# L.S  COLLEGE MUZAFFARPUR

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# CO-ORDINATION OF COMPOUNDS

Coordination compounds are chemical compounds that consist of an array of anions or neutral molecules that are bound to a central atom via coordinate covalent bonds. Coordination compounds are also referred to as **coordination complexes**. These molecules or ions that are bound to the central atom are referred to as ligands (also known as complexing agents).

Many coordination compounds contain a metallic element as the central atom and are therefore referred to as metal complexes. These types of coordination complex generally consist of a transition element as the central atom. It can be noted that the central atom in these complexes is called the coordination centre.

## Important Terms Involving Coordination Compounds

The definitions of some important terms in the chemistry of coordination compounds can be found below.

### Coordination Entity

A chemical compound in which the central ion or atom (or the coordination centre) is bound to a set number of atoms, molecules, or ions is called a **coordination entity**.

Some examples of such coordination entities include [CoCl3(NH3)3], and [Fe(CN)6]4-.

### Central Atoms and Central Ions

As discussed earlier, the atoms and ions to which a set number of atoms, molecules, or ions are bound are referred to as the **central atoms** and the **central ions**.

In coordination compounds, the central atoms or ions are typically Lewis Acids and can, therefore, act as electron-pair acceptors.

### Ligands

The atoms, molecules, or ions that are bound to the coordination centre or the central atom/ion are referred to as **ligands**.

These ligands can either be a simple ion or molecule (such as Cl– or NH3) or in the form of relatively large molecules, such as ethane-1,2-diamine (NH2-CH2-CH2-NH2).

### Coordination Number

The **coordination number** of the central atom in the coordination compound refers to the total number of sigma bonds through which the ligands are bound to the coordination centre.

**For example,** in the coordination complex given by [Ni(NH3)4]2+, the coordination number of nickel is 4.

### Coordination Sphere

The non-ionizable part of a complex compound which consists of central transition metal ion surrounded by neighbouring atoms or groups enclosed in square bracket.

The coordination centre, the ligands attached to the coordination centre, and the net charge of the chemical compound as a whole, form the **coordination sphere** when written together.

This coordination sphere is usually accompanied by a counter ion (the ionizable groups that attach to charged coordination complexes).

**Example:** [Co(NH3)6]C/3 – coordination sphere

## Coordination Polyhedron

The geometric shape formed by the attachment of the ligands to the coordination centre is called the **coordination polyhedron**.

Examples of such spatial arrangements in coordination compounds include tetrahedral and square planar.

## Oxidation Number

The oxidation number of the central atom can be calculated by finding the charge associated with it when all the electron pairs that are donated by the ligands are removed from it.

For example, the oxidation number of the platinum atom in the complex $[PtCl_6]^{2-}$ is +4.

## Homoleptic and Heteroleptic Complex

- When the coordination centre is bound to only one type of electron pair donating ligand group, the coordination complex is called a **homoleptic complex**, for example: $[Cu(CN)_4]^{3-}$.
- When the central atom is bound to many different types of ligands, the coordination compound in question is called a **heteroleptic complex**, an example for which is $[Co(NH_3)_4Cl_2]^+$.

# Properties of Coordination Compounds

The general properties of coordination compounds are discussed in this subsection.

- The coordination compounds formed by the transition elements are coloured due to the presence of unpaired electrons that absorb light in their electronic transitions. For example, the complexes containing Iron(II) can exhibit green and pale green colours, but the coordination compounds containing iron(III) have a brown or yellowish-brown colour.
- When the coordination centre is a metal, the corresponding coordination complexes have a magnetic nature due to the presence of unpaired electrons.
- Coordination compounds exhibit a variety of chemical reactivity. They can be a part of inner-sphere electron transfer reactions as well as outer-sphere electron transfers.
- Complex compounds with certain ligands have the ability to aid in the transformation of molecules in a catalytic or a stoichiometric manner.

# Double Salts and Coordination Complex

## Double Salts

Double salts are completely ionizable in aqueous solutions and each ion in the solution gives the corresponding confirmatory test.

