Dev Academy
Yamunanagar (Haryana)

Comprehensive Notes

Coordination Compounds

Class 12

CHEMISTRY

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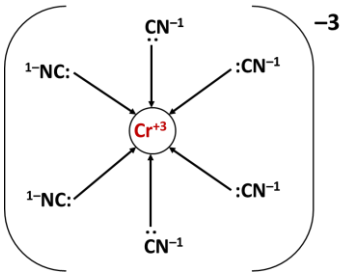
Introduction

- **A Coordination compound** is **the product** of a **Lewis acid–base reaction** in which anions or neutral molecules (called ligands) **donate lone pairs of electrons** to a central metal atom (or ion), **forming coordinate covalent bonds**.
    - **In simple terms:**
      They are compounds in which a **central metal atom/ion** is linked to a number of ions or neutral molecules (called **ligands**) through **coordinate covalent bonds**.



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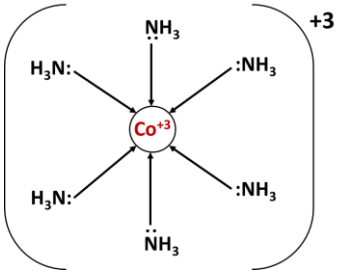
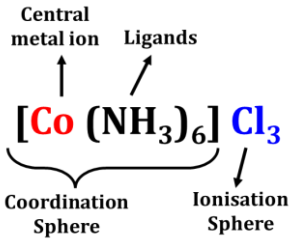


(II)

- **Transition metals** have strong tendency to form a large number of **coordination compounds or complexes**.
- **Representation of a Coordination Compound:**



- **Alfred Werner** was a **Swiss chemist** who is regarded as the **father of coordination chemistry**.
- He was awarded the **Nobel Prize in Chemistry 1913** for this work.

Werner's Theory of Coordination Compounds

- Alfred Werner **prepared and characterized** a large number of coordination compounds and **studied their physical and chemical behaviour** using simple experimental methods (i.e., Precipitation).
- He introduced the concept of: **Primary valency** (ionisable), and **Secondary valency** (non-ionisable).

Werner's Experiment (Precipitation Studies)

- Werner studied several **cobalt–ammonia complexes** obtained by reacting **Cobalt chloride ($CoCl_3$)** with **Ammonia (NH_3)**.
- When such **cobalt–ammonia complexes** are treated with excess **Silver nitrate ($AgNO_3$)** solution, the **number of moles of silver chloride (AgCl) precipitated** indicates the number of **ionisable chloride ions** present **outside** the coordination sphere.

$$[\text{Cobalt-ammonia}]\ Cl_{\mathbf{n}} \ + \ \text{excess}\ AgNO_3 \longrightarrow \ \mathbf{n}\ AgCl_{(ppt)}$$

- **Example:**
  - $CoCl_3 \cdot 6NH_3$ + excess $AgNO_3$ ⟶ 3 moles of AgCl
    - It means the compound has **3 ionisable Cl^{-1} ions**.
    - Hence, the formula of compound is : **$[Co(NH_3)_6]Cl_3$**
  - $CoCl_3 \cdot 5NH_3$ + excess $AgNO_3$ ⟶ 2 moles of AgCl
    - It means the compound has **2 ionisable Cl^{-1} ions**.
    - Hence, the formula of compound is : **$[CoCl(NH_3)_5]Cl_2$**
  - $CoCl_3 \cdot 4NH_3$ + excess $AgNO_3$ ⟶ 1 moles of AgCl
    - It means the compound has **1 ionisable Cl^{-1} ions**.
    - Hence, the formula of compound is : **$[CoCl_2(NH_3)_4]Cl$**

Compound	Colour	Moles of AgCl formed from 1 mole of compound	Formula of the complex
$CoCl_3.6NH_3$	Yellow	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3.5NH_3$	Purple	2	$[CoCl(NH_3)_5]\ Cl_2$
$CoCl_3.4NH_3$	Violet	1	$[CoCl_2(NH_3)_4]\ Cl$
$CoCl_3.4NH_3$	Green	1	$[CoCl_2(NH_3)_4]\ Cl$

Note:
The **two different colours** (violet and green) of **$[CoCl_2(NH_3)_4]\ Cl$** are due to the existence of **geometrical isomers (cis and trans forms)**.

