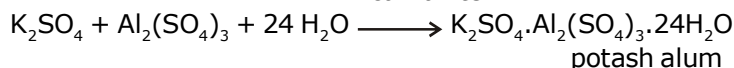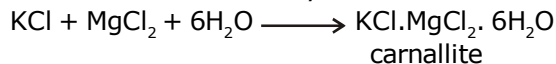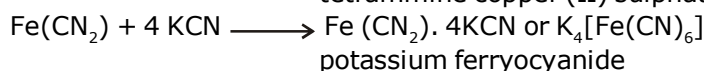# COORDINATION COMPOUND
KEY CONCEPTS

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.

Double salts : Those which retain their identity in solutions are called double salts. For example.

$$KCl + MgCl_2 + 6H_2O \longrightarrow KCl.MgCl_2. 6H_2O$$
$$\text{carnallite}$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24 H_2O \longrightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$$
$$\text{potash alum}$$

Complex compounds : Those which loose their identity in solution (complexes). For example.

$$CuSO_4 + 4 NH_3 \longrightarrow CuSO_4.4 NH_3 \text{ or } [Cu(NH_3)_4]SO_4$$
$$\text{tetrammine copper (II) sulphate}$$

$$Fe(CN_2) + 4 KCN \longrightarrow Fe(CN_2). 4KCN \text{ or } K_4[Fe(CN)_6]$$
$$\text{potassium ferryocyanide}$$

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 potassium alum shows the properties of K^+, Al^{3+} and SO_4^{2-} ions. These are both examples of double salts which exist only in the crystalline state. When the other two examples of coordination compounds are dissolved they do not form simple ions, Cu^{2+} / Fe^{2+} and CN^-, but instead their complex ions are formed.

Representation of Complex Ion :

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

when
   M = Central Metal atom /ion (usually of d-block)
   L = Ligand
   x = No. of ligands
   $_{n\pm}$ = charge on coordination

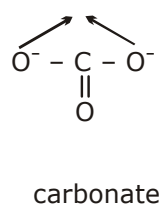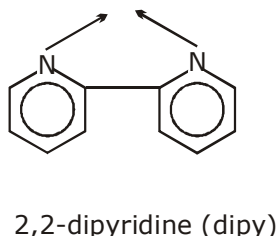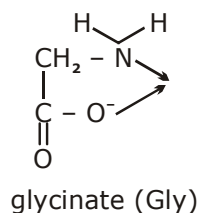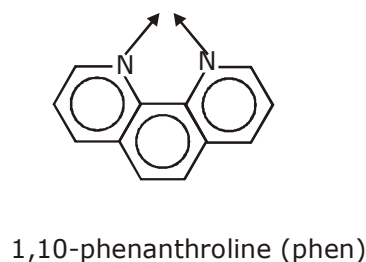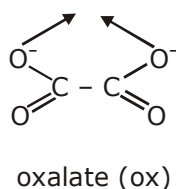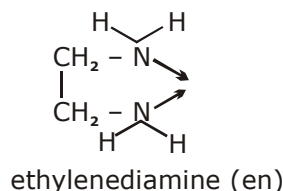Outside region apart from coordination sphere is called ionisation sphere.

1. **Central metal atom/ion :** Central ion acts as an acceptor (Lewis acid) and has to 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 form co-ordination compounds readily. Thus, 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 co-ordinate or dative bond free ligands have at least one lone pair.

$$H - \overset{\cdot\cdot}{\underset{|}{N}} - H \qquad H - \overset{\cdot\cdot}{\underset{|}{O}}: \qquad : C \equiv \overset{\ominus}{N} : \qquad : \overset{\cdot\cdot}{\underset{\cdot\cdot}{C}} : ^-$$
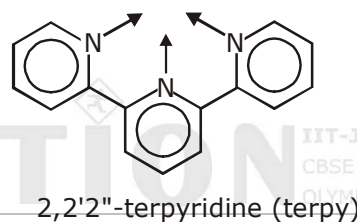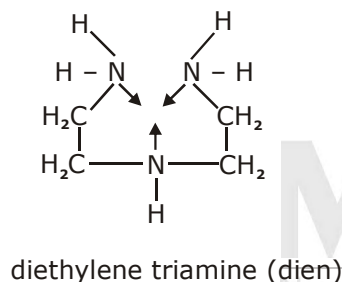$$\quad\ \ H \qquad\qquad\quad H$$

The lignads are thus Lewis bases and the central metal ions / natoms are Lewis acids.

Ligands can be of following types depending on the number of donor atoms pesent in them.