**Example:** Potash Alum is double sulphate. It is K2SO4.Al2(SO4)$_3$.24H2O on Ionization it gives:

$K^+$, $SO_2^{-4}$ and $Al^{+3}$ ions which response to the corresponding tests.

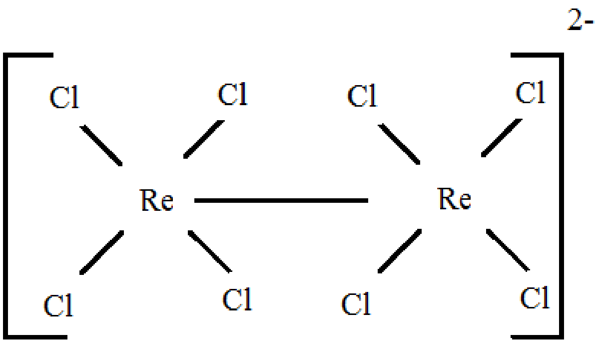
### Coordination Complex

Co-ordinate complex are incompletely ionizable in the aqueous solutions. These give a complexion which does not show complete ionization.

**Example:** Potassium Ferrocyanide. $[K_4Fe(CN)_6]$ It ionizes to give $K^+$ and $[Fe(CN)_6]^{-4}$ [ferro cyanide ions]

## Types of Coordination Complexes

- **Cationic complexes:** In this co-ordination sphere is a cation. Example: [Co(NH3)6]Cl3
- **Anionic complexes:** In this co-ordination sphere is Anion. Example: K4[Fe(CH)6]
- **Neutral Complexes:** In this co-ordination sphere is neither cation or anion. Example: [Ni(CO)4]
- **Homoleptic complex:** The complex consist of a similar type of ligands. Example: K4[Fe(CN)6]
- **Heteroleptic complexes:** These consists of different types of ligands. Example: [Co(NH3)5Cl]SO4
- **Mononuclear complexes:** In this co-ordination sphere has single transition metal ion. Example: K4[Fe(CN)6]
- **Polynuclear complexes:** More than one transition metal ion is present. Example:



**Polynuclear complexes**

## IUPAC Nomenclature of Coordination Compounds

### Rules For Naming Coordination Compound

The standard rules that must be followed in the nomenclature of coordination compounds are described below.

1. The ligands are always written before the central metal ion in the naming of complex coordination complexes.
2. When the coordination centre is bound to more than one ligand, the names of the ligands are written in an alphabetical order which is not affected by the numerical prefixes that must be applied to the ligands.

3. When there are many monodentate ligands present in the coordination compound, the prefixes that give insight into the number of ligands are of the type: di-, tri-, tetra-, and so on.
4. When there are many polydentate ligands attached to the central metal ion, the prefixes are of the form bis-, tris-, and so on.
5. The names of the anions present in a coordination compound must end with the letter ‘o’, which generally replaces the letter ‘e’. Therefore, the sulfate anion must be written as ‘sulfato’ and the chloride anion must be written as ‘chlorido’.
6. The following neutral ligands are assigned specific names in coordination compounds: NH3 (ammine), H2O (aqua or aquo), CO (carbonyl), NO (nitrosyl).
7. After the ligands are named, the name of the central metal atom is written. If the complex has an anionic charge associated with it, the suffix ‘-ate’ is applied.
8. When writing the name of the central metallic atom in an anionic complex, priority is given to the Latin name of the metal if it exists (with the exception of mercury).
9. The oxidation state of the central metal atom/ion must be specified with the help of roman numerals that are enclosed in a set of parentheses.
10. If the coordination compound is accompanied by a counter ion, the cationic entity must be written before the anionic entity.

⇒ **Also Read:** Nomenclature of Organic Compounds

## Examples of Naming Coordination Compounds

Some examples of the nomenclature of coordination compounds can be found below.

- $K_4[Fe(CN)_6]$: Potassium hexa cyanide ferrate (II)
- $[Ni(CN)_4]^{-2}$: Tetra cyanie Nickelate (II) ion.
- $[Zn(OH)_4]^{-2}$: Tetra hydroxide zincate (II) ion.
- $[Ni(CO)_4]$: Tetra carbonyl Nickel (O).

