CO-ORDINATION CHEMISTRY

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The branch of inorganic chemistry that deals with the study of coordination compounds.

Addition or molecular compounds

When solution of two or more simple stable salts are mixed together in simple molecular proportion and the solution thus obtained is allowed to evaporate, crystals of a new compound are formed. This new compound is called addition or molecular compound.

Simple compounds	Addition compounds

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

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \xrightarrow{\text{Carnollite}} K_2SO_4.Al_2(SO_4)_3.24H_2O$$

TYPE OF ADDITION COMPOUNDS :

Addition compounds are of two types

1. Double salts. These are the addition compounds which are stable in the solid state but give their constituent ions when dissolved in water or in any other ionic solvent. In these compounds the individual properties of the constituent ions are not lost. e.g. $KCl.\ MgCl_2.\ 6H_2O$
2. Coordination (or complex) compounds. These are the addition compounds which donot give all their constituent ions when dissolved in water. In these compounds the individual properties of some constituent ions are lost.

$$K_3[Fe(CN)_6] \rightleftharpoons \underset{\text{simple cation}}{3K^+} + \underset{\text{complex anion}}{\left[Fe(CN)_6\right]^{3-}}$$

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons \underset{\text{complex cation}}{[Co(NH_3)_6]^{3+}} + \underset{\text{simple anion}}{3Cl^-}$$

Difference between double salt and a coordination compound

Double salt

1. Double salts exist only in solid state and dissociate into ions in aqueous solution or in any other solvent.
2. They lose their identity in solution.
3. The properties of the double salt are essentially the same as those of constituent compounds.
4. In a double salt, metal ions exhibit their normal valency.

COORINATION COMPOUND

1. Coordination compounds exist in the solid state.
2. When dissolved in water or any other solvent they do not completely lose their identity in solution.
3. The properties of coordination compound are different from the constituents.
4. In coordination compound, metal ion is surrounded by a number of oppositely charged ions or neutral molecules.

Postulates of Werner’s Coordination Theory

1. In co–ordination compounds, metal atoms exhibit two types of valencies namely, the primary valency and the secondary valency.

   The primary valency is ionizable whereas the secondary valency is non–ionizable. In modern terminology, the primary valency corresponds to oxidation state and the secondary valency corresponds to coordination number.
2. Every metal atom has a fixed number of secondary valencies i.e. it has a fixed coordination number.
3. The metal atom tends to satisfy both its primary as well as secondary valencies. Primary valencies are satisfied by negative ions whereas secondary valencies are satisfied either by negative ions or by neutral molecules. In certain cases, a negative ion may satisfy both types of valencies.
4. The secondary valencies are always directed towards the fixed positions in space and this leads to definite geometry of the coordination compound. In other words, second valencies have characteristic spatial arrangements corresponding to different coordination numbers. In the modern terminology, such spactial arrangements are called coordination polyhedra.

   The secondary valencies, thus, determine the stereochemistry of the complex. On the other hand, the primary valency is non–directional.

Important terms in co–ordination chemistry

Central Metal atom or ion : A complex ion contains a metal atom or ion known as the central metal atom or ion. It is sometimes also called a nuclear atom.

Coordination sphere: The central metal atom or ion and the ligands that are directly attached to it are enclosed in a square bracket. This has been called coordination sphere or first sphere of attraction. It behaves as a single unit.

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$$

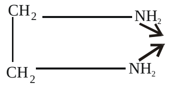
The charge on the complex ion is the algebraic sum of the charges carried by central metal ion and the legends attached to it.

1. Ligands: The neutral molecules anions or cations which are directly linked with the central metal atom or ion in a complex ion are called ligands. The ligands are attached to the central metal ion or atom through coordinate bonds or dative linkage.

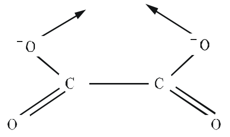
   Types of Ligands : On the basis of denticity ligands are classified as :

   (i) Mono or unidentate ligands: They supply only one electron pair to central metal atom or ion. F^-, Cl^-, Br, H_2O NH_3, CN^- NO_2^-, OH^-, CO, etc., are monodentate ligands.

