

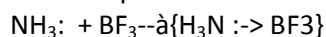
Class 12th Chapter 9 Coordination Compounds Revision Notes & Important Question (www.free-education.in)

Introduction

The Coordination compounds are very important in day to day life, many compounds exist as coordination compounds as they have special type of linkage that is coordinate bond. It is formed between electron rich and electron deficient species.

Coordinate bond: It is a bond in which sharing of electrons occurs but not mutual sharing. In this the shared pair is donated by only one atom and the one that **donates** is donor and the other which accepts is **acceptor**.

For example:



In this NH_3 is donor atom as it has lone pair and BF_3 is acceptor as it is electron deficient compound.

The branch of chemistry that deals with the study of coordination compounds are called as " **coordinate chemistry** "

Examples of some coordinate compounds like:

- Hemoglobin – coordination compound of iron (Fe)
- Chlorophyll – coordination compound of magnesium (Mg)
- Vitamin B12- coordination compound of cobalt (Co)

Most of time coordination compounds are confused with double salts but there exists a lot difference between the two.

Double salts

Double salt is the association of many substances or we can say they mainly contain two salts in equimolar concentration.

1. like Mohr's salt $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
2. Potash alum $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ etc.

In coordination compound once the compound is formed its ions than the compound as a whole do not lose its identity but when dissolved in water they show different properties whereas in case of double salts they don't show different properties but loses their identity in water

$\{\text{Co}(\text{NH}_3)_6\}\text{Cl}_3 \rightarrow \text{Co}(\text{NH}_3)_6 + 3\text{Cl}$ (coordination compound in water)

$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} \rightarrow \text{Fe}^{2+}, \text{NH}_4^+, \text{SO}_4^{2-}, \text{H}^+, \text{OH}^-$ ions (double salt in water)

- Coordination compounds exist in solid as well as aqueous state whereas the double salts exist in solid state and in aqueous state they dissociate into ions.
- The coordination compounds exist in extended octet whereas in double salts they exist in their own valences.

Terminology involved

central metal atom:

- it is the acceptor metal atom present in the coordination compound
- It is mostly d block element
- It act as an acceptor as it has vacant d orbital
- Due to accepting nature they act as Lewis acids

For example in complex: $\{\text{Co}(\text{NH}_3)_6\}\text{Cl}_3$ in this Co is central metal atom

Ligands:

- They are donor atom may be single atom or group of atoms
- They are negatively charged or neutral species with lone pair Br^-, Cl^- etc or neutral like $\text{NH}_3, \text{NO}, \text{CO}$ etc
- They act as Lewis bases
- We can also call ligands as nucleophile as they are nucleus loving

For example in complex: $\{\text{Co}(\text{NH}_3)_6\}\text{Cl}_3$ in this NH_3 is ligand

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coordination sphere:

- It is the combination of atom and ligands.

Example: in $[\text{Co}(\text{NH}_3)_6\text{Cl}_3]$

$[\text{Co}(\text{NH}_3)_6]$ is coordination entity or complex

- They are written in square brackets [coordination entity]
- This coordination sphere may be positively charged, negatively charged
- If it is positively charged then it is called as **cationic entity** and in case of negative charge it is **anionic entity or complex**.

Example: $[\text{Co}(\text{NH}_3)_6]^{3+}$ cationic entity $[\text{Ag}(\text{CN})_6]^-$ anionic entity

counter ion:

- The atom or group of atoms written outside bracket is called counter ion.

Example: in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

Cl_3 is a counter ion or the ionizable part when dissolved in water

- If coordination sphere is with positive charge then counter ion is with negative charge or vice versa.

Coordination entity

- The central metal atom and ligands attached to it forms coordination entity and is written within square brackets

Example : in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

In this $[\text{Co}(\text{NH}_3)_6]$ is coordination entity

Nature of ligands: Their nature is determined by the property denticity

Denticity

it determines the total number of donor atoms in a molecule.