## What are Ligands in Coordination Compounds?

The surrounding atoms, ion and molecule around the central transition metal ion are known as Ligands. They act as Lewis base and donate electron pairs to transition metal ion thus a dative bond is formed between ligands and the transition metal ion. Hence these compounds are coordination complexes.

Also Read: Ligands

## Types of Ligands

Based on the nature of the bond between the ligand and the central atom, ligands are classified as follows:

- Anionic ligands: $CN^-$, $Br^-$, $Cl^-$
- Cationic ligands: $NO^+$
- Neutral ligands: CO, $H_2O$, $NH_3$

**Ligands can be further classified as:**

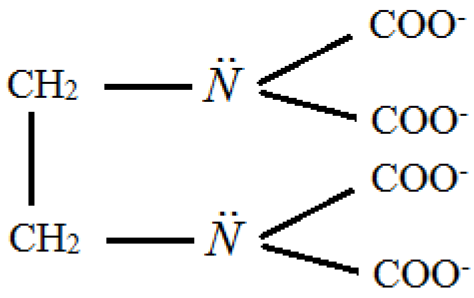
## Unidentate Ligands

The ligands which only have one atom that can bind to the coordination centre are called unidentate ligands. Ammonia (NH3) is a great example of a unidentate ligand. Some common unidentate are $Cl^-$, $H_2O$ etc.

## Bidentate Ligands

Ligands which have the ability to bind to the central atom via two separate donor atoms, such as ethane-1,2-diamine, are referred to as bidentate ligands.

Oxalate ion is a bidentate as it can bond through two atoms to the central atom in a coordination compound and Ethane-1, 2-diamine:



## Polydentate Ligands

Some ligands have many donor atoms that can bind to the coordination centre. These ligands are often referred to as polydentate ligands.

A great example of a polydentate ligand is the EDTA4- ion (ethylene diamine tetraacetate ion), which can bind to the coordination centre via its four oxygen atoms and two nitrogen atoms.

## Chelate Ligand

When a polydentate ligand attaches itself to the same central metal atom through two or more donor atoms, it is known as a chelate ligand. The atoms that ligate to the metal ion are termed as the denticity of such ligands.

## Ambidentate Ligand

Some ligands have the ability to bind to the central atom via the atoms of two different elements.

For example, the SCN– ion can bind to a ligand via the nitrogen atom or via the sulfur atom. Such ligands are known as ambidentate ligands.

# Isomerism in Coordination Compounds

Two or more compounds that have the same chemical formula but a different arrangement of atoms are known as isomers. Due to this difference in the arrangement of atoms, coordination compounds pre-dominantly exhibit two types of isomerism namely, **stereo-isomerism and structural isomerism**.

## Stereoisomerism

Coordination compounds which have the same chemical and chemical bonds but have different spatial arrangement are known as stereoisomers. These are further divided into optical isomerism and geometrical isomerism.

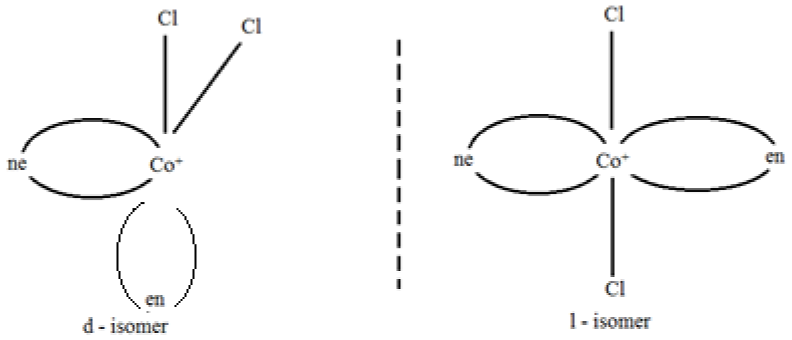
## Optical Isomerism in Coordination Compounds

The isomer which forms non-super imposable mirror image is known as optical isomers or enantiomers. These are of two types

- The isomer that rotates plane-polarized light towards clockwise direction is dextro or ‘d’ or ‘+’ isomer.
- The isomer that rotates plane-polarized light to anti-clockwise direction is leavo isomer or ‘l’, ‘-‘ isomer.