(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. Exmplaes are

diethylene triamine (dien)   2,2'2"-terpyridine (terpy)

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

Nitriloacetate   Triethylene tetramine (trien)
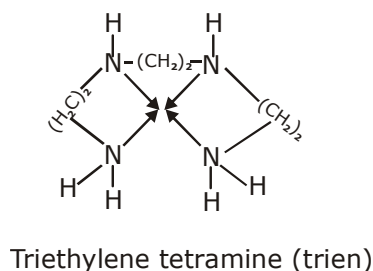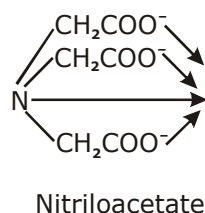
(v) Pentadentate Ligands They have five donor atoms. For example, ethylenediamine triacetate ion.

ethylendiamine triacetate ion

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

ethylenediamine tetraacetate (EDTA)

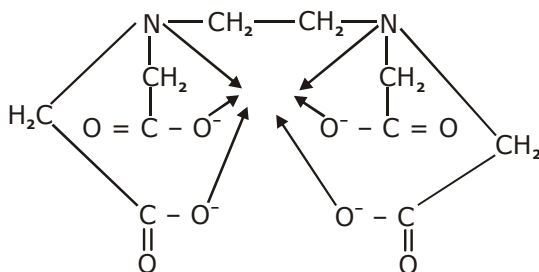**(Vii) Ambidentate ligands :** There are cerain ligands which have two or more donor atoms but in forming complexes, only one donor atom is attached to the metal / ion. Such ligands are called ambidentate ligands. Some examples of such ligands are

M	$\longleftarrow NO_2^-$	M	$\longleftarrow ONO^-$
	nitrite – N		nitrite –O
M	$\longleftarrow CN^-$	M	$\longleftarrow NC^-$
	cyanide		isocyanide
M	$\longleftarrow SCN^-$	M	$\longleftarrow NCS^-$
	thiocyanide		isothiocyanide

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

3. Co-ordination sphere The central metal atom and the ligands directly attached to it are collectively termed as the co-ordination sphere. Co-ordination 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. Co-ordination number (CN) The co-ordination number (CN) of a metal atom /ion in a complex is the total number of e^- pairs accetpted by central metal atom /ion from ligands through coordinate bond. Some common co-ordination numbers of metal ions are summarised in the following Table (1) and examples of complexes of various co-ordination number are given in Table (2).

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Table (1) Co-ordination number of metal ion

Metal ion	Co-ordinaton 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 co-ordination numbers

Complex	Co-ordinaton 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

5. **Oxidation number/oxidation state (O.S.) of central metal ion** It is a number(numerical value) which represents the electric charge on the central metal atom of a complex ion. 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 a 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^- ion (univalent ion), that is 6 represents the co-ordination number of Fe cation. The oxidation state of iron can be determined easily as below, knowing that cyanids ions is unidentate and the complex on the whole carries −4 charge.

$$[Fe(CN)_6]^{-4}$$
$$x + (-6) = -4$$
$$\therefore \qquad\qquad x = +2$$

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

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

(iii) $Ni(CO)_4$ Here the co-ordination number of Ni is 4 since carbonyl group is unidentate. Further since the complex as well as the ligands has no charge, nickel atom must also be neutral ,that is it is in zero oxidation state.

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

$$E.A.N = Z - O.S. + 2 \times C.N.$$

Sidgwick also suggested that the metal ion will continue accepting electron pairs till the total number of electrons in the metal ion and those donated by ligands is equal to that of 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 comlex, 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 NOMENCLATURE OF COMPLEXES :
The rules for the systematic naming of co-ordination 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	H^- hydrido	HS^- mercapto
Cl^-	chloro /chlorido	OH^- hydroxo/hydroxido	S^{2-} sulphido
Br^-	bromo / bromido	O^{2-} oxo / oxido	CN^- cyano / Cyanido
I^-	iodo / iodido	O_2^{2-} peroxo / Peroxido	

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)

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(v)   Neutral ligands have No special ending and usually common ligands 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 numeral 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.

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 link 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 it is bonded.

(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 preceded by the number of these groups in Arabic numericals. These rules are illustrated by the following examples.

(a)   **Complex cations**   **IUPAC name**
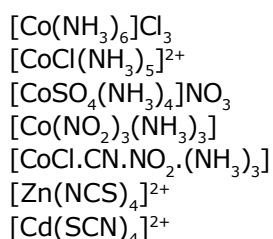
$[Co(NH_3)_6]Cl_3$ Hexaamminecobalt(III) chloride
$[CoCl(NH_3)_5]^{2+}$ Pentaamminechloridocobalt(III) ion
$[CoSO_4(NH_3)_4]NO_3$ Tetraamminesulphatocobalt(III) nitrate
$[Co(NO_2)_3(NH_3)_3]$ Triamminetrinitrito-N-cobalt(III)
$[CoCl.CN.NO_2.(NH_3)_3]$ Triammine-chloro-cyano-nitro-N-cobalt(III)
$[Zn(NCS)_4]^{2+}$ Tetrathiocyannato-N-zinc(II) ion.
$[Cd(SCN)_4]^{2+}$ Tetrathiocyanato-S-cadmium(II) ion.

