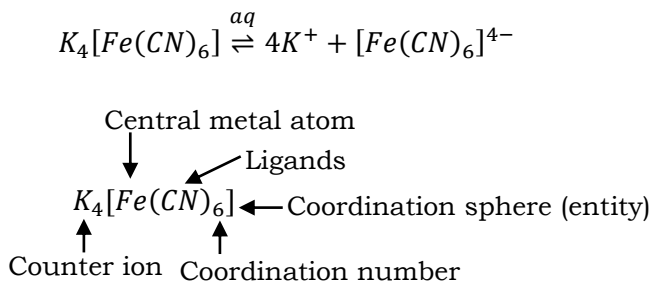


CHAPTER -03

Coordination Compounds

Coordination compounds are those molecular compounds which retain their identity in solid state as well as in dissolved state. In these compounds, the central metal atom or ion is linked by ions or molecules with **coordinate bonds**. e.g. potassium ferrocyanide, $K_4[Fe(CN)_6]$.



Double Salts

These are the addition molecular compounds which are stable in solid state but dissociate into constituent ions in the solution. e.g. Mohr's salt, $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$ get dissociated into Fe^{2+} , NH_4^+ and SO_4^{2-} ions.

Terms Related to Coordination Compounds

1. Complex Ion or Coordination Entity

It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or neutral molecules.

- (i) **Cationic complex entity** It is the complex ion which carries positive charge, e.g. $[Pt(NH_3)_4]^{2+}$.
- (ii) **Anionic complex entity** It is the complex ion which carries negative charge, e.g. $[Fe(CN)_6]^{4-}$.

2. Central Atom or Ion

The atom or ion to which a fixed number of ions or groups are bound, is called central atom or ion. It is also referred as Lewis acid. e.g. in $[NiCl_2(H_2O)_4]$, Ni is central metal atom. It is generally transition element or inner-transition element. These central atoms/ions are also referred to as Lewis acids.

3. Ligands

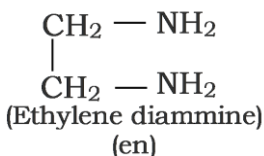
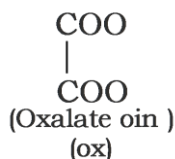
Ligand is electron donating species (ions or molecules) bound to the central atom in the coordination entity.

These may be charged or neutral. Ligands are of the following types:

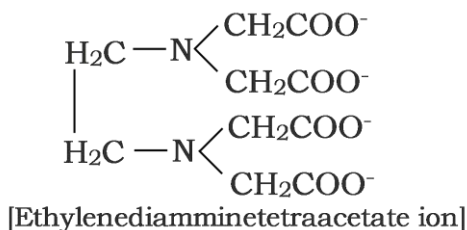
(i) **Unidentate** It is a ligand, which has one donor site, i.e. the ligand bound to a metal ion through a single donor site, e.g. H_2O, NH_3 , etc.

(ii) **Didentate** It is the ligand, which has two donor sites.

e.g.



(iii) **Polydentate** It is the ligand, which has several donor sites. e.g. $[EDTA]^{4-}$ is hexadentate ligand.



(iv) **Ambidentate ligands** These are the monodentate ligands which can ligate through two different sites, e.g. NO_2, SCN , etc.

(v) Chelating ligands Di or polydentate ligands cause cyclisation around the metal atom which are known as chelates. Such ligands use two or more donor atoms to bind a single metal ion and are known as chelating ligands.

More the number of chelate rings, more is the stability of complex.

The stabilisation of coordination compounds due to chelation is known as chelate effect.

┌ π -acid ligands are those ligands which can form σ -bond and π -bond by accepting an appreciable amount of π electron density from metal atom pulling electrons to empty π or π^* -orbitals. ┘

4. Coordination Number

It is defined as the number of coordinate bonds formed by central metal atom, with the ligands.

e.g. in $[PtCl_6]^{2-}$, Pt has coordination number 6.

In case of monodentate ligands,

Coordination number = number of ligands

In polydentate ligands,

Coordination number = number of ligands \times denticity

5. Coordination Sphere

The central metal/ion and the ligands attached to it, are enclosed in square bracket which is known as coordination sphere. The ionisable group written outside the bracket is known as counter ions.

6. Coordination Polyhedron

The spatial arrangement of the ligands which are directly attached to the central atom or ion, is called coordination polyhedron around the central atom or ion. e.g. $[Co(NH_3)_6]^{3+}$ is octahedral, $[Ni(CO)_4]$ is tetrahedral and $[PtCl_4]^{2-}$ is square planar.