The equimolar mixture of ‘d’ and ‘l’ isomer is known as the racemic mixture.

**Example of Optical Isomerism**:



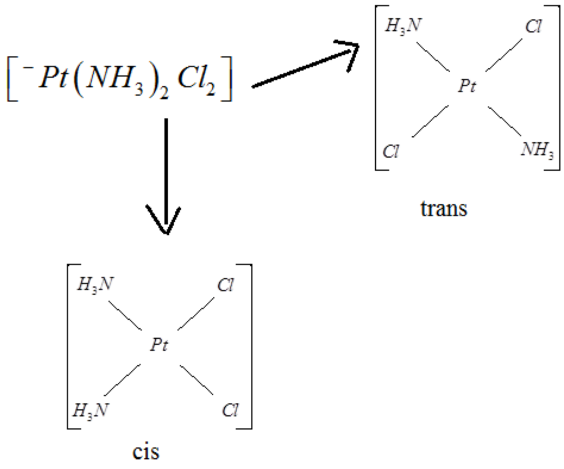
## Geometrical Isomerism

Geometrical isomerism is observed in heteroleptic complexes (complexes with more than one type of ligands) due to different possible geometric arrangements of the ligands.

This behaviour is mainly observed in coordination compounds having coordination numbers equal to 4 and 6. Geometrical isomerism of complexes with **coordination number 4**:

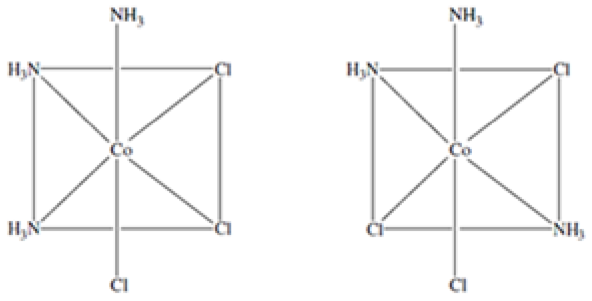
- ML4 tetrahedral complexes do not show cis-trans isomerism since ligands are in different directions.
- MABCD has 3 geometrical isomers. 2-cis and 1-trans.
- MA2B2 complex shows cis and trans isomers.

**Example:**



ML6 octahedral complex does not show geometrical isomerism. MA2B4 complex shows cis-trans isomerism.

**Example:** [Co(NH3)4Cl2]+



MA3B3 complex shows facial-meridional isomerism

## Structural Isomerism

Structural isomerism is exhibited by the coordination compounds having the same chemical formula but a different arrangement of atoms. These are further divided into four types:

### Linkage Isomerism

Linkage isomerism is exhibited by coordination compounds having Ambidentate ligands.

**For example**$[Co(NH_3)_5No]So_4$ and $[Co(NH_3)_5ONO]So_4$

### Coordination Isomerism

Incoordination isomerism, the interchange of ligands between cationic and anionic entities of different metal ions present in coordination compounds takes place.

**For example:** $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH3)_6][Co(CN)_6]$.

### Ionisation Isomerism

Ionisation isomerism arises when the counter ion in a complex salt which is a potential ligand replaces the ligand.

**For example:** $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$.

### Solvate Isomerism

Solvate isomers are a special case of ionisation isomerism in which compounds differ depending on the number of the solvent molecule directly bonded to the metal ion.