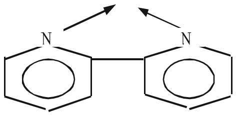
   (ii) Bidentate Ligands : Bidentate Ligands form two co-ordinate bonds with central metal atom/ ion



Ethylenediamine (en)

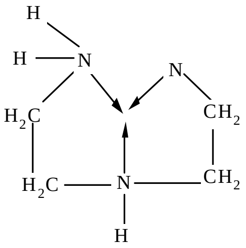


Oxalate (ox)

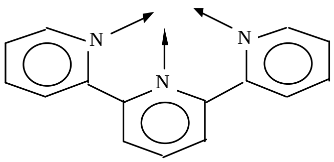


2,2 ′- Dipyridyl (Dipy)

   (iii) Tridentate ligands: Tridentate Ligands from three coordinate bonds with centralmetal atom/ion

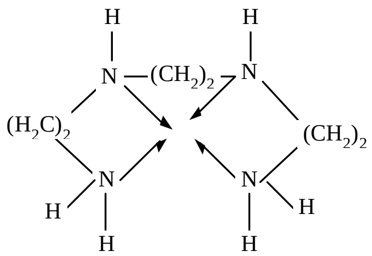


Diethylene triamine (dien)



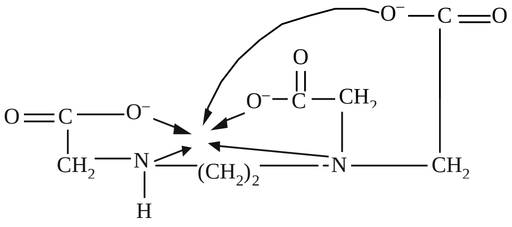
2, 2′, 2″ - Terpyridine (terpy)

(iv) Tetradentate ligands: Tetradentate Ligands from four coordinate bonds with centralmetal atom/ion



Triethylene tetramine
(trien)

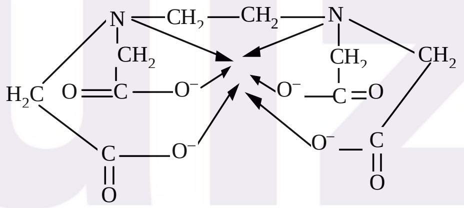
(iv) Pentadentate ligads: Pentadentate Ligands from five coordinate bonds with centralmetal atom/ion



Ethylenediamine triacetate ion

$(EDTA)^{3-}$

(v) Hexadentate ligands: Hexadentate Ligands from six coordinate bonds with centralmetal atom/ion



Ethylenediamine tetracetate ion $(EDTA)^{4-}$

<u>Note:</u> (i) The ligands that form two or more coordinate bonds with centalmetal atom/ion are called polydentate or multidentate ligands.

(ii) A multidentate ligands is known as a chelating ligands if on coordination it results in formation of a closed or cyclic ring. The complexes thus formed are called chelates. The chelates are comparatively more stable than ordinary complexes.

(iii) Polydentate ligands have flexdentate character. It is not jnecessary that all the donor atoms presetn in the polydentate ligands should form coordinate bonds with central metal atom or ion.

(iv) There are certain ligands which have two or more donor atoms but in forming complexes only one donor atom is attached to metal ion. Such ligands are called ambidentate ligands.

M ⟵ CN Cyano	M ⟵ NC Isocyano
M ⟵ SCN Thiocyanide	M ⟵ NCS Isothiocyanide

Chelating Ligands and Chelates

A chelating ligand is a bidendate or polydentate ligand which is attached to the same central metal atom by two or more of its donor atoms resulting in the formation of a complex having a strain free ring structure. The complex having a the ring structure is called chelate or chelated complex. The chelate is also called by various other names like cyclic complex, ring–type complex etc. The formation of a chelate is called chelation or cyclisation.

Factors affecting the stability of chelates

Following are important factors which influence the stability of chelates.