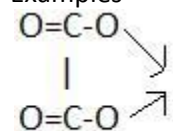
On the basis of the property denticity ligands are :

- **Monodentate / unidentate:** is that which has one donor atom

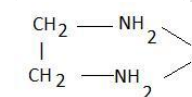
Examples : CN^- , OH^- , Cl^- , Br^- , NH_3 , H_2O , CO etc

- **Di-dentate:** if it has two donor atoms

Examples



(OXALATE ION)



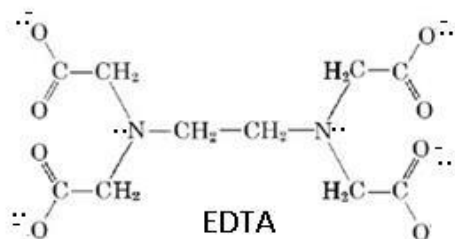
(ethylenediamine)

- **Polydentate :** if it has 3 or more donor atoms in it DIETHYLENE TRIAMINE (tridentate)

$\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$

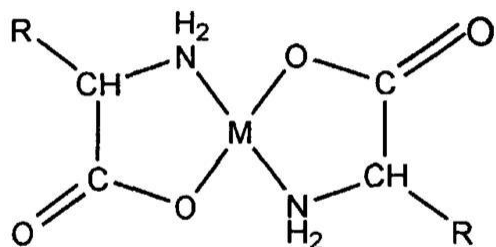
Hexadentate: ethylenediamine tetra acetic acid (EDTA)

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chelate: when the ligand has two or more donor atoms and they are arranged in such a way that they give rise to a ring like structure than the effect is called chelating and the ring formed is chelate .

For example:



uses of chelates:

- They are used in softening of hard water
- In qualitative analysis for detection of metal
- In separation of lanthanoids and actinoids

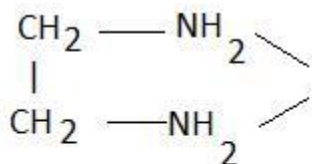
Ambidentate ligand: that have two donor atoms but doesn't show chelation. This group bond at a time by one atom.

For example: CN⁻, NO₂ etc

Symmetrical and unsymmetrical ligands :

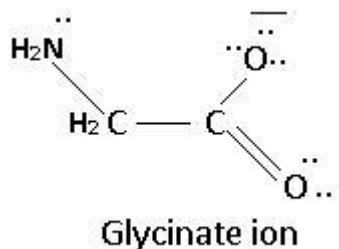
Symmetrical ligands: if ligands attached to central atom are of same type

Example: ethylenediamine etc.



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Unsymmetrical ligands: if ligands attached are of different type.



Example: glycinate ion etc.

Coordination number: it is the number of ligands bonded with the central metal atom for example: IN $[\text{Ag}(\text{CN})_2]^-$ "the no. Of ligands attached are 2 therefore coordination no. is 2".

Oxidation number: it is the residual charge left on the atom when all other atoms are removed from it .it is calculated by assigning appropriate charges to ligands and then equating the sum of the charges on the central atom and the ligands equal to the charge on the coordination sphere.

For example: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in this oxidation state of NH_3 is 0 and for Cl is -1, and ooxidation state of Co is taken as x then

$$(x-3) \times 1=0 \text{ or } x=+3$$

another example: $[\text{Cu}(\text{CN})_4]^{3-}$ in this oxidation state of Cu is taken as x, CN as -1 so,
 $x + (-1 \times 4) = -3$ or $x=+1$

Homo-leptic and hetero-leptic compounds

Homoleptic: are those which have same kind of ligands attached to central metal atom

Example:in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is homoleptic as ligands are same

terolyptic: when ligands attached are of different type

Example: in $[\text{CoCl}_3(\text{NH}_3)_3]^{3+}$ is heterolytic because ligands attached are of different types.

Nomenclature of coordination compounds

Like for ionic compounds the naming is done by writing first cation name and then naming anion.

For example: NaCl is ionic and written as sodium chloride that is in name first part is cationic and other is anionic.

In the same way coordination compounds consist of two parts:Cation and anion. While naming,the name of cationic part is written first followed by anionic part. There are certain set of rules that are followed while writing name of cation.

Naming for cationic species: in which coordination sphere is positively charged

- Name of cation is written first

Let's say the coordination sphere is cationic that is with positive charge for example $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ for the naming of coordination entity is done first and later the counter ion .so in given complex the name of $[\text{Co}(\text{NH}_3)_6]$ is written first than the counter ion Cl

- In case of coordination entity: the name of ligands is written first and then the central metal atom. Forexample, in this $[\text{Co}(\text{NH}_3)_6]$ the name of NH_3 is written first than for Co.
- If the ligands are homoleptic than you can write in any manner but if they are heterodetic than the alphabetical order is followed

For example: in complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]$ the name of ligands is written in alphabetical order that is for ammine firstand then chloro.