7. Oxidation Number of Central Atom

The charge of the complex if all the ligands are removed along with the electron pairs that are shared with the central atom, is called oxidation number of central atom.

e.g. $[Cu(CN)_4]^{3-}$, oxidation number of copper is +1, and represented as $Cu(I)$.

Types of Complexes

Homoleptic Complexes

Complexes in which the metal atom or ion is linked to only one kind of donor atoms, are called homoleptic complexes. e.g. $[Co(NH_3)_6]^{3+}$.

Heteroleptic Complexes

Complexes in which the metal atom or ion is linked to more than one kind of donor atoms are called heteroleptic complexes. e.g. $[Co(NH_3)_4Cl_2]^+$.

Labile and Inert Complexes

Complexes in which the ligand substitution is fast are known as labile complexes and in which ligand substitution is slow, are known as inert complexes.

Effective Atomic Number (EAN)

This concept was proposed by Sidgwick. In a complex, the EAN of metal atom is equal to the total number of electrons present in it.

$$EAN = Z - ON \text{ of metal} + 2 \times CN$$

(where, Z = atomic number of metal atom

ON = oxidation number of metal

and CN = coordination number of complex)

An ion with central metal atom having EAN equal to next inert gas will be more stable.

IUPAC Naming of Complex Compounds

Naming is based on set of rules given by IUPAC.

1. Name of the compound is written in two parts (i) name of cation, and (ii) name of anion.

2. The cation is named first in both positively and negatively charged coordination complexes.
3. The dissimilar ligands are named in an alphabetical order before the name of central metal atom or ion.
4. For more than one similar ligands, the prefixes di, tri, tetra, etc are added before its name. If the di, tri, etc already appear in the complex then bis, tris, tetrakis are used.
5. If the complex part is anion, the name of the central metal ends with suffix 'ate'.
6. Names of the anionic ligands end in 'O', names of positive ligands end with 'ium' and names of neutral ligands remains as such. But exception are there as we use aqua for H_2O , ammine for NH_3 , carbonyl for CO and nitrosyl for NO .
7. Oxidation state for the metal in cation, anion or neutral coordination compounds is indicated by Roman numeral in parentheses.
8. The name of the complex part is written as one word.
9. If the complex ion is a cation, the metal is named same as the element.
10. The neutral complex molecule is named similar to that of the complex cation.

Some examples are

- (i) $[Cr(NH_3)_3(H_2O)_3]Cl_3$
triamminetriaquachromium (III) chloride
- (ii) $[Co(H_2NCH_2CH_2NH_2)_3](SO_4)_3$
tris (ethane-1,2-diammine) cobalt (III) sulphate
- (iii) $[Ag(NH_3)_2][Ag(CN)_2]$
diamminesilver (I) dicyanoargentate(I)
- (iv) $K_4[Fe(CN)_6]$
potassiumhexacyanoferrate (II)

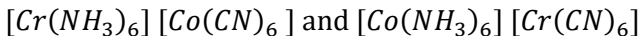
Isomerism in Coordination Compounds

Coordination compounds exhibit the following types of isomerism:

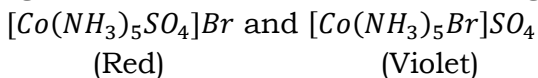
1. Structural Isomerism

In this isomerism, isomers have different bonding pattern. Different types of structural isomers are

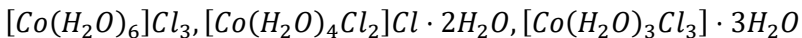
- (i) **Linkage isomerism** This type of isomerism is shown by the coordination compounds having ambidentate ligands. e.g. $[Co(NH_3)_5(NO_2)]Cl$ and $[Co(NH_3)_5(ONO)]Cl$ or pentammine nitrito-N-cobalt (III) chloride and pentamminenitrito-O-cobalt (III) chloride.
- (ii) **Coordination isomerism** This type of isomerism arises from the interchange of ligands between cationic and anionic complexes of different metal ions present in a complex, e.g.



- (iii) **Ionisation isomerism** This isomerism arises due to exchange of ionisable anion with anionic ligand, e.g.



- (iv) **Solvate isomerism** This is also known as hydrate isomerism. In this isomerism, water is taken as solvent. It has different number of water molecules in the coordination sphere and outside it, e.g.



