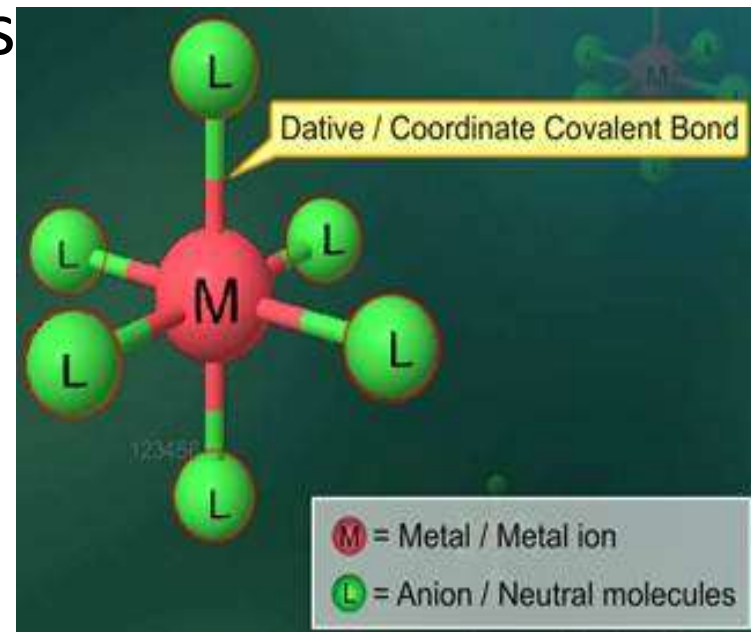


# Coordination compound

By azim

# Coordination compound

- Complex compounds are a special class of compounds in which the metal atoms (or) ions are bound to a number of anions (or) neutral molecules.
- In modern terminology, these compounds are called coordination compounds
- Coordination compounds (or) complex compounds are a type of addition compounds.



On the basis of nature, addition (or) molecular compounds are divided into two categories. They are double salts and coordination (or) complex compounds.

*differences between double salt and co-ordination compound.*

<i>Double Salt</i>	<i>Co-ordination compound</i>
<ol style="list-style-type: none"><li>1. These exist only in solid state and dissociate into constituent species in their solution.</li><li>2. They lose their identity in dissolved state.</li><li>3. Their properties are essentially the same as those of constituent species.</li><li>4. In double salts the metal atom/ion exhibit normal valency.</li></ol>	<ol style="list-style-type: none"><li>1. They retain their identity in solid as well as in solution state.</li><li>2. They do not lose their identity in dissolved state.</li><li>3. Their properties are different from those of their constituents. For example <math>K_4[Fe(CN)_6]</math> does not show the test of <math>Fe^{2+}</math> and <math>CN^-</math> ions.</li><li>4. In co-ordination <b>compounds</b>, the number negative ions or molecules surrounding the central metal atom is beyond its normal valency.</li></ol>

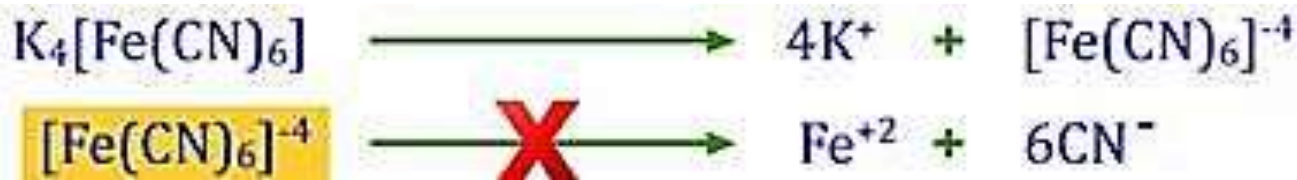
Mohr's salt:  $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$  double salt.

# Double salt and coordination compound

- Ex: An aqueous solution of potash alum will give the tests for  $K^+$ ,  $Al^{+3}$ , and  $SO_4^{-2}$

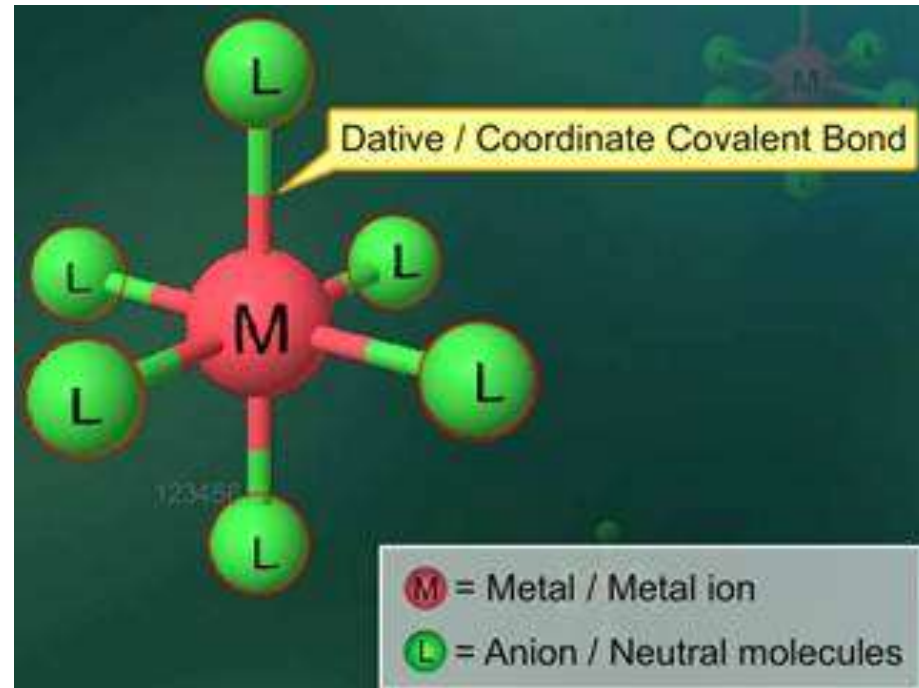


- On the other hand, coordination compounds are molecular compounds that retain their identity even when dissolved in water.
- Ex: When potassium ferrocyanide is dissolved in water, it does not give the usual tests for  $Fe^{+2}$  and  $CN^{-1}$ , indicating that,  $[Fe(CN)_6]^{-4}$  does not dissociate into  $Fe^{+2}$  and  $CN^{-1}$ .



# Complexes compound

- Compounds that have complex ions are called complex compounds.
- As the central metal ion in the complex ion forms dative (or) coordinate covalent bonds with the species surrounding it, complex ions are also known as coordinate ions and hence the corresponding compounds are known as coordinate compounds.



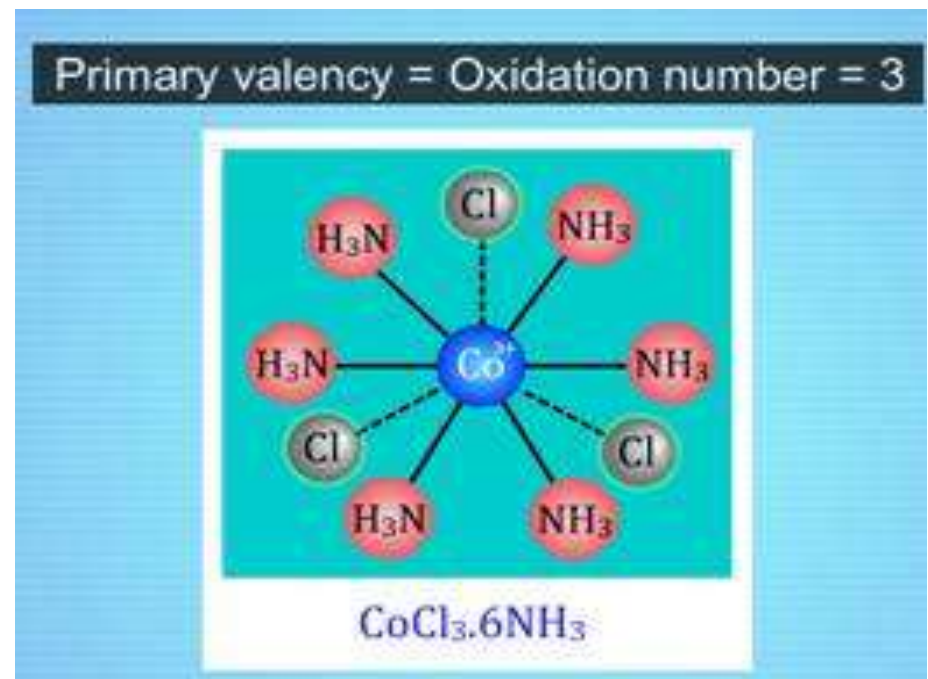
# Werner's Theory:

- Alfred Werner a Swiss chemist put forward a theory to explain the formation of complex compounds.
- It was the first successful explanation, became famous as the coordination theory of complex compounds, which is also known as Werner's theory.

# Postulates:

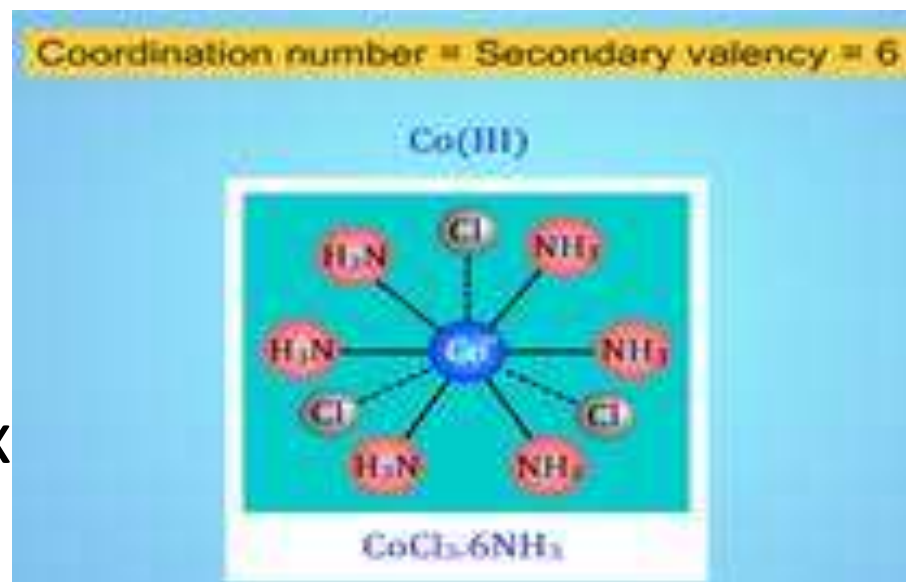
- The central metal atom (or) ion in a coordination compound exhibits two types of valencies - primary and secondary.
- Primary valencies are ionisable and correspond to the number of charges on the complex ion.

Primary valencies apply equally well to simple salts and to complexes and are satisfied by negative ions.



# Postulates:

- Secondary valencies correspond to the valencies that a metal atom (or) ion towards neutral molecules (or) negative ions in the formation of its complex ions.
- Secondary valencies are directional and so a complex has a particular shape. The number and arrangement of ligands in space determines the stereochemistry of a complex



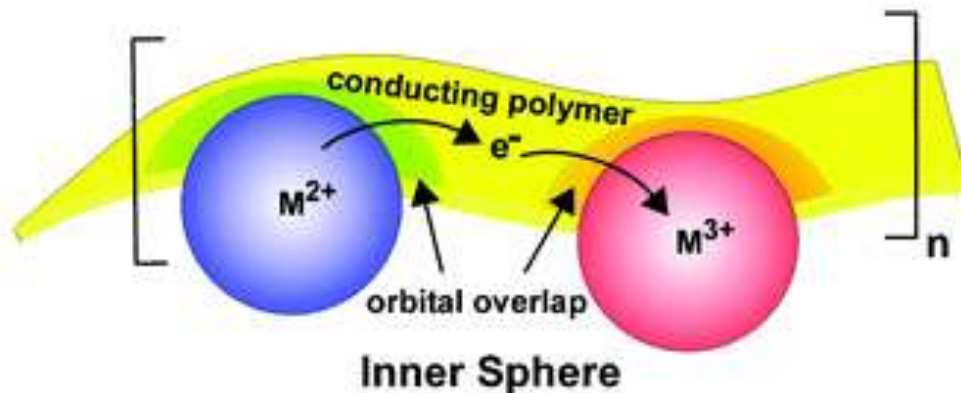
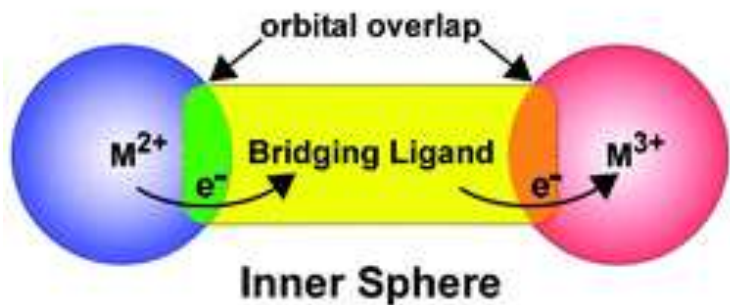
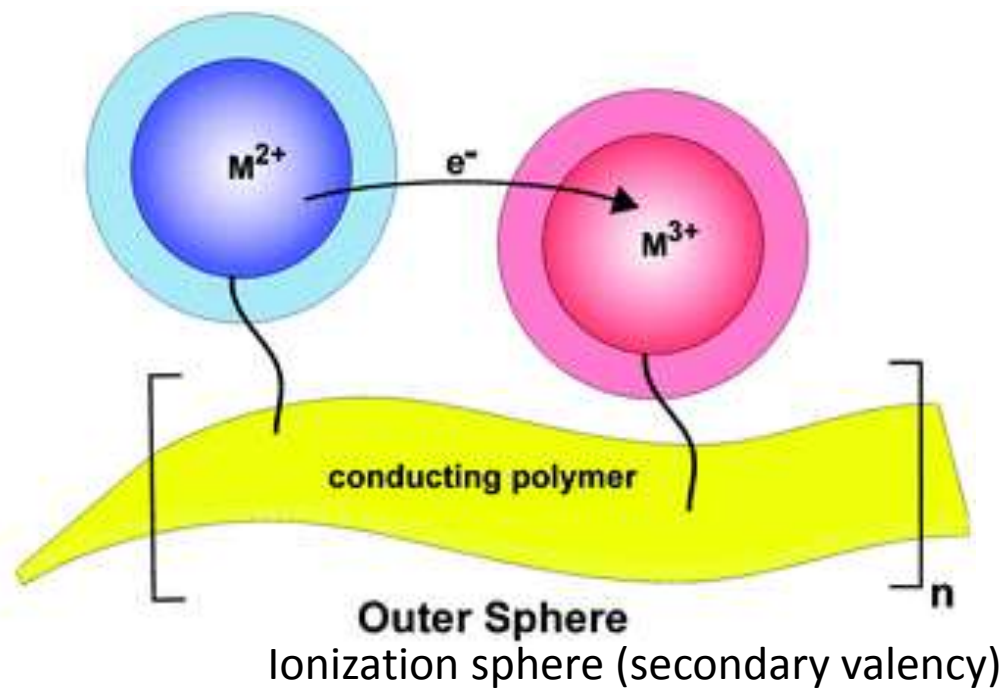
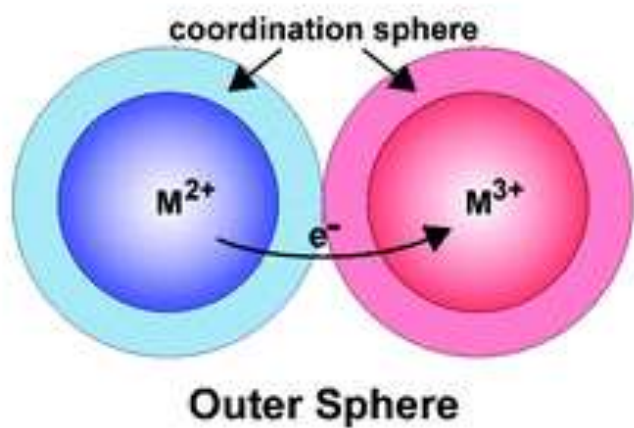
# Werner's Theory:

- The postulates of Werner's coordination theory were actually based on experimental evidence rather than theoretical.
- Although Werner's theory successfully explains the bonding features in coordination compounds, it has drawbacks.

## **Drawbacks:**

- It doesn't explain why only certain elements form coordination compounds.
- It does not explain why the bonds in coordination compounds have directional properties.
- It does not explain the colour, and the magnetic and optical properties of complexes.

# Warner's modern electronic theory of valence



# Application of werner theory to Co[III] amines



- On heating with HCl at 373k, cobalt amines doesnot evlove NH3.
- Primary valence of Co is 3 and secondary is 6.
- All the compound differ in their reactivity.

# Werner's Theory

Werner proposed putting all molecules and ions within the sphere in brackets and those "free" anions (that dissociate from the complex ion when dissolved in water) outside the brackets.

TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl <sup>-</sup> Ions per Formula Unit	Modern Formulation
CoCl <sub>3</sub> ·6 NH <sub>3</sub>	Orange	4	3	[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>
CoCl <sub>3</sub> ·5 NH <sub>3</sub>	Purple	3	2	[Co(NH <sub>3</sub> ) <sub>5</sub> Cl]Cl <sub>2</sub>
CoCl <sub>3</sub> ·4 NH <sub>3</sub>	Green	2	1	<i>trans</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Cl
CoCl <sub>3</sub> ·4 NH <sub>3</sub>	Violet	2	1	<i>cis</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Cl

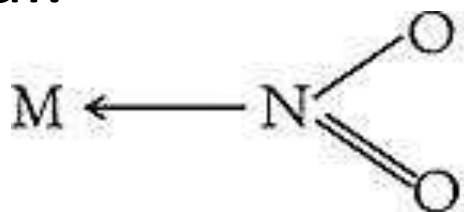
# Ligands

- The molecule or ions which are coordinated to the metal atom or ion.
- Eg.  $K_4[Fe(CN)_6]$ , the 6 cyanide group coordinated by  $Fe^{2+}$  and are the ligands.
- Ligand can be negative ions, positive ions or neutral molecules.
- Ligand are lewis base.
- Central metal atom or ion is lewis acid.

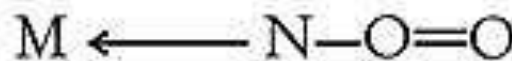
# Type of ligands

1. mono or unidentate ligands
2. Poly or multidentate ligand
- 3. Ambidentate ligands:-**

If a ligand has 2 or more donor atoms, complex is formed only 1 donor atom is attached to the metal.



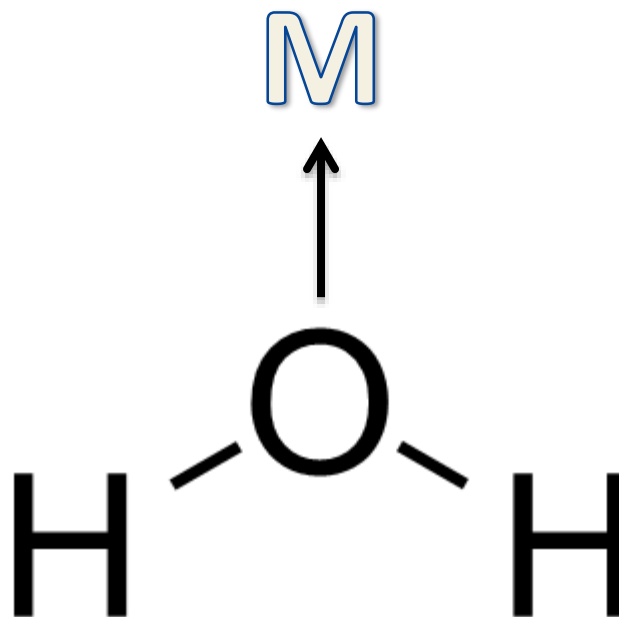
nitrito-N  
(In yellow complex)  
I



nitrito-O  
(In red complex)  
II

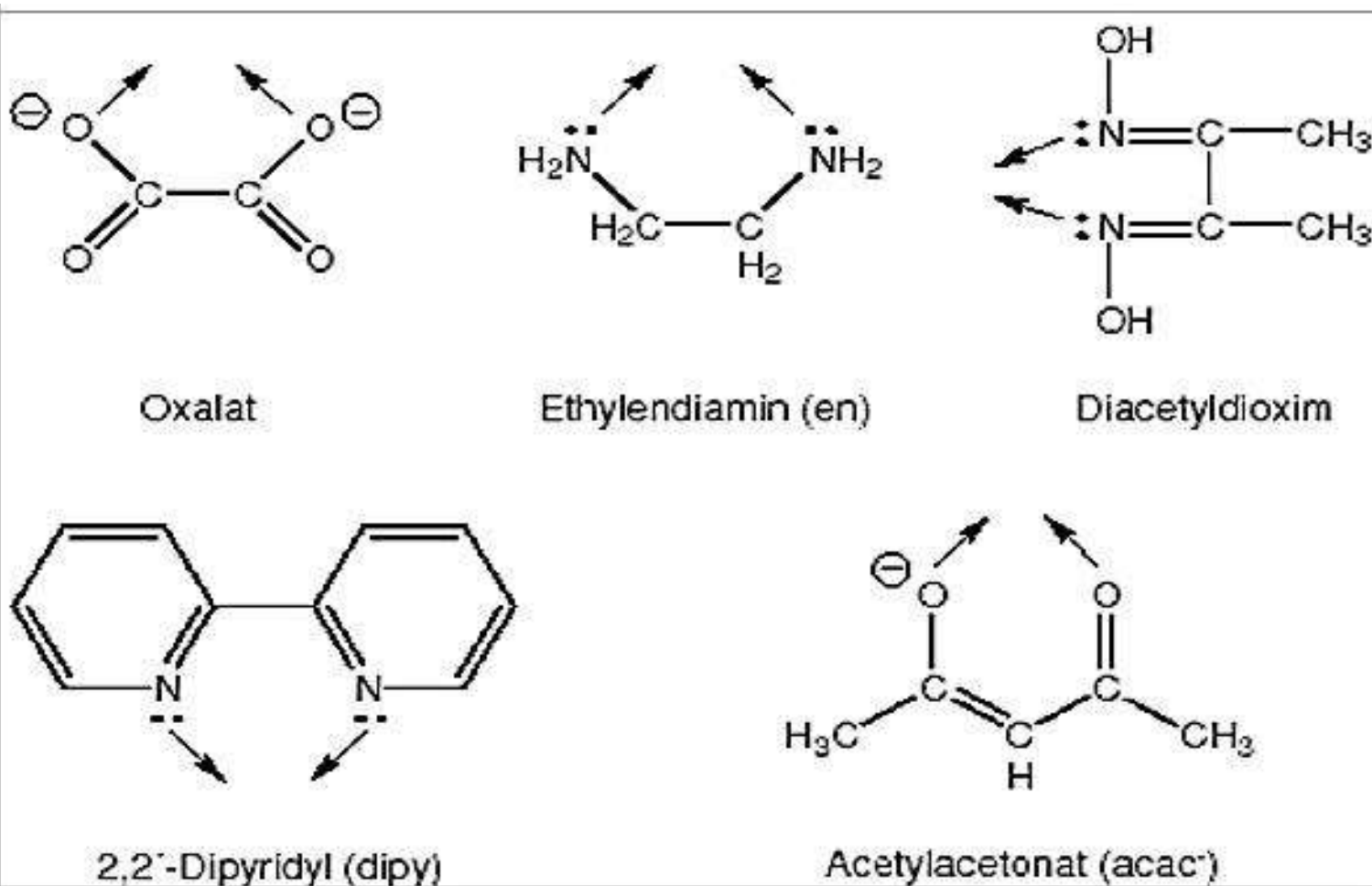
# 1. mono or unidentate ligands

- one donor atom or one point of attachment and can coordinate with the metal ion at only one site in a complex.
- Eg.  $\text{Cl}^-$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  etc.



## 2. Poly or multidentate ligand

2 or more donor atom or points of attachments. Polydentate ligands are further classified as bi, tri,....hexa dentate.



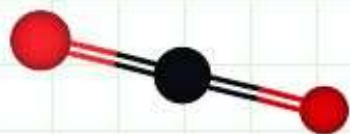
# Coordination Number

**CN** - Number of ligand atoms bonded directly to the central metal ion.  
Specific for given metal ion in particular Oxidation #.

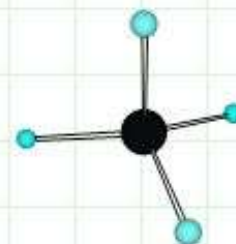
i.e., $[\text{Co}(\text{NH}_3)_6]^+$	CN = 6	Ligand # = 6
$[\text{Ag}(\text{NH}_3)_2]^+$	CN = 2	Ligand # = 2
$[\text{Co}(\text{en})_3]^+$	CN = 6	Ligand # = 3

Geometry of Complex is related to CN.

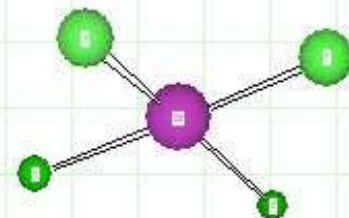
CN = 2 Linear



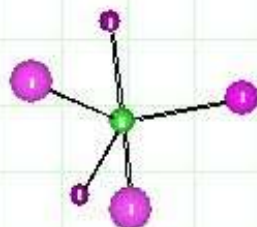
CN = 4 Tetrahedral ( $d^{10}$ )



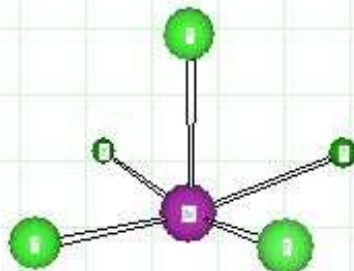
Sq Planar ( $d^8$ )



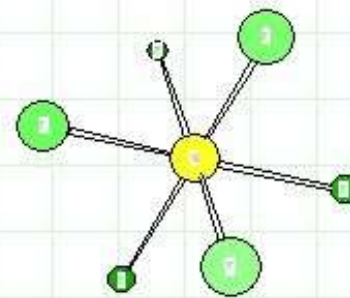
CN = 5 Trigonal bipyramidal



Square Pyramide

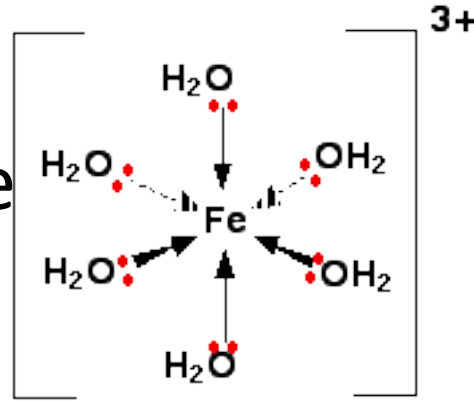


CN = 6 Octahedral

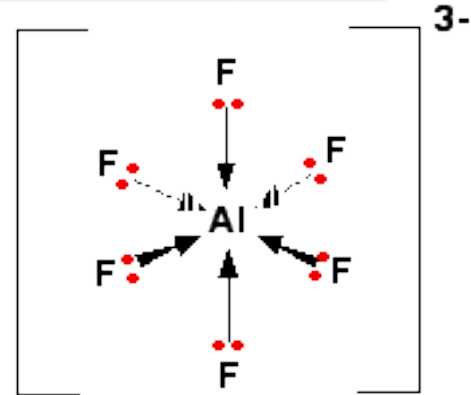


# Complex ion

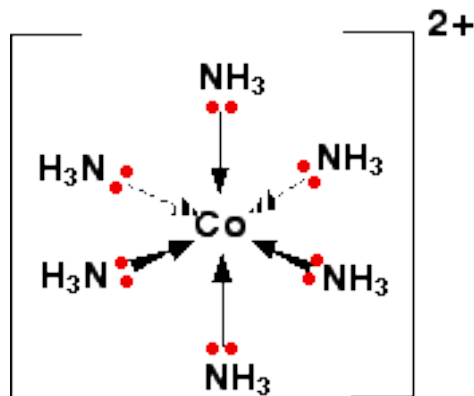
A **complex ion** has a metal **ion** at its Centre with a number of other molecules or **ions** surrounding it.



