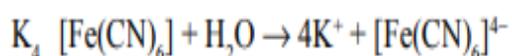


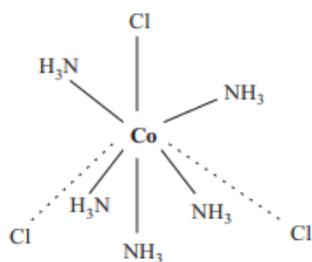
## COORDINATION COMPOUNDS

✚ **Introduction:** Complex compounds or coordination compounds are those molecular compounds which retain their identity in solid as well as in solution are known as complex compounds. In these compounds metal atoms are bound to a number of anions.



### WERNER'S COORDINATION THEORY

- In complex compounds, metal atom exhibit two types of valencies  $\bar{n}$  primary valency and secondary valency.
- Primary valencies are satisfied by anions only while secondary valencies are satisfied by ligands. Primary valency depends upon oxidation number of central metal atom while secondary valency represents coordination number of central metal atom.
- Primary valencies are ionisable and are non-directional while secondary valencies are non-ionisable and directional. Therefore, geometry of complex is decided by secondary valencies.



Primary valence (ionizable) (-----)  
Secondary valence (non-ionizable) (———)

### DEFINITION OF SOME IMPORTANT TERMS

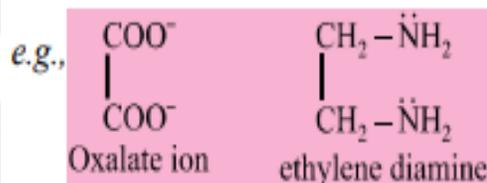
✚ **Ligands:** The ions or molecules bound to the central atom/ion in the coordination entity are called ligands.

✚ **Types of Ligands: (i) Unidentate,** a ligand which is bound to a metal ion through a single donor atom.

*e.g.,*  $H_2O, NH_3, CO, Cl^-, NH_2^-$  etc.

○

(ii) **Didentate,** a ligand which is bound to a metal ion through a two donor atoms.



(iii) **Polydentate,** a ligand which is bound to a metal ion through a several donor atoms.

*e.g.,* ethylene diamine tetraacetate ion  $[EDTA]^{4-}$ .

(iv) **Ambidentate** ligands, which can ligate through two different atoms.

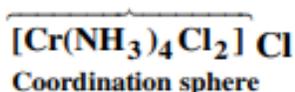
*e.g.,*  $-NO_2 - ONO, -SCN - NCS$  etc.

(v) **Chelate ligands,** these may be a di- or polydentate ligand which form closed ring with central metal ion. Closed ring is known as chelate ring. Number of more chelate ring in complex, complex will be more stable. The number of such ligating groups is called the denticity

✚ **Coordination number:** The coordination number in coordination compounds is

defined as the number of ligand (donor) atoms/ions surrounding the central metal atom in a complex ion. For example, the coordination number of cobalt in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is six.

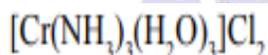
- ✚ **Coordination sphere:** The central metal atom and the ligands which are directly attached to it are enclosed in a square bracket and are collectively termed as coordination sphere.



- 
- ✚ **Oxidation number:** The net charge on a complex ion is the sum of the charges on the central atom and its surrounding ligands. In the  $[\text{PtCl}_6]^{2-}$  ion for example, each chloride ion has an oxidation number of  $-1$ , so the oxidation number of Pt must be  $+4$ .
- ✚ Paramagnetism due to presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum.