Rules for writing the name of the ligand:

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- If the ligand names end with 'ate' or 'ite' than e is replaced by o

Like for oxalate it is written as oxalato, sulphite as sulphato

- If ligand name end with 'ide' than ide is replaced by 'o'

Example for chloride it becomes chlorido

- Neutral ligands are name as such like for water it is aqua, for ammonia it is ammine
- If more than one ligand is present than alphabetical order is followed and di, tri, tetra is prefixed before the name of ligand.

For example: in complex $[\text{Co}(\text{NH}_3)_6]$ ligand name will be hexamine that is hexa for 6

- For polydentate ligands they include numerical prefix –like di is replaced by bi, tri is replaced by tris, tetra is replaced by tetra is so on

For example: $[\text{CoCl}_2(\text{en})_2]$ Cl in this the ligands are dichlorobisethylenediamine

In case of Central metal atom:

Oxidation state of central metal atom is written in numeral after the name of central metal atom

For example: in complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ it is hexamine cobalt (III) that is cobalt (III) is central metal atom with its Oxidation state in numeral

- if complex is cationic than normally the name is used: example is same as given above
- if complex is anionic than metal atom name ends with ate

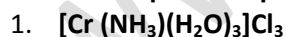
for example: in complex $\text{K}_3[\text{Fe}(\text{CN})_6]$ in this the name is written as potassium hexacyanoferrate(III) that is in this example coordination entity is anionic complex and the name of central metal atom is written with ate followed by Oxidation state in numeral

- if complex is neutral than the normal central metal atom name is used

some commonly used ligands:

- bromo Br^-
- fluoro F^-
- oxo
- hydroxo OH^-
- cyano CN^-
- carbonato CO_3^{2-}
- acetate CH_3COO^-
- ammine NH_3
- aqua H_2O
- nitrosyl NO
- carbonyl CO
- dioxygen O_2
- dinitrogen N_2
- pyridine $\text{C}_5\text{H}_5\text{N}$
- ethylene diamine $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$

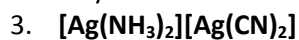
some examples of iupac naming:



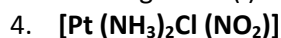
Triamminetriaquachromium(III)chloride



Trisethylenediaminecobalt(III)sulphate



Diamine argentum(i)dicyanoargentate(i)



Diaminechloronitroplatinum(III)

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5. $K_3[Cr(C_2O_4)_3]$

Potassiumtrioxalatochromate(III)

Isomerism in Coordination Compounds

Isomerism is the phenomenon in which compounds have same molecular formula but different structures and these different structures are called as isomers. Isomers are those that have different physical and chemical properties.

There are two types of isomers:

- Structural isomerism
- Stereoisomerism

Structural isomerism: Different types are as follows:-

- ionization isomerism
- Hydrate isomerism
- Coordination isomerism
- Linkage isomerism

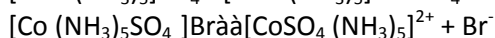
Stereoisomerism: Different types are as follows:-

- geometrical isomerism
- Optical isomerism

Structural isomerism: The compounds have same molecular phenomenon but different structures

- **Ionization isomerism:** they differ in productions of ions in aqueous solution

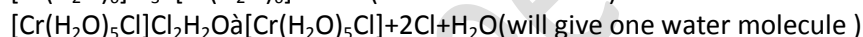
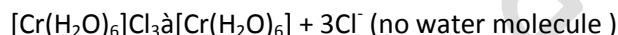
For example: $[CoBr(NH_3)_5]SO_4$ and $[Co(NH_3)_5SO_4]Br$ are ionization isomers when dissolved in water



- **Hydrate or solvate isomerism:** in this they differ in number of molecules of water of crystallization

For example: $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ are hydrate isomers

When dissolved in water



- **Coordination isomerism:** they differ in coordination entities

For example: $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $[Co(CN)_6]$ $[Cr(NH_3)_6]$ are coordination isomers

- **Linkage isomerism:** it is in case of ambidentate ligands and in this they differ in the point of attachment.

For example, in case of CN (cyano) and in case of NC (isocyano)

- **Stereoisomerism:** in these compounds have same molecular formula but differ in spatial arrangements of ligands.