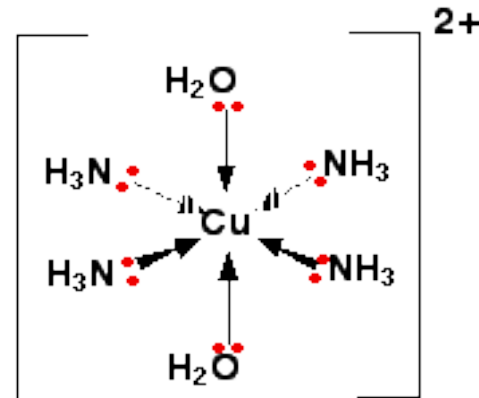
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$



$[\text{AlF}_6]^{3-}$



$[\text{Co}(\text{NH}_3)_6]^{2+}$

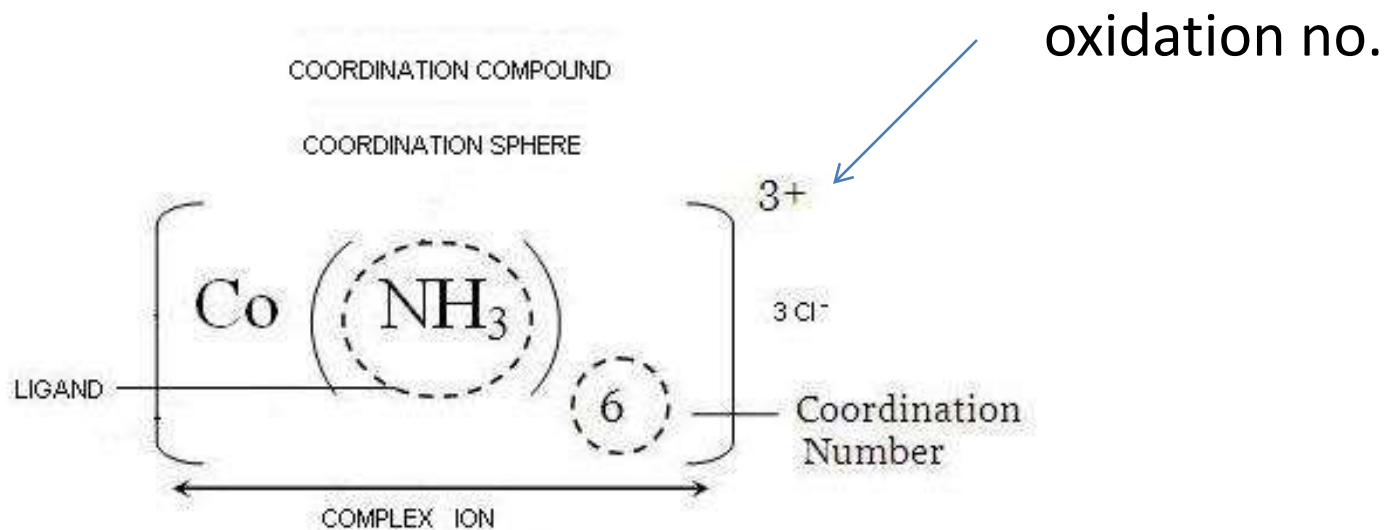


$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$

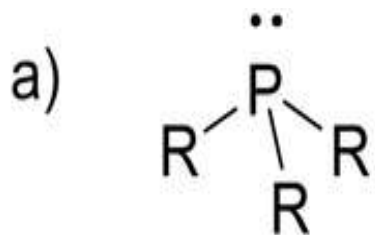
# Coordination entity

- Metal atom or ion bonded to fixed number of ions or molecules. For eg.
- $[\text{CoCl}_3(\text{NH}_3)_3]$  fixed Cl and  $\text{NH}_3$  ion.

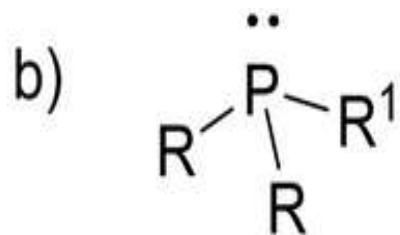
# Coordination sphere



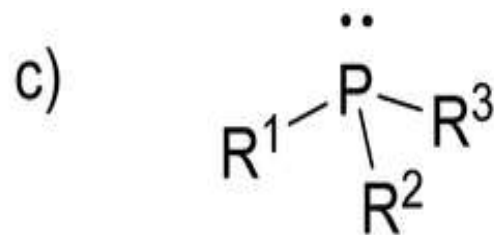
# Homoleptic- one kind of donor grp attached to metal ion or atom.



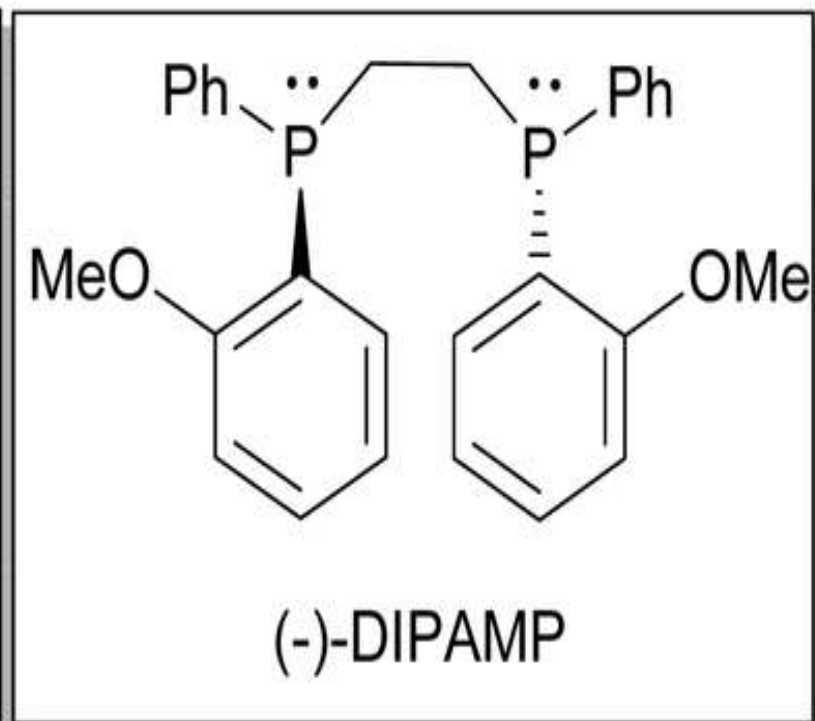
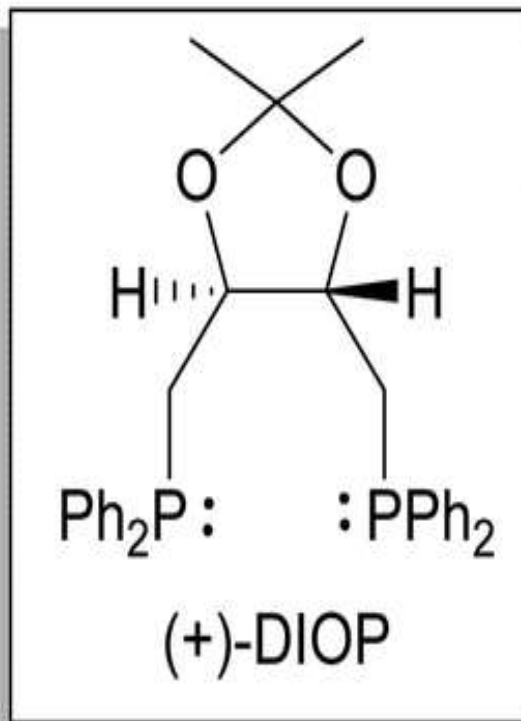
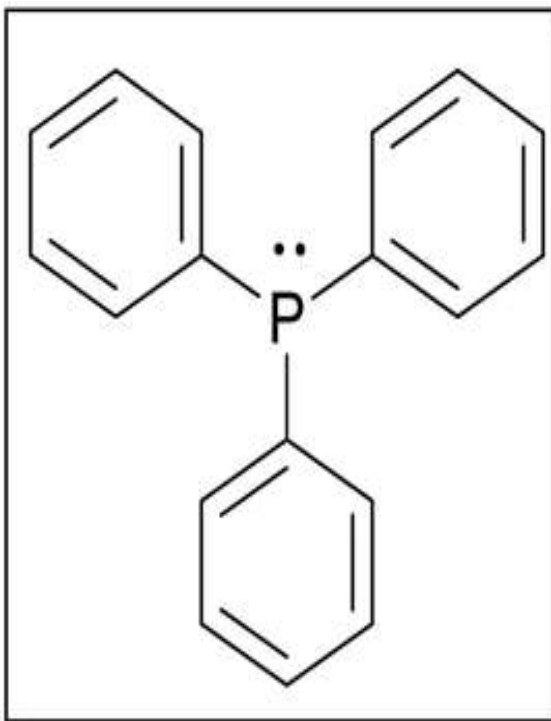
Homoleptic



Heteroleptic



Asymmetric



# Charge number of complex ion

- The net charge carried by complex ion.

Charge number of  $[\text{Fe}(\text{CN})_6]^{4-}$

= charge of  $\text{Fe}^{2+}$  + 6 x charge on  $\text{CN}^-$  ion

= +2 + 6 (-1) = -4.

# Coordination polyhedron

The spatial arrangement of ligand atoms, directly attached to the central atom/ion.



Square planar



Tetrahedral



Trigonal  
bipyramidal



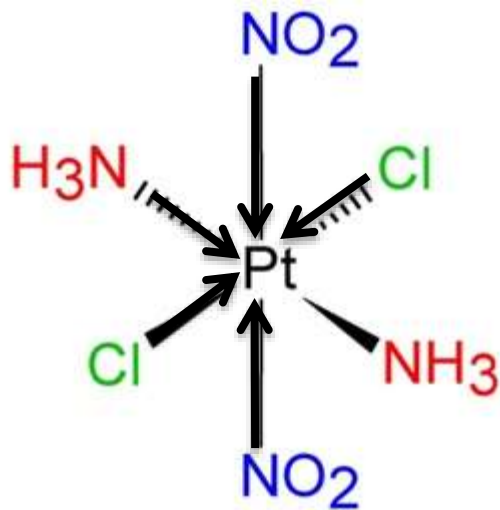
Square  
pyramidal



Octahedral

# Sidgwick's electronic theory

- The ligand donate the electron pair to the central metal ion and thus form a number of coordinate bond.



# Effective atomic number (EAN)

- **$EAN = Z - X + Y$**

Where,

Z = atomic no. of the metal.

X = no. of electron lost during the formation of the metal ion from its atom.

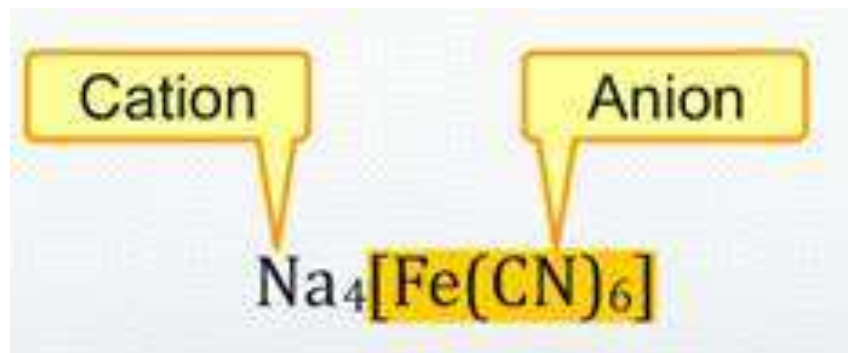
Y = no. of electrons donated by the ligands.

Eg.  $[\text{Fe}(\text{CN})_6]^{-4}$ , Fe oxidation = +2 & Z = 26

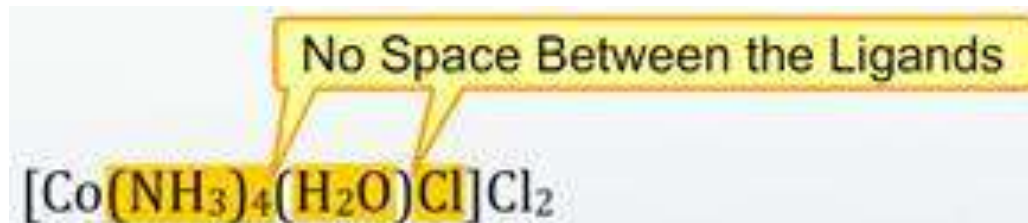
$$[\text{Fe}(\text{CN})_6]^{-4} = 26 - 2 + 6(2) = 36$$

# Nomenclature writing complex compound

- The formula of the cation, whether it is simple (or) complex is written first followed by that of the anion.

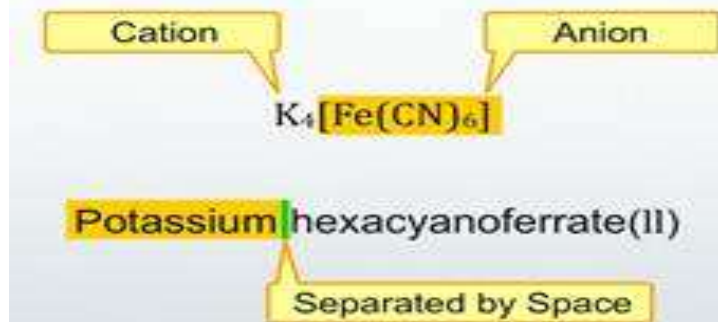


- Within a coordination sphere the metal atom as well as the ligands are listed without any space between them.



