CO-ORDINATION COMPOUNDS

Introduction

We know that when two or more stable compounds are allowed to combine in their stoichiometric ratio, we get molecular or addition compounds. Addition compounds are of two types

1. Double salt
2. Coordination compounds

Double salts

These are addition compounds which are stable in solid state but breakup into its constituents in dissolve state. Carnallite $kCl.MgCl_2.6H_2O$ is double salt whose aqueous solution shows the properties of K^+, Mg^{+2} and Cl^- ions.

Coordination compounds They are the addition compounds which retain their identity in the solid as well as in the dissolved state. Example of this type is $[Ni(NH_3)_6]Cl_2$, If we dissolve this complex compound, we get the ions as under.

$[Ni(NH_3)_6]Cl_2$ ————> $[Ni(NH_3)_6]^{2+}$ + $2Cl^-$
complex ion

Here the species in square bracket does not ionise and it remains as a single entity. Here Ni is central metal ion and NH_3 is ligand. Here the coordination number of Ni is 6 because six, NH_3 ligands are bonded with Ni by coordinate bond. Metals are having two types of valancies, primary and secondry valancy. Primary linkage is ionizable and secondry linkage is nonionizable. Secondry linkage is due to coordinate bonds formed by ligands and central metal atom or ion.

Ligands are of three types

v. Unidentate
vi. Bidentate
vii. Polydentate

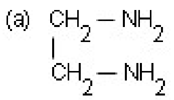
viii. Unidentate ligards

If the ligand is having one donor site, then the ligand is called unidentate. Examples are NH_3, H_2O, Cl^-, CN^-, OH^- etc.

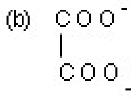
Name of ligand	**Donar site or atom**
Ammonia NH_3	N
Water H_2O	O
Hydroxide ion OH^-	O
Halide ion X^-	X
Carbonyl CO	O
Nitrosyl NO	N
Cyanide ion CN^-	N or C
Nitro NO_2^-	N
Nitrito ONO^-	O
Thiocynate SCN^-	S or N

x. Bidentate ligand

Ligands which have two donar atoms and can domate to the central ion from these two positions are called bidentate ligands. Examples are



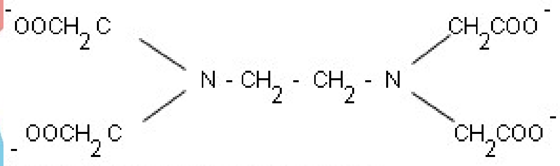
Ethylenediamine (en)



Oxalate ron (ox)

xi. Polydentate ligands

Ligands having more than two donar atoms are called polydentate ligands. These may be tridentate, tetradentate, Pentadentate and hexadenate depending upon the donar atoms present in the ligand is three, four, five and six respectively. EDTA is an example of hexadentate.



Ethylenediamine tetracetable (EDTA)
Here domaratoms are N and O.

COORDINATION COMPOUNDS : NOMENCLATURE

IUPAC rules for naming the coordination compounds are as under

- If the compound is ionic, the name of the cation is mentioned first followed by the name of anion.

  Example $K_3[Fe(CN)_6]$
  Potasiumhexacyanoferrate

(III) and for $[Ni(NH_3)_4 Cl_2]$, its name will be as under
Tetraamminedichloronickel

(II) here oxydation state of nicket is two and we have to write in roman numeral.

- Name of the ligand are acted first followed by the name of the central metal atom.
- When the complex is cation or neutral, the name of the metal is written without any characteristic ending. But when the complex ion is anion, then the name of central metal atom ends in ate.

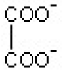
Example

a. $[Co(NH_3)_6]Cl_3$ Here complex ion is $[Co(NH_3)_6]^{3+}$ and it is cation. Its name will be hexaaminine cobalt(III) ion and name of compound is hexaammine cobalt(III) chloride.

b. $K[Pt(NH_3)Cl_5]$ Here the complex ion is anion and its name will be potasium ammine pentachloroplatinate(IV).

- The names of negative ligands end in -O and names of positive ligand end in ium. The neutral ligands are named as such.

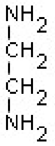
Example (a) Negative ligand end in -O

Ligand	Name	Ligand	Name
F^-	Fluoro	SO_4^{2-}	Sulphato
Cl^-	Chloro	CO_3^{2-}	Carbonato
Br^-	Bromo	Clo_3^-	Chlorato
OH^-	hydroxo	SCN^-	Thiocyanato
CN^-	Cyano	NCS^-	Isothiocyanato
O_2^{2-}	Peroxo	H^-	Hydrido
O^{2-}	Oxo	NO_3^-	Nitrato
NO_2^-	Nitro	$S_2O_3^{2-}$	Thiosulphato
ONO^-	Nitrito	 $\begin{matrix}COO^-\\ \vert\\ COO^-\end{matrix}$	Oxalato
N_3^-	Azido		

(b) Positive ligands end in ium

Ligand	Name
NO^+	Nitrosonium
NO_2^+	Nitronium.
$NH_2\text{-}N^+H_3$	Hydrazinium

(c) Neutral ligands are named as such

 $\begin{matrix}NH_2\\ \vert\\ CH_2\\ \vert\\ CH_2\\ \vert\\ NH_2\end{matrix}$	Ethylenediamine
C_6H_5N	Pyridine
$(C_6H_5)_3P$	Triphenylphosphine

But - for H_2O we will write aquo.

NH_3	Ammine
CO	Carbonyl
No	Nitrosyl

Name of the different ligards in the same complex compound will be in alphabetical order.

- Prefix mono, di, tri etc. are used to indicate the number of individual ligands in the complex. If the ligand is a complex molecule then for two ligands we write bis. Similarity for three complex ligands we write tris and for four complex ligands we will write tetrakis. After writting bis, tris or tetrakis we write the name of ligand in parentheses. **Example (a)** $[Co(en)_3]Cl_3$ = Name will be Tris (ethylene diamine) cobalt(III) chloride.
- Oxidation state of metal in cation, anion or neutral complex is indicated by roman numeral in parentheses.

ISOMERISM IN COORDINATION COMPOUNDS

Compounds having same molecular formula but different structures are called isomers and the phenomenon is known as isomerism. Isomers are divided into two categories

v. Structural isomers
  i. Ionisation isomers
  ii. Coordination isomers
  iii. Linkage isomers
w. Stereo isomers

STRUCTURAL ISOMERS

Ionization isomers

Compounds which have same molecular formula but give different ions in solution are called ionization isomers.

Example

$[Co(NH_3)_5Br]^{2+}SO_4^{2-}$

Bromo pentammine cobalt (III) sulphate (Voilet colour)

$[Co(NH_3)_5SO_4]^+Br^-$

Sulphatolentammine cobalt (III) Bromide (red colour)

In the above example the violet colour compound gives SO_4^{2-} ion in solution and red colour compound gives Br^- ion in solution. Both compounds are having same molecular formulae. They are called ionization isomers.

Coordination isomers

This type of isomerism occurs when both the cation and anion are complexes.

For example -

$[Co(en)_3][Cr(CN)_6]$ and $[Cr(en)_3][Co(CN)_6]$

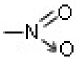
Here ligands are interchanged but both compounds are having same molecular formula. Name of $[Co(en)_3][Cr(CN)_6]$

Tris (ethylene diamine) Cobalt (III) hexa cyano chromatd (III).

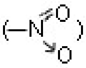
Similarly name of $[Cr(en)_3]$ $[Co(CN)_6]$ is tris (ethylens diamine) chromium (III) hexacyano cobaltate (III).

Linkage isomers

Thus types of isomers are obtained when one ligand attached with central metal atom in two ways. For example NO_2^- in a ligand and it can attach to central metal atom through nitrogen or oxygen. If it is bond through nitrogen structure of

ligand will be  and if it is through O, then structure of ligand will be - O - N = O.