### RULES OF NOMENCLATURE OF COORDINATION COMPOUNDS

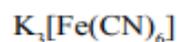
- ✚ **Cationic Complex:**



triamminetriaquachromium (III) chloride

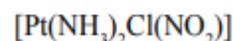
- Prefixes mono, di, tri, etc. are used to indicate the number of the individual ligands and ligands are named in an alphabetical order.
- Central metal atom and oxidation state indicated by Roman numeral in parenthesis.
- Name of ionisable anion

- ✚ **Anionic Complex:**



Potassium hexacyanoferrate (III)

- Name of ionisable metal and oxidation state.
- Name of ligand in an alphabetical order
- Central metal atom + ate and oxidation state



Diammine chloronitrito-N-platinum (II)

- Name of ligands in an alphabetical order
- Central metal atom and oxidation state

### VALENCE BOND THEORY

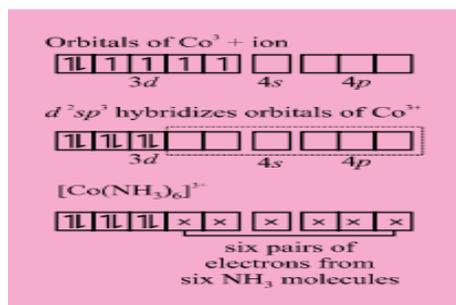
- ✚ According to this theory, the metal atom or ion under the influence of ligands form inner orbital and outer orbital complex. These hybridized orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

- Six ligands (unidentate) (octahedral entity) Generally central atom belongs 3d series and ligands can be monodentate or didentate but coordination number should be six and shape of complexes will be octahedral and form two types of complexes.

- Inner orbital complexes**, which are formed due to participation of  $(n-1)d$  orbitals in hybridisation is  $(d^2sp^3)$  and shape of complex will be octahedral.

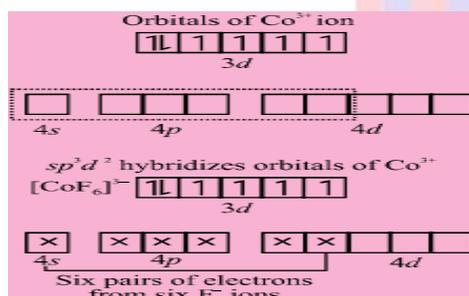
- Outer orbital complexes**, which are formed due to participation of  $nd$  orbitals in hybridisation is  $(sp^3d^2)$ . Generally halides ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ),  $\text{SCN}^-$ ,  $\text{S}^{2-}$  form outer orbital complexes and other ligands form inner orbital complexes.

e.g., Inner orbital complex,  $[\text{Co}(\text{NH}_3)_6]^{3+}$



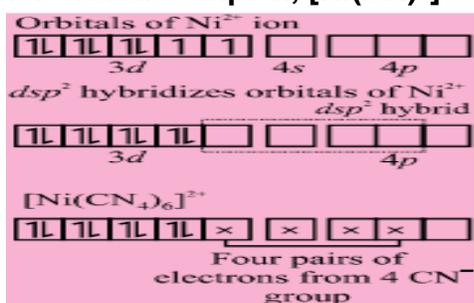
- All electrons are paired therefore, complex will be diamagnetic in nature.

e.g., Outer orbital complex,  $[\text{CoF}_6]^{3-}$

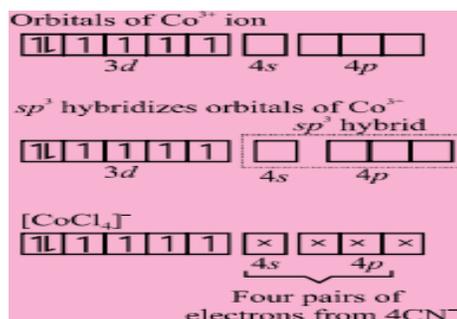


- Complex has unpaired electrons; therefore, complex will be paramagnetic in nature.
- Generally halides ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) ligands,  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Co}(\text{CO})_4]$ ,  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  complexes form outer orbital complexes and other form inner orbital complexes. For example,