It is of two types:

- Geometrical isomerism
- Optical isomerism

Geometrical isomerism: it is due to difference in the geometrical arrangements of ligands around central metal atom.

it is of further two types :

- Cis
- Trans

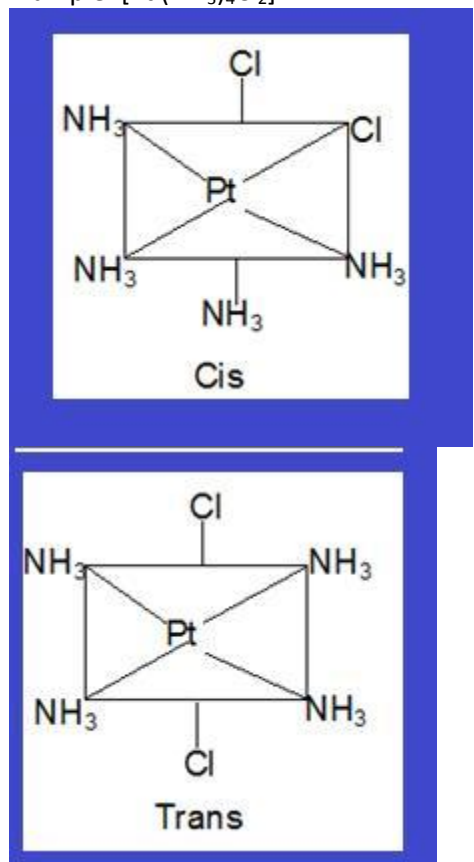
Cis : when the similar ligands are on adjacent position

Trans : when the similar ligands are on opposite positions

Cis and trans isomers are shown below (this is shown by compounds with coordination number 4 and 6)

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Example: $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]$



○ Another type of Geometrical isomerism that occurs in octahedral compounds in Ma_3b_3 like $[\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3]$. It can be of two types :

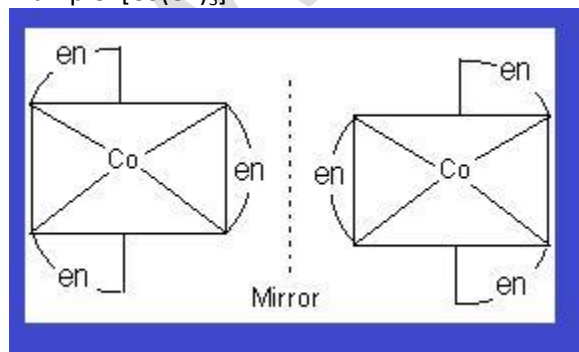
- Facial
- Meridional

Fac :In this three donor atoms of same ligands occupy adjacent positions at corners of an octahedral face

mer :In this three donor atoms of same ligands occupy positions around the meridian of an octahedron.

- **Optical isomers**:they can also show optical isomerism if chiral center is present in them .if they possess chiral center they can rotate the plane of polarized light .

Example: $[\text{Co}(\text{en})_3]$

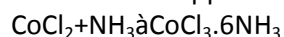


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Bonding in coordination compounds

The first theory in order to explain it was given by **Alfred Werner in 1892**.

He performed various experiments to show that the surrounding atoms exist around central atom. He actually conducted ppt. studies



When $\text{CoCl}_3 \cdot 6\text{NH}_3$ was precipitated with AgNO_3 it gave 3 moles of AgCl this shows that 3 Chloride ions are not directly bonded with cobalt that is why it was precipitated with silver nitrate which gave him the idea about primary and secondary valences' and accordingly he postulated his theory.

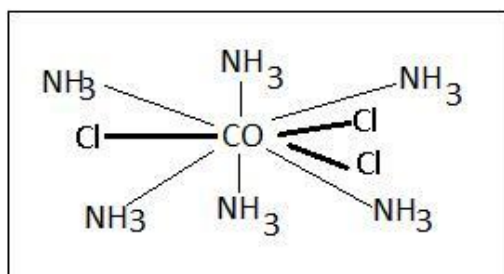
Werner's theory

According to the theory the postulates are:

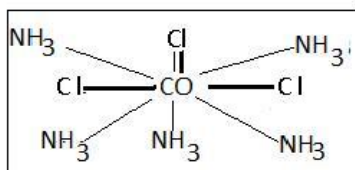
1. Metal exhibit 2 types of vacancies: primary valency and secondary valency
2. Primary valency gives the information about oxidation state and secondary valency gives the information about coordination number
3. Primary valency is variable whereas secondary valency is always fixed
4. Secondary valency that is coordination number determines the geometry of molecule or we can say polyhedral of the molecule.
5. Metal stabilize all its vacancies