1. Size of the chelate ring. Chelates having six membered rings including the metal atomare more stable than those having five–membered rings which in turn are more stable than the chelates with four membered rings and so on.
2. Number of chelate rings. Greater in the number of chelate rings, greater is the stability of the chelate.
3. Resonance effects. Resonance enhances the stability of the chelate.
4. Chelate effect. The chelated complexes are known to be more stable than the non–chelated complexes. This effect is known as chelate effect.

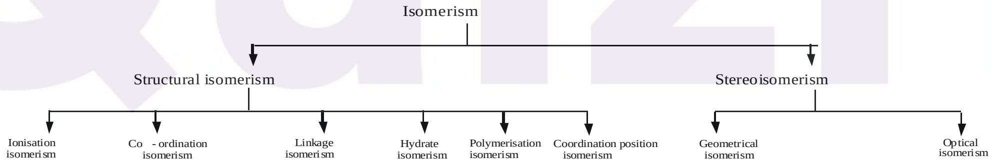
Coordination number: The number of atoms of the ligands that are directly bound to the central metal atom or ion by coordinate bonds is known as the coordination number of the metal atom or ion.

$$\underbrace{\left[Cu(NH_3)_4\right]}_{\text{Co-Ordination sphere}}\ \underbrace{SO_4}_{\text{Ionisation sphere}}$$

$$\begin{aligned} &\text{Central Metal ion} &&= Cu^{2+} \\ &\text{Ligand} &&= NH_3 \\ &\text{Co-ordination Number} &&= 6 \end{aligned}$$

ISOMERISM IN CO–ORDINATION COMPOUNDS

Compounds having the same molecular formula but different structures or spatial arrangements are called isomers and the phenomenon is referred as isomerism.



STRUCTURAL ISOMERISM

The isomers which have same molecular formula but different structural arrangement of atoms or groups of atoms around the central metal ion are called structural isomers and such phenomenon is said to be structural isomerism.

1. Ionisation isomerism: The compounds which have same molecular formula but give different ions in solution are called ionisaion isomers.

   e.g. (i) $[Co(NH_3)_4Cl_2]\ NO_2$ & $[Co(NH_3)_4\ Cl(NO_2)]Cl$

   (ii) $[Co(NH_3)_5\ (NO_3)\ ]\ SO_4$ & $[Co(NH_3)_5\ (SO_4)]NO_3$

2. Coordination isomerism: The type of isomerism occurs in compounds containing both cationic and anionic entities as a complex ion. Coordination isomers differ in the distribution of ligands in the coordination entity of cationic and anionic parts. The examples are

   (i) $[Co(NH_3)_6]\ [Cr(NH)_6]$ and $[Cr(NH_3)_6]\ [Co(CN)_6]$

   (ii) $[Cu(NH_3)_4]\ [PtCl_4]$ and $[Pt(NH_3)_4]\ [CuCl_4]$

3. Linkage Isomerism : The compounds which have the same molecular formula but differ in the mode of attachment of a ligand to the metal atom or ion are called linkage isomers.

e.g. $\left[CO\left(NH_3\right)_5 NO_2\right]Cl_2$ and $\left[CO\left(NH_3\right)_5 (ONO)\right]Cl_2$

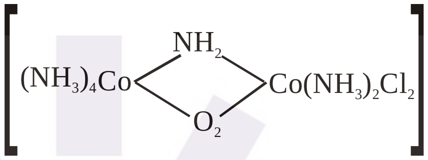
4. Hydrate Isomerism : The compounds which have the same molecular formula but differ in the number of water molecules present as ligands or as molecules of hydration are called hydrate isomers.

The following two isomers are hydrate isomers.