Example : $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$ Name of firstone is pentaminine nitro cobalt (III) chloride and name of second compound is pentammine nitrito cobalt (III) chloride. The unidentate ligands which can bind to the central metal atom through two possible donor atoms are also called ambident ligands. Some examples are as under

(a) Nitro () and Nitrito (– ON = O)

(b) Cyano (– CN) and Isocyano (– NC)

(c) Thiocyanato (– CNS) and Isothocyanato (– NCS)

Stereo isomers

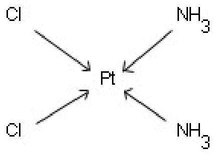
Stereoisomers are those isomers which have the same position of atoms or groups but they differ in the spetial arrangements around the central metal atom. They are of two types

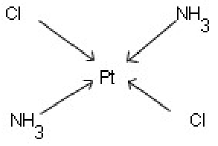
x. Geometrical isomers

y. Optical isomers

GEOMETRICAL ISOMERS

If the same kind of ligands occupy position adjacent to each other it is called **cis** form and if the ligands are opposite to each other it is called **trans** form. $[Pt(NH_3)_2Cl_2]$ exist in cis and trans forms

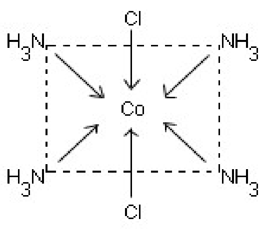




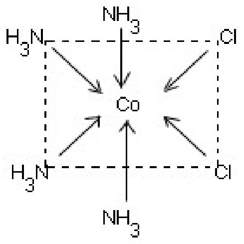
cis form trans form

Square planar complexes show this type of isomerism. Tetrahedral complxes do not show geometrical isomerism because the relative position of ligands with respect to each other will be the same.

Octahedral complexes with coordination number six also exist in cis and trans form. We can take an example of $[CO(NH_3)_4Cl_2]^+$



Trans form (Green)



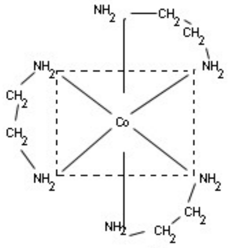
CIS form (Blue violet)

Optical isomers

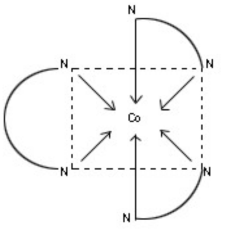
This type of isomerism is exhibited by the chiral molecules i.e molecules which do not have plane of symmetry. These isomers are non-superimposable mirror images of each other. They are optically active and rotate the plane of polarized light equally but in opposite directions.

The isomers which rotate the plane of polarised light towards right is called dextrorotatory (d) and isomers which rotate the plane of polarised light towards left is called laevoratory (l)

Complexes with coordination number six having bidentate ligands provide example of optical isomerism. Example $[Co(en)_3]^{3+}$ can be written in the following way

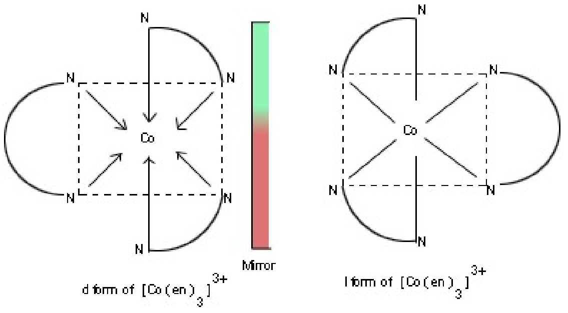


$[Co(en)_3]^{3+}$



$[Co(en)_3]^{3+}$

$[Co(en)_3]^{3+}$ exist in dextro and levo form. Its configuration will be as under.



d and l form of isomers are called enantiomers.

BONDING IN COORDINATION COMPOUNDS

Werner was the first to explain the bonding in coordination compounds. Howevers with the development of modern theories like valance bond theory, ligand field theory molecular orbital theory, it has been possible to explain the properties of these compounds such as colour, geometry and magnetic properties etc. Here we will discuss valence bond theory which is very simple. This was proposed by Pauling.

According to Pauling, the metal atom or ion can use the 3d, 4s, 4p orbital for hybridization to yield a set of equivalent orbitals of definite geometry like square planar, tetrahedral, octahedral and so on. These hybridized orbitals are allowed to overlap with those ligands orbitals that can donate an electron pair for bonding. Here, it may be noted that d orbital involved in the hybridization may be either inner d orbitals i.e. (n-1)d or outer d orbital i.e nd. For example in the case of octahedral hybridization it may be d^2sp^3 or sp^3d^2

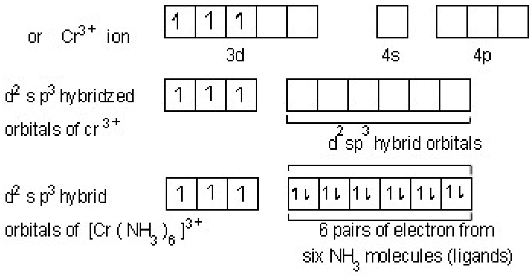
(a) $[Cr(NH_3)_6]^{3+}$

Here we know the electronic configuration of Cr.

Here in the complex ion Cr having three plus charge.

$_{24}Cr = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

$_{24}Cr^{3+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$



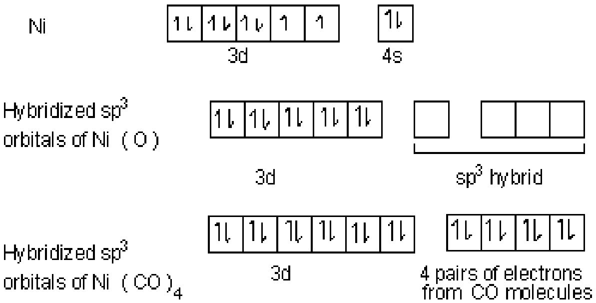
here six pairs of electron, one from each NH_3 molecule occupy the six hybrid orbitals. The presence of three unpaired electrons in the remaining orbital of Cr (III) makes the complex ion or compound in paramagnetic in nature.

(b) $Ni(CO)_4$ Tetra Corbonyl Nickel(O)

here atomic number of Ni is 28 and oxidation state of Ni in $Ni(CO)_4$ is zero.

$_{28}Ni = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

or



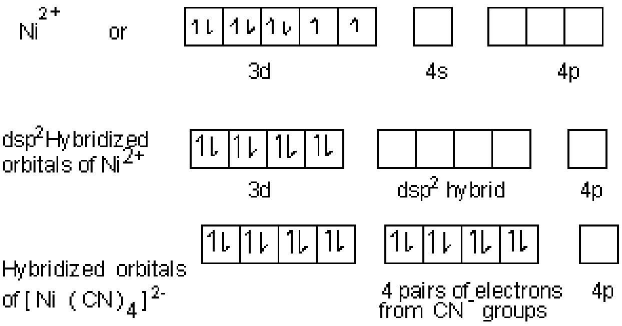
In the above compound s and p orbital of Ni hybridized as sp^3 to give four equivalent orbitals, arranged tetrahedrally. Each CO group (ligand) donate a pair of electron to form tetrahedral complex. Magnetic studies reveal that the compound is diamagnetic in nature and thus supports the forced pairing of 4s electrons with 3d electrons.

(c) $[Ni(CN)_4]^{2-}$ Tetracyano Nickalate (II) ion.

here Ni is in Ni^{2+} state

$Ni = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

$Ni^{2+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$



the complex ion $[Ni(CN)_4]^{2-}$ is diamognetic as seen from the absence of unpaired electrons. Compound has square planar geometry.