Depending upon this theory various structures of coordination compound was explained :

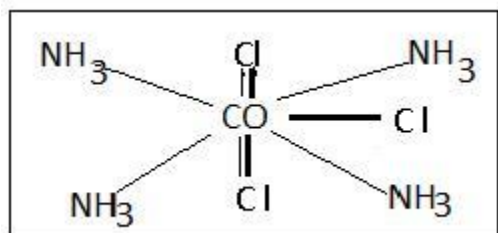
In $\text{CoCl}_3 \cdot (\text{NH}_3)_6$ In this NH_3 is secondary valency and Cl is primary valency



In $\text{CoCl}_3 \cdot (\text{NH}_3)_5$ the ionizable chlorides are only 2



In $\text{CoCl}_3 \cdot (\text{NH}_3)_4$ the ionizable ions are only one chloride ion



Please note the dark lines shows ionizable part and light lines show non ionizable part in all the figures.

Limitations of Werner's theory:

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He was able to explain many facts about coordination compounds but failed to give any information about why only certain elements participate in coordinate bond, why the coordination entity has special geometry ... Due to these reasons other theory was proposed that is valence bond theory

Valence bond theory

It was given by Pauling in 1931

1. He proposed the idea of donating lone pair to central metal atom.
2. Bonding in coordination compound occur due to overlap of orbital of ligand with vacant orbital of central metal atom
3. All the vacant d orbitals have same energy. but the degeneracy of d orbital breaks when ligand approaches
4. Hybridization is considered while drawing polyhedral
5. Metal ions in presence of ligands can use their (n-1)d ns np or ns np Nd.

If the inner d orbital is used than the complex is regarded as inner orbital complex and if outer d orbital is used than the complex is outer orbital complex.

6. The ligands decide which orbitals out of these to be used and accordingly the geometry is decided.

If hybridization

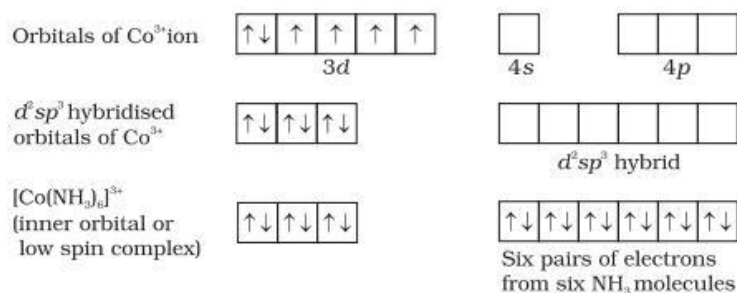
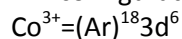
- o sp^3 - tetrahedral
- o dsp^2 -square planar
- o Sp^3d -trigonal bipyramidal
- o Sp^3d^2 - octahedral
- o d^2sp^3 -octahedral

For example:

For any coordination compound: To find the shape using valence bond theory following steps to be followed

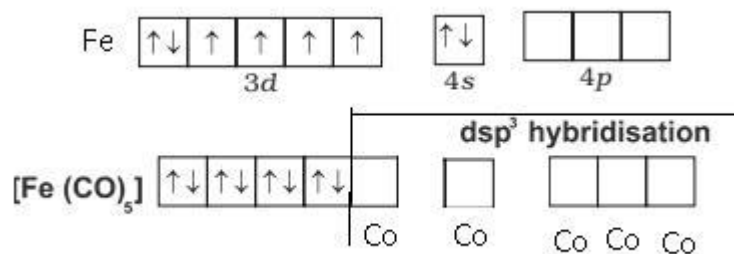
1. Remove the electrons from the metal and form it the ion
2. Rearrange metal electrons if necessary
3. Hybridization
4. Overlapping of hybrid orbitals of metal with ligand

Let us take one example: of example $[Co(NH_3)_6]^{3+}$. In this central metal atom Co atomic no. is 27. The electronic configuration of Co = $(Ar)^{18}3d^74s^2$