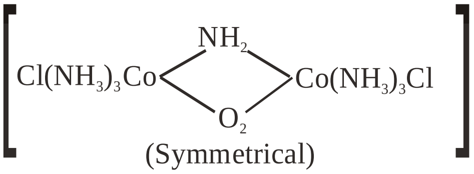
$[Co(en)_2 (H_2O) Cl]Cl_2$ and $[Co(en)_2 Cl_2]Cl.H_2O$
$[Co(NH_3)_4 (H_2O)Cl]Cl_2$ and $[Co(NH_3)_4 Cl_2]Cl.H_2O$
$[Cr(py)_2(H_2O)_2 Cl_2]Cl$ and $[Cr(py)_2H_2O.Cl_3].H_2O$

5. Coordination position isomerism

This type of isomerism is shown by those complex compounds which contain bridging ligands and arises when the non–bridging ligands are differently placed round the central metal atom. Thus (I) and (II) are coordination position isomers to each other, since NH_3 molecules and Cl^- ions (non–bridging ligands) are differently placed round the two Co^{3+} ions.



(Unsymmetrical)



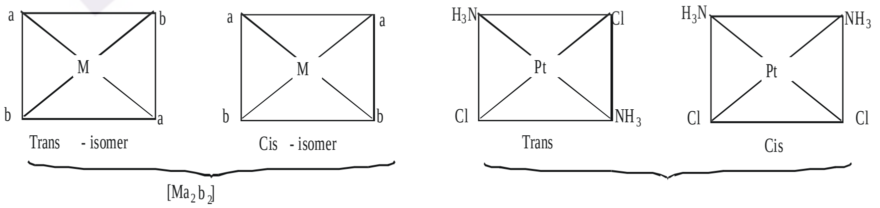
(Symmetrical)

Stereo Isomerism or space Isomerism

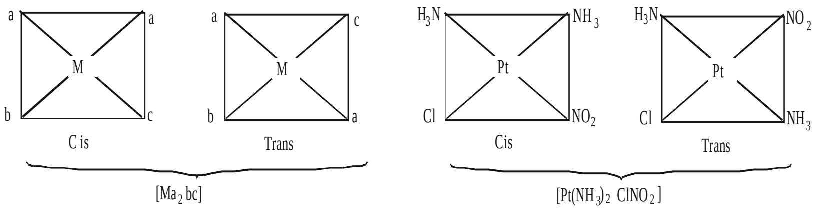
Compounds having same molecular formula, same structural formula but different stereo forms are said to be stereoisomers and such phenomenon is said to be stereo isomerism.

(A) Geometrical Isomerism: This is type of isomerism arises due to ligands occupying different position around the central metal atom or ion. The ligands occupy positions either adjacent or opposite to one another. This type of isomerism is also known as cis–trans isomerism.

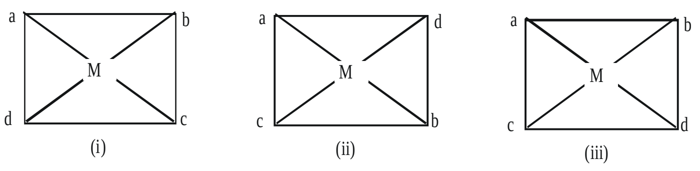
(i) Complexes with general formula, Ma_2b_2 (where both 'a' and 'b' are monodentate) can have cis– and trans–isomers.



(ii) Complexes with general formula Ma_2bc can have cis and trans–isomers.

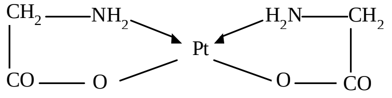


(iii) Complexes with general formula, Mabcd, can have three isomers.

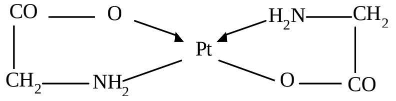


Example: $[Pt(NH_3)\ (NH_2OH)\ (NO_2)\ (py)]\ NO_2$

(iv) Square planar complexes having unsymmetrical bidentate ligands can also show geometrical isomerism. For example, platinum glycinato complex, $[Pt(Gly)_2]$, exhibit geometrical isomerism.

