$	2.0×10^{27}
$[Fe(CN)_6]^{3-}$	7.69×10^{43}

Factors affecting stability of complex compounds :

(i) The values of stability constant differ widely depending on the nature of the metal ion and the ligand. In general higher the charge density on the central ion, greater the stability of its complexes.

(ii) More basic a ligand, the greater is the ease with which it can donate its lone pairs of electrons and therefore, greater is the stability of the complexes formed by it.

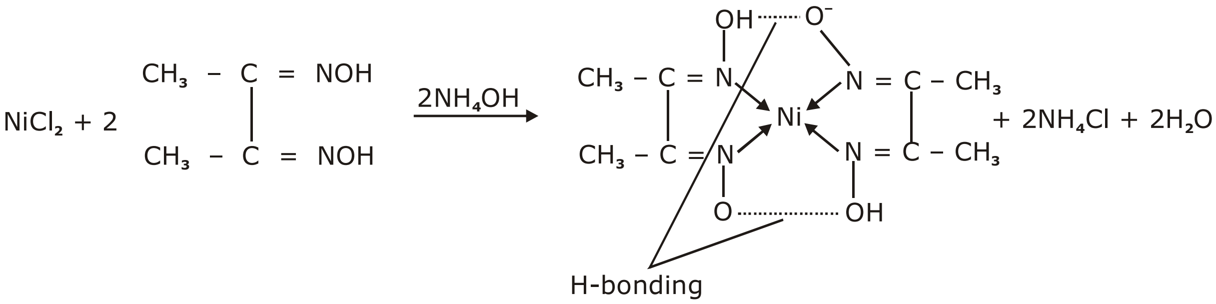
eg. The cyano and ammine complexes are far more stable than those formed by halide ions. This is due to the fact that NH_3 and CN^- are strong Lewis bases.

(iii) Chelating ligands form more stable complexes as compared to mondentate ligands.

Application of complexes

The complexes are of immense importance on account of their applications in various fields. During complex formation there are drastic changes in the properties of metal atom/ion, these changes in properties are made use of in the application of metal complexes.

(i) The detection and estimation of Ni^{2+} is based on the formation of a scarlet red complex with dimethyl glyoxime.



(a) Fe^{3+} is detected by the formation of a blood red coloured complex with KSCN.

$$Fe^{3+} + 3KSCN \longrightarrow \underset{\text{blood red colour}}{Fe(SCN)_3} + 3K^+$$

or

$$[Fe(H_2O)_5(SCN)]^{2+}$$

(b) Many ligands (organic reagents) are used for the gravimetric estimation of number of metal ions.

Metal ion to be estimated	Cu^{2+}	Ni^{2+}	Fe^{3+}	Al^{3+}	Co^{2+}
Organic reagents used	Benzoin oxime	Dimethyl glyoxime	1,20-phenanthroline	8-hydroxy quinoline	α-nitroso β-naphthol

(c) EDTA is used as a complexing agent in volumetric analysis of metal ions like Ca^{2+}, Mg^{2+} and Zn^{2+}.

(d) The coordination compounds of the transition metals exhibit a variety of colours. This property is utilised in colorimetric analysis for the estimation of many metals.

(ii)

(a) Metallurgical process : Silver and gold are extracted by the use of complex formation. Silver ore is treated with sodium cyanide solution by continuous passing of air through the solution. Silver dissolves as a cyanide complex and silver is precipitated by the addition of scrap zinc.

$$\underset{\text{argentine}}{Ag_2S} + 4NaCN \xrightleftharpoons{\text{Air}} \underset{\text{sodium argentocyanide}}{2Na[Ag(CN)_2]} + NaS \xrightarrow{O_2(\text{Air})} Na_2SO_4 + S$$

$$2Na[Ag(CN)_2] + Zn \xrightleftharpoons{\text{Air}} \underset{\text{sodium tetracyanozincate(II)}}{Na_2[Zn(CN)_4]} + 2Ag$$

(b) Native Gold and Silver also dissolve in NaCN solution in presence of the oxygen (air).

$$4Ag + 8NaCN + O_2 + 2H_2O \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

Silver and Gold are precipitated by addition of scrap zinc. Nickel is extracted by converting it into a volatile complex, nickel carbonyl, by use of carbon monoxide (Mond's process). The complex decomposes on heating again into pure nickel and carbon monoxide.

$$Ni + 4CO \longrightarrow Ni(CO)_4 \xrightarrow{\text{heating}} Ni + 4\,CO$$

(iii) **Photography:** In photography, the image on the negative is fixed by dissolving all the remaining silver bromide with hypo solution in the form of a soluble complex.

$$AgBr + 2Na_2S_2O_3 \longrightarrow \underset{\text{(soluble)}}{Na_3[Ag(S_2O_3)_2]} + \underset{\text{(soluble)}}{NaBr}$$

(iv) **Electroplating:** Metal complexes release metal slowly and give a uniform coating of the metal on the desired object. Cyano complexes of silver, gold, copper and other metals are used for the electrodeposition of these metals.