### 1. Inner orbital complex, $[\text{Ni}(\text{CN})_4]^{2-}$



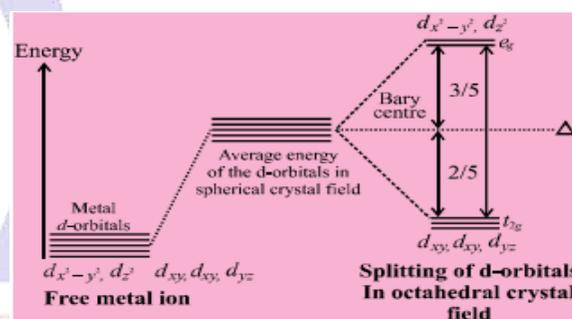
### 2. Outer orbital complex, $[\text{CoCl}_4]^-$



## CRYSTAL FIELD THEORY

- The five d-orbitals are split into lower and higher energy level due to approach of ligands is known as crystal field theory. The five d-orbitals in a gaseous metal atom/ion have same energy.

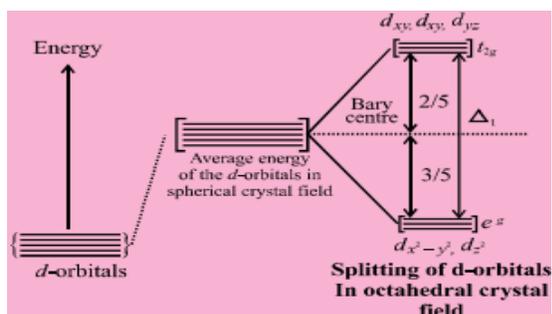
(i) Crystal field splitting in octahedral coordination entities.



- Energy separation is denoted by  $\Delta_o$  (the subscript o is for octahedral).
- The energy of the two  $e_g$  orbitals (higher energy orbitals) will increase by  $(3/5)\Delta_o$  and that of the three  $t_{2g}$  (lower energy orbitals) will decrease by  $(2/5)\Delta_o$ .
- If  $\Delta_o < p$ , the fourth electron enters one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^1$ . Ligands for which  $\Delta_o < p$  are known as weak field ligands and form high spin complexes.
- If  $\Delta_o > p$ , it becomes more energetically favorable for the fourth electron to occupy a  $t_{2g}$  orbital with configuration  $t_{2g}^4 e_g^0$ . Ligands which produce this effect

are known as strong field ligands and form low spin complexes, where  $p$  represents the energy required for electron pairing in a single orbital.

(ii) Crystal field splitting in tetrahedral coordination entities.



In tetrahedral coordination entities,  $\Delta_t = (4/9)\Delta_o$ , consequently the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

Due to less crystal field stabilization energy, it is not possible to pair electrons and so all the tetrahedral complexes are high spin.

## ISOMERISM

Compounds which have the same molecular formula, but different structural formulae are said to be isomers. There are many types of isomerism possible. The isomerism can be classified as:

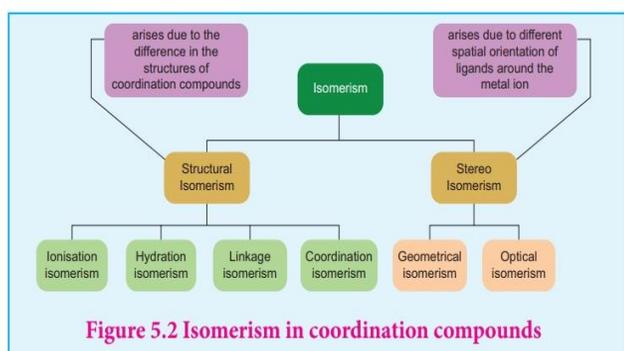


Figure 5.2 Isomerism in coordination compounds

## APPLICATIONS OF COORDINATION COMPOUNDS

A major application of coordination compounds is their use as catalysts, which serve to alter the rate of chemical reactions. Certain complex metal catalysts, for example, play a key role in the production of polyethylene and polypropylene.