2. Stereoisomerism

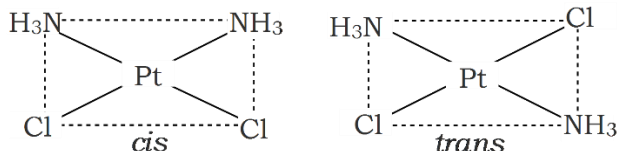
Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. These are of two types :

- (i) **Geometrical isomerism** Geometrical isomers are further of two types i.e. *cis* and *trans* isomers. This isomerism is common in complexes with coordination number 4 and 6.

Geometrical isomerism in complexes with coordination number 4

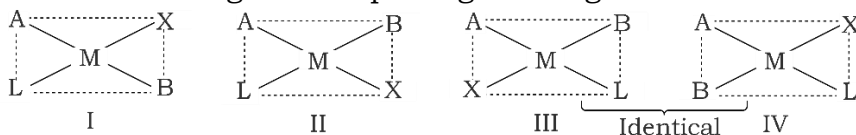
- (i) Tetrahedral complexes do not show geometrical isomerism.

- (ii) Square planar complexes of formula $[MX_2L_2]$ (X and L are unidentate) show geometrical isomerism. The two X ligands may be arranged adjacent to each other in a *cis* isomer, or opposite to each other in a *trans*-isomer, e.g.



- (iii) Square planar complex of the type $[MABXL]$ (where A , B , X , L , are unidentate ligands) shows three isomers, two *cis* and one *trans*.

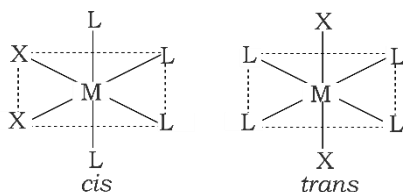
The structures of these isomers can be written by fixing the position of one ligand and placing other ligands *trans* to it.



e.g. $[Pt(\text{NH}_3)(\text{Br})(\text{Cl})(\text{Py})]$

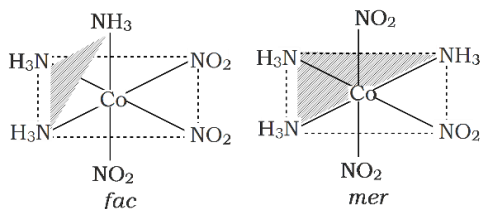
Geometrical isomerism in complexes with coordination number 6

Octahedral complexes of formula $[MX_2L_4]$, in which the two X ligands may be oriented *cis* or *trans* to each other, e.g. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.



Octahedral complexes of formula $[MX_2A_2]$, where X are unidentate ligands and A are didentate ligand, form *cis* and *trans* isomers, e.g. $[\text{CoCl}_2(\text{en})_2]$.

In octahedral complexes of formula $[MA_3X_3]$, if three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, it is known as **facial (fac) isomer**, when the positions are around the meridian of the octahedron, it is known as **meridional (mer) isomer**. e.g. $[Co(NH_3)_3(NO_2)_3]$



- (ii) **Optical isomerism** These are the complexes which have chiral structures. It arises when mirror images cannot be superimposed on one another. These mirror images are called enantiomers. The two forms are called *dextro (d)* and *laevo (l)* forms.

Tetrahedral complexes with formula $[M(AB)_2]$ show optical isomers and octahedral complexes (*cis* form) exhibit optical isomerism.

Bonding in Coordination Compounds

Werner's Theory

Metals exhibit two types of valencies in the formation of complexes. These are primary valencies and secondary valencies.

1. Primary valencies correspond to oxidation number (ON) of the metal and are satisfied by anions. These are ionisable and non-directional.
2. Secondary valencies correspond to coordination number (CN) of the metal atom and are satisfied by ligands. These are non-ionisable and directional. Hence, geometry is decided by these valencies.
3. Metal ion should satisfy both primary and secondary valencies.

Limitations

Werner theory was unable to account for the following.

- (i) Definite geometry of coordination compounds.
- (ii) Presence of magnetic and optical properties of coordination compounds.

To overcome the limitations of Werner's theory, various theories were put forward such as valence bond theory, crystal field theory.

Valence Bond Theory (VBT)

This theory was proposed by L. Pauling in 1930 s. According to this theory, when a complex is formed, the metal ion/atom provides empty orbitals to the surrounding ligands. Coordination number shows the number of such empty orbitals, i.e. number of empty orbitals is equal to the coordination number. These empty orbitals hybridised before participation in bonding and the nature of hybridisation depends on the nature of metal and on the nature of approaching ligand.