# Nomenclature naming

- In ionic coordination compounds the cation is named first and separated by a space from the anion.



- If the coordination entity is either neutral (or) cationic then usual name of the metal is used. But, when the coordination entity is an anion then name of the metal ends with the suffix 'ate'.

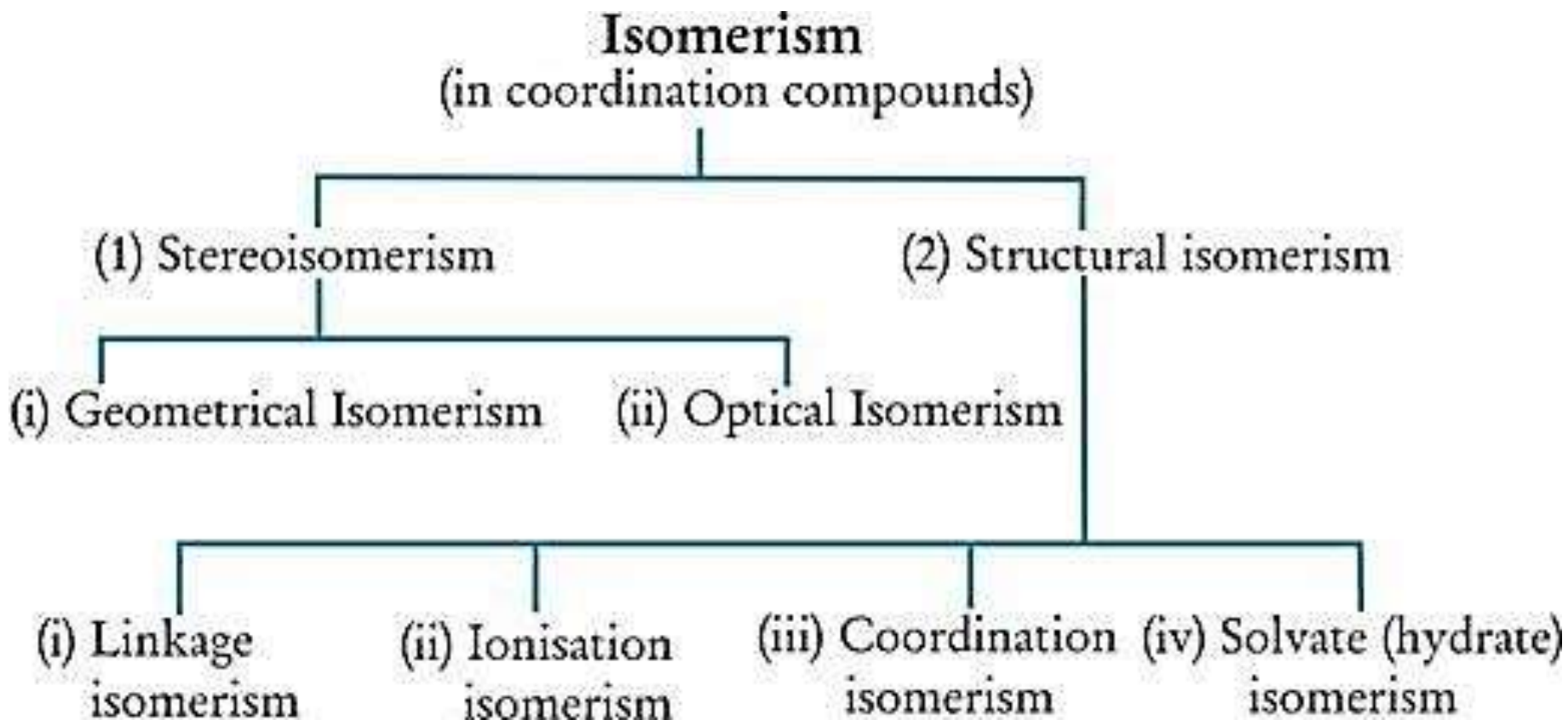


Sodium triamminetrichloridoplatinate (II)

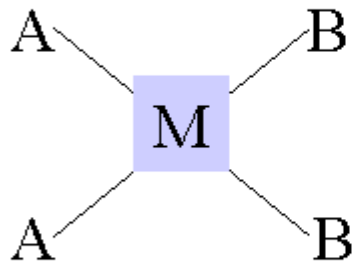
# Nomenclature naming

- $\text{Li}[\text{AlH}_4]$  Lithium hydrido aluminate(III)
- $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$  sodium hexanitrito –N  
cobaltate
- $[\text{Ag}(\text{NH}_3)_2]\text{NO}$  Diammine silver(I) nitrate
- $\text{K}[\text{Au}(\text{CN})_4]^-$  potassium tetracyanoaurate(III) ion
- $[\text{Ni}(\text{CN})_4]^{2-}$  teteracyanonickellate(II) ion

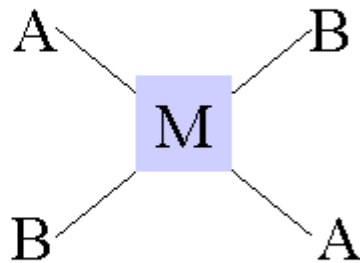
# Isomerism in coordination compound



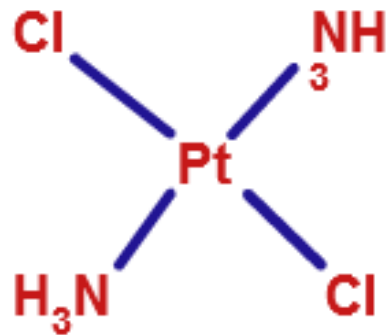
# 1. Geometrical isomerism



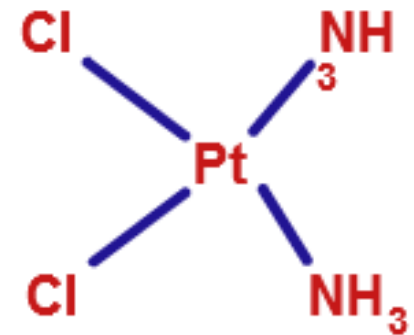
*cis*



*trans*



*trans*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>

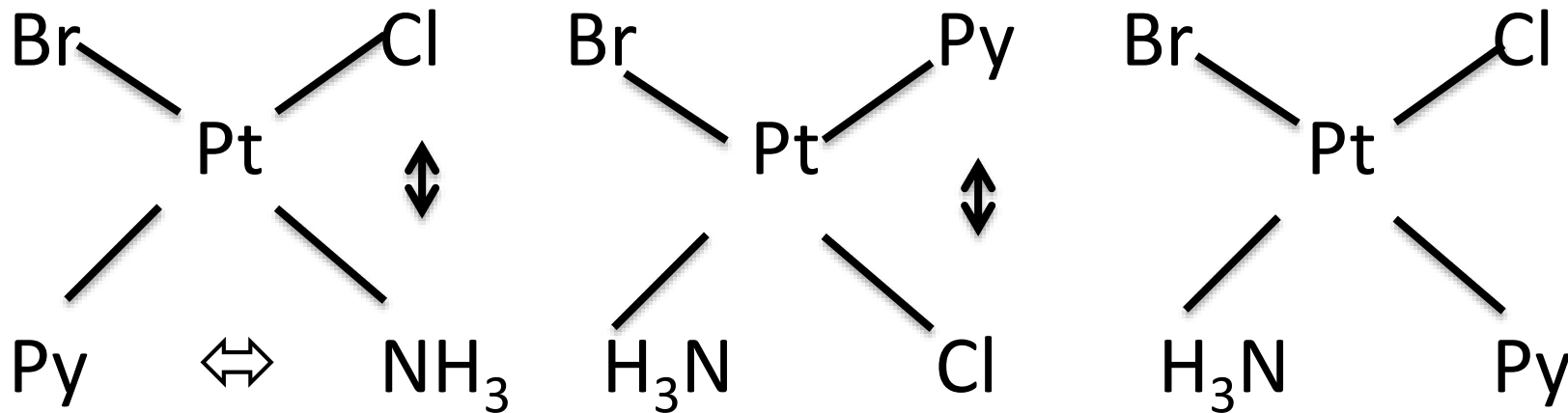


*cis*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>

# 1. Geometrical isomerism

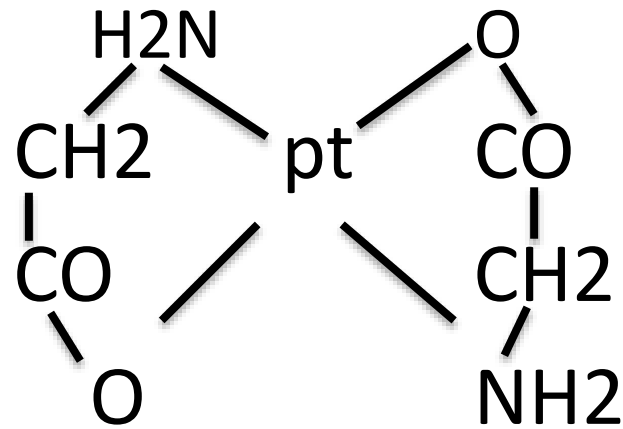
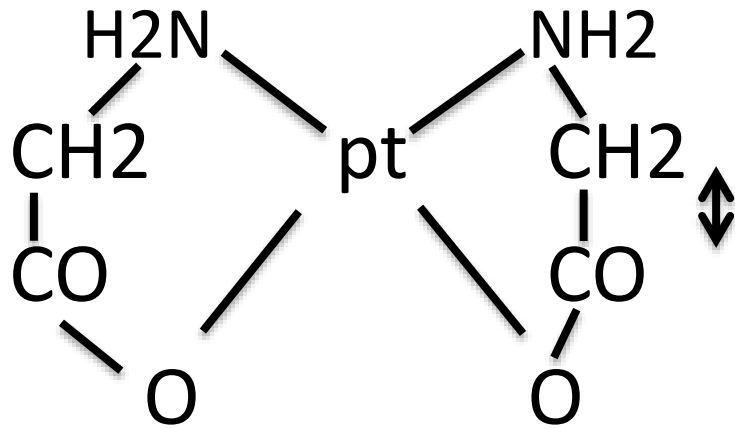
$[\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2\text{Py}]$  diamminebromo  
chloroplatinum(II).

$(\text{Ma}_2\text{b}_2)^{n+}$



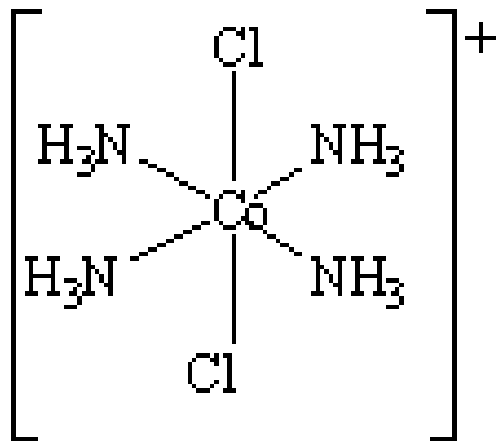
# 1. Geometrical isomerism

- $[Mabcd]^{n+}$  for eg.  $[Pt(gly)_2]$  (glycino)

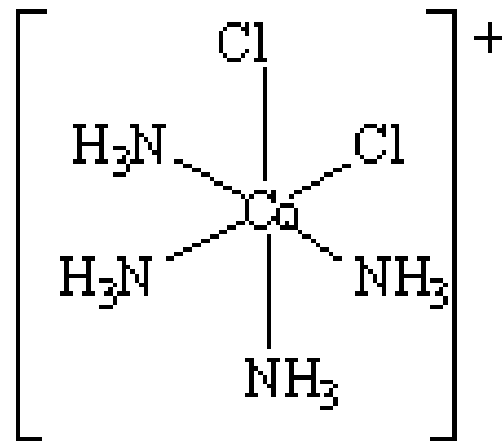


# six coordination compounds

- Complexes of the type  $[Ma_4b_2]^{m+}$



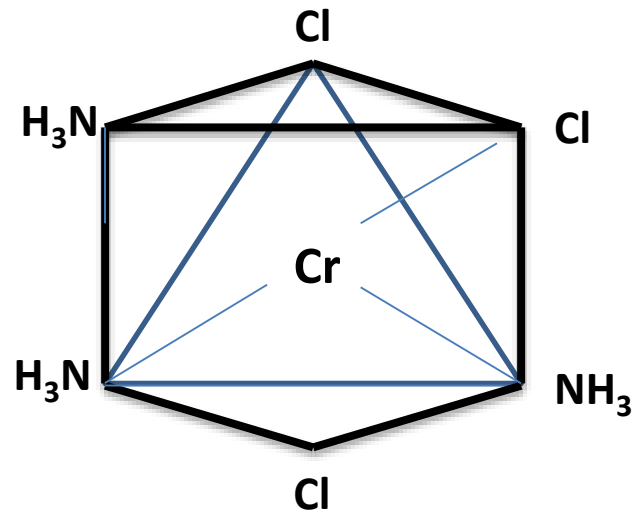
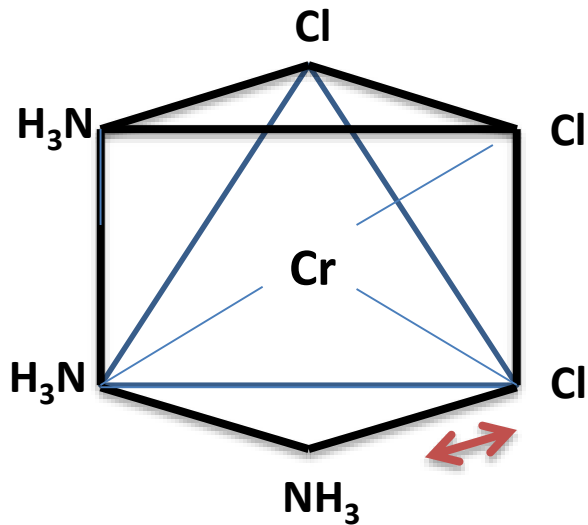
Trans -  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$