They are used in estimation of hardness of water as calcium and, magnesium ions form **complexes** with EDTA.

It is used in estimation and detection of metal ions.

It is used in medicines like cis platin is used in treatment of cancer.

Some examples of coordination complex metalloenzymes are: Zinc-complex enzymes like carbonic anhydrase, important to buffering reactions in blood. Copper-complex enzymes important to iron storage and producing pigments in hair, skin, and eyes.

## Colour in Coordination Compounds

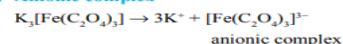
In complex compounds d-orbitals split in two sets  $t_{2g}$  and  $e_g$ . These have different energies. The difference in energies lies in visible region and electron jump from ground state  $t_{2g}$  level to higher state  $e_g$  level. This is known as d-d transition and it is responsible for colour of coordination compounds.

Table : Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities

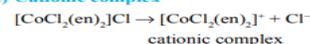
Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[\text{CoCl}(\text{NH}_3)_4]^{2+}$	535	Yellow	Violet
$[\text{Co}(\text{NH}_3)_6(\text{H}_2\text{O})]^{3+}$	500	Blue Green	Red
$[\text{Co}(\text{NH}_3)_4]^{2+}$	475	Blue	Yellow Orange
$[\text{Co}(\text{CN})_6]^{3-}$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

## Types of Complex

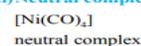
(i) **Anionic complex**



(ii) **Cationic complex**



(iii) **Neutral complex**



**Check Yourself**

- Trunbull's blue is  
(A) Ferricyanide (B) Ferrous ferricyanide  
(C) Ferrous cyanide (D)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$
- Primary and secondary valency of Pt in  $[\text{Pt}(\text{en})_2\text{Cl}_2]$  are  
(A) 4, 4 (B) 4, 6  
(C) 6, 4 (D) 2, 6
- The complex ions  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$  and  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$  are called  
(A) Ionization isomers  
(B) Linkage isomers  
(C) Co-ordination isomers  
(D) Geometrical isomers
- Which of the following has square planar structure?  
(A)  $[\text{NiCl}_4]^{2-}$  (B)  $[\text{Ni}(\text{CO})_4]$   
(C)  $[\text{Ni}(\text{CN})_4]^{2-}$  (D) None of these
- Which of the following has magnesium?  
(A) Chlorophyll  
(B) Haemocyanin  
(C) Carbonic anhydrate  
(D) Vitamin B<sub>12</sub>

**Test Yourself**

**Question:** Using IUPAC norms write the formulae for the following coordination compounds:

- Tetracarbonylnickel(O)
- Potassium tetracyanidoferrate(II)

**Answer:**

- $[\text{Ni}(\text{CO})_4]$
- $\text{K}_2[\text{Fe}(\text{CN})_4]$

**Stretch Yourself**

1. Why tetrahedral complexes high are spin?
2. Write down the IUPAC name of the complex  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ . What type of isomerism is shown by this complex?
3. Predict the number of unpaired electrons in hexaaquamanganese(II) ion. [Atomic number of Mn = 25]
4. Write the chemical formula and shape of hexamminecobalt(III) sulphate.
5. A  $\text{CuSO}_4$  solution is mixed with  $(\text{NH}_4)_2\text{SO}_4$  solution in the ratio of 1:4 does not give test for  $\text{Cu}^{2+}$  ion, why?

**Answers****Check Yourself**

**Answer: 1(A); 2(C); 3(B); 4(D); 5(B)**

**Stretch Yourself**

1. It is because of small splitting energy gap, electrons are not forced to pair; therefore, there is large number of unpaired electrons, i.e. high spin.
2. Dichloro Bis-(ethane-1,2 diamine) Cobalt (III). It will show geometrical as well as optical isomerism.
3. It has 5 unpaired electrons.
4.  $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$ , octahedral.
5.  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  is formed which does not have free  $\text{Cu}^{2+}$  ions.