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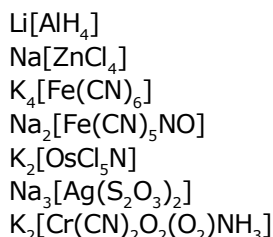
$Li[AlH_4]$ Lithium tetrahydridoaluminate(III)
$Na[ZnCl_4]$ Sodium tetrachloridozincate(II)
$K_4[Fe(CN)_6]$ Potassium hexacyanidoferrate(II)
$Na_2[Fe(CN)_5NO]$ Sodium pentacyanidonitrosyliumferrate(II)
$K_2[OsCl_5N]$ Potassium pentachloridonitridoosmate(VI)
$Na_3[Ag(S_2O_3)_2]$ Sodium bis(thiosulphato)argentate(I)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

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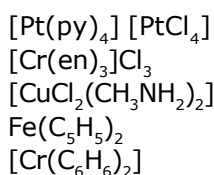
$[Pt(py)_4] [PtCl_4]$	tetrapyridineplatinum(II) tetrachloridoplatinate(II)
$[Cr(en)_3]Cl_3$	d or ℓ Tris(ethylenediamine) chromium(III)chloride
$[CuCl_2(CH_3NH_2)_2]$	Dichloridodimethylaminecopper(II)
$Fe(C_5H_5)_2$	Bis(η^5–cyclopentadienyl)iron(II)
$[Cr(C_6H_6)_2]$	Bis(η^6-benzene)chromium(0)

(d)   Bridging groups
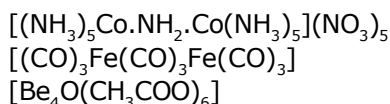
$[(NH_3)_5Co.NH_2.Co(NH_3)_5](NO_3)_5$	μ-amidobis[pentaamminecobalt(III) nitrate
$[(CO)_3Fe(CO)_3Fe(CO)_3]$	Tri-μ-carbonyl-bis [tricarbonyliron(0)]
$[Be_4O(CH_3COO)_6]$	Hexa-μ- acetato(O,O')-μ_4-oxidotetraberyllium(II) (basic baryllium acetate)

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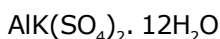
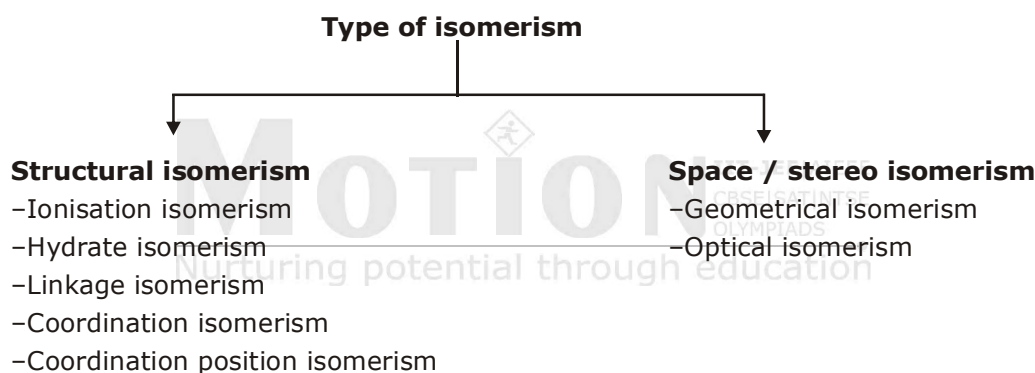|	
$AlK(SO_4)_2. 12H_2O$	Aluminium potassium sulphate 12-water

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 named 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 negativeligands, Neutral ligands, positive ligands]$^{n\pm}$

ISOMERISM IN COMPLEXES :

Complex compounds that have the same molecular formula but have different structural /spacial arrangements of ligands are called isomers. These are of two types, namely structural and stereo isomers.

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

(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 creamcoloured 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 $[Co(en)_2Cl.SCN]NO_2$.

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

$$[Cr(H_2O)_6]Cl_3$$
$$[Cr(H_2O)_5Cl]Cl_2.H_2O$$
$$[Cr(H_2O)_4Cl_2]Cl.2H_2O$$
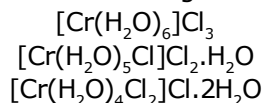
(iii) **Linkage Isomerism** This type of isomersim arises when the ligand attached to the central metal ion of a complex in different ways. Such ligands are called ambidient ligands. Nitrite ion has electron pairs available for co-ordination both on N and O atoms.
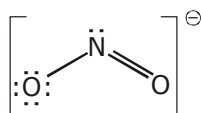
Examples

(a) $[Co(NH_3)_5 ONO]Cl_2$ and $[Co(NH_3)_5 NO_2] Cl_2$
pentaamminenitrito-o-cobalt(III) chloride   pentaamminenitrito-N-cobalt-(III)-chloride
(red)   (yellow)

(b) $[Mn(CO_5).SCN]^+$ and $[Mn(CO_5) (NCS]^+$
pentacarbonylthiocyanto   pentacarbonylthiocyanato
–S-manganese (II) ion   –N-manganese (II) ion

(iv) Co-ordination 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 co-ordination isomers.