Inner orbital Complexes or Outer Orbital Complexes

When outer d -orbital nd shells are used in bonding, the complexes are called **outer orbital complexes**. They are formed due to weak field ligands or high spin ligands and hybridisation is sp^3d^2 . They have octahedral geometry.

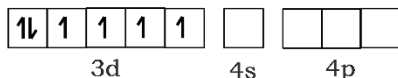
When d -orbitals of $(n - 1)$ shell are used, these are known as **inner orbital complex**.

They are formed due to strong field ligands or low spin ligands and hybridisation is d^2sp^3 . They have also octahedral geometry.

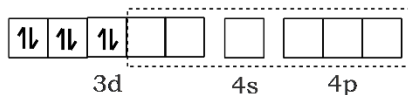
1. 6-ligands (unidentate), octahedral entity

- (i) **Inner orbital complex** $[Co(NH_3)_6]^{3+}$

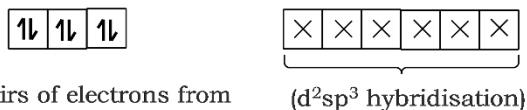
Orbitals of Co^{3+} ion



d^2sp^3 hybridised orbitals of Co^{3+}



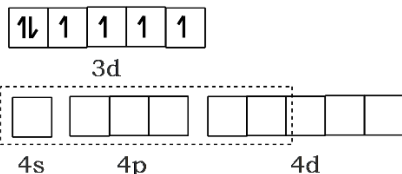
$[\text{Co}(\text{NH}_3)_6]^{3+}$



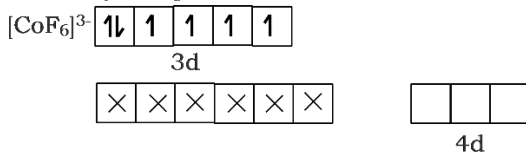
All electrons are paired, therefore complex will be diamagnetic in nature.

(ii) **Outer orbital complex, $[\text{CoF}_6]^{3-}$**

Orbitals of Co^{3+} ion



sp^3d^2 hybridised orbitals of Co^{3+}



Six pairs of electrons from six F ligands (sp^3d^2 hybridisation)

Complex has unpaired electrons, therefore, it will be paramagnetic in nature.

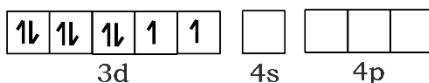
2. 4-ligands (unidentate) tetrahedral entity

| S. No. | Inner orbital complexes | Outer orbital complexes |
|--------|----------------------------------|---------------------------------|
| (a) | Strong field or low spin ligands | Weak field or high spin ligands |

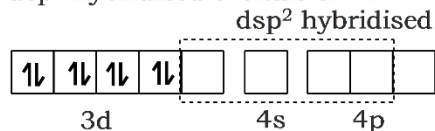
| | | |
|-----|---|---|
| (b) | Hybridisation is dsp^2 (where one orbital of $3d$, one orbital of $4s$ and two orbitals of $4p$) | Hybridisation is sp^3 (where one orbital of $4s$ and three orbitals of $4p$) |
| (c) | Square planar shape | Tetrahedral shape |

(i) Inner orbital complex, $[Ni(CN)_4]^{2-}$

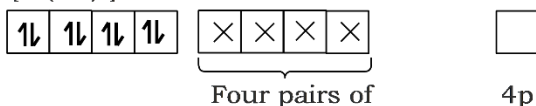
Orbitals of Ni^{2+} ion



dsp^2 hybridised orbitals of Ni^{2+}



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

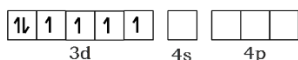


groups

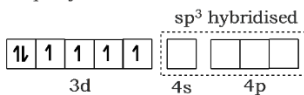
All electrons are paired so complex will be diamagnetic in nature.

(ii) Outer orbital complex, $[CoCl_4]^-$

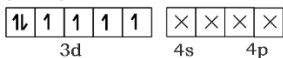
Orbitals of Co^{3+} ion



sp^3 hybridised orbitals of Co^{3+}



$[CoCl_4]^-$



Four pairs of electrons from $4Cl^-$
(sp^3 hybridisation)

Since, complex has unpaired electrons, so it will be paramagnetic in nature.