Cis -  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

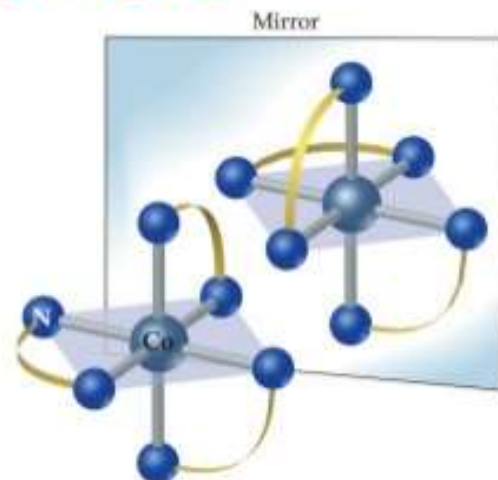
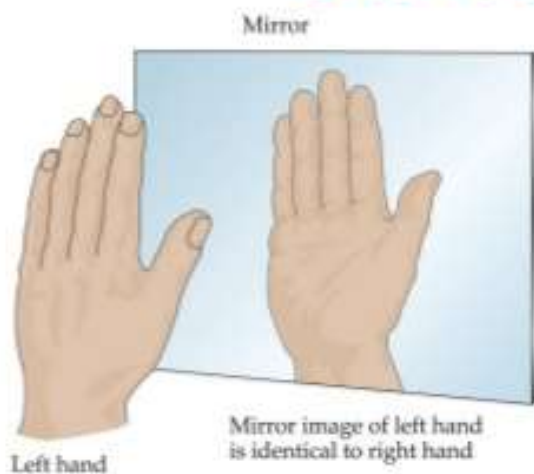
# Complexes of the type

- $[Ma_3b_3]^n$
- eg.  $[CrCl_3(NH_3)_3]$



# Optical isomerism

## Stereoisomers



- Other stereoisomers, called optical isomers or enantiomers, are mirror images of each other.
- Just as a right hand will not fit into a left glove, two enantiomers cannot be superimposed on each other.

# Six coordination compounds

- Octahedral complexes containing only monodentate ligands:
- A)  $[M(AA)_3]^n$  eg.  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$   
trioxalatochromium (III) anion
- B)  $[M(AA)_2a_2]^n$  eg.  $[\text{CoCl}_2(\text{en})_2]^+$   
cis-Dichlorobis(ethylenediamine)cobalt(III) chloride
- C)  $[M(AA)_2ab]^n$  eg.  $[\text{CoCl}(\text{en})_2(\text{NH}_3)]^{2+}$

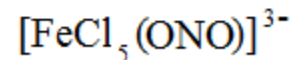
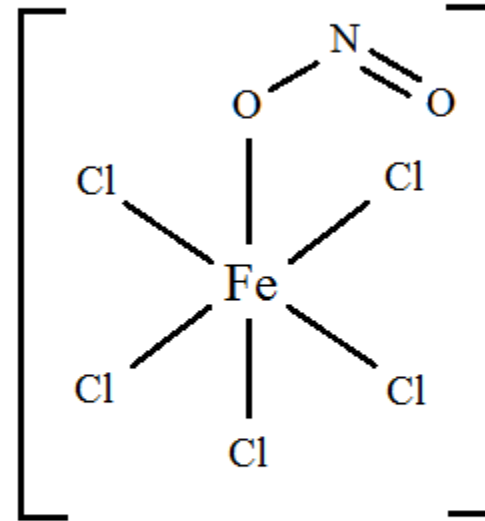
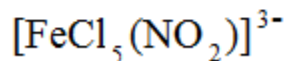
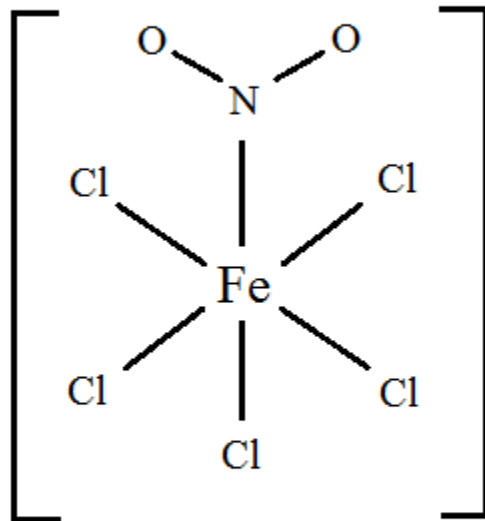
# 1. Ionisation isomerism

- Ions present in coordination compound.
- $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$       **red violet**       $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+ + \text{Br}^-$
- $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$       **Red**       $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} + \text{SO}_4^{2-}$

## 2. Linkage isomerism

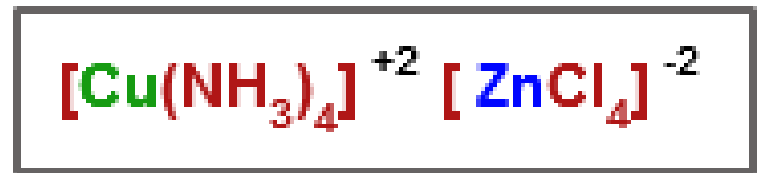
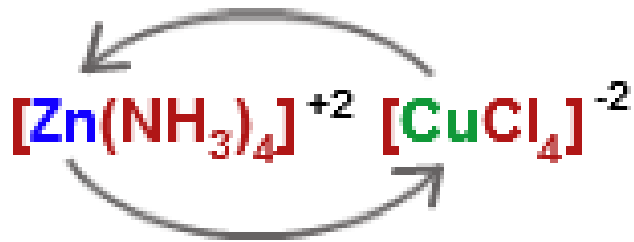
- Same M.F but differ in linkage of the ligand.

### LINKAGE ISOMERS



### 3. Coordination isomerism

- Interchange of ligand.

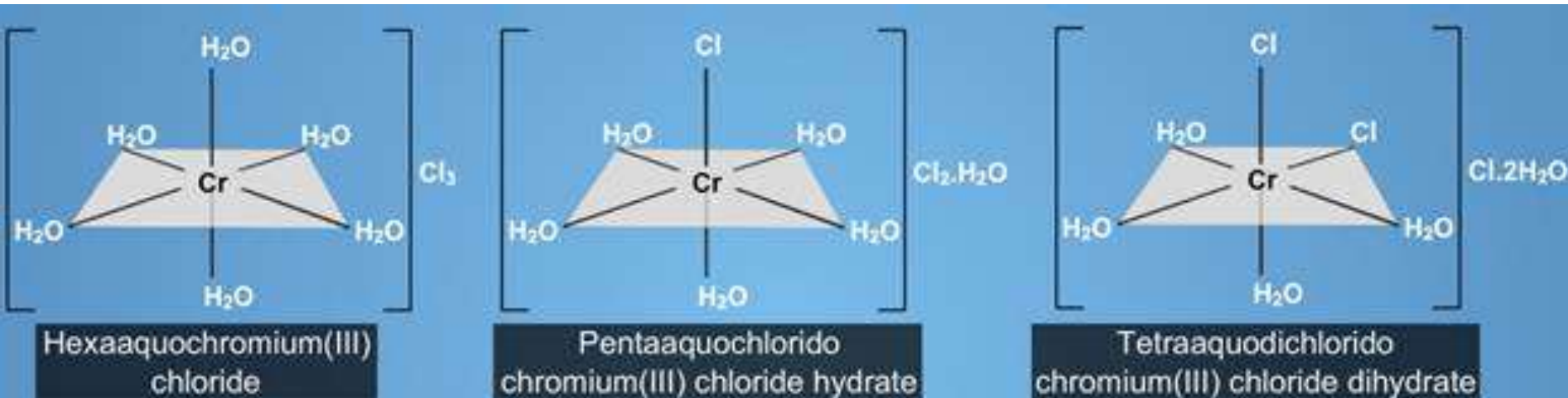


**TetraamineZinc(II)**  
**TetraamineCuprate(II)**

**Tetraamine Copper(II)**  
**Tetraamine Zincate(II)**

# 4. hydrate isomerism

- Same M.F but differ in water molecule inside and outside.
- Ex:  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$



# Bonding in coordination compound

1. Valence bond theory(VBT)
2. Crystal field theory(CFT)
3. Ligand field theory(LFT)
4. Molecular orbital theory(MOT)

# 1. Valence bond theory(VBT)

- Linus Pauling 1931.
- The valence bond theory satisfactorily explains the structure and magnetic properties of a large number of coordination compounds.

## **Salient features of the theory:**

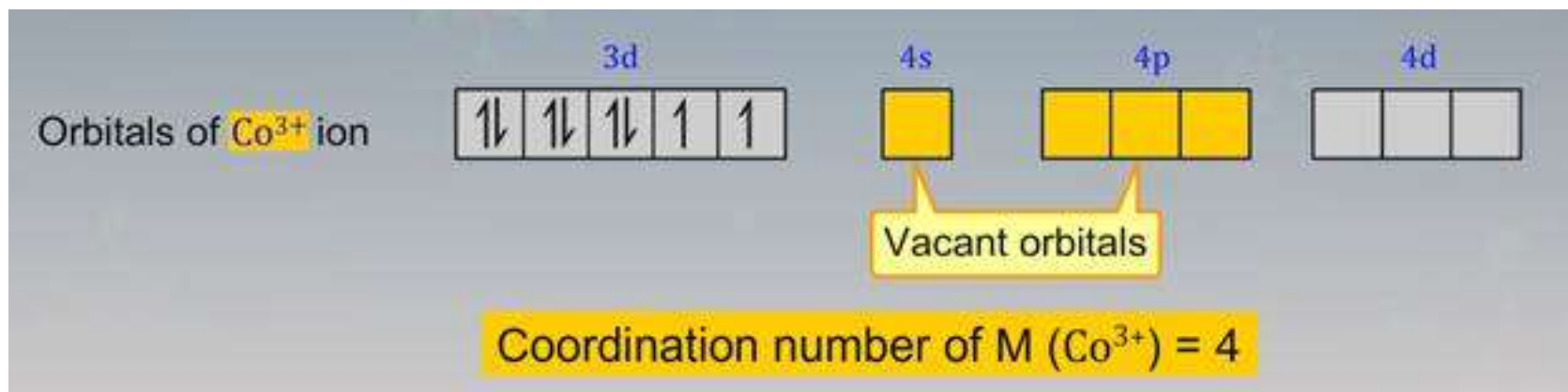
- The central metal atom (or) ion has the required number of vacant orbitals for accommodating the electrons donated by the ligands. The number of vacant orbitals is equal to the coordination number of the metal ion for a particular complex.

**Vacant orbital s, p, d, f.**

# **Salient features of the VBT theory:**

- This vacant orbital goes hybridization to form same no. of hybrid orbitals.**
- Each ligand has at least one orbital containing lone pair of electrons.**
- Vacant hybrid orbital filled with ligand to form coordination bond.**
- Coordinate bond is stronger if the overlapping between the orbitals is greater.**

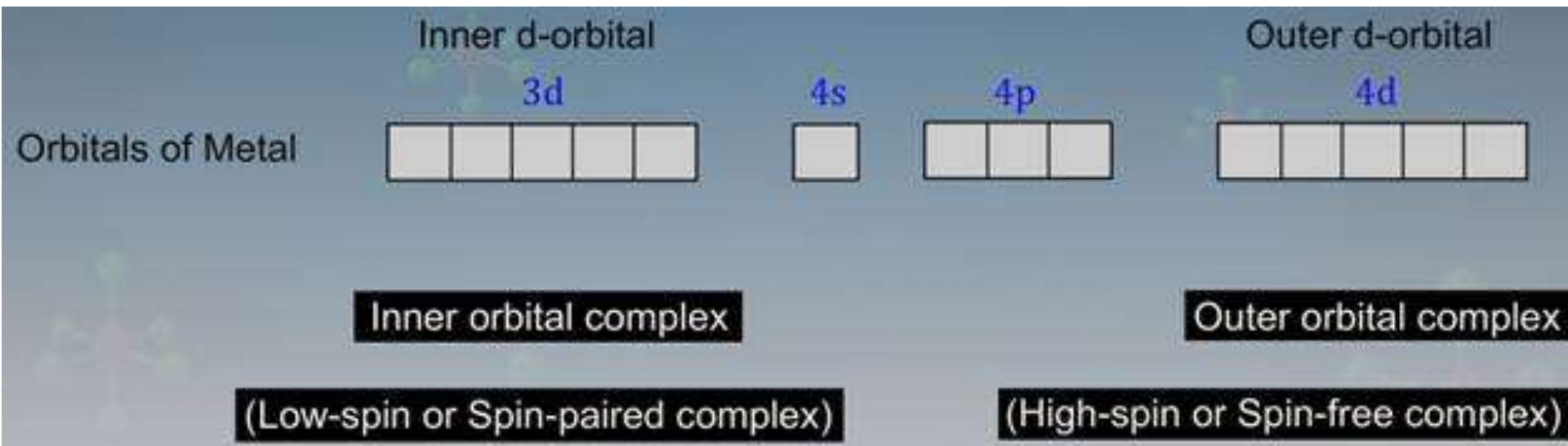
- The vacant orbitals of the metal atom (or) ion undergo suitable hybridisation to yield a set of equivalent hybrid orbitals of definite geometry.