(v) **Co-ordination Position Isomerism** In polynuclear complexes, an interchange of ligands between the metal nuclei gives rise to co-ordinaton position isomerism, for example.
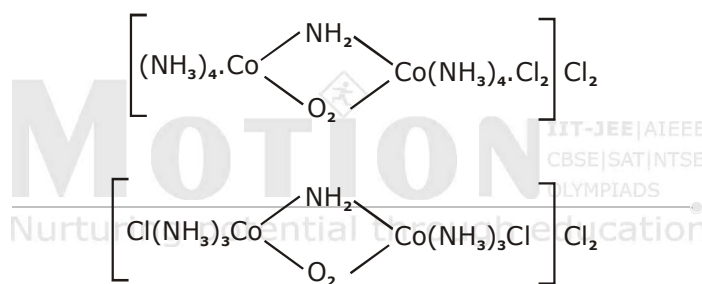
Co-ordination position isomers

Polymerisation Isomerism : This is not 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.
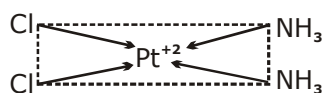
Geometrical is Isomerism Geometrical isomers are the isomers in which the atoms are joined to one another in the same way but differ in space because some ligands occupy different relative positions in space.

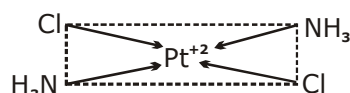## Geometrical Isomerism in complex compound having C.N. = 4

Tetrahedron complexes (sp^3 hydrididation) never exhibit geometry isomerism, however, it is very common in square planer complexes (dsp^2 hybridisationn).

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.
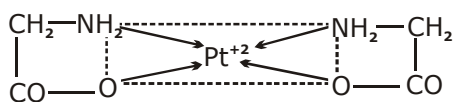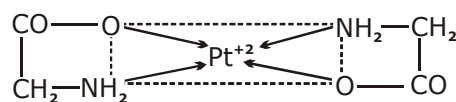
cis form   trans- form

Geometrcial Isomerism in Complex compound having co-ordination number 6

(a) $[Co(NH_3)_4Cl_2]^+$ can exist as
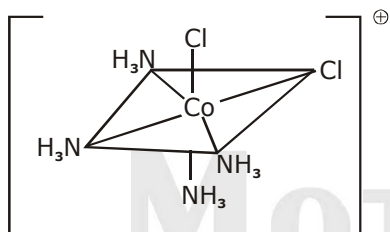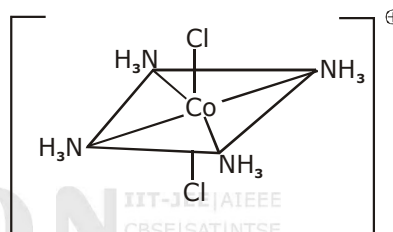
cis form (violet)   trans form (green)

(b) $[Pt(NH_3)_2Cl_2Br_2]$ can exist as

cis   trans

There are many more trans arrangements.

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(ii)   **Optical Isomerism** If a molecule is asymmetric then it cannot be superimposed on its mirror image. These forms are called optical isomers. They are called either dextro or laevo compounds depending on the direction in which they rotate the plane polarised light in polarimeter.

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

(iv) $[Co(en)_2Cl_2{}^+]^\oplus$ exist as cis-and trans-isomers. But only cis-isomer can have d and ℓ optical isomers.

trans form (optically inactive)

mirror

cis-d-form   cis-ℓ-form

cis-dichlorobis (ethylenediamine) cobalt (III) ion
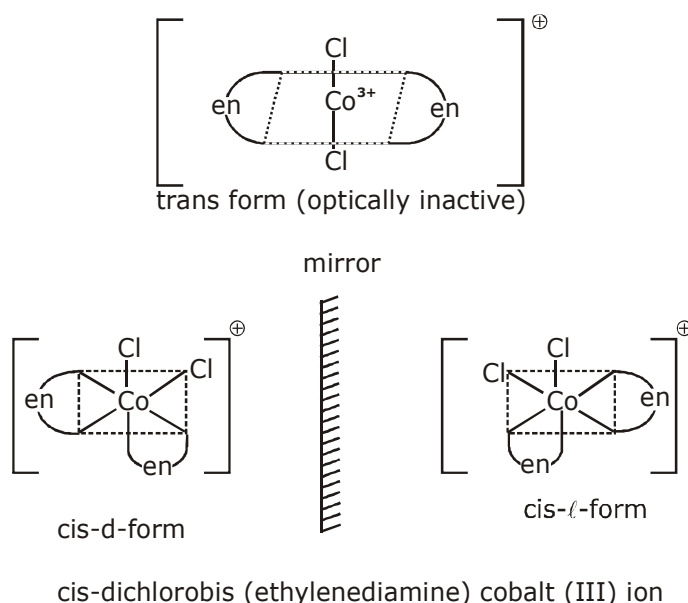
(v)   Optical isomers of $[Co(en)_3]^{3+}$ are

mirror
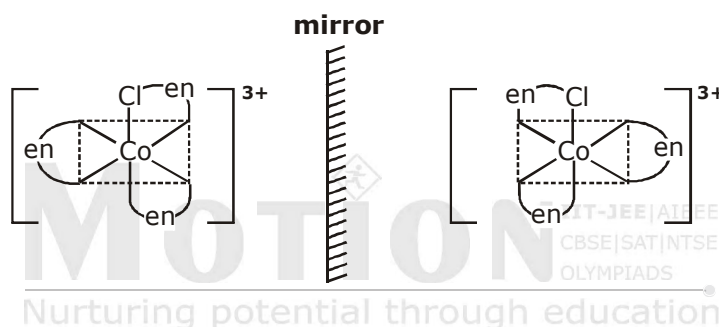
BONDING IN COMPLEXES

Werner's Co-ordination Theory :