(v) **Biological processes:** Metal complexes are of immense importance in biological processes. Haemoglobin, the red blood pigment, which acts as oxygen carrier to different parts of the body is a complex of iron (II). Vitamin B_{12} is a complex of cobalt metal. The green colouring matter of plants, called chlorophyll, is a complex of magnesium. It acts as a catalyst in photosynthesis.

Organometallic compound

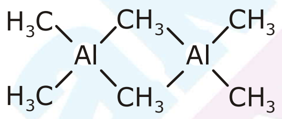
Introduction

Organometallic compounds are defined as those compounds in which the carbon atoms of organic (usually alkyl or aryl) groups are directly bonded to metal atoms. The compounds of elements such as boron, phosphorus, silicon, germanium and antimony with organic groups are also included in organometallics. Many organometallic compounds are important reagents which are used for the synthesis of organic compounds.

(a) Grignard reagents, R – Mg – X where R is an alkyl or aryl group and X is a halogen.

(b) Zinc compounds of the formula R_2Zn such as $(C_2H_5)_2Zn$. (isolated by Frankland).

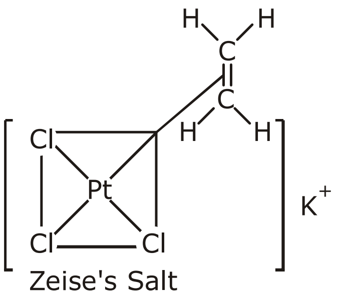
Other similar compound are $(CH_3)_4Sn$, $(C_2H_5)_4Pb$, $Al_2(CH_3)_6$, $Al_2(C_2H_5)_6$, $Pb(CH_3)_4$ etc.



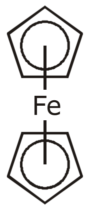
$Al_2(CH_3)_6$ is a dimeric compound and has a structure similar to diborane, (B_2H_6). It is an electron deficient compound and two methyl groups act as bridges between two aluminium atoms.

Pi-bonded organometallic compounds : These are the compounds of metals with alkenes, alkynes, benzene and other ring compounds. In these complexes, the metal and ligand form a bond that involves the π-electrons of the ligand. Three common examples are Zeise's salt, ferrocene and dibenzene chromium.

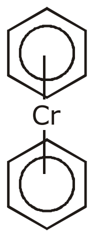
These are shown below.



Zeise's Salt
$K\{PtCl_3(\eta^2-C_2H_4)\}$



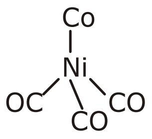
Ferrocene
$Fe(\eta^5-C_5H_5)_2$

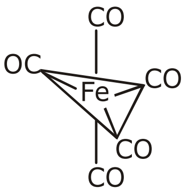


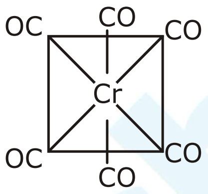
Dibenzene chromium
$Cr(\eta^6-C_6H_6)_2$

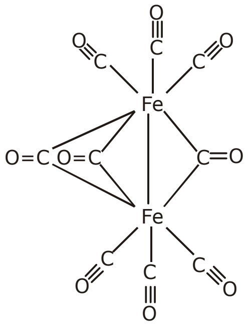
The number of carbon atoms bonded to the metal in these compounds is indicated by the greek letter η(eta) with a number. The prefixes η^2, η^5 and η^6 indicate that 2, 5 and 6 carbon atoms are bonded to the metal in the compound.

Sigma and Pi bonded organometallic compounds : Metal carbonyl compounds formed between metal and carbon monoxide, belong to this class. These compounds possess both σ-and π-bonding. Generally oxidation state of metal atoms in these compounds is zero. Carbonyls may be mononuclear, bridged or polynuclear.