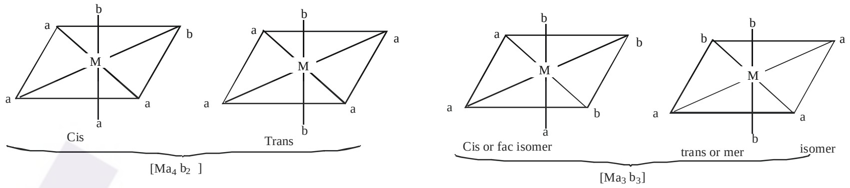


Cis-isomer



Trans-isomer

Octahedral complexes of the type Ma_4b_2, Ma_4bc and $Ma_3\ b_3$ exhibit geometrical isomerism. In Ma_3b_3, if groups occupy one of the octahedral faces, it is facial facisomer while if the position of trio of donor atoms are around the maridian of octahedral, it is called meridional or mer–isomer.



Example: $[Co\ (NH_3)_4\ Cl_2]Cl$, $[Co(NH_3)_3\ Cl_3]$

Note:

1. Octahedral complexes of general formula, Mabcdef, can have fifteen geometrical isomers.
2. Geometrical isomerism is not observed in complexes of coordination number 2 and 3.
3. Geometrical isomerism is not observed in complexes of coordination number 4 of tetrahedral geometry.
4. The complexes of general formulae, Ma_3b or Mab_3, or Ma_4 of square planar geometry do not show geometrical isomerism.
5. The complexes of general formula, Ma_6 and Ma_5b, of octahedral geometry do not show geometrical isomerism.

(B) Optical Isomerism: A coordination compound which can rotate the plane of polarised light is said to be optically active. When the coordination compounds have same molecular formula, same structural formula but differ in their abilities to rotate directions of the plane of polarised light are said to exhibit optical isomerism and molecules are optical isomers. The optical isomers are pair of molecules which are non–superimposable mirror images of each other. The essential requirement for a substance to be optically active is that the substance should not have a plane of symmetry in its structure. The isomer which rotates the plane of polarised light to right direction is termed dextro (d–form) while the isomer which rotates the plane of polarised light to left direction is termed laevo (l–form). The two optically active isomers are collectively called enantiomers. Enantimers are mirror image to each other and their physical properties are different.

Optically isomers rarelyoccur in square planar complexes on account of the presence of axis of symmetry.

Optically isomerism is very common in octahedral complexes. Octahedral complexes of general formulae.

$\left[Ma_2b_2c_2\right]^{n\pm}, \left[Mabcdef\right], \left[M(AA)_3\right]^{n\pm}, \left[M(AA)_2a_2\right]^{n\pm}$, (where AA = symmetrical bidentate ligands)

$[M(AA)_2ab]^{n\pm}$ and $[M(AA)_3]^{n\pm}$ (where AB unsymmetrical ligands) show optical isomerism.

Trans forms of $[M(AA)_2a_2]^{n\pm}$ does not show optical isomerism.

Valence Bond Theory (VBT)

This theory was developed by Pauling. It describes the binding in terms of hybridized orbitals of the central metal atom or ion. The theory mainly deals with the geometry and magnetic properties of complexes. This theory is based on the following assumptions.

1. The central metal atom or ion in the complex makes available an adequate number of empty orbitals for the formation of coordinate bonds with suitable ligands. the number of empty orbitals made available for the purpose is equal to the coordination number of the central ion.
2. The appropriate atomic orbitals (s, p and d) of the metal hybridise to give an equal number of new orbitals of equivalent energy, called hybrid orbitals. The hybrid orbitals are directed towards the ligand positions according to the geometry of the complex.
3. The d orbitals involed in the hybridisation may be inner, viz., (n – 1)d orbitals or the outer, viz., nd orbitals. For example, octahedral hybridisation may be either $(n-1)d^2sp^3$ or $nsnp^3nd^2$. The complexes thus formed are referred to as low spin and high spin complexes, respectively.
4. Each ligand has at least one orbital containing a lone pair of electrons.
5. The empty hybrid orbitals of metal atom or ion overlap with the fully filled orbitals of the ligand, forming the ligand–metal coordinate bond. The number of such bonds varies with the number of empty orbitals made available by the central ion.

LIMITATIONS OF VALENCE BOND THEORY

(i) It involves a number of assumptions.