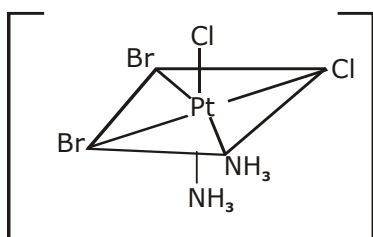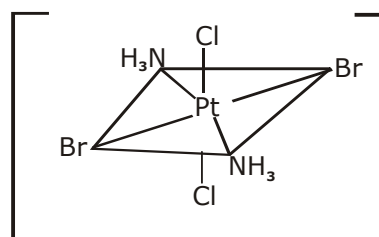Alfred Werner put forward his concept of secondary valency for advancing a correct explanation for the characteristics of the coordination compounds. The fundamental postulates of Werner's theory are as follows.

(i)   Metal possess two types of valencies, namely, primary (principal or ionisable) valency and secondary (auxillary or non-ioisable) 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 thick lines.

(ii)   Every metal cation in complex compound has a fixed number of secondary valencies for example Pt^{4+} cationhas its six secondary valency.

(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, where as secondary valency has directional character, there fore a complex ion has its definite geometry eg. $[Co(NH_3)_6]^{3+}$ – octahedron.

(v)   It is the directional nature of secondary valency due to which co-ordination compound exhibits the phenomenon of isomerism.

Werner's Representation of Complexes

Consider the case of $CoCl_3.xNH_3$ where primary valency = +3 and seconary valency = 6.
Various structures are summarised in Table -4.

	Werner complexes	Modern formula	Ionisation	Secondary valency satisfied by	Primary valency staisfied 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^-)	three (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)**
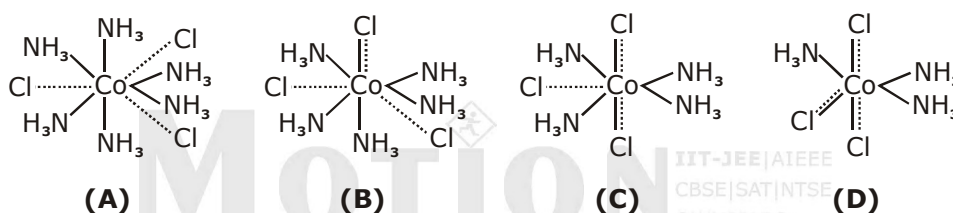
Valence Bond Theory :

It was developed by Pauling. The salient features of the 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.

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

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

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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 determind series is obtained named as spectrochemical series.

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < EtOH < CH_3COO^- \approx C_2O_4^{2-} < H_2O$$

————————————— Weak field ligands —————————————

$$< EDTA < NH_3 \approx py < en < dipy < phen < NO_2^- \, CN^- < CO$$

——————————— Strong field ligands ———————————

(v) The central metal ion has a number of empty orbitals for accommodating electrons donated by the ligands.
The number of empty orbitals is equal to the co-ordination number of the metal ion for a particular complex.

(vi) The atomic orbital (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 orbial complexes, respectively.

Limitations of valence bond theory

(i) Correct magnetic moment of complex compounds can not 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.
Such an electron can be easily lost then why does not $[Cu(NH_3)_4]^{2+}$ complex 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 the 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 remain 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 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 the 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 point to three adjacent corners of the octahedron as shown fig.

The iobes 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 directons will increase the energy of the $d_{x^2-y^2}$ and d_{z^2} orbitals (which point along the axes) than it increses the energy of the dxy, dxz and dyz orbitals (which points between the axes). 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.
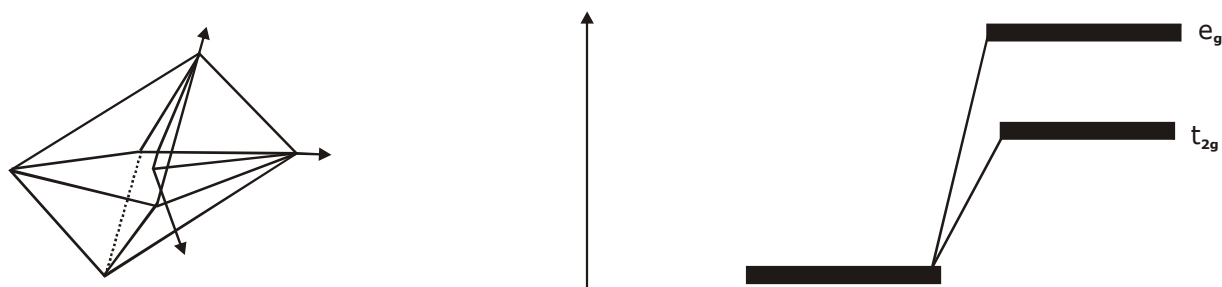