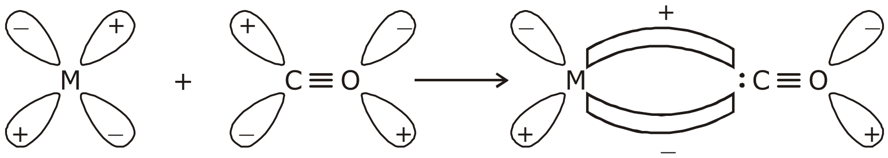


Tetracarbonylnickel(0) Pentacarbonyliron(0) Hexacarbonylchromium(0) [Fe(CO)$_9$]

[Ni(CO)$_4$] [Fe(CO)$_5$] [Cr(CO)$_6$]

In a metal carbonyl, the metal-carbon bond possesses both the σ-and π-character. A σ-bond between metal and carbon atom is formed when a vacant hybrid orbital of the metal atom overlap with an orbital on C atom of carbon monoxide containing a lone pair of electrons.

Formation of π-bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding π* orbital of C atom of carbon monoxide. This overlap is also called back donation of electrons by metal atom to carbon.



The π-overlap is perpendicular to the nodal plane of σ-bond.

In olefinic complexes, the bonding π-orbital electrons are donated to the empty orbital of the metal atom and at the same time to the back bonding π-orbital of the olefin.

Points to be remembered :

(i) The closed ring complexes formed by polydentate ligands are called Chelates. Chelation leads to stability.

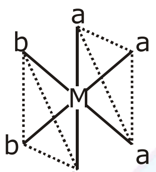
(ii) Estimation of nickel (II) is done by complexing with dimethyl glyoxime (DMG) whereas Ca^{+2} and Mg^{2+} ions are done by titrating against EDTA.

(iii) Complex in which ligands can be substituted by other ligands are called labile complexes. For example $[Cu(NH_3)_4]^{2+}$ is a labile complex because NH_3 ligands can be substituted by CN^- ligands.

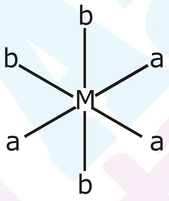
$$\underset{\text{(less stable)}}{[Cu(NH_3)_4]^{2+}} + 4\,CN^- \rightarrow \underset{\text{(more stable)}}{[Cu(CN)_4]_2} + 4NH_3$$

(iv) Another type of geometrical isomerism is also shown by octahedral complexes of the type Ma_3b_3.

If each trio of donor atoms occupy adjacent positions at the corner of an octahedral face, then it is called facial (fac) isomer and when the position are around the meridian of the octahedron, then it is called meridional (mer) isomer.



fac-form



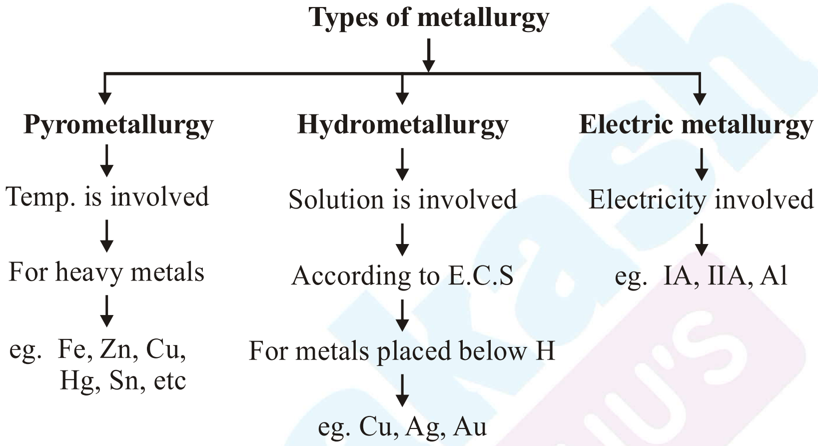
mer-form

(v) Haemoglobin is a complex of Fe, chlorophyll is a complex of Mg, vitamin B_{12} is a complex of Co.

MEATLLURGY

The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy.