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

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

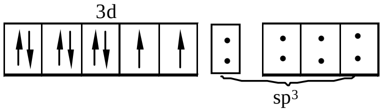
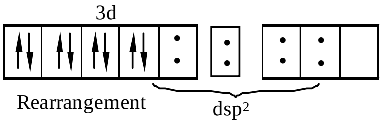
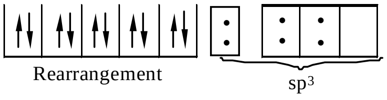
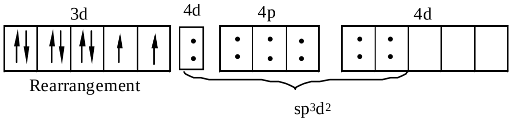
(iv) This theory does not explain the spectral properties of the coordination compounds.

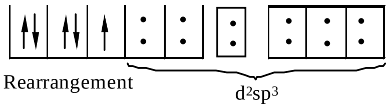
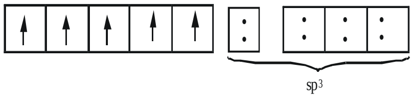
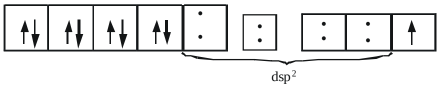
(v) It does not explain the thermodynamic and kinetic stabilities of different coordination compounds.

(vi) It does not make exact predictions regarding the tetrahedral or square planar structures of 4–coordinate complexes.

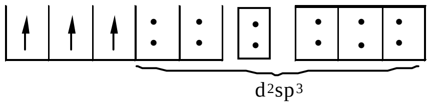
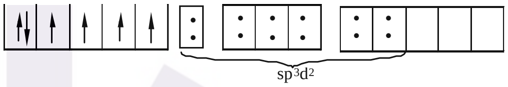
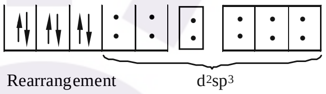
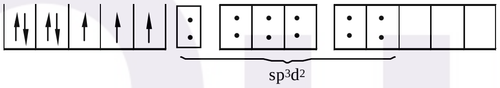
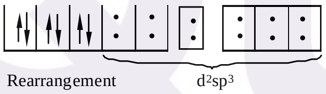
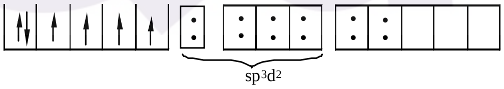
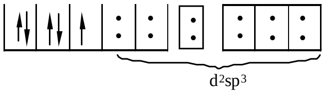
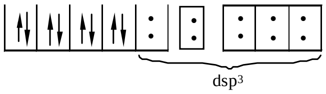
(vii) It does not distinguish between weak and strong ligands.

Geometry and magnetic nature of some of the complexes

Complex	Configuration(2)	Oxidation (3) state of metal	Type of (4) hybridization	Geometry (5) shape	No. of unpaired electrons	Magnetic (7) nature
$[NiCl_4]^{2-}$		+2	sp^3	Tetrahedral	2	Paramagnetic
$[Ni(CN)_4]^{2+}$		+2	dsp^2	Square planar	0	Diamagnetic
$Ni(CO)_4$		0	sp^3	Tetrahedral	0	Diamagnetic
$[Ni(NH_3)_6]^{2+}$		+2	sp^3d^2(outer)	Octahedral	2	Paramagnetic

$[Mn(CN)_6]^{4+}$		+2	d^2sp^3(Inner)	Octahedral	1	Paramagnetic
$[MnCl_4]^{2-}$		+2	sp^3	Tetrahedral	5	Paramagnetic
$[Cu(NH_3)_4]^{2+}$		+2	dsp^2	square planar	1	Paramagnetic