Fig. The directions in an octahedral complex

Free metal ion (five degenerate d orbitals) Fig Crystal field spliting of energy levels in an octahedral field

metal ion in octahedral field

It follows that the e_g orbitals are $+0.6\ \Delta_0$ above the average level, and the t_{2g} orbitals $-0.4\ \Delta_0$ below the average level.
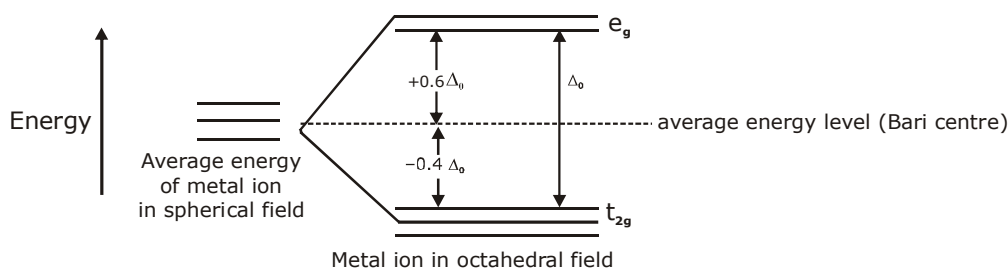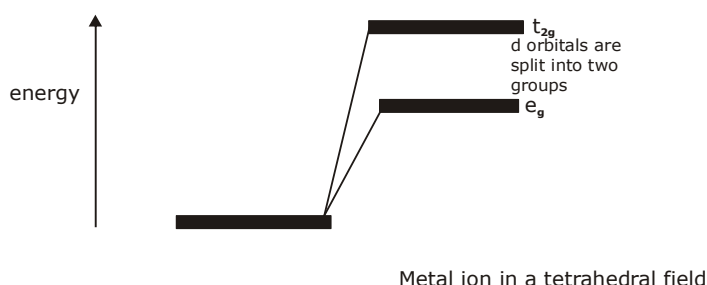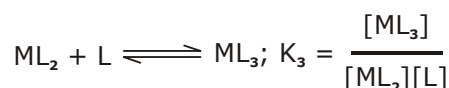

Fig. Diagram of the energy levels of d -orbitals in a octahedralfield

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Tetrahedral Complexes A regular tetrahedron is related to a cube. One atom is at the centre of the cube, and 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 centres 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 (the Bari centre) and the e_g orbitals are 0.6 Δ_t below the average level.
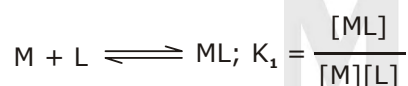

Metal ion in a tetrahedral field

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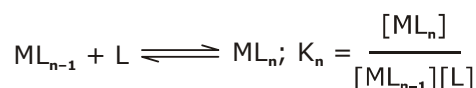
Stability of complexes

A co-ordination 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=co-ordination number of metal ion) supposed to take place by the following n cosecutive steps.

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

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

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

....

....

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

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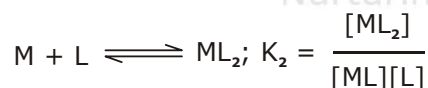
K_1, K_2, K_3........K_n are called stepwise stability constants. With a few exceptions, the values of successive stability constants decrease regularly from K_1 to K_n. The overall stability constant K is given as

$$M + nL \rightleftharpoons ML_n;$$
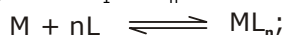
$$K = K_1 K_2 K_3 \ldots K_n = \frac{[ML_n]}{[M][L]^n}$$

The higher the overall stability constant value of the complex, the more stable it is. Alternatively, 1/K values called instability constant explain 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 Table.

Table : Stability constants 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. The greater the stability of its complexes.

(ii)   the more basic a ligands, 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) The higher the oxidation state of the metal, the more stable is the complex. The charge density of Co^{3+} ion is more than Co^{2+} ion and thus, $[Co(NH_3)_6]^{3+}$ is more stable than $[Co(NH_3)_6]^{2+}$. Similarly, $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(CN)_6]^{4-}$.

(iv)   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.