STABILITY OF COORDINATION COMPOUNDS

The formation of a coordination compounds involve the reaction between a metal or metal ion and ligands. If the force or bonding between metal ion and ligand is strong, then we get a stable complex.

Generally complex ions are highly stable. But some times complex ions may dissociate to a small extent. The reaction between metal and a ligand can be represented by the following equllibrium.

$$M^{a+} + nL^{x-} \rightleftharpoons [ML_n]^{b+}$$

here b+ = a+ + n (x-)

$$K_s = \frac{[(MLn)^{b+}]}{[M^{a+}]\,[L^{x-}]^n}$$

here Ks is called stability constant. If the value of Ks is more then it can be said that complex ion is more stable. The magnitude of the stability constant gives an indication of the stability of the complexes in solution.

K value of some complexes are as under

$$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} \quad K_s = 4.5 \times 10^{11}$$

$$Cu^{2+} + 4\,CN^- \rightleftharpoons [Cu(CN)_4]^{2-} \quad K_s = 2.0 \times 10^{27}$$

here Ks for $[Cu(CN)_4]^{2-}$ is very high and indicates that complex $[Cu(CH)_4]^{2-}$ is more stable than $[Cu(NH_3)_4]^{2+}$ here CN^- is a relatively stronger ligand than NH_3 and thus forms more stable complex. If the charge density om the central metal ion is more, then it will form a stable complex. Similarly more basic ligand will form more stable complex ion because they can donate the electron easily.

APPLICATION OF COORDINATION COMPOUNDS

Coordination compounds find many application in our life. The ability of metal ions to form complexes with different molecules (ligands) have different physico-chemical properties which can be used in many ways.

z. Hardness of water is estimated by simple titration with EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. As the stability constants of calcium and magnesium complexes of EDTA are different, selective estimation of these ions is possible.

aa. Many coordination complexes are used as electrolytes for electroplating. These complexes delives the metal ions in controled manner. For example, for silver plating the complex $K[Ag(CH)_2]$ is used.

bb. Silver and gold are extracted from their respective ores by treatment with NaCN solution.

$Ag^+(aq) + 2NaCN(aq)$ ———> $Na[Ag(CN)_2](aq) + Na^+$

$Au^+(aq) + 2NaCN(aq)$ ———> $Na[Au(CN)_2](aq) + Na^+$

cc. Ni^{2+} ions are estimated as their ued complex with dimethyl glyoxime (DMG). Ca^{2+} and Mg^{2+} ions are estimated as their complexes with CDTA. The complex of Ca^{2+} with EDTA is used to treat lead poisioning. Inside the body calcium in the complex is replaced by Pb and more stable Pb - EDTA complex is eliminated through urine.

dd. The Pt complex cis platin cis - $[Pt(NH_3)_2Cl_2]$ is used as an antitumar agent in the treatment of cancer.

ee. Many biological important natural compounds exist as coordination complexes. For example Chlorophypl - a complex of Mg^{2+}

Haemoglobin - a complex of Fe^{2+}

Vitamin B12 - a complex of CO^{2+}

COMPOUNDS CONTAINING METAL CARBON BOND

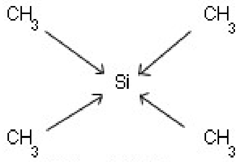
Organometallic compounds have one or more metal carbon bonds. Thus compounds which are having metal carbon bonds are called organo metallic compound. The compounds of metalloids such as Ge, Sb and non- metallic elements such as B and Si are also included under this classification. Many organo metallic compounds are important reagents which are used for the synthesis of organic compounds.

Organometallic compounds are of two types

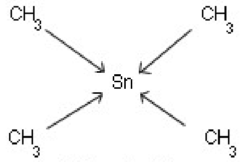
ff. σ bonded compounds

gg. π bonded compounds.

hh **σ bonded compounds** In these compounds organic group is bonded to a metal atom through a normal 2 electron covalent bond. Some examples are



Tetramethyl Silane



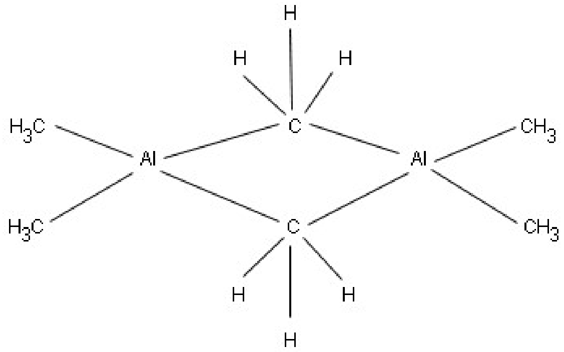
Tetramethyl Tin

$(C_2H_5)_4Pb$
Tetraethyl Lead

$(CH_3)_2Cd$
Dimethyl cadmium

$(CH_3)_3Al$
Tetramethyl aluminium

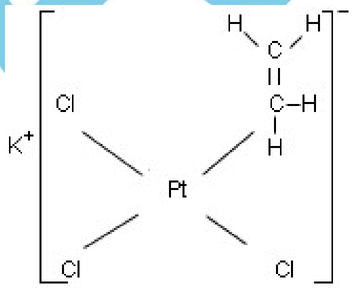
Trimethyl aluminium exists as a stable dimer as shown below



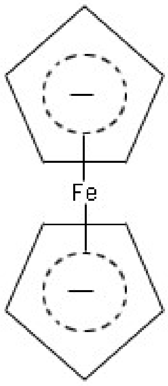
Trimethyl aluminium (Dimer)

ii. π bonded organometallic compounds

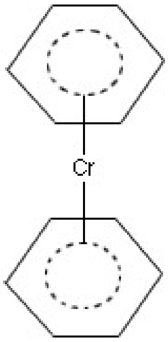
This type of compouds are generally formed by transition metals. They are formed by π electrons. π electrons are donated to metal or metal ions. Some examples are as under



Zeise's salt $K[PtCl_3\text{-}(\eta^2\text{-}C_2H_4)]$



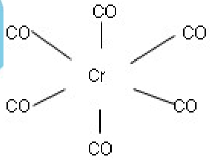
Ferrocene $Fe(\eta^5\text{-}C_5H_5)_2$
Bis (cyclopentadienyl) from (II)



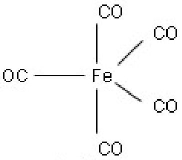
Bis (Benzene) chromium (o)
$Cr(\eta^6\text{-}C_6H_6)_2$

here η is read as eta. η^2 means that two carbons are attached with metal.

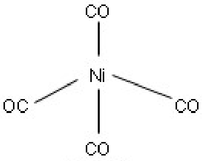
Another important class of organometallic compounds consists of metal carbonyl in which carbon monoxide(CO) acts as ligand. The metal carbon bond in metal carbonyls bonds in metal - carbonyls possess both σ and π charactes.