One electron is shifted from 3d– to 4p–orbital

$[Cr(NH_3)_6]^{3+}$		+3	d^2sp^3(Inner)	Octahedral	3	Paramagnetic
$[CoF_6]^{3-}$		+3	sp^3d^2(Outer)	Octahedral	4	Paramagnetic
$[Co(NH_3)_6]^{3+}$		+3	d^2sp^3(inner)	Octahedral	0	Diamagnetic
$[Co(H_2O)_6]^{2+}$		+2	sp^3d^2(outer)	Octahedral	3	Paramagnetic
$[Fe(CN)_6]^{4-}$		+2	d^2sp^3	Octahedral	0	Diamagnetic
$[Fe(H_2O)_6]^{2+}$		+2	sp^3d^2(outer)	Octahedral	4	Paramagnetic
$[Fe(CN)_6]^{3-}$		+3	d^2sp^3(Inner)	Octahedral	1	Paramagnetic
$Fe(CO)_5$		0	dsp^3(Inner)	Trigonal bipyramidal	0	Diamagnetic

Crystal Field Theory :

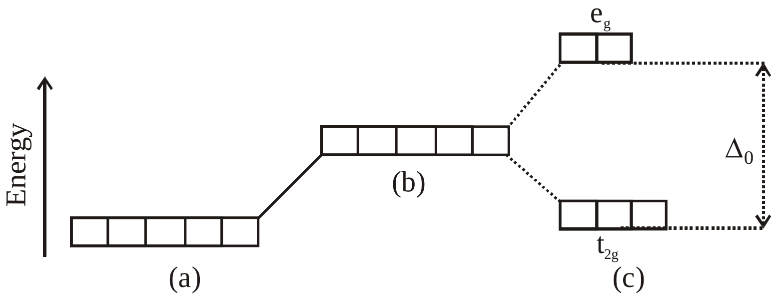
(i) The central metal cation is surrounded by ligands which contains one or more ion pairs of electrons.

(ii) The ionic ligands e.g. F^-, Cl^-, CN^- etc.) are regarded as negative point charges (also called point charges) and the neutrla ligand (e.g. H_2O, NH_3, etc) are regarded point dipoles or simply dipoles i.e. according to this theory neutral ligands are dipolar point dipoles or simply dipoles, i.e. according to this theory neutral ligands are dipolar. If the ligand is neutral, the negative end of this ligand dipole is oriented towards the metal cation.

(iii) The CFT does not provide for electrons to enter the metal orbitals.Thus the metal ion and the ligands do not mix their orbitals or share electrons, i.e it does not consider any orbital overlap.

(iv) According to CFT, the bonding between the metal cation and ligand is not covalent but it is regarded as purely electrostatic.

Splitting of d–orbital in Different Field :

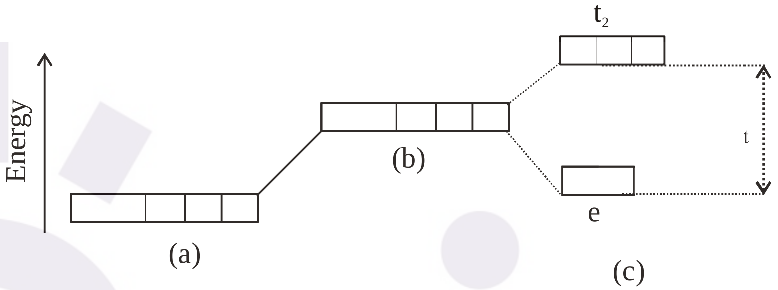


(Crystal field splitting of d-ortbials in an octahedral field)

(a) Five degenerate d-orbitals of free metal cation

(b) Hypothetical degenerate d-orbitals at higher energy level under spherically symmetrical ligand field

(c) Splitting of di-orbitals under the influence of ligands



(Crystal field splitting of d-ortbials in tetrahedral field)

(a) Five degenerate d-orbitals of free metal cation

(b) Hypothetical degenerate d-orbitals at higher energy level under spherically symmetrical ligand field

(c) Splitting of di-orbitals under the influence of ligands

Factors affecting stability of Complexes :

(i) Charge on the central metal atom or ion - Higher the charge greater is the stabiliity e.g. Pt^{4+} complexes are more stable than those of Pt^{2+} complex.

(ii) Position of metal in d-block - A metal belonging to 4-d series makes more stable complexes than thoseof metal of 3d-series. Similarly 5d-series metal make most stable complexes.