Limitations of VBT

This theory could not explain the quantization of the magnetic data, existence of inner orbital and outer orbital complex, change of magnetic moment with temperature and colour of complexes.

Crystal Field Theory (CFT)

This theory was proposed by H. Bethe in 1929 and van **Vleck**. **Orgel**, in 1935, applied this theory to coordination compounds. In this theory, ligands are treated as point charges in case of anions and dipoles in case of neutral molecules.

The five *d*-orbitals are classified as

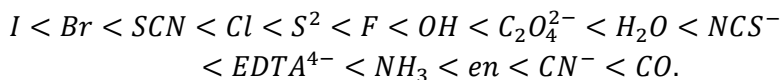
- (i) Three *d*-orbitals i.e. d_{xy} , d_{yz} and d_{zx} are oriented between the coordinate axes and are called t_{2g} -orbitals.
- (ii) The other two *d*-orbitals, i.e. $d_{x^2-y^2}$ and d_{z^2} oriented along the axes are called e_g -orbitals.

Due to approach of ligands, the five degenerate *d*-orbitals split. Splitting of *d*-orbitals depends on the nature of the crystal field.

┌ The energy difference between t_{2g} and e_g level is designated
by Δ and is called **crystal field splitting energy**. ┐

By using spectroscopic data for a number of coordination compounds, having the same metal ions but different ligand, the crystal field splitting for each ligand has been calculated. A series in which ligand are arranged in order of increasing magnitude of crystal field splitting, is called **spectrochemical series**.

Spectrochemical series



Crystal Field Splitting in Octahedral Complexes

In case of octahedral complexes, energy separation is denoted by Δ_0 (where subscript *o* is for octahedral).

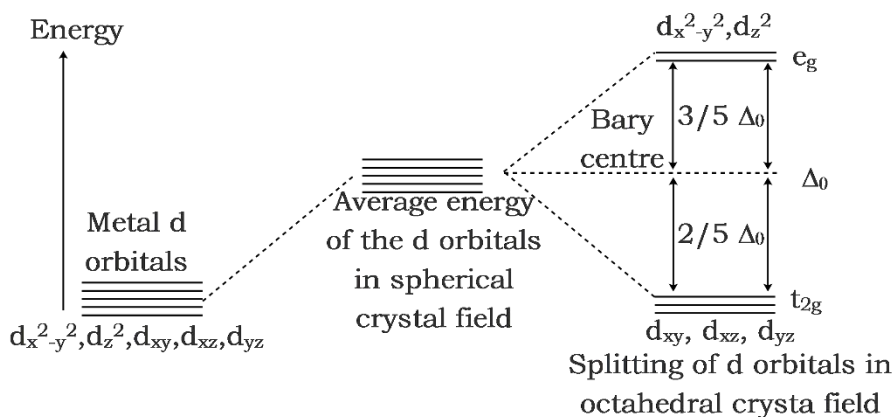
In octahedral complexes, the six-ligands approach the central metal ion along the axis of $d_{x^2-y^2}$ and d_{z^2} orbitals. These are e_g orbitals.

Energy of e_g set of orbitals > energy of t_{2g} set of orbitals.

The energy of e_g orbitals will increase by $(3/5)\Delta_0$ and t_{2g} will decrease by $(2/5)\Delta_0$.

If $\Delta_0 < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_0 < P$ are known as weak field ligands and form high spin complexes.

If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. (where, P = energy required for e pairing in an orbital). Ligands which produce this effect are known as strong field ligands and form low spin complexes.



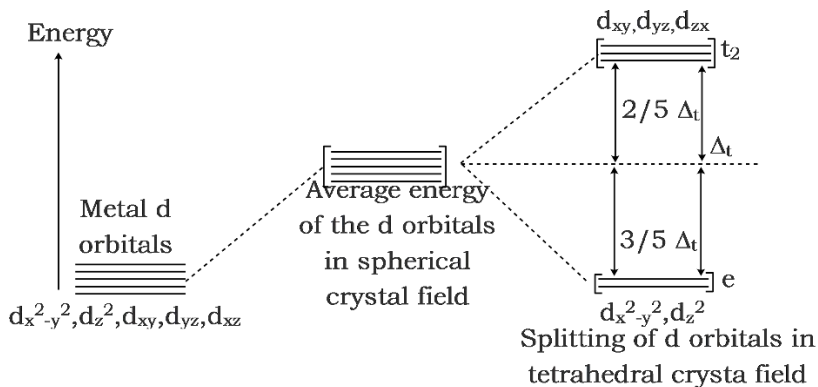
Crystal Field Splitting in Tetrahedral Complexes

In tetrahedral complexes, four ligands may be imagined to occupy the alternate corners of the cube and the metal ion at the center of the cube.