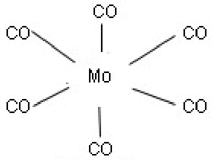
$Fe(CO)_6$



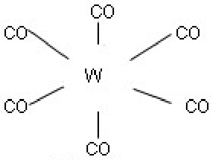
$Fe(CO)_5$



$Ni(CO)_4$



$Mo(CO)_6$



$W(CO)_6$

SYNTHESIS OF ORGANOMETALLIC COMPOUNDS

1. Metal likes Li, Na, K, Mg, Zn, Cd react directly with alkyl - halides in the presence of some suitable solvent such as diethyl ether.

$$R - x + Mg \xrightarrow{C_2H_5 - O - C_2H_5} \underset{\text{Brignard Reagent}}{R - Mg - x}$$

$$R - x + 2M \xrightarrow{C_2H_5 - O - C_2H_5} R - M + Mx$$

Where M = Li, Na, K and X = Cl, Br, I

$$CH_3 - CH_2 - CH_2 - CH_2 - Br + 2Li$$

$$\Big\downarrow C_2H_5 - O - C_2H_5$$

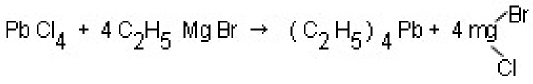
$$CH_3 - CH_2 - CH_2 - CH_2 - Li + LiBr$$

n - Butyl lithium

$$2C_2H_5Br + Zn \longrightarrow \underset{\text{Diethyl Zinc}}{(C_2H_5)_2Zn} + ZnBr_2$$

2. Reaction of an organometallic reagent with metal halides. By this way we get some more useful organometallic compounds.

$$SnCl_4 + 4BuLi \rightarrow Bu_4Sn + 4LiCl$$



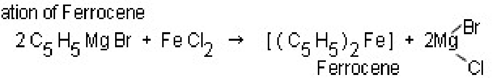
$$PbCl_4 + 4C_2H_5MgBr \rightarrow (C_2H_5)_4Pb + 4mg\genfrac{}{}{0pt}{}{Br}{Cl}$$

3. Preparation of π complex.

Preparation of Zeise's salt

$$H_2C = CH_2 + K_2P + Cl_4 \rightarrow \underset{\text{Zeise's salt}}{K^+[PtCl_3(C_2H_4)]^-} + KCl$$

Preparation of Ferrocene



$$2C_5H_5MgBr + FeCl_2 \rightarrow \underset{\text{Ferrocene}}{[(C_5H_5)_2Fe]} + 2Mg\genfrac{}{}{0pt}{}{Br}{Cl}$$

Preparation of Bis (Benzene) chromium

$$2C_6H_6 + Cr\,(\text{vapours}) \rightarrow \underset{\text{Bis (Benzene) chromium}}{[(C_6H_6)_2Cr]}$$

4. Preparation of metal carbonyls - Finely divided Ni reacts with CO at room temperature to form $Ni(CO)_4$.

$Ni + 4CO$ ———> $Ni(CO)_4$

Iron reacts with CO at high temperature and pressure. $Fe + 5CO$ ———> $Fe(CO)_5$

Ni can be purified by first converting the Ni in to volatile $Ni(CO)_4$ and then its decomposition is employed in mond process.

$$Ni(CO)_4 \xrightarrow{\Delta} Ni + 4CO\uparrow$$

APPLICATION OF ORGAOMETALLIC COMPOUNDS

They have extensive applications.

- As homogeneous catalysis - They are used as homogeneous catalysis for reaction in solution. Wilkinson's catalyst $(Ph_3P)_3RhCl$ is used as a homogeneous catalyst for the hydrogenation of alkenes.

- As hetrogeneous catalysis - Ziegler Natta catalyst (Solution of $TiCl_4$ and $(C_2H_5)_3Al$) is used as a catalyst for the polymerization of olefins.

- Organometallic compounds such as R - Li, R - Mg - X and R_2Cd are used in many organic synthesis.

- $(C_2H_5)_4Pb$ is used as a anti knocking compound in gasoline (Petrol)

- Many organometallic compounds are finding use in agriculture. For example C_2H_5HgCl is used as a fungicide.

- Organosilicon compounds are used in medicines.

- Aryl arsenic compounds are used as chemotherapeutic agents.

- Silicon rubbers have high termal stability, resistance to oxidation and chemical attack, are used in modern surgery for the purpose of production of artificial body parts.

- Organometallic compounds are used in purification of metals. For example nickel carbonyl is used in the purification of Ni by mond process.

SOLVED PROBLEMS

Q.1 Define the terms: coordination entity, central metal, ligand, donor atom, coordination number and oxidation number.

Ans. **(i) Coordination entity.** It constitutes a central metal at atom / ion, generally of a metal, to which are attached a fixed number of other atoms or groups each of which is called a ligand. It may be a neutral or a charged species. e.g. $[Co(NH_3)_6]^{3+}$, $[PtCl_4]^{2-}$, $[Fe(CN)_6]^{3-}$, $[NiCl_2(H_2O)_4]$ etc.

(ii) Central metal. It is the atom or ion in a complex to which a fixed number of ligands are bonded in a definite geometrical arrangement around it e.g. in $[Fe(CN)_6]^{4-}$, the central metal ion is Fe^{2+}.

(iii) Ligands. It is an ion or a molecule that is bound to the central metal atom or ion of the complex. It generally has a lone pair of electrons e.g. Br^-, Cl^-, CN^-, OH^-, O^{2-}, NH_3, H_2O etc.

(iv) Donor atom. The atom which donates the pair of electrons to the central metal atom is called donor atom e.g. In NH_3, N is the donor atom. In H_2O, O is the donor atom.

(v) Coordination Number. The number of ligands directly bonded to the central metal ion in definite geometric arrangement is the coordination number of the metal atom e.g. In $[Co(NH_3)_6]^{3+}$ the 6 NH_3, molecules are bonded to Co^{3+} atom so coordination number of Co^{+3} is six.

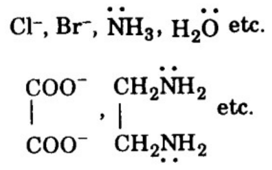
(vi) Oxidation Number. It is the charge on the central atom that it would carry when all the ligands are removed. e.g. in $[Co(NH_3)_6]^{3+}$ the oxidation number of cobalt (Co) is + 3.

Q.2 What is meant by the denticity of a ligand? Give examples of a unidentate and a didentate ligand.

Ans. **Denticity of a Ligand.** It is the number of sigma (σ) electron pair donor groups. It may be 1, 2, 3, 4, 6 etc.

Denticity **Nomenclature**

Example



Cl^-, Br^-, $\ddot{N}H_3$, $H_2\ddot{O}$ etc.

$$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix} , \begin{matrix} CH_2\ddot{N}H_2 \\ | \\ CH_2\ddot{N}H_2 \end{matrix} \text{ etc.}$$

1.	uni dentate	2.	bi dentate
3.	tridentate	4.	tridentate
5.	tetradentate	6.	hexadentate.

Q.3 Which postulates did Werner use to explain the bonding in coordination compounds? What is the main weakness of Werner's theory?

Ans. Main postulates of Werner's Theory.

(i) Metals possess two types of valencies i.e. primary (ionisable) and secondary (non – ionisable).

(ii) Primary valencies are satisfied by negative ions and it is equal to the oxidation state of the metal ion.

(iii) The secondary valencies can be satisfied by neutral or negative ions / groups. It is equal to the coordination number of the metal and is a fixed number.

(iv) The ions / groups bound by secondary linakge have characteristic spatial arrangement corresponding to different oxidation numbers. Such arrangements are called coordination polyhedra.

On the basis of these postulates, Werner formulated the coordination compounds **$CoCl_3.6NH_3$, $CoCl_3.5NH_3$, $CoCl_3.4NH_3$** as **$[Co(NH_3)_6]Cl_3$; $[Co(NH_3)_5Cl]Cl_2$; $[Co(NH_3)_4Cl_2]Cl$.**

Main Weaknesses of Werner's Theory

(i) It failed to explain as to why certain elements possess the property of forming coordination complexes.

(ii) It failed to explain the directional properties of bonds in coordination compounds.

(iii) It failed to explain the characteristic magnetic and optical property of the coordination compounds.

Q.4 **What is understood by:**

(a) a chelating ligand,

(b) an ambidentate ligand?

Answer using specific examples.

Ans. **(a) Chelating Ligand.** When the coordination of more than one sigma – electron pair donor group (i.e. bidentate or polydentate) from the ligand to the same metal ion occur, it is called chelation and such a ligand is called as **chelating lignad** e.g. $C_2O_4^{2-}$ (oxalato).