(iii) Basic nature of ligands - Higher the base strength of a ligand more stable complex it can make. The order of ligand strengths is called spectrochemical series.

(iv) Presence of chelate rings – Ring complexes formed by bidentate or polydentate ligands are generally more stable.

Prep^n of Co–ordination Compounds:

Coordination compounds are generally prepared by the application of the following methods

(i) Ligand substitution reaction : A reaction involving the replacement of the ligands attached to the central metal ion in the complex by other ligands is called a ligand substition reaction.

$$\underset{\text{Light blue}}{\left[Cu(H_2O)_4\right]^{2+}}(aq) + 4NH_{(aq)} \rightarrow \underset{\text{Deep blue}}{\left[Cu(NH_3)_4\right]^{2+}}(aq) + 4H_2O(l)$$

(ii) Direct mixing of reagnet :

$$PtCl_2 + 2H_2N - \underset{(en)}{C}H_2 - CH_2 - NH_2 \rightarrow \underset{\text{(Dichloro bis ethylene diamine platium II)}}{[Pt(en)_2Cl_2]}$$

Organometallic Compounds

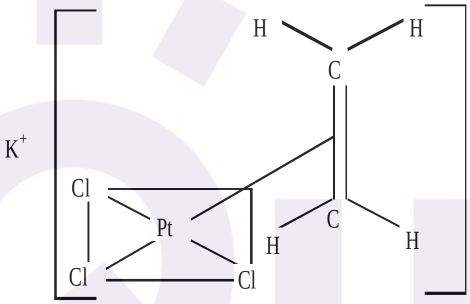
These are the compounds in which a metal atom or a metalloid (Ge, Sb) or anon-metal atom like B, Si, P, etc. (less elecronegative than C) is directly linked to a carbon atom of a hydrocarbon radical or molecule. Organometallic compounds contain at least one.

(1) Metal - Carbon bond, (2) Metalloid - Carbon bond, (3) Non metal – Carbon bond

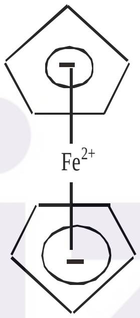
Organometallic compounds may be classified in three classes:

1. Sigma (σ) bonded complexes,
2. Pi (π) bonded complexes,
3. Complexes containing both σ – and π –bonding characteristics.

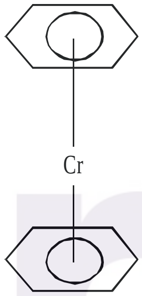
1. Sigma bonded complexes: In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond.
   - (i) Grignard reagents, R – Mg – X where R is an alkyl or aryl group and X is a halogen.
   - (ii) Zinc compounds of the formula R_2Zn such as $(C_2H_5)_2Zn$. This was first isolated by Frankland in 1849. Other similar compounds are $(CH_3)_4Sn$, $(C_2H_5)_4$ Pb, $Al_2(CH_3)_6$, $Al_2(C_2H_5)_6$. $Pb(CH_3)_4$, etc.
2. π –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.



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

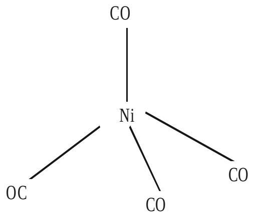


Ferrocene
$Fe(\eta^5\text{-}C_5H_5)_2$

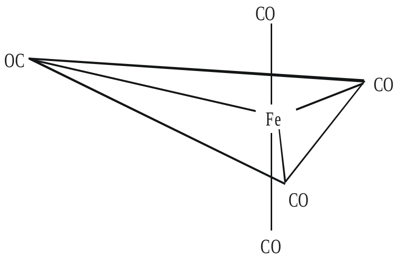


Dibenzene choromium
$Cr(\eta^6\text{–}C_6H_6)_2$

3. σ – and π – bonded organometallic compounds: Metal carbonyls, compounds formed between metal and carbon monoxide belong to this class. These compounds possess both s–and p–bonding. The oxidation state of metal atoms in these compounds is zero.



tetracabony nickel (0)
$Ni(CO)_4$



pentacarbonyl ion (0)
$Fe(CO)_5$