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$$NiCl_2 + 2 \begin{array}{c} CH_3 - C = NOH \\ | \\ CH_3 - C = NOH \end{array} \xrightarrow{NH_4OH} \quad \text{(Ni complex with H-bonding)} \quad + 2NH_4Cl + 2H_2O$$

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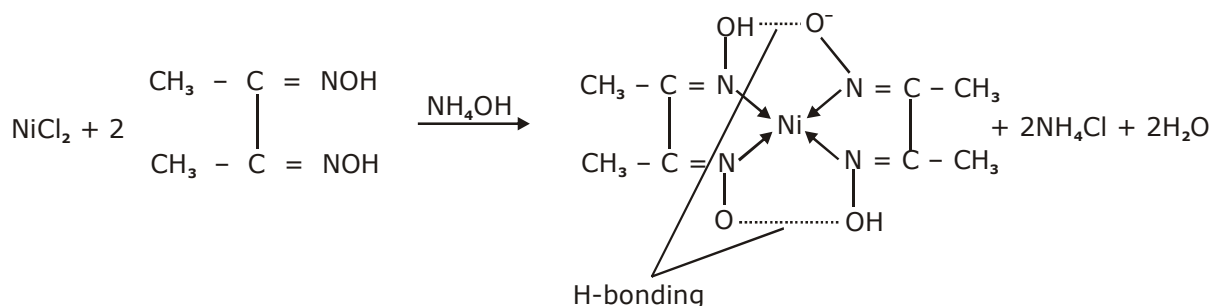
(a) Fe^{3+} is detected by formation of a blood red coloured complex with KSCN.

$$Fe^{3+} + 3KSCN \longrightarrow Fe(SCN)_3 + 3K^+$$
$$\text{blood red colour}$$
$$\text{or}$$
$$[Fe(H_2O)_5(SCN)]^{2+}$$
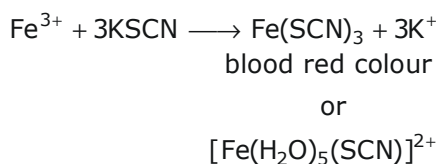
(b) Many ligands (organic reagents) are used for the gravimetric estimation of number of metal ions.

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

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

(d) The co-ordination 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 with continuous passing of air through the solution. Silver dissolves as a cyanide complex and silver is precipitated by the addition of scrap zinc.

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

$$2Na[Ag(CN)_2] + Zn \overset{Air}{\rightleftharpoons} \underset{\text{sodium tetracyanozincate(II)}}{Na_2[Zn(CN)_4]} + 2Ag$$
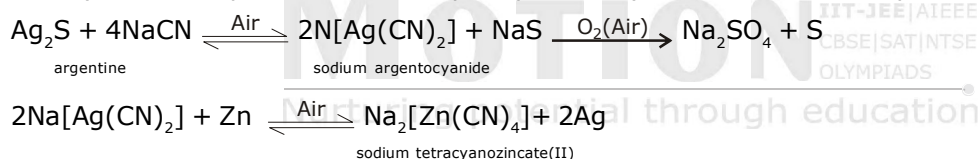
(b) Native Gold and Silver also dissolve in NaCN solution in presence of the oxygen (air).
$$4\,Ag + 8\,NaCN + O_2 + 2H_2O \longrightarrow 3Na[Ag(CN)_2] + 3NaOH$$
Silver and Gold are precipitated by addition of scrap zinc. Nickel is extracted by converting it into a volatile complex, nickel carbonyl, by use of carbon monoxide (Mond's process). The complex decomposes on heating again into pure nickel and carbon monoxide.

$$Ni + 4CO \longrightarrow Ni(CO)_4 \xrightarrow{\text{heating}} Ni + 4\,CO$$
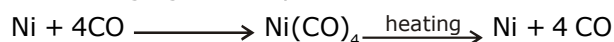
(iii) **Photography** In photography, the image on the negative is fixed by dissolving all the remaining silver bromide with hypo solution in the form of a soluble complex.
$$AgBr + 2Na_2S_2O_3 \longrightarrow \underset{\text{(soluble)}}{Na_3[Ag(S_2O_3)_2]} + \underset{\text{(soluble)}}{NaBr}$$
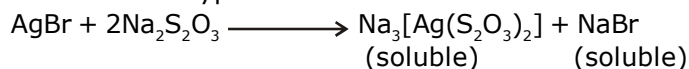
(iv) **Electroplating** Metal complexes release metal slowly and give a uniform coating of the metal on the desired object Cyano complexes of silver, gold copper and other metals are used for the electrodeposition of these metals,

(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 COMPOUNDS

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.

Classification of Organometallic Compounds
Organometallic compounds are classified in three classes.

(i) Sigma bonded organometallic compounds: In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond, For Examples:

(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$_2$Zn such as $(C_2H_5)_2$Zn. (isolated by Frankland).

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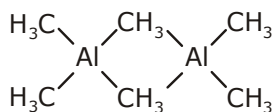

$Al_2(CH_3)_6$ is a dimeric compound and has a structure similar to diborane, (B_2H_6). It is an electron deficient compound and two methyl groups act as bridges between two aluminium atoms.

(ii) 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
$Cr(\eta^6 - C_6H_6)_2$
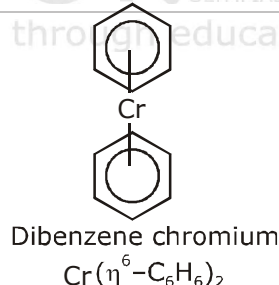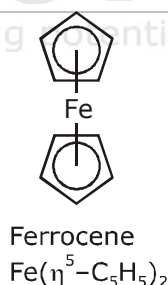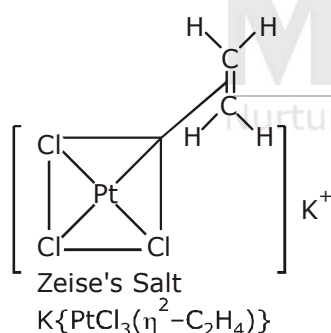
The number of carbon atoms bonded to the metal in these compounds is indicated by the greek letter η(eta) with a number. The prefixes η^2, η^5 and η^6 indicate that 2, 5 and 6 carbon atoms are the metal in the compound.