# Geometrical shape depend upon the hybridization of the metal orbital.

C.N.	Hybridised orbitals	Molecular geometry	Example
2	$sp$	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$ , $[\text{Ag}(\text{CN})_2]^-$
3	$sp^2$	Trigonal planar	$[\text{HgI}_3]^-$
4	$sp^3$	Tetrahedral	$[\text{Ni}(\text{CO})_4]$ , $\text{Zn}[(\text{NH}_3)_4]^{2+}$ , $[\text{NiX}_4]^{2-}$ , $[\text{MnX}_4]^{2-}$ $[\text{Cd}(\text{CN})_4]^{2-}$ , $[\text{FeCl}_4]^{2-}$ , $[\text{CuCl}_4]^{2-}$
4	$dsp^2$ $d$ -orbital used is $d_{x^2-y^2}$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Ni}(\text{NH}_3)_4]^{2+}$ , $[\text{Pt}(\text{NH}_3)_4]^{2+}$ $[\text{Pt}(\text{Cl}_4)]^{2-}$ , $[\text{PdCl}_4]^{2-}$ , $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ , $[\text{PdCl}_4]^{2-}$ , $[\text{Cu}(\text{NH}_3)_4]^{2+}$
5	$dsp^3$ $d$ -orbital used is $d_{z^2}$ of inner <i>i.e.</i> $(n-1)^{\text{th}}$ shell	Trigonal bipyramidal	$[\text{CuCl}_5]^{3-}$ , $[\text{Fe}(\text{CO})_5]$

If  $(n-1)d$  orbitals are used for hybridization, the complexes are called inner complexes and  $nd$  orbitals are called outer complexes.



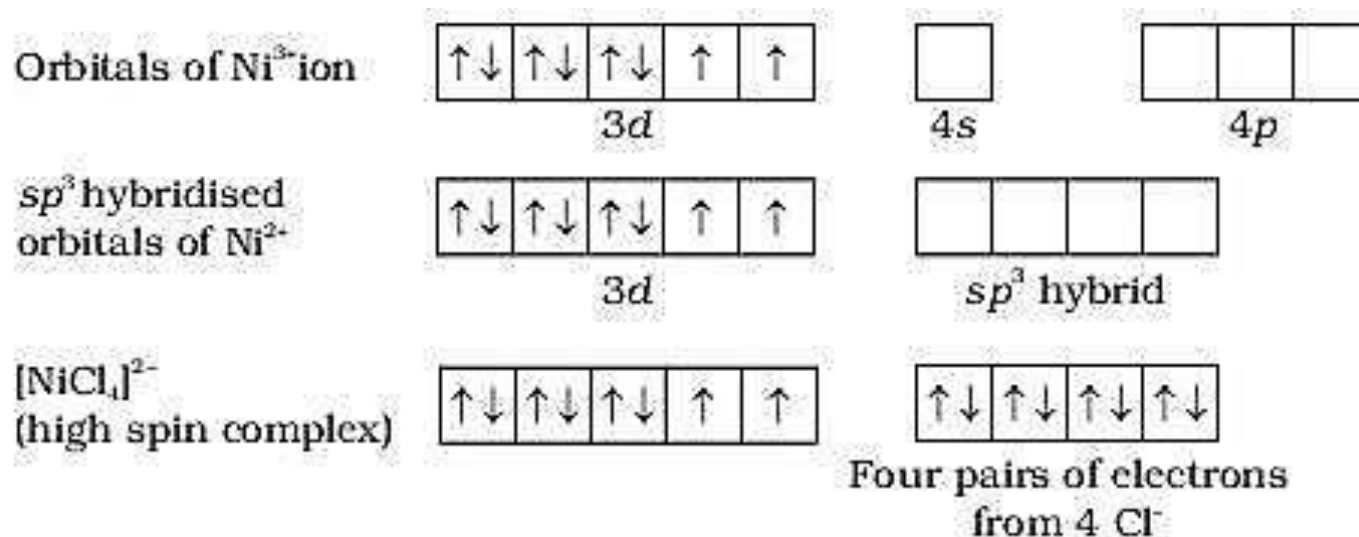
- When strong field ligands like  $\text{NH}_3$  and  $\text{CN}^-$  are involved in the formation of complexes, they causes pairing electrons present in metal ions. This process is called as spin pairing.

# Structure of complex compounds based on VBT

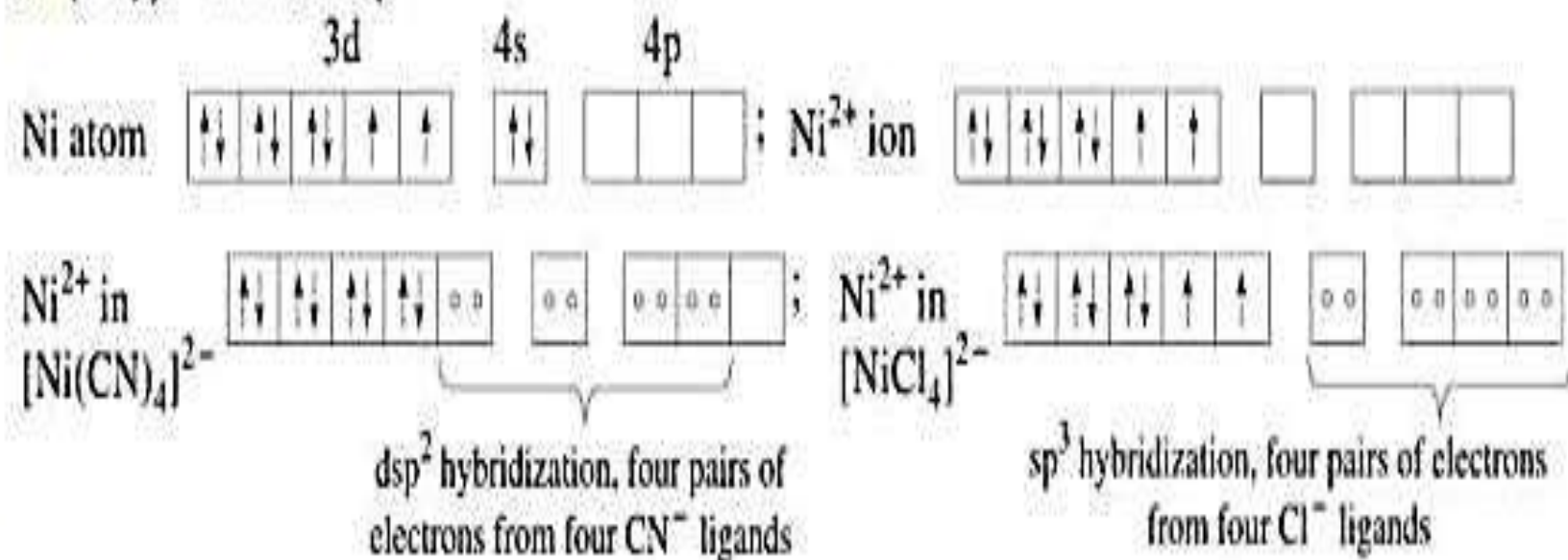
1. Structure of nickel tetracarbonyl  $[\text{Ni}(\text{CO})_4]$
2. Formation of  $[\text{NiCl}_4]^{2-}$
3. Structure of  $[\text{Ni}(\text{CN})_4]^{2-}$
4. Structure of  $[\text{CoF}_6]^{3-}$
5. Structure of  $[\text{Co}(\text{NH}_3)_6]^{3+}$

# Formation of $[\text{NiCl}_4]^{2-}$

- Oxidation is +2. each chlorine ion donate 2 electron. Ni-  $3d^8 4s^2$ .
- Paramagnetic contain 2 unpaired electron.



### $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{NiCl}_4]^{2-}$



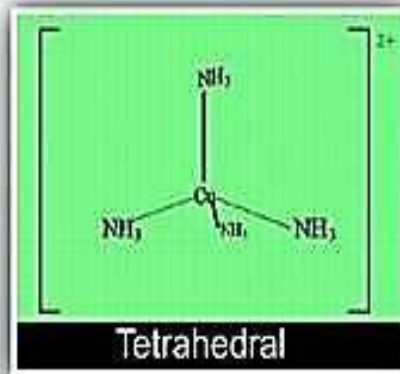
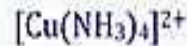
$[\text{Ni}(\text{CN})_4]^{2-}$  is a square planar ( $dsp^2$  hybridization) and diamagnetic (no unpaired electrons) while  $[\text{NiCl}_4]^{2-}$  is tetrahedral ( $sp^3$  hybridization) and paramagnetic (two unpaired electrons). The  $\text{CN}^-$  ligand is strong and it forces the two unpaired electrons to pair up.

# Drawbacks of the valence bond theory:

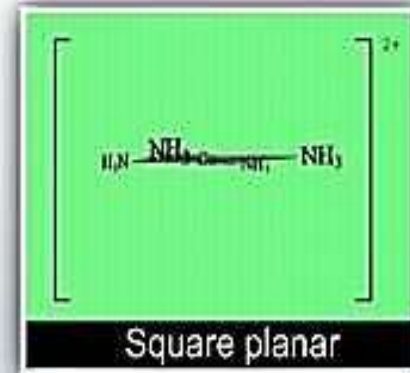
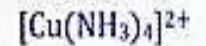
- a) Does not explain the colour of coordination compound.
- b) cannot explain magnetic behavior based on geometry.
- c) does not explain why some called inner and outer complex same metal ion in the same oxidation state.
- d) Fails to predict the exact geometry of the complexes with the coordination number four.

Example:

According to valence bond theory:



According to X-ray analysis:



# Drawbacks of the valence bond theory:

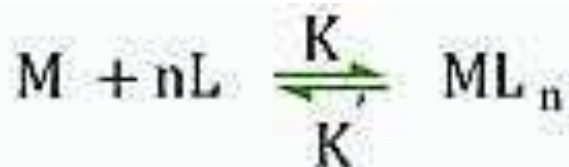
e) Doesnot distinguish weak field and strong field of ligand.

f) It cannot predict exactly the tetrahedral and square planar structure of 4-cordinate.

# Stability of coordination compounds

- Thermodynamic equilibrium constant.
- Stability depend upon the interaction between metal and ligand.
- If interaction strong thermodynamic stability strong.
- Reaction between metal ion and ligand is based Lewis acid and base.
- The greater the value of stability constant, more stable is the complex.

# Stability of coordination compounds



Apply law of mass action

$$K = \frac{[ML_n]}{[M][L]^n}$$

$K$  = Formation equilibrium constant

$K \propto$  Stability of complex

$$K' = \frac{1}{K}$$

$K'$  = Instability constant or the dissociation constant

# Stability of coordination compounds

System	Stability
$\text{Cd}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cd}(\text{NH}_3)_4]^{2+}$	$1.3 \times 10^7$
$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$	$1.6 \times 10^7$
$\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}$	$4.5 \times 10^{11}$
$\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2]^-$	$5.5 \times 10^{18}$
$\text{Cu}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Cu}(\text{CN})_4]^{2-}$	$2.0 \times 10^{33}$

**CN<sup>-</sup> is more stable than ammine complex.**

**It concludes that cyano is a stronger ligand than ammine.**

**Stability depends upon**

1. Charge density of the central metal ion (ionic radii)
2. Nature of ligand

# Crystal field theory (CFT)

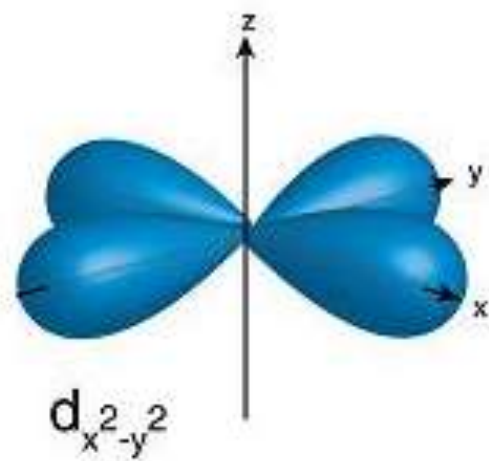
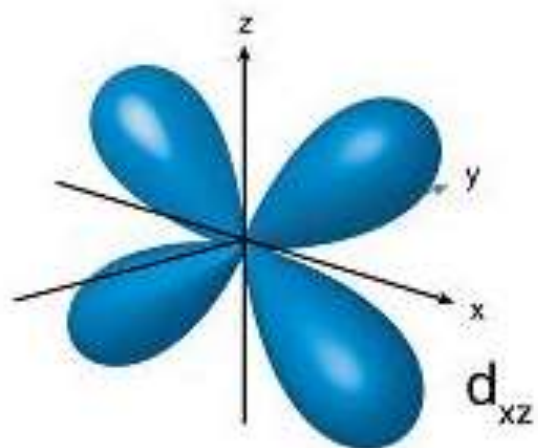
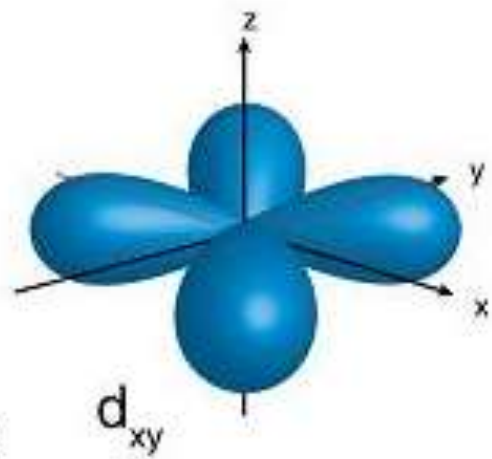
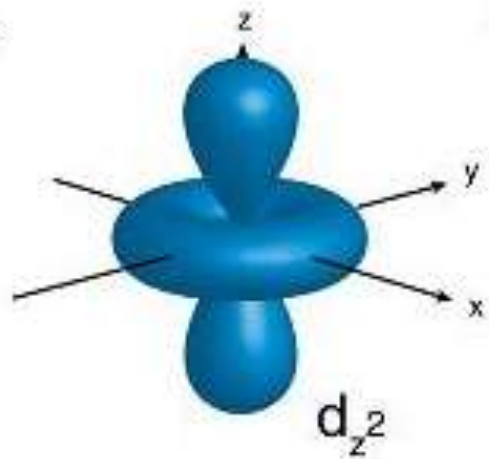
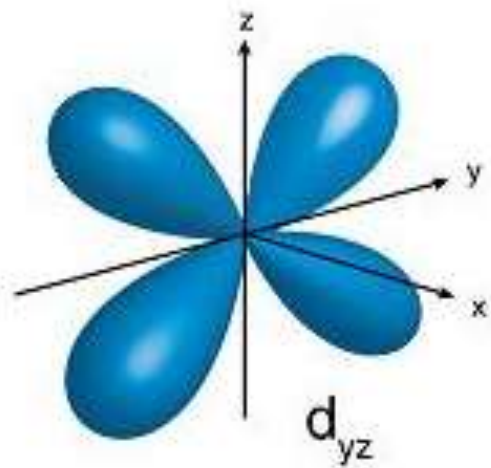
- The crystal field theory was proposed by Hans Bethe and VanVleck.
- Crystal field theory assumes that the interaction between metal ion and the ligand is purely electrostatic.