(b) Ambident Ligands. The monodentate ligand which can coordinate with the central metal atom through more than one site are called ambident ligands e.g. CN^-, NO_2^- etc.

Q.5 **Complete the following statements for the coordination entity (complex ion) $[CrCl_2(OX)_2]^{3-}$:**

(a) OX is abbreviation for

____

(b) The oxidation number of chromium is

____

(c) The coordination number of chromium is __________________

(d) ______________ **is a didentate ligand.**

Ans. **(a)** Oxalate ion 
$\left(\begin{array}{c} COO^- \\ | \\ COO^- \end{array}\right)$ or $C_2O_4^{2-}$

(b) + 3

(c) 6

(d) oxalate ion or $C_2O_4^{2-}$ ion.

Q.6 **Specify the oxidation numbers of the metals in the following coordination entities:**

(a) $[Co(CN)(H_2O)(en)_2]^{2+}$

(b) $[PtCl_4]^{2-}$

(c) $[CrCl_3(NH_3)_3]$

(d) $[CoBr_2(en)_2]^+$ **(e) $K_3[Fe(CN)_6]$.**

Ans. **(a)** $[Co(CN)(H_2O)(en)_2]^{3+}$ – O. N. of Co is **+3**

(b) $[PtCl_4]^{2-}$ – The O. N. of Pt is **+2**

(c) $[CrCl_3\ (NH_3)_3]$ – The O. N. of Cr is **+3**

(d) $[CoBr_2\ (en)_2]^+$ – The O. N. of Co is **+3**

(e) $K_3\ [Fe(CN)_6]$ – The O. N. of Fe is **+3.**

Q.7 **Using IUPAC norms write the formulae for the following:**

(a) Tetrahydroxozincate (III)

(b) Hexaamine cobalt (III) sulphate

(c) Potassiumtetrachloropalladate (II)

(d) Potassium tri (oxalato) chromate (III)

(e) Diamminedichloroplatinum (II)

(f) Hexaammineplatinum (IV)

(g) Potassium tetracyanonickelate (II)

(h) Tetrabromocuprate (II)

(i) Pentaamminenitrito – O – cobalt (III)

(j) Penetaamminenitrito – N – cobalt (III)

Ans. **(a)** $[Zn\ (OH)_4]^{2-}$ **(b)** $[Co\ (NH_3)_6]_2(SO_4)_3$

(c) $K_2\ [PdCl_4]$ **(d)** $K_2\ [Cr(C_2O_4)_2]$

(e) $[PtCl_2\ (NH)_3]_2$ **(f)** $[Pt\ (NH_3)_6]^{4+}$

(g) $K_2\ [Ni(CN)_4]$ **(h)** $[CuBr_4]^{2-}$

(i) $[Co(ON)(NH_3)_5]^{2+}$ **(j)** $[Co\ (NH_3)_5\ (NO_2)]_{2+}$.

Q.8 **Using IUPAC norms write the systematic names of the following:**

(a) $[Co\ (NH_3)_6]\ Cl_3$

(b) $[CoCl(NO_2)\ (NH_3)_4]Cl$

(c) $[Ni(NH_3)_6]Cl_2$

(d) $[PtCl\ (NH_2\ CH_3)\ (NH_3)_2]Cl$

(e) $[Mn(H_2O)_6]^{2+}$

(f) $[Co(en)_3]^{3+}$

(g) $[Ti(H_2O)_6]^{3+}$

(h) $[NiCl_4]^{2-}$

(i) $[Ni(CO)_4]$

Ans. **(a)** Hexammine cobalt (III) chloride

(b) Tetrammine chloro nitro cobalt (III) chloride

(c) Hexaamine chloro (methylamine) platinum (II) chloride

(d) Diammine chloro (methylamine) platinum (II) chloride

(e) Hexaaqua managanese (II)

(f) Tris (ethylenediamine) cobalt (II)

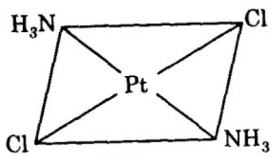
(g) Hexaaqua titanium (III)

(h) Tetrachoro nicklate (II)

(i) Tetracarbonyl nickel (O).

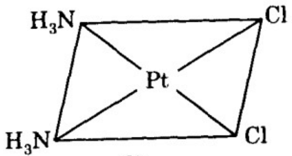
Q.9 **Explain with examples geometric and optical isomerism.**

Ans. **Geometrical Isomerism.** This type of isomerism arises in coordination compounds due to the difference in geometrical arrangement of the ligands around the central metal atom / ion. This is also known as cis – trans isomerism.



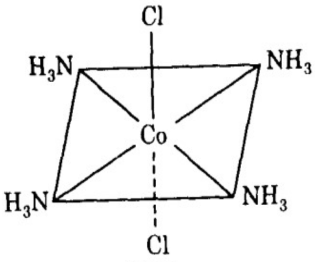
Trans-

In tetra coordinate square planar complex the cis – isomer has the same groups on the same side where as in trans – isomer the same groups are on opposite sides. e.g.

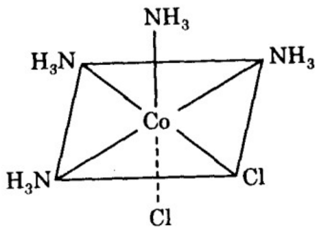


Cis-

This type of isomerism is also shown by octahedral complexes e.g. $Co(NH_3)_4Cl_2$

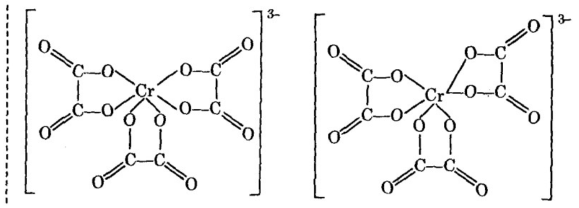


Trans-



Cis-

Optical Isomerism. Optical isomers are non – superimposable mirror images of each other. They possess the property of **chirality.** They have identical physical and chemical properties but differ in **optical rotation.** One of them rotates the plane polarized light toward right and is called dextro – rotatory (d – isomer) and the other rotates plane polarized right towards left and is called laevo rotroty (l – isomer) e.g. $[Cr(C_2O_4)_3]^{3-}$



Q.10 Specify which out of the following complex structures exhibit geometric isomerism:

(a) linear (b) square – planar

(c) tetrahedral (d) octahedral

Ans. The following will show geometrical isomerism.

(b) – Square planar

(d) – tetrahedral.

Q.11 How many geometric isomers are possible in the following coordination entities:

(a) $[Cr(OX)_3]^{3-}$ (b) $[CoCl_3(NH_3)_3]$

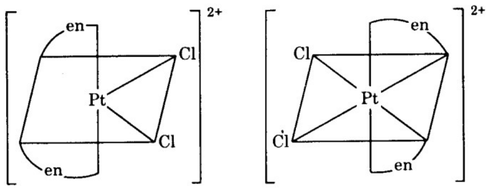
Ans. (a) Two **(b)** Two

Q.12 Draw the structure of optical isomers of:

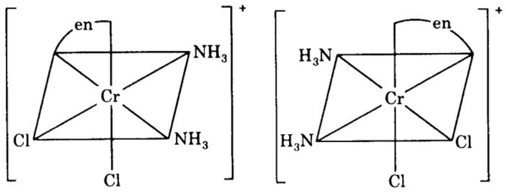
(a) $[Cr(OX)_3]^{3-}$ (b) $[PtCl_2(en)_2]^{2+}$

(c) $[CrCl_2(en)(NH_3)_2]^{+}$

Ans. (a) Refer to Q. 9.