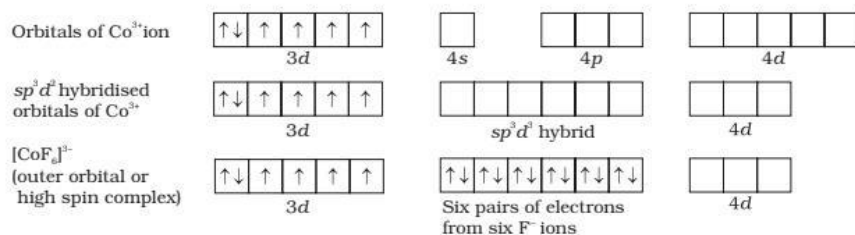


Example $[Fe(CO)_5]$: (inner orbital complex and diamagnetic)

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EXAMPLE: in $[\text{CoF}_6]^{3-}$ (outer orbital complex and paramagnetic)



Drawbacks of valence bond theory:

1. This theory couldn't have valid reason behind that why some complexes of metal oxidation state is inner orbital while in some other complexes the same metal atom ion in same state form outer orbital complex.
2. The magnetic behavior explained wasn't satisfactory
3. This theory couldn't give the information about color of compounds
4. This theory failed to distinguish between strong and weak ligand

TO OVERCOME THE SHORT COMINGS A NEW THEORY WAS PROPOSED: CRYSTAL FIELD THEORY

Crystal field splitting theory

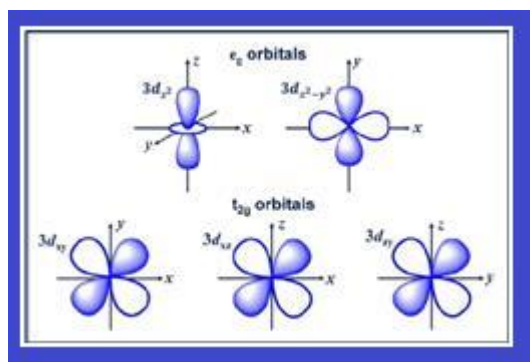
It was given by Hans Bethe and John van Vleck

Postulates

1. It assumes the central metal atom and ligands as point charges
2. When a complex is formed: central metal atom positive charge
Ligands –have negative charge
3. This theory considers the interaction between central metal atom and ligand is purely electrostatic
4. When a complex is formed the central metal atom is surrounded by oppositely charged ligands
5. No hybridization takes place
6. To form a bond the ligand molecule must approach towards central metal atom
7. In absence of external magnetic field, the d orbital of central metal atom is degenerate but this degeneracy breaks when ligand approaches.
8. The d orbital splits into two sets:

Axial set	non-axial set
d_{xy}, d_{yz}, d_{zx}	$d_{x^2-y^2}, d_z^2$

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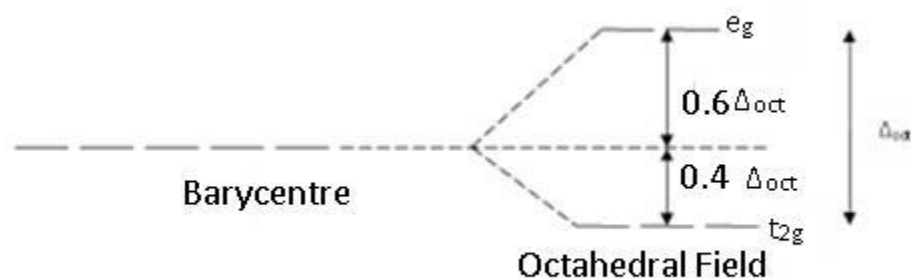


This is crystal field splitting.

9. Repulsive forces occur between electrons of metal and with lone pair ligands due to which energy of electron fluctuate or changes.

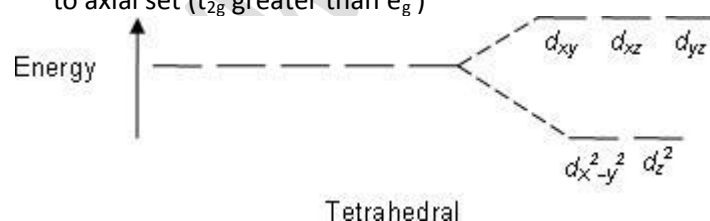
For octahedral complexes

To form octahedral complex the ligands, have to approach central metal atom along the coordination axis. During the approach the d orbitals whose lobes lie along the axis will experience more repulsion due to this their energy will increase and the other non axial set will suffer less repulsion. as a result, the non-axial will have less energy as compare to axial set (e_g greater than t_{2g})