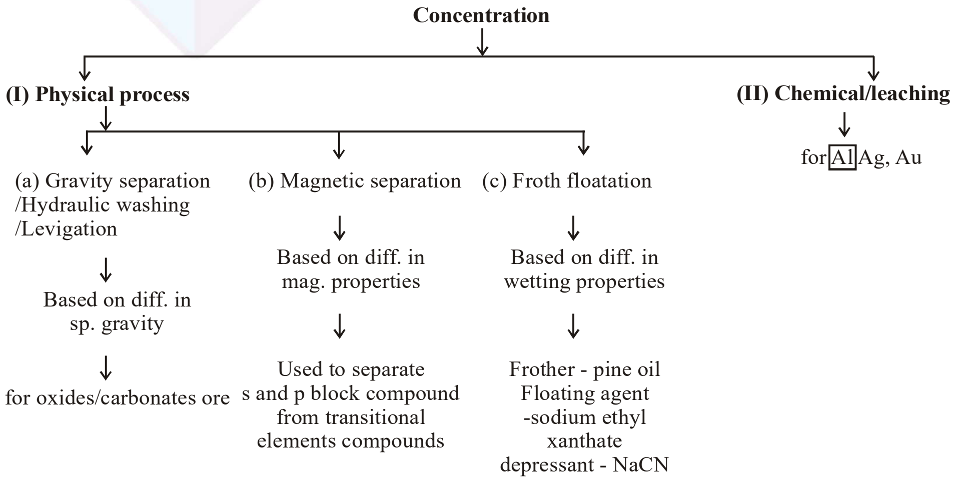
Ore : Minerals from which metal can be extracted economically & easily.



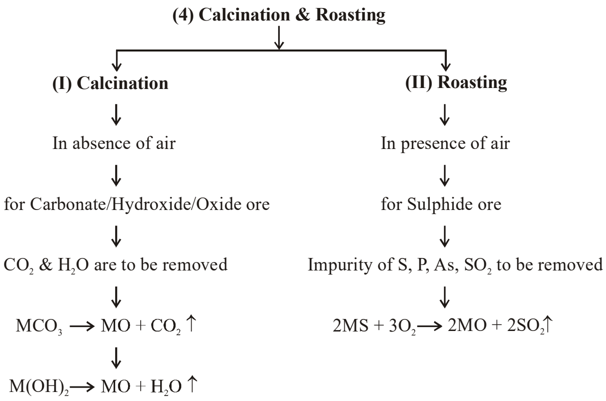
Metallurgical Process :

1. **Mining :** Ore obtain in big lumps (less reactive)
2. **Crushing/grinding/pulverization :** big lumps convert into powder (more reactive)
3. **Concentration :** To remove matrix/gangue (major impurities) from

ore to increases the concentration of ore particle in ore sample.

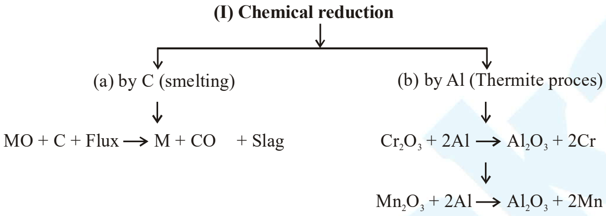


Ag, Au, are concentrated by cyanide process.

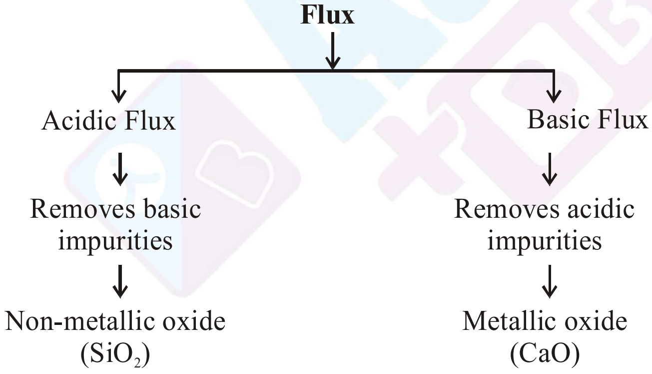


5. Reduction :

To obtains metal (95 to 98%) from metal oxide.



Flux - substance to convert non-fusibl we impurities to fusible one.



Imp. point - At high temp. C is reducing agent.
- At low temp. CO is reducing agent.

(II) Self reduction

↓

For Cu, Pb, Hg

↓

For sulphide ore only

(III) Metal displacement reduction

↓

Metal placed below H. in E.C.S

↓

$\boxed{\text{Ag, Au,}}$ Cu

↓

(i) Cyano complex or Mac-Arther process

$$Ag_2S + 4NaCN \xrightarrow{2O_2} 2Na[Ag(CN)_2] + Na_2SO_4$$

$$2Au + 4KCN + H_2O \xrightarrow{O_2} 2K[Au(CN)_2] + 2KOH$$

(ii) Reduction to free metal

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

$$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2Au\downarrow$$

(IV) Electrolytic reduction

↓

For IA, IIA, Al

↓

Electrolysis of molten sol.