(b)



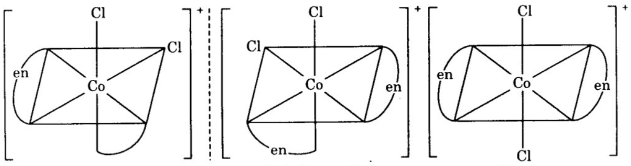
(c) Optical Isomerism. Optical isomers are non – superimposable mirror images of each other. They possess the property of **chirality.** They have identical physical and chemical properties but differ in **optical rotation.** One of them rotates the plane polarized light toward right and is called dextro – rotatory (d – isomer) and the other rotates plane polarized right towards left and is called laevo rotroty (l – isomer) e.g. $[Cr(C_2O_4)_3]^{3-}$

Q.13 **Draw all the isomers (geometric and optical) of:**

(a) $[CoCl_2(en)_2]^+$

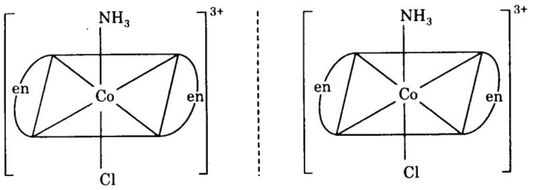
(b) $[CoCl(en)_2(NH_3)]^{2+}$

(c) $[CoCl_2(en)(NH_3)_2]^+$

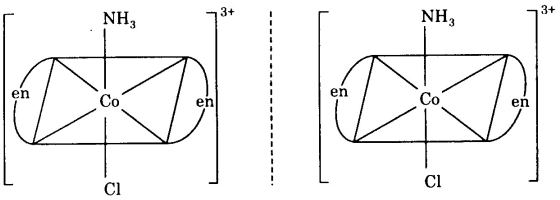


Cis- Optical isomer of *cis-* *Trans-*

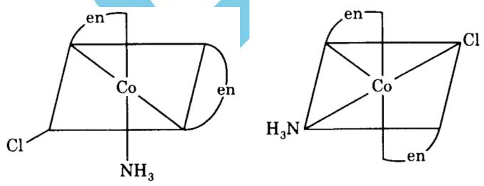
Ans. **(a)**

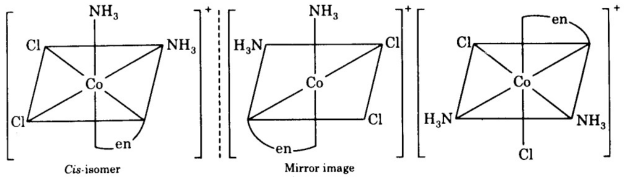


(b) Optical Isomers



Geometrical Isomers





Cis-isomer Mirror image of *cis*-isomer

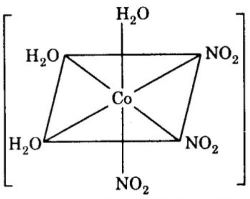
Q.14 **Draw the structures of:**

(a) **Cis – dichlorotetracyano – chromate (III)**

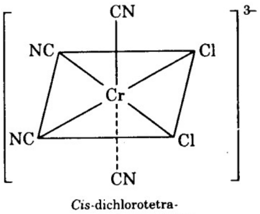
(b) **Mer – triamminetri chlorocobalt (III)**

(c) **Fac – triaquatrinitor – N – cobalt (III).**

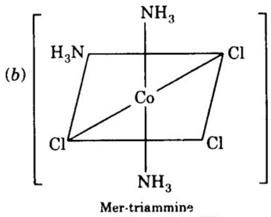
Ans.



Fac-Triaquatrinitro—N-cobalt (III)



Cis-dichlorotetra-
cyano chromate (III)



Mer-triammine
trichloro cobalt (III)

Q.15 **Illustrate with an example each of the following:**

(a) **ionization isomerism**

(b) **linkage isomerism**

(c) **coordination isomerism.**

Ans. **(a)** $[Co(NO_3)(NH_3)_5]SO_4$ and $[Co(NH_3)_5SO_4]\ NO_3$ are ionization isomers.

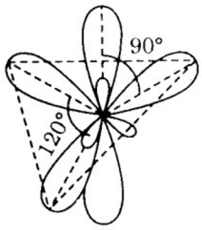
(b) $[Co(NH_3)_5ONO]^{2+}$ and $[Co(NH_3)_5NO_2]^{2+}$ linage isomers.

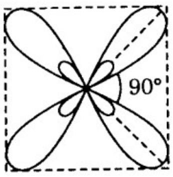
(c) $[Cr(NH_3)_6]Co(CN)_6]$ and $[Co(NH_3)_6]$ $[Cr(CN)_6]$ are coordination isomers.

Q.16 **Sketch the geometrical shapes of the following sets of hybrid orbitals:**

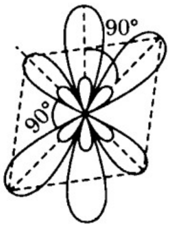
(a) dsp² **(b) dsp³**

(c) d²sp³ **(d) sp³**

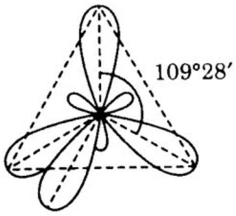




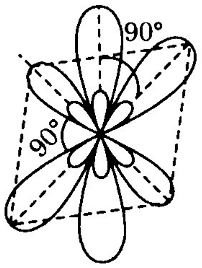
Ans. (a) dsp^2



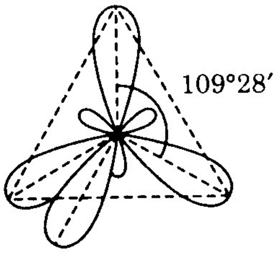
(b) sp^3d or dsp^3



(c) sp^3d^2 or d^2sp^3

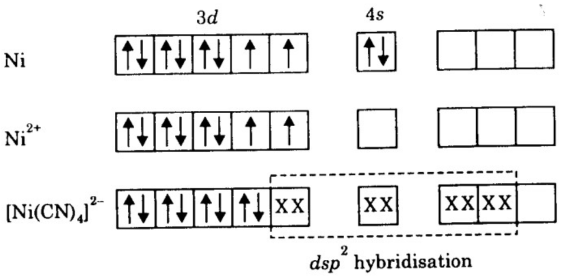


(d) sp^3



Q.17 **Explain on the basis of valence bond theory, the experimental finding that $[Ni(CN)_4]^{2-}$ ion with a square – planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.**

Ans. **$[Ni(CN)_4]^{2-}$**



Where XX represents the lone pair of electrons from CN^-.

Because of dsp^2 hybridization, it is square planar complex.

Since there is no unpaired electron so it is diamagnetic.

$[NiCl_4]^{2-}$

XX is electron pair donated by each Cl.

Because of sp^3 hybridization it is tetrahedral due to the presence of two unpaired electrons it is paramagnetic.

Q.18 **Write the correct formulae for the following coordination compounds:**

(a) $CrCl_3$**.$6H_2O$ (violet, with 3 chloride ions / unit formula)**

(b) $CrCl_3.6H_2O$ (light green colour, with 2 chloride ions / unit formula)

(c) $CrCl_3.6H_2O$ (dark green colour, with 1 chloride ions / unit formula)

[Hint: Some of these compounds may exist as hydrates].

Ans. **(a)** $[Cr(H_2O)_6]Cl_3$

(b) $[Cr(H_2O)_5Cl]Cl_2.H_2O$

(c) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

Q.19 **Aqueous copper sulphate solution (blue in colour) gives:**

(a) A green precipitate with aqueous potassium fluoride, and

(b) A bright green solution with aqueous potassium chloride.

Explain these experimental results.

Ans. The green precipitate is of CuF_2.