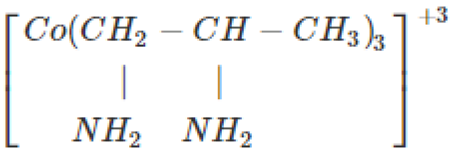
**For example:**

- $[Co(H_2O)_6]Cl_3$
- $[Co(H_2O)_5Cl]Cl_2.H_2O$
- $[Co(H_2O)_4Cl_2]Cl.2H_2O$
- $[Co(H_2O)_3Cl_3].3H_2O$

### Ligand Isomerism

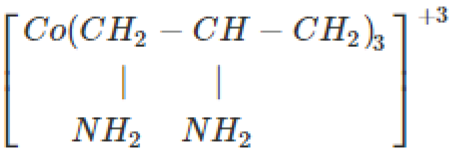
In this type, ligands show isomerism.

**For Example:**



$$\left[Co(\underset{NH_2}{\underset{|}{CH_2}}-\underset{NH_2}{\underset{|}{CH}}-CH_3)_3\right]^{+3}$$

*and*



$$\left[Co(\underset{NH_2}{\underset{|}{CH_2}}-\underset{NH_2}{\underset{|}{CH}}-CH_2)_3\right]^{+3}$$

## Werner's Theory

Alfred Werner in 1898 proposed Werner's theory explaining the structure of coordination compounds.

**Werner's Experiment:** By mixing AgNO3 (silver nitrate) with $CoCl_3·6NH_3$, all three chloride ions got converted to AgCl (silver chloride). However, when AgNO3 was mixed with $CoCl_3·5NH_3$, two moles of AgCl were formed.

Further, on mixing $CoCl_3·4NH_3$ with $AgNO_3$, one mole of AgCL was formed. Based on this observation, the following Werner's theory was postulated:

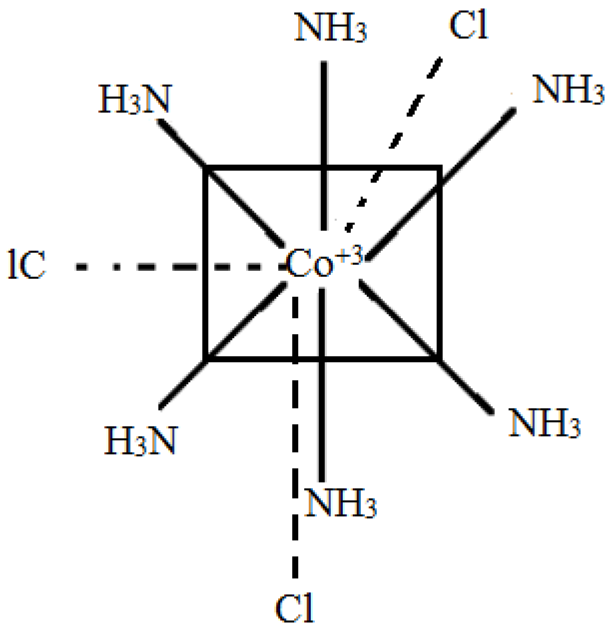
## Postulates of Werner's Theory

- The central metal atom in the coordination compound exhibits two types of valency, namely, primary and secondary linkages or valencies.
- Primary linkages are ionizable and are satisfied by the negative ions.
- Secondary linkages are non-ionizable. These are satisfied by negative ions. Also, the secondary valence is fixed for any metal and is equal to its coordination number.
- The ions bounded by the secondary linkages to the metal exhibit characteristic spatial arrangements corresponding to different coordination numbers.

## Difference between Primary and Secondary Valency in Coordination Compounds

| **Werner's Theory** | |
|---|---|
| **Primary valency** | **Secondary valency** |
| These are ionizable | These are Non-ionizable |
| Satisfied by charged ions | Satisfied by ligands |
| **Primary valency** does not help in the structure of complex | **Secondary valency** helps in structure |
| It can also function as a secondary valence | It can not function as a primary valency |

**Example:** CoC{{l}_{3}}.6N{{H}_{3}}$CoCl_3.6NH_3$ is Werner complex.



Such spatial arrangement is termed as coordination polyhedra. The terms inside the square brackets are coordination complexes and the ions outside the square brackets are counter-ions.