## *Silent features of CFT*

- Central metal atom or ion is surrounded by various ligands which are either negative charge or neutral molecule.
- Electrostatic interaction between ML.

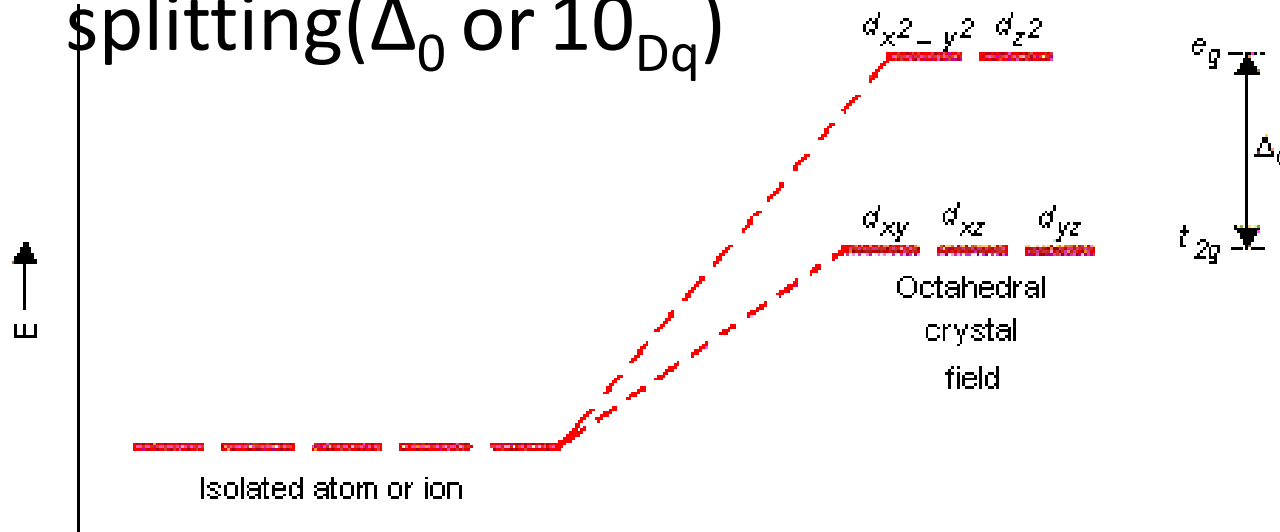
Eg.  $\text{Fe}^-$  and  $\text{Co}^{3+}$ .

- Central metal atom have 5 degenerated orbital  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ,  $d_{(x^2-y^2)}$ ,  $d_{z^2}$ .



# *Silent features of CFT*

- When the ligands approach the metal ion, due to repulsion forces, the degeneracy of d-orbitals is destroyed and they split into two groups of different energy level  $t_{2g}$  and  $e_g$  orbital. This effect is called crystal field splitting ( $\Delta_0$  or  $10Dq$ )



## *Silent features of CFT*

- Due to repulsion, the orbitals along the axes of ligands acquire higher energy while those lying in between the ligands acquire less energy.
- It doesn't show the overlapping.
- From the Crystal field stability energy the stability of the complexes can be known.

# Defination

- **Crystal field splitting-**

Splitting of 5 degenerated d-orbital.

- **Crystal filed stabilization energy(CFSE)-**

Change in energy achieved by filling up electron in orbital in complex metal atom.

# Definition

- **High spin complex-(spin free)**

Greater no. of unpaired electrons and hence higher value of resultant spin and magnetic moment is called.

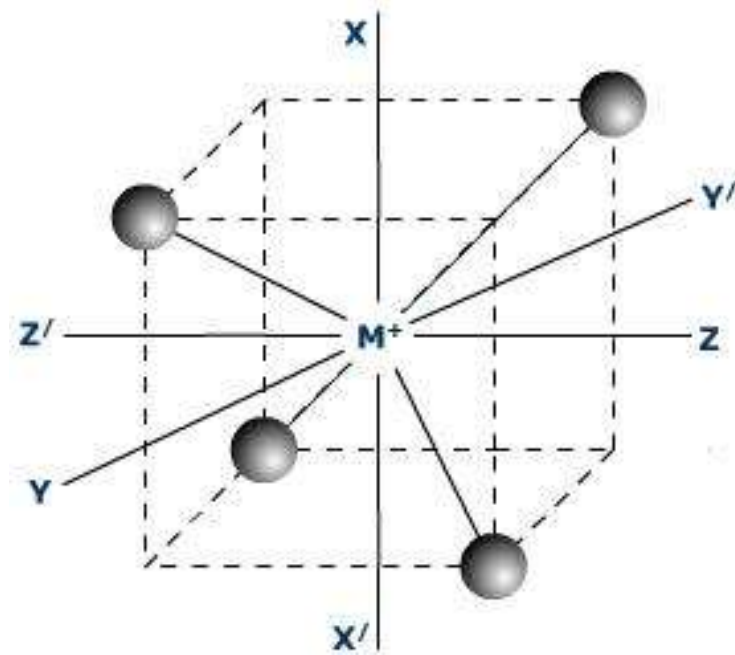
- **Low spin complex-**

- **Pairing energy-**

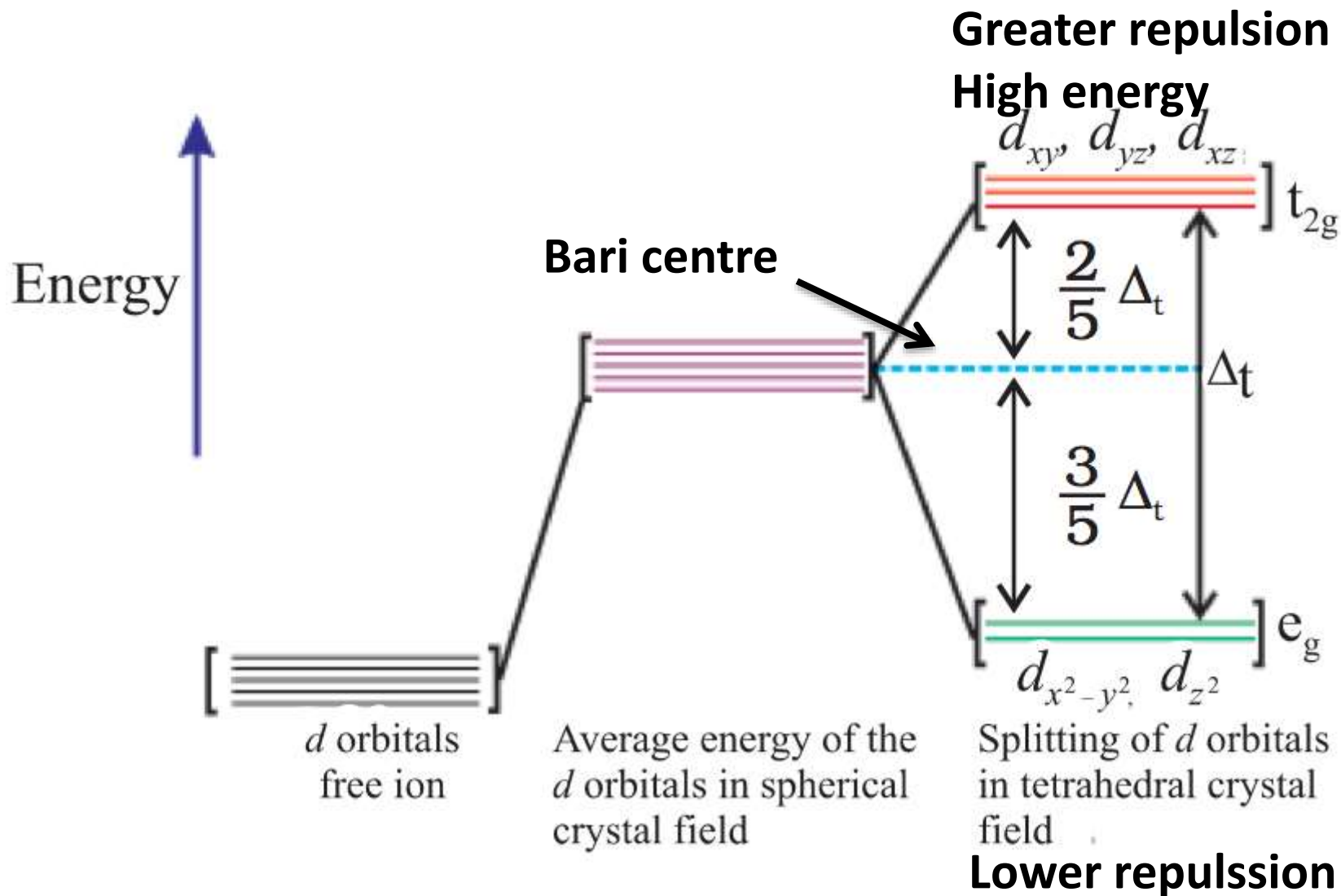
The energy required to pair 2 electron against the electron electron repulsion in the same orbital of a metal atom.

# Application of CFT to tetrahedral complexes

- In the tetrahedral complex,  $[MX_4]^n$ , the metal atom or ion is placed at centre of the regular tetrahedron and the 4 ligands, are placed at four corners of the tetrahedron.
- Ligand approach the central Metal atom in between 3 coordinate  $x, y, z$ .



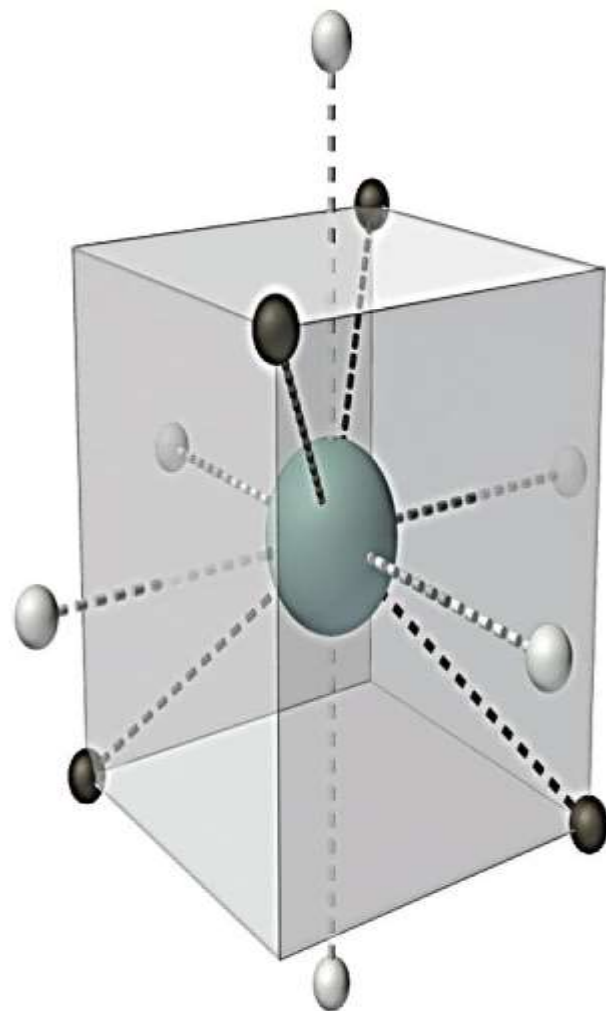
In case of strong field ligands, the electrons prefer to pair up in  $e_g$  orbital giving low spin complexes while in case of weak field ligands, the electrons prefer to enter higher energy  $t_{2g}$  orbitals giving more unpaired electrons and hence form high spin complexes.