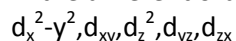
Tetrahedral complex:

The ligands have to approach central metal atom in between the coordination axis. during the approach the d orbital's whose lobes lie along the axis will experience less repulsion due to this their energy will increase and the other non axial set will suffer more repulsion. as a result, the non-axial will have more energy as compared to axial set (t_{2g} greater than e_g)

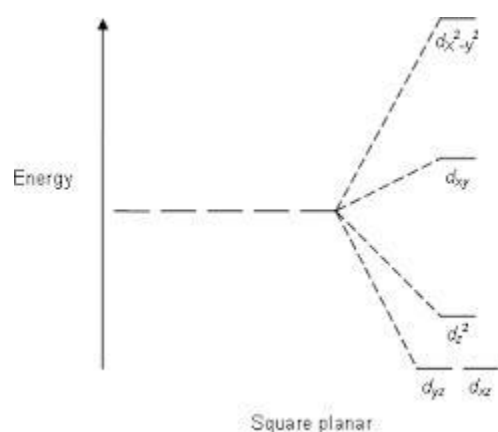


square planar complex:

In the different order is seen i.e



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Please note for all the complexes:

for strong ligands : the CFSE is more therefore pairing will occur

for weak ligands : the CFSE is less

Organo-metallic compounds

They are those compounds in which metal or metalloid or a non-metal is directly linked to carbon atom of a hydrocarbon.

For example: $(C_2H_5)_2Zn$ etc

Please note that metal cyanides and metal carbides are not organometallic compounds as in them carbon atom is not directly joined to metal.

Types of organometallic compounds:

- Sigma organometallic compounds
- Pi organometallic compounds

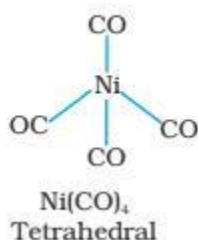
Sigma and pi organometallic compounds In detail:

- Sigma organo-metallic compounds: these are the compounds obtained by bonding of non-metal with metalloid elements with carbon. for example: $RMgX$, $(CH_3)_3Al$ etc.
- Pi organo- metallic compound: these compounds are formed mainly by transition elements. Normal sigma bond is formed through the pi electron cloud of organic molecule. For example : ferrocene ,zeisse's salt etc
- Sigma and pi organo-metallic compound: these compounds are formed by transition metal carbonyls .for example : $Ni(CO)_4$, $Fe(CO)_5$ etc

Shapes of these structures are shown below:

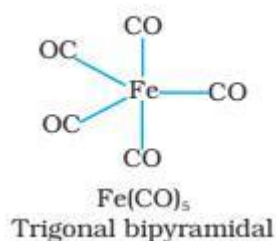
For example :

1. **Shape of $[Ni(CO)_4]$**

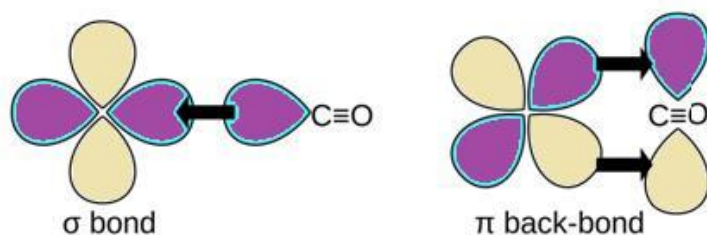


Shape of $[Fe(CO)_5]$

Class 12th Chapter 9 Coordination Compounds Revision Notes & Important Question (www.free-education.in)



Considering bonding in metal carbonyls: these compounds possess both s and p characters. The M-C sigma bond is formed by donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of metal. The M-C pi bond is formed by the donation of pair of electrons from the filled d orbital of metal into vacant antibonding pi orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and metal as shown below:-



Applications of coordination compounds

1. They are used in estimation of hardness of water as calcium and, magnesium ions form complexes with EDTA.
2. It is used in estimation and detection of metal ions. for example: Ni^{2+} ions is estimated using dimethyl glyoxime
3. It is used in Extraction of metals
4. It is used in medicines like cis platin is used in treatment of cancer
5. It is used in animal and in plant world like hemoglobin is a complex of iron, chlorophyll is a complex of magnesium and so on