## Limitations of Werner's Theory

1. It fails to explain the magnetic, colour and optical properties shown by coordination compounds.
2. It failed to explain the reason why all elements don't form coordination compounds.
3. It failed to explain the directional properties of bonds in coordination compounds.
4. This theory does not explain the stability of the complex
5. This theory could not explain the nature of complexes

## Effective Atomic Number Rule

Effective Atomic Number Rule is proposed by Sidgwick. The total number of electrons passed by central transition metal ion after the donation of electrons by the ligand an effective atomic number.

A complex is stable if the effective atomic number is equal to the atomic number of nearest inert gas.

**Example: Calculate the effective atomic number of the following complexes:**

- K4[Fe(CN)6]
- [Co(NH3)]Cl3

**1. K4[Fe(CN)6]**

Number of electrons in Fe2+ = 24

Number of electrons by Six CN = 2×6 = 12

Total number of electrons possessed by Fe2+ = 24 + 12

Therefore, the effective atomic number = 36.

**2. [Co(NH3)]Cl3**

Number of electrons in Co+3 = 24

Number of electrons by Six NH3 = 2×6 = 12

Total number of electrons possessed by Co+3 = 24 + 12

Therefore, the effective atomic number = 36.

## Magnetic Properties of Complexes

1. The complex in which central transition metal ion has unpaired electrons is Paramagnetic.
2. The complex in which central transition metal ion has no unpaired electrons is diamagnetic.
3. The magnetic moment of a complex is calculated by the spin only formula

M = √[n(n+2)] BM

BM = Bohr Magneton

The magnetic moment of complex compounds depends upon:

- Type of hybridization.
- The oxidation state of central transition metal ion.
- The number of unpaired electrons.

## Spectro Chemical Series

The series of increasing order of field strength of ligands is known as Spectrochemical series. It is $I^{-}$ < $Br^{-}$ < $SCN^{-}$ < $Cl^{-}$ < $S^{-2}$ < $F^{-}$ < $OH^{-}$ < $C2O^{-2}4$ < H2O < NCS− < $(EDTA)^{-4}$ < NH3 < en < CN < CO

## Stability of Complexes

A complex is formed in several steps. Each process step is reversible and the equilibrium constant is known as stepwise formation constant. Let us consider the formation of complex ML4

$$M + L_1 \overset{K_1}{\rightleftharpoons} ML_1$$

$$ML_1 + L \overset{K_2}{\rightleftharpoons} ML_2$$

$$ML_2 + L \overset{K_3}{\rightleftharpoons} ML_3$$

$$ML_3 + L \overset{K_4}{\rightleftharpoons} ML_4$$

The overall formation constant or stability constant, β = K1 × K2 × K3 × K4 and 1/β = Instability constant

## Factors Affecting Stability of Complexes

1. Small size and high nuclear charge of central transition metal ion,
2. Crystal field stabilizing energy (CFSE) should be more.
3. Complexes containing chelating ligands are more stable.
4. Octahedral complexes are generally more stable than tetrahedral.

**Also, Check ⇒** Crystal Field Theory

## Colour of Complexes

Complexes in which central transition metal ion contains unpaired electrons shows colour. It is 'd – d' transition. The colour of complexes depends upon:

- Number of unpaired electrons in transition metal ion
- Nature of ligands
- The oxidation state of central transition metal ion
- The wavelength of light absorbed and emitted
- The proportion of ligands in the coordination sphere

**Example:** [Ni(H2O)6]+2+en(aq)→[Ni(H2O)4en]$^{+2}$ – Green Pale blue

## Bonding in Metal Complexes [Metal Carbonyls]

Complexes in which carbon monoxide acts as ligands are metal carbonyls

**Example:** $[Ni(CO)_4]$ Tetracarbonyl Nickel (0) and $[Fe(CO)_5]$ Penta Carbonyl Iron (0) In these complexes, complexes, a′σ' bond is formed by the overlapping of vacant 'd' orbital of metal ion and filled orbital of C-atom (carbon).

A π bond is formed by the lateral overlapping of filled inner orbitals of metal ion and vacant of the carbon atom. Thus synergic bonding exist in metal carbonyls