↓

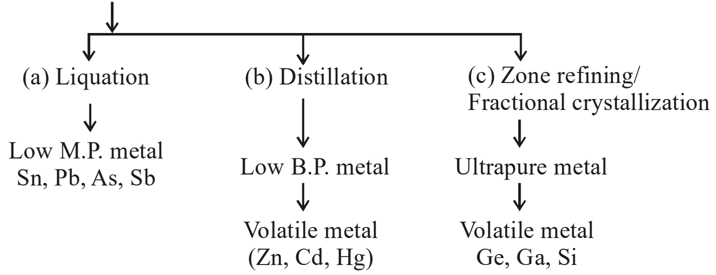
(i) Extraction of Al (Hall-Heroult Process)
- Al can be extracted from Al_2O_3
- To decrease fusion temp. of Al_2O_3, $Na_3\ AlF_6$ & CaF_2 is to added
- $Na_3\ AlF_6$ and CaF_2 (Neutral flux) increase the conductivity and reduce the fusion temp.

(ii) Extraction of Na (Down cell process)
- Na can be extracted from NaCl
- Neutral flux ($CaCl_2$) to be added to decrease the fusion temp. of NaCl
- Neutral flux - substance used to increase the conductivity of NaCl
- Decrease the fusion temp. of ionic compounds of (IA, IIA, Al) which is more than the melting point of metal.

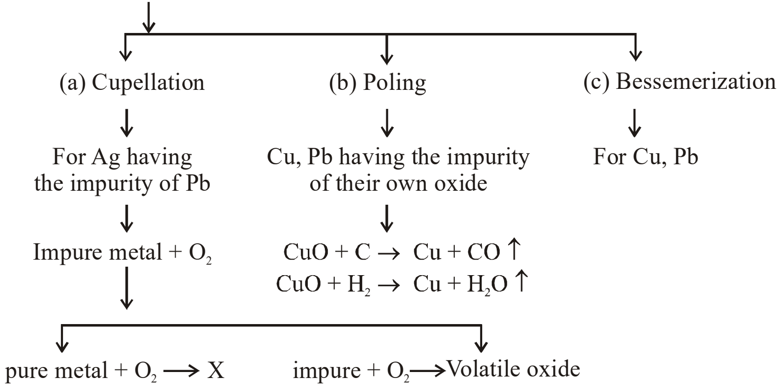
Refining : To obtain metal (99.98%) pure

↓

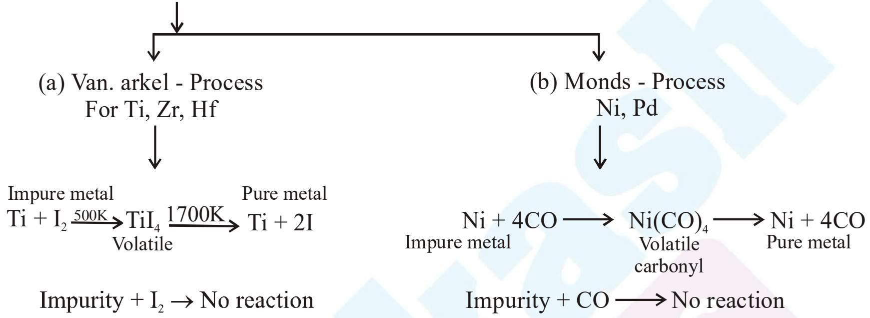
(I) Physical Process



(II) Chemical Process



(II) Thermal decomposition



(IV) Electrolytic refining

↓

Anode - made up of impure metal (Impurity deposited below anode as anode mud)
Cathode - made up of pure metal (pure metal deposited)

Thermodynamics principle of metallurgy

The graphical representation of Gibbs energy was first used by H.I.T. Ellingham. This provide a sound basis for considering be choice of reducing agent in the reduction of oxides. This is known as Ellingham diagram such diagram help us in predicting the feasibility of thermal reduction of an ore.

The criteria of feasibility is that at a given temperature, Gibbs energy of reaction must be negative.

$$Cu^{2+} \quad + \quad 2e^{-} \xrightarrow{\text{reduction}} Cu$$

Electrons (from electrolyte)	Electrons (from cathode)	Pure copper metal (deposited at cathode)