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(iii) **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.
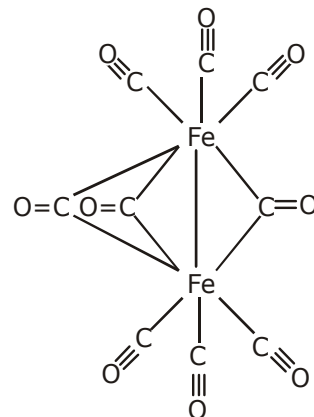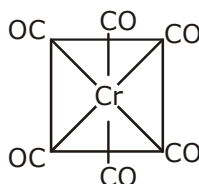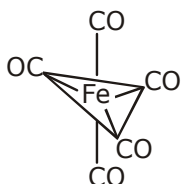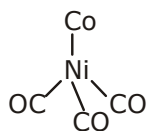

Tetracarbonyl nickel(0)   Pentacarbonyl iron(0)   Hexacarbonyl chromium(0)   Fe(CO)$_9$

Ni(CO)$_4$ Fe(CO)$_5$ Cr(CO)$_6$
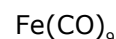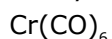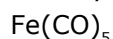
In a metal carbonyl, the metal-carbon bond possesses both the σ-and π-character. A σ-bond between metal and carbon atom is formed when a vacant hybrid orbital of the metal atom overlap with an orbital on C atom of carbon monoxide containing a lone pair of electrons.
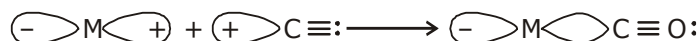
Formation of p-bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding π* orbital of C atom of carbon monoxide. This overlap is also called back donation of electrons by metal atom to carbon.
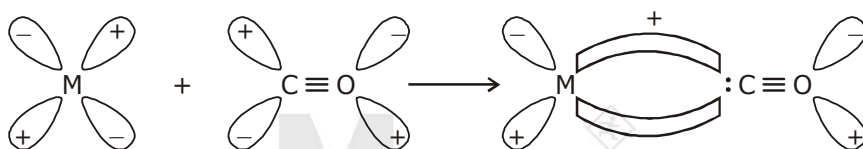
The π-overlap is perpendicular to the nodal plane of σ-bond.

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 p-orbital of the olefin.
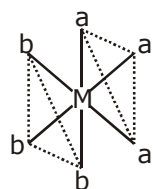
Applications of Organometallic Compounds

(i) Tetra ethyl lead (TEL) is used as antiknock compound in gasoline.

(ii) Wilkinson's catalyst [Rh(PPh$_3$)$_3$Cl] is use as homogeneous catalyst in the hydrogenation of alkenes.

(iii) The extraction and purification of nickel is based on the formation of organometallic compound Ni(CO)$_4$. The formation of Ni(CO)$_4$ at 50-80ºC and its decomposition at 150-180ºC is used in the extraction of nickel by MONDS PROCESS.

(iv) Zeigler Natta catalyst (trialkyl aluminium + titanium tetrachloride) acts as a heterogeneous catalyst in the polymerisation of ethylene in to polyethylene polymer.

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394 - Rajeev Gandhi Nagar Kota, Ph. No. 0744-2209671, 93141-87482, 93527-21564
IVRS No. 0744-2439051, 0744-2439052, 0744-2439053, www.motioniitjee.com, email-hr.motioniitjee@gmail.com

Points to be remembered:

(i) $CH_3B(OCH_3)$ is an organometallic compound but $B(OCH_3)$ is not.

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

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

(iv) 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.

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

    (less stable)   (more stable)

(v) 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.
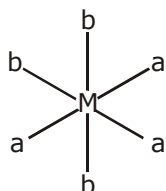
fac-form   Mer-form

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

(vii) σ-bond organometallic compounds generally contains a non-transition metal linked to carbon atom of alkyl group by σ bond. For example eg. R-MgX.

(viii) p-bonded organometallics are formed by donation of p-electrons of double bond to the metal atom. For example Zeise's salt $K[PtCl_3\eta^2\,C_2H_4]$ and Ferrocene $Fe(\eta^5-C_5H_5)_2$

(ix) Grignard's reagent is one of the most useful organometallic compounds. Due to the high polarity of ($C^{\delta-}$–$Mg^{\delta+}$) bond, it can be used to synthesise many organic compounds.

394 - Rajeev Gandhi Nagar Kota, Ph. No. 0744-2209671, 93141-87482, 93527-21564
IVRS No. 0744-2439051, 0744-2439052, 0744-2439053, www.motioniitjee.com, email-hr.motioniitjee@gmail.com

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