$CuSO_4 + 2KF\ (aq) \rightarrow CuF_2\downarrow + K_2SO_4$

(green)

The green colour solution is due to $K_2[CuCl_4]$

$CuSO_4 + 4KCl \rightarrow K_2\ (CuCl_4) + K_2SO_4$

(green solution) (Soluble complex)

Q.20 **What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when H_2S (g) is passed through this solution?**

Ans. KCN reacts with $CuSO_4$ to form $K_2\ [Cu(CN)_4] + K_2SO_4$

Complex

The coordination entity is $[Cu(CN)_4]^{2-}$

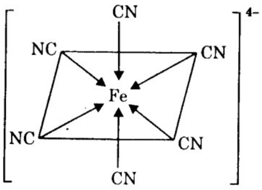
Since the complex ion does not yield Cu^{2+} ions and remains as a single entity so not ppt. of CuS is obtained when H_2S is passed through this solution.

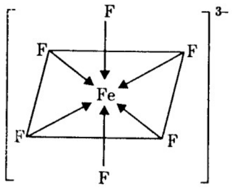
Q.21 **Discus the nature of bonding in the following coordination entities on the basis of valence bond theory:**

(a) $[Fe(CN)_6]^{4-}$ **(b) $[FeF_6]^{3-}$**

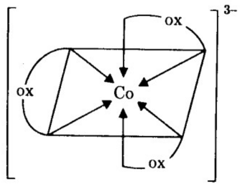
(c) $[Co(OX)_3]^{3-}$ **(d) $[CoF_6]^{3-}$.**

Ans. **(a)** Since it is a complex compound so it has coordinate bonds between ligands CN^- and central metal Fe^{2+}

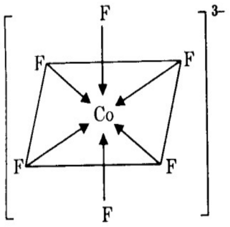




(b) Coordinate bonds between Fe^{3+} and F^-



(c) Coordinate bonds between Co^{3+} and $C_2O_4^{2-}$ (lignad)



(d) Coordinate bonds between Co^{3+} and F^-.

Q.22 **Write the valence bond description of:**
(a) $[Ni(CN)_4]^{2-}$ **(b)** $[Ni\,Cl_4]^{2-}$**.**

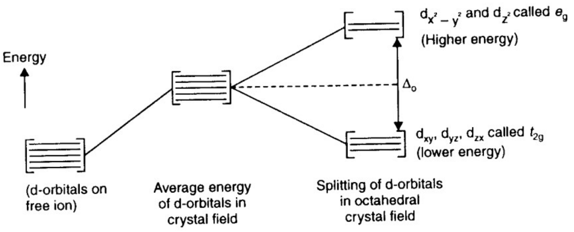
Ans. Refer to Q. 17 of this section.

Q.23 **What is understood by the generalization, 'magnetic criteria of the bond type'? Illustrate your answer with suitable examples.**

Ans. By magnetic criterion of bond type we means that it is possible to predict the geometry of the coordinate entity if we know its magnetic behaviour. e.g. $[Ni(CN)_4]^{2-}$ is diamagnetic, so we can predict that it has undergone dsp^2 hybridization and has a square planar geometry but since $[NiCl_4]^{2-}$ is paramagnetic; so it has sp^3 hybridization and thus tetrahedral shape.

Q.24 **Draw figure to show splitting of degenerate d orbitals in an octahedral crystal field.**

Ans. Te splitting of d – orbital in an octahedral field is shown below.

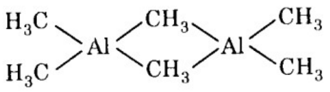


Q.25 **State the essential requirements for regarding a compound as an organometallic. Which amongst the following are organometallic compounds:**
(a) $B(CH_3)_3$ **(b)** $B(OCH_3)_3$
(c) $SiCl_3(CH_3)$ **(d)** $N(CH_3)_3$

Ans. The essential requirement for regarding a compound as organometallic compound is that it must have a metal – carbon bond
Of the given compounds (a) and (c) may be classified as organometallic compounds.

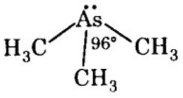
Q.26 **Write the formulae of the following:**
(a) **methyllithium**
(b) **tetramethysilane**
(c) **trimethylbismuth**
(d) **trimethylarsane**
(e) **hexamethyldialuminium**
(f) **trimethylboron.**

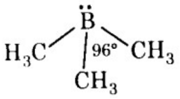
Ans.

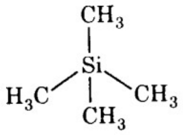


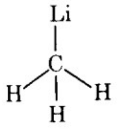
26. **(a)** $H_3C - Li$ **(b)** $Si(CH_3)_4$
(c) $Bi(CH_3)_3$
(d) $As(CH_3)_3$ **(e)** $Al_2(CH_3)_6$ i.e.
(f) $B(CH_3)_n$

Q.27 **Sketch the structure of the organometallic compounds given in 10.26.**

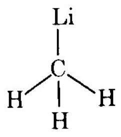




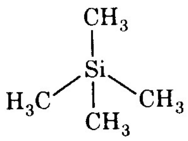




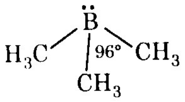
Ans. **(a)**



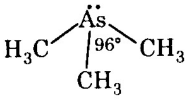
(b)



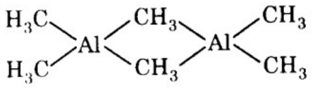
(c)



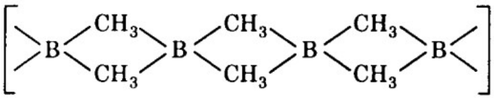
(d)



(e)



(f)

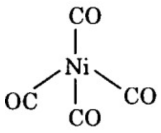


Q.28 **Give IUPAC name and draw the structure of:**

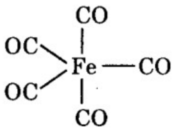
(a) **$Ni(CO)_4$** **(b)** **$Fe(CO)_5$**

(c) **$[PtCl_3(C_2H_2)]^-$** **(d)** **$[Cr(CO)_6]$.**

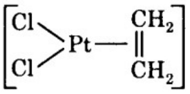
Ans. **(a)** Tetracarbonyl – nickel (O);



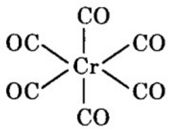
(b) Pentacarbonyl iron (O);



(c) Trichloroetheneplatinate (II). It is known as zeise salt.



(d) Hexacarbonyl chromium (O).



Q.29 **Assign oxidation number to the metal atom in the compounds given in 10.28.**

Ans. **(a)** Ni = 0 **(b)** Fe = 0

(c) Pt = + 2 **(d)** Cr = 0.

Q.30 **Discuss the nature of bonding in $[Ni(CO)_4]$.**

Ans. In $Ni(CO)_4$, we find that both σ or π bonds are formed. Sigma (σ) bonds is formed by donation of lone pair of electron by CO to vacant d – orbitals of nickel. The pi (π) bonds is formed by back donation of pair of electrons from filled d – orbitals of nickel to vacant anitbonding orbital of CO.

Q.31 **Discuss briefly the role of coordination compounds in:**

(a) **biological systems,**

(b) **analytical chemistry,**

(c) **medicinal chemistry, and**

(d) **extraction / metallurgy of metals.**

Ans. **Role of coordination compounds**

(a) In biological systems. Haemoglobin, a complex of iron acts as carrier of oxygen in animals and human beings. Chlorophyll, a complex of Mg is helpful in the process of photosynthesis. It is present in green plants.

(b) In Analytical chemistry. To determine the harness of water we use EDTA. In laboratory EDTA (a complex compound) is used in the estimation of Ca^{2+}, Mg^{2+} ions. Another complex known as DMG (Dimethyl glyoxime) is used in the estimations of Ni^{2+}.