In such complexes d -orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

Energy of t_2 set of orbitals $>$ Energy of e set of orbitals.

Orbital splitting energies are so low that pairing of electrons are not possible so these form high spin complexes.



Colour in Coordination Compounds

The crystal field theory attributes the colour of the coordination compounds due to $d-d$ transition of the electron, i.e. electron jump from t_{2g} level to higher e_g level.

In the absence of ligands, crystal field splitting does not occur and hence the substance is colourless.

e.g. $[Ti(H_2O)_6]^{3+}$ — Violet in colour

$[Cu(H_2O)_4]^{2+}$ — Blue in colour, etc.

Limitations of CFT

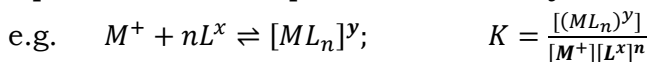
1. It does not consider the formation of p bonding in complexes.
2. It is also unable to account satisfactorily for the relative strengths of ligands, e.g. it does not explain why H_2O is stronger ligand than OH .
3. It gives no account of the partially covalent nature of metal-metal bonds.

Ligand Field or Molecular Orbital Theory

This theory was put forward by Hund and Mulliken. According to this theory, all the atomic orbitals of the atom participating in molecule formation get mixed to give rise an equivalent number of new orbitals, called the molecular orbitals. The electrons are now under the influence of all the nuclei.

Stability of Coordination Compounds

The stability of complex in solution refers to the degree of association between the two species involved in the state of equilibrium. It is expressed as stability constant (K).



The factors on which stability of the complex depends :

- (i) **Charge on the central metal atom** As the magnitude of charge on metal atom increases, stability of the complex increases.
- (ii) **Nature of metal ion** The stability order is $3d < 4d < 5d$ series.
- (iii) **Basic nature of ligands** Strong field ligands form stable complex.

The instability constant or the **dissociation constant** of compounds is defined as the reciprocal of the formation or stability constant.

Importance and Applications of Coordination Compounds

1. They are used in many qualitative and quantitative analysis.
2. Hardness of water is estimated by simple titration with Na_2EDTA .
3. Purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.
4. They have great importance in biological systems.
5. They are used as catalyst for many industrial processes.
6. In medicinal chemistry, there is a growing interest of chelating therapy.

Organometallic Compounds

They contain one or more metal-carbon bond in their molecules. They are of the following types:

1. Sigma (σ) Bonded Compounds

Metal-carbon bond is sigma bond, e.g. $(\text{C}_2\text{H}_5)_4\text{Pb}$, $\text{Zn}(\text{C}_2\text{H}_5)_2$, $\text{R}-\text{Mg}-\text{X}$, etc.

2. Pi(π) Bonded Compounds

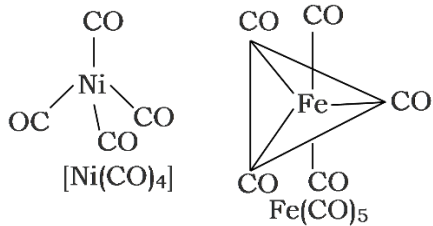
In which molecules/ions containing π bonds act as a ligand, e.g. ferrocene, dibenzene chromium and Zeise's salt.

┌ Zeise's salts is $\text{K}[\text{PtCl}_3(\eta^2 - \text{C}_2\text{H}_4)]$ in which ethylene acts as a ligand which do not have a lone pair of electron.

In ferrocene, $\text{Fe}(\eta^5 - \text{C}_5\text{H}_5)_2$, η represents the number of carbon atoms with which metal ion is directly attached. ┘

3. σ and π Bonded Compounds

Metal carbonyls are their examples. Metal-carbon bond of metal carbonyls have both σ and π -bond character. They have CO molecule as ligand, e.g.



「 Wilkinson's catalyst ($\text{Rh}(\text{PPh}_3)_3\text{Cl}$) is used as homogeneous catalyst in the hydrogenation of alkenes. *Zeigler-Natta* catalyst [$\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}$] acts as heterogeneous catalyst in the polymerisation of ethylene.