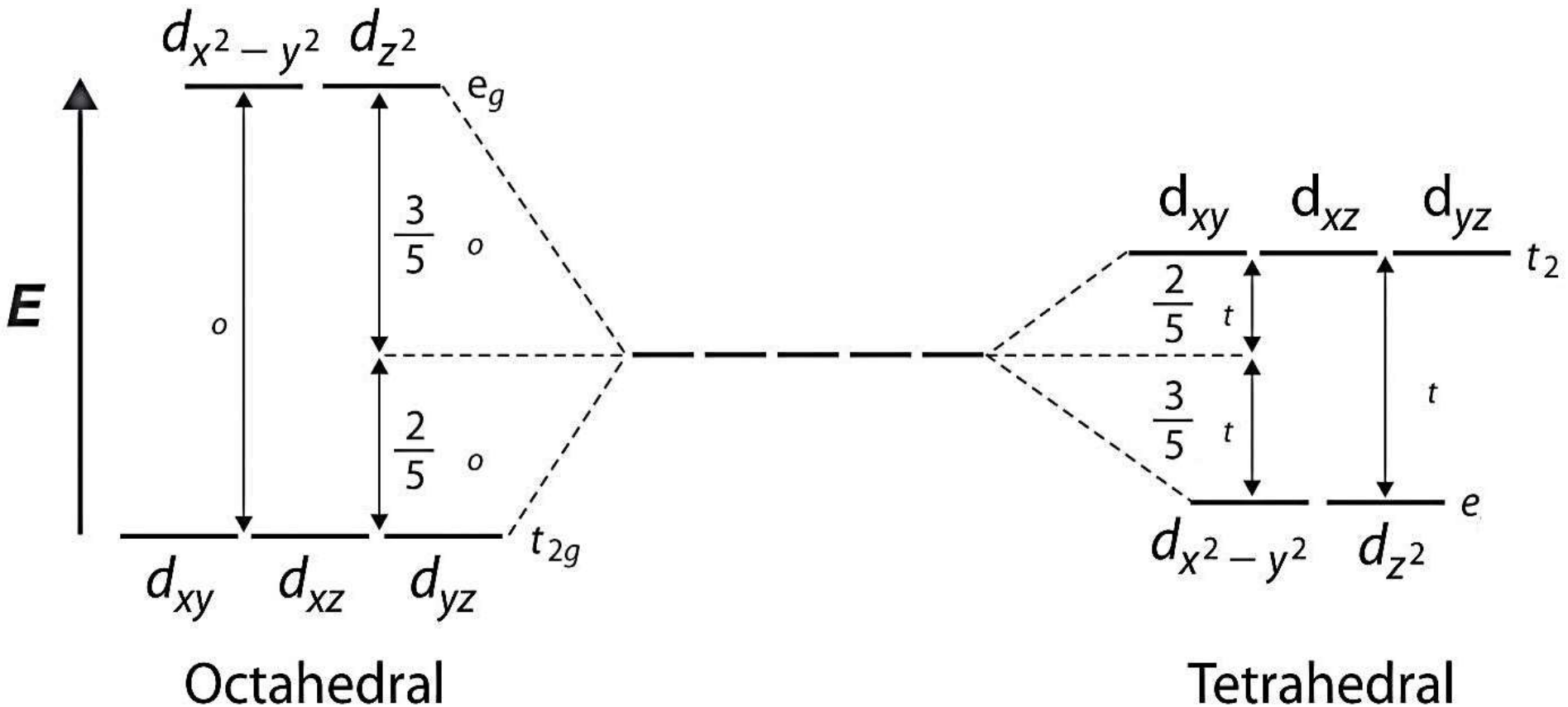
# Application of Crystal field theory to octahedral complexes

$[MX_6]^n$  the metal atom or ion is placed at the centre of regular octahedron while 6 ligands occupy the positions at 6 vertices octahedron.

- Two orbital  $d_{x^2-y^2}$  and  $d_{z^2}$  are Axial greater repulsion and  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$  less repulsion.



Five d orbitals lose degeneracy and split into two point groups. The group  $t_{2g}$  lower energy while  $e_g$  group have higher energy.



# Application of Crystal field theory to octahedral complexes

- Experimental calculation show that the energy of  $t_{2g}$  orbital is lowered by  $0.4\Delta_0$  or  $4D_q$  and energy of  $e_g$  orbital is increased by  $0.6\Delta_0$  or  $6D_q$ . Thus energy difference between  $t_{2g}$  and  $e_g$  orbitals is  $\Delta_0$  or  $10D_q$  which is crystal field splitting energy.
- CFSE increases with the increasing strength of ligands and oxidation state of central metal ion.

# Limitation of crystal field theory

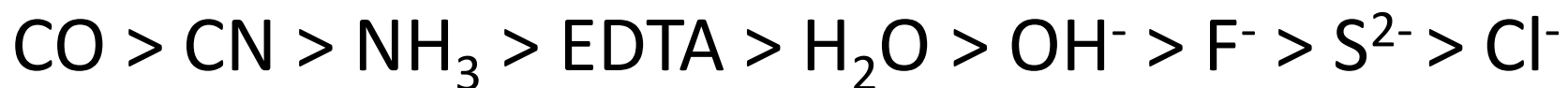
- Does not explain the s and p orbital.
- Does not explain  $\pi$  bonding.
- Cannot explain partly covalent nature of the metal ligand bond.
- Spectrochemical series water is a stronger ligand than  $\text{OH}^-$  which is not explained satisfactorily.

# Spectrochemical series

- The arrangement of various ligands in the decreasing order of their field strength and the splitting power of d-orbitals of the metal atom.
- Strong field ligand have higher splitting power of d orbital, hence higher crystal field splitting energy  $\Delta_0$ , while weak.....
- the field strength of ligand does not depend upon the geometry of the complex or nature of central metal atom or ion

# Spectrochemical series

- The decreasing order of field strength of some of the ligands is,

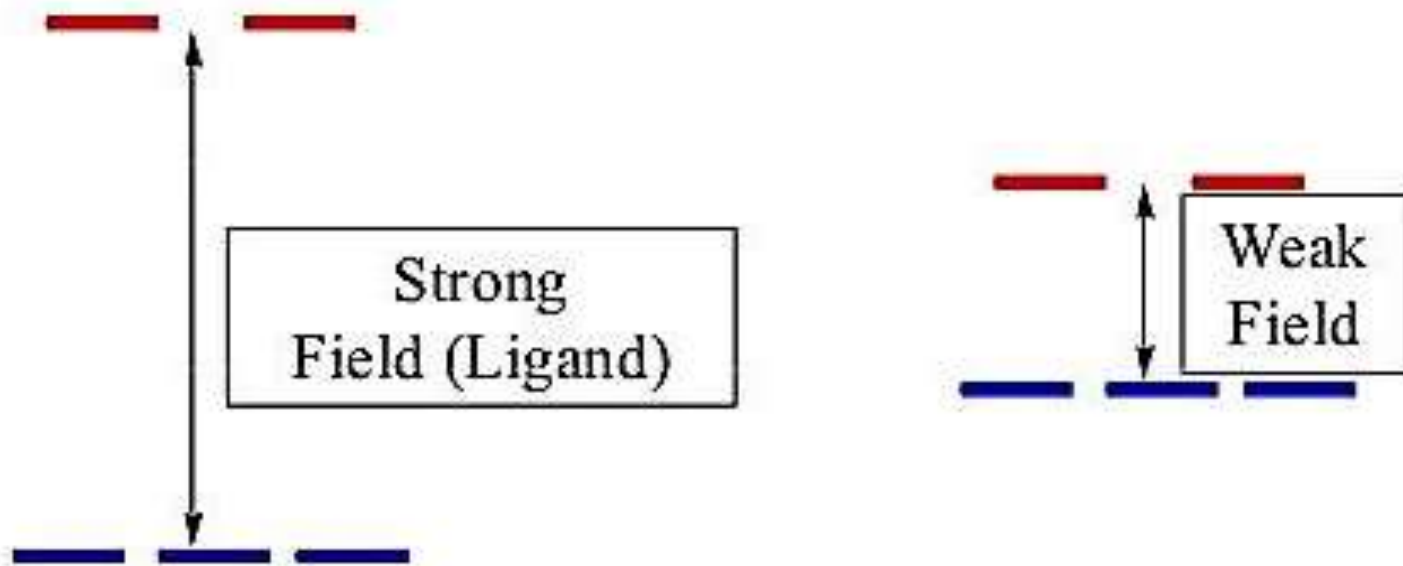


This series depends on the power of splitting the d orbitals and is called spectrochemical series.

## Spectrochemical Series


An arrangement of ligands according to their ability to increase  $\Delta$  for a given metal center

Weak – I<sup>-</sup>, Br<sup>-</sup>, SCN<sup>-</sup>, Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>, F<sup>-</sup>, H<sub>2</sub>NC(O)NH<sub>2</sub>, OH<sup>-</sup>, ox<sup>2-</sup>, O<sup>2-</sup>, H<sub>2</sub>O, NCS<sup>-</sup>, py, NH<sub>3</sub>, en, bpy, phen, NO<sub>2</sub><sup>-</sup>, CH<sub>3</sub><sup>-</sup>, C<sub>6</sub>H<sub>5</sub><sup>-</sup>, CN<sup>-</sup>, CO – Strong



# Colours in coordination compound

- Transition metal atoms (or) ions with one (or) more unpaired electrons and their complexes exhibit colour both in their solid and in solution states.
- If absorption occurs then the transmitted light bears a colour complementary to the colour of the light absorbed.

Coordination Entity	Wavelength of Light Absorbed (nm)	Colour of Light Absorbed	Colour of Coordination Entity
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	535	Yellow 	Violet 
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	500	Blue Green 	Red 
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue 	Yellow Orange 
$[\text{Co}(\text{CN})_6]^{3-}$	310	Ultraviolet 	Pale Yellow 
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$	600	Red 	Blue 
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	498	Blue Green 	Purple 

# Application of coordination compounds

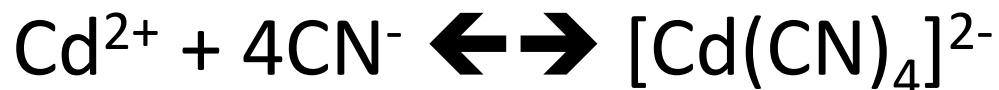
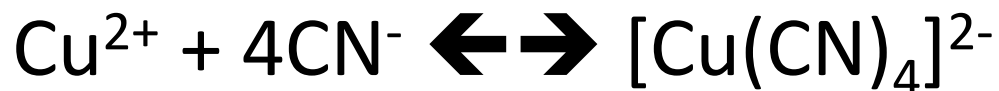
- 1. Extraction of metal:**
- 2. Analytical chemistry:**
- 3. Biological importance**
- 4. In medicine**
- 5. In electroplating**
- 6. For estimation of hardness of water**
- 7. In modifying the redox behavior of metal ions**

# 1. Extraction of metal:

- Technique used for noble metal like Ag & Au.
- Noble metals like silver and gold are extracted from their ore by the formation of cyanide complexes - dicyanoargentite(I) and dicyanoaurate (I).
- $\text{Ag}_2\text{S} + 4\text{NaCN} \rightleftharpoons 2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{S}$
- $2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \rightleftharpoons \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag}\downarrow$

## 2. Analytical chemistry:

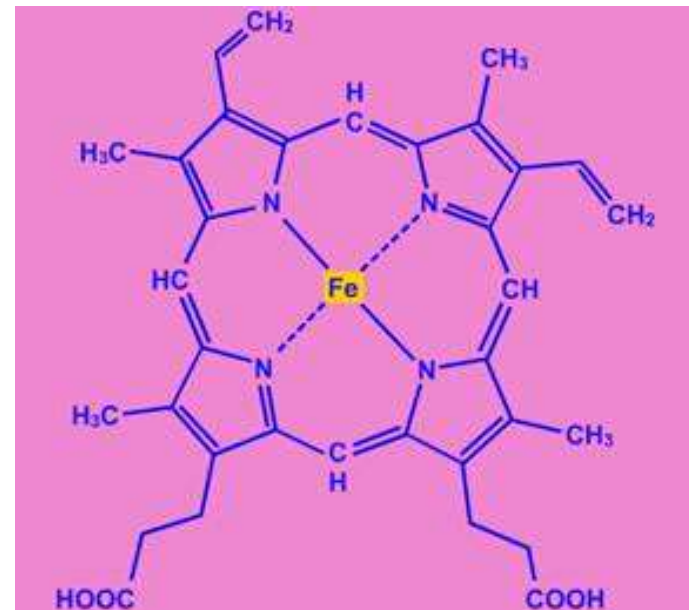
- Qualitative and quantitative analysis.
- In the qualitative methods of analysis, complex formation is of immense importance in the identification and separation of most inorganic ions.



Since Cu is more stable than Cd. Therefore, on passing  $\text{H}_2\text{S}$  only  $\text{CdS}$  is precipitated. Thus  $\text{Cd}^{2+}$  ion easily detected in the presence of  $\text{Cu}^{2+}$  ions.

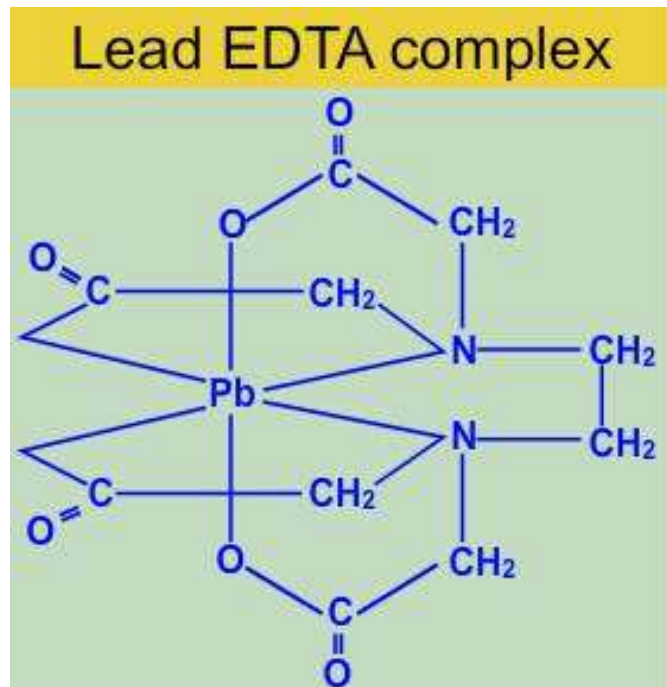
# 3. Biological Importance

- Significant role in plant(chlorophyll-Mg) and animal Vitamin-B12.
- Haemoglobin, red pigment of blood that acts as the Oxygen carrier is a coordination compound of iron



## 4. In medicine

- Treatment of cancer – cisplatin
- Platinum, cis  $[\text{PtCl}_2(\text{NH}_3)_2]$
- EDTA is used to treat lead poisoning.



# 5. Hardness of water

- The hardness of water is estimated by titration with the sodium salt of EDTA. During titration, the calcium and magnesium ions in hard water form the stable complexes, Calcium EDTA and Magnesium EDTA. Stability is different.