(c) In Medicines. Cis – platin another coordination compound is used as an anti – cancer agent in the treatment of cancer.

(d) In Metallurgy. In the metallurgy of Ag and Au we first prepare their cyanide complexes which are then reduced with zinc metal to get pure Ag or Au.

EXERCISE-I UNSOLVED PROBLEMS

Q.1 $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why

Q.2 $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

Q.3 Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

Q.4 Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.

Q.5 The hexaaquomanganese (II) ion contains five unpaired electrons while the hexacyano ion contains only one unpaired electron. Explain using crystal field theory.

Q.6 Calculate the overall complex dissociation equilibrium constant for the $Cu\,(NH_4)^{2+}_4$ ion, given that β_4 for this complex is 2.1×10^{13}.

Q.7 Explain the bonding in coordination compounds in terms of Werner's positulates.

Q.8 $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1 : 1 molar ratio gives the lest of Fe^{2+} but $CuSO_4$ soluiton mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ion. Explain why ?

Q.9 Explain with two examples each of the following Coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

Q.10 What is meant by unidentate, didentate and ambidentate ligands ? Give two example for each.

Q.11 Specify the oxidation numbers of the metals in the following coordination entities.
(i) $[Co(H_2O)\,(CN)\,(en)_2]^{2+}$
(ii) $[PtCl_4]^{2-}$ (iii) $[Cr(NH_3)_3Cl_3]$
(iv) $[CoBr_2\,(en)_2]^{+}$ (v) $K_3\,Fe\,(CN)_6$

Q.12 Using IUPAC norms, write the formulae of the following :
(i) Tetrahydroxozincate (II)
(ii) Hexaamminecobalt (III) sulphate
(iii) Potassium tetrachloridopalladate (II)
(iv) Potassiumtrioxalatochromate (III)
(v) Diamminedichloridoplatinum (II)
(vi) Hexaammineplatinum (IV)
(vii) Potassium tetracyanonickelate (II)
(viii) Tetrabromidocuprate (II)
(ix) Pentaamminenitrito-O-cobalt (III)
(x) Pentaamminenitrito-N-cobalt (III)

Q.13 List the various types of isomerism possible for coordination compounds, giving an example of each.

Q.14 How many geometrical isomers are possible in the following coordination entities ?

Q.15 Draw the structure of optical isomers of
(i) $[PtCl_2]\,(en)_2]^{2+}$
(ii) $[Cr(NH_3)_2Cl_2(en)_2]^{+}$

Q.16 Draw all the isomers (geometrical and optical) of
(i) $[Co(NH_3)Cl(en)_2]^{2+}$
(ii) $[Co(NH_3)_2Cl_2(en)]^{+}$

Q.17 Write all the geometrical isomers of $[Pt(NH_3)\,(Br)\,(Cl)\,(py)]$ and how many of these will exhibit optical isomerism ?

Q.18 Aqueous copper sulphate solution (blue in colour) gives (i) a green precipitate with aqueous potassium fluoride, and (ii) a bright green solution with aqueous potassium chloride. Explain these experimental results.

Q.19 What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate ? why is that no precipitate of copper sulphide is obtained when H_2S (g) is passed through this solution ?

Q.20 Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory :
(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$
(ii) $[Co(C_2O_4)_3]^{3-}$ (iv) $[NiCl_4]^{2-}$

Q.21 Draw a figure to show splitting of degenerated orbital in an octahedral crystal field.

Q.22 What is spectrochemical series ? Explain the difference between a weak field ligand and a strong field ligand.

EXERCISE-II BOARD PROBLEMS

Q.1 Describe for any two of the following complex ions, the type of hybridization, shape and magnetic property :
(i) $[Fe(H_2O)_6]^{2+}$ (ii) $[Co(NH_3)_6]^{3+}$
(iii) $[NiCl_4]^{2-}$
(At. Nos. Fe = 26, Co = 27, Ni = 28)

Q.2 (a) What is a ligand ? Give an example of a bidentate ligand.
(b) Explain as to how the two complexes of nickel, $[Ni(CN)_4]^{2-}$ and $Ni(CO)_4$, have different structures but do not differ in their magnetic behaviour. (Ni = 28)

Q.3 For the complex $[Fe(en)_2Cl_2]Cl$, (en = ethylene diamine), identify
(i) the oxidation number of iron.
(ii) the hybrid orbitals and shape of the complex
(iii) the magnetic behaviour of the complex
(iv) the number of geometrical isomers.
(v) whether there is an optical isomer also, and
(vi) name of complex. (At. no. of Fe = 26)

Q.4 Compare the following complexes with respect to their shape, magnetic behaviour and the hybrid orbitals involved :
(i) $[CoF_4]^{2-}$ (ii) $[Cr(H_2O)_2(C_2O_4)_2]^-$
(iii) $[Ni(CO)_4]$
(Atomic number : Co = 27, Cr = 24, Ni = 28)

Q.5 Giving a suitable example for each, explain the following :
(i) Crystal field splitting
(ii) Linkage isomerism
(iii) Ambidentate ligand.

Q.6 Compare the following complexes with respect to their molecular shape and magnetic behaviour
(i) $[Cr(NH_3)_6]^{3+}$ (ii) $[Fe(CN)_6]^{4-}$
(iii) $[NiCl_4]^{2-}$
(At. No. Cr = 24, Fe = 26, Ni = 28)

Q.7 (a) What happen when
(i) chlorine gas is passed through a hot concentrated solution of NaOH ?
(ii) sulphur dioxide gas is passed through an aqueous solution of a Fe(III) salt ?
(b) Answer the following :
(i) What is the basicity of H_3PO_3 and why
(ii) Why does fluorine not play the role of a central atom in interhalogen compounds ?
(iii) Why do noble gases have very low boiling points ?

Q.8 Write the state of hybridization, the shape and the magnetic behaviour of the following complex entities.
(i) $[Cr(NH_3)_4Cl_2]Cl$ (ii) $[Co(en)_3]Cl_3$
(iii) $K_2[Ni(CN)_4]$

Q.9 Name the following coordination compounds and draw their structures :
(i) $[CoCl_2(en)_2]Cl$ (ii) $[Pt(NH_3)_2]Cl(NO_2)]$
(At. no. Co = 27, Pt = 78)

Q.10 For the complex $[Fe(en)_2Cl_2]Cl$, identify the following :
(i) Oxidation number of iron.
(ii) Hybrid orbitals and shape of the complex
(iii) Magnetic behaviour of the complex
(iv) Number of its geometrical isomers
(v) Whether there may be optical isomer also
(vi Name of the complex

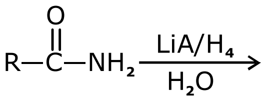
Q.11 State reasons for each of the following :
(i) All the P—Cl bonds in PCl_5 molecule are not equivalent.
(ii) Sulphur has greater tendency for catention than oxygen.

Q.12 State reasons for each of the following :
(i) The N—O bond in NO_2^- is shorter than the N—O bond in NO_3^-.
(ii) SF_6 is kineticaly an inert substance.

Q.13 Complete the following chemical equations :

(i) $CH_3CH_2Cl \xrightarrow{NaCN} (A) \xrightarrow[Ni/H_2]{reduction} (B)$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(iii) 
$R—\overset{O}{\overset{||}{C}}—NH_2 \xrightarrow[H_2O]{LiA/H_4}$

Q.14 For the complex $[NiCl_4]^{2-}$, write
(i) the IUPAC name.
(ii) the hybridization type.
(iii) the shape of the complex.
(Atomic no. of Ni = 28)

OR

What is meant by crystal field splitting energy ? On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when
(i) $\Delta_0 > P$ (ii) $\Delta_0 < P$