Conductance Measurements

- The **molar conductance** of a solution depends on the **number of ions** produced by **one mole of a compound** when dissolved in water.
- Greater the number of ions, **higher** will be the **molar conductivity**.
- By comparing the molar conductance with known electrolytes, we can determine the **number of ions furnished by each complex**.
- Example:

Compound	Colour	Electrolytic Type	Total number of ions produced	Inference
$CoCl_3.6NH_3$	Yellow	1 : 3	4	$[Co(NH_3)_6]^{+3} + 3Cl^{-1}$
$CoCl_3.5NH_3$	Purple	1 : 2	3	$[CoCl(NH_3)_5]^{+2} + 2Cl^{-1}$
$CoCl_3.4NH_3$	Violet	1 : 1	2	$[CoCl_2(NH_3)_4]^{+1} + Cl^{-1}$
$CoCl_3.4NH_3$	Green	1 : 1	2	$[CoCl_2(NH_3)_4]^{+1} + Cl^{-1}$

Postulates of Werner's Theory

- A **metal atom (or ion)** in coordination compounds exhibits **two types of valencies** :–
  (i) Primary valency (ii) Secondary valency
- **Primary Valency:**
  - **Ionisable** in nature.
  - Corresponds to the **oxidation state** of the metal.
  - Satisfied only by **negative ions**.
  - **Non-directional** in character.

- **Secondary Valency (or Auxiliary Valency):**
  - **Non-ionisable** in nature.
  - Corresponds to the **coordination number** of the metal.
  - Every metal has a **fixed number** of secondary valencies.
  - Satisfied by **negative ions or neutral molecules** (called ligands).
  - **Directional** in character, giving the compound a **definite geometry** (i.e., octahedral, tetrahedral etc.)
- The metal atom tends to satisfy **both its primary and secondary valencies**.

NOTE
A coordination complex **does not show the properties of** the individual **central metal ion** and **the ligands**. This is because metal ion and ligands are **not free in solution**. They are **tightly bound** within the complex.

Basic observations:

Metal	Primary Valency	Secondary Valency
Chromium (Cr)	+2 , +3	6
Manganese (Mn)	+2 , +3 , +4	6
Iron (Fe)	+2 , +3	6
Cobalt (Co)	+2 , +3	6
Nickel (Ni)	+2 , +3	4 , 5 , 6
	+4	6
Copper (Cu)	+1	4
	+2	4 , 5 , 6
Zinc (Zn)	+2	4
Platinum (Pt)	+2	4
	+4	6

Limitations of Werner's Theory

- It could not explain **why only certain elements** form coordination compounds.
- It did not explain **why complexes have definite geometries**.
- It failed to explain the **magnetic and optical properties** of coordination compounds.
- It did not explain the **origin of colour** in coordination compounds.

Difference Between Coordination Complex and a Double Salt

Double Salts

- Double salts are **ionic compounds** formed by the combination of **two simple salts** that **completely dissociate into their constituent ions** when dissolved in water.
- They **lose their molecular identity** in solution.
- **Example:**
  - **Mohr's salt :** $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \longrightarrow Fe^{+2} + 2SO_4^{-2} + 2NH_4^{+} + 6H_2O$
  - **Carnallite :** $KCl \cdot MgCl_2 \cdot 6H_2O \longrightarrow K^{+} + Mg^{+2} + 3Cl^{-1} + 6H_2O$
  - **Potash alum :** $K_2SO_4 \cdot Al_2(SO_4)_3.24H_2O \longrightarrow 2K^{+} + 2Al^{+3} + 4SO_4^{-2} + 24H_2O$

Coordination Complexes

- Coordination complexes **do not dissociate completely** into simple ions.
- They **retain their molecular identity** in aqueous solution.
- **Example:**
  - **Potassium ferrocyanide (Complex) :** $K_4[Fe(CN)_6] \longrightarrow [Fe(CN)_6]^{-4} + 4K^{+}$

Practice Problems

1. One mole of $CoCl_3 \cdot 4NH_3$ gives one mole of AgCl when treated with excess $AgNO_3$. Write the formula of this compound and state how many chloride ions are outside the coordination sphere.
2. Explain how conductance measurements support Werner's theory of primary and secondary valencies.
3. Why does the compound $[Co(NH_3)_6]Cl_3$ not give a test for Co^{3+} or NH_3, even though it contains both?
4. Write the formula and coordination entity for the compound formed when one mole of $CoCl_3 \cdot 6NH_3$ gives three moles of AgCl on treatment with excess $AgNO_3$.
5. Why are primary valencies ionisable, whereas secondary valencies are non-ionisable?
6. How are primary and secondary valencies satisfied in coordination compounds? Give one example.
7. State two experimental evidences that support Werner's distinction between primary and secondary valencies.
8. Mention two main limitations of Werner's Coordination Theory.
9. What are the major differences between coordination complexes and double salts?
10. On the basis of the following observations made with aqueous solutions, assign secondary valences to metals in the following compounds:

Formula	Moles of AgCl precipitated per mole of the compounds with excess $AgNO_3$
(i) $PdCl_2.4NH_3$	2
(ii) $NiCl_2.6H_2O$	2
(iii) $PtCl_4.2HCl$	0
(iv) $CoCl_3.4NH_3$	1
(v) $PtCl_2.2NH_3$	0

Some Basic Terms Used in Coordination Compounds

Coordination Entity or Coordination Sphere

- A **coordination entity** (or **coordination sphere**) consists of a **central metal atom/ion** bonded to a definite number of **ligands (ions or neutral molecules)** through coordinate bonds.
- The entire coordination entity is written inside **square brackets [ ]**, which represent the **non-ionizable part** of the compound.
- Based on **the charge** present on a coordination entity, it may be of **three types**: cationic, anionic, or neutral.
    - **Example:**
        - **Cationic :** $[Co(NH_3)_6]^{+3}$, $[Cr(en)_3]^{+3}$
        - **Anionic :** $[Fe(CN)_6]^{-3}$, $[Mn(CN)_6]^{-4}$
        - **Neutral :** $[Ni(CO)_4]$

Ligands

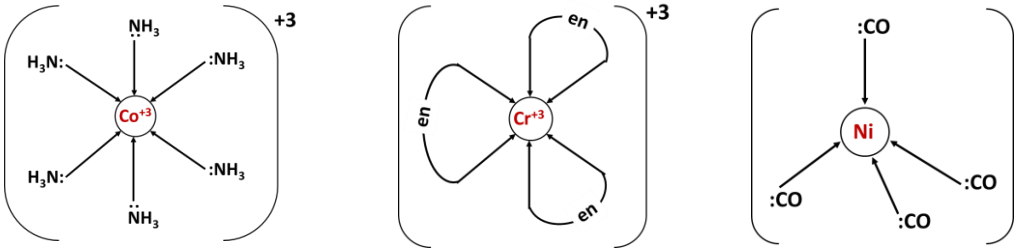
- **Ligands** are ions or molecules that **donate a pair of electrons** to the central metal atom/ion to form **coordinate covalent bonds**.
- They act as **Lewis bases** (electron pair donors).
- Based on the **number of lone pairs donated**, ligands are further classified as **monodentate**, **bidentate**, or **polydentate**.
- **Example:**
    - CN^{-1} and NH_3 are **monodentate ligands** in the complexes $[Fe(CN)_6]^{-3}$ and $[Co(NH_3)_6]^{+3}$, respectively.
    - Ethane-1,2-diamine (en) is a **bidentate ligand** in the complex $[Cr(en)_3]^{+3}$.

Central Metal Atom or Ion

- The central metal atom/ion **accepts a pair of electrons** from ligands and behaves as a **Lewis acid**.
- It is typically a **transition metal** (like Fe, Co, Cu, Ni, etc.), which is usually present **as an ion** (e.g., Fe^{+3}, Co^{+2}) but can **occasionally be in the zero-oxidation state**.
- **Example:**
    - In the complex $[Co(NH_3)_6]^{+3}$, the central metal is the **cobalt ion** (Co^{+3}) .
    - In the complex $[Ni(CO)_4]$, the central metal is the **nickel atom** (Ni).
- The C.M.I. determines the **coordination number**, **geometry**, and **magnetic properties** of the complex.

Coordination Number

- The **coordination number** of a central metal atom/ion is the **number of donor atoms** (not ligands) directly bonded to it.
- It represents the **total number of coordinate bonds** formed by the central atom.
- Common coordination numbers are **4, 5, and 6**.
- **Example:**
    - In complex, $[Co(NH_3)_6]^{+3}$, coordination number is **6**.
    - In complex, $[Cr(en)_3]^{+3}$, coordination number is **6**.
    - In complex, $[Ni(CO)_4]$, coordination number is **4**.



Note:
For **monodentate** ligands; coordination number = number of ligands.
For **bidentate** ligands; coordination number = 2 × number of ligands.

Oxidation State (or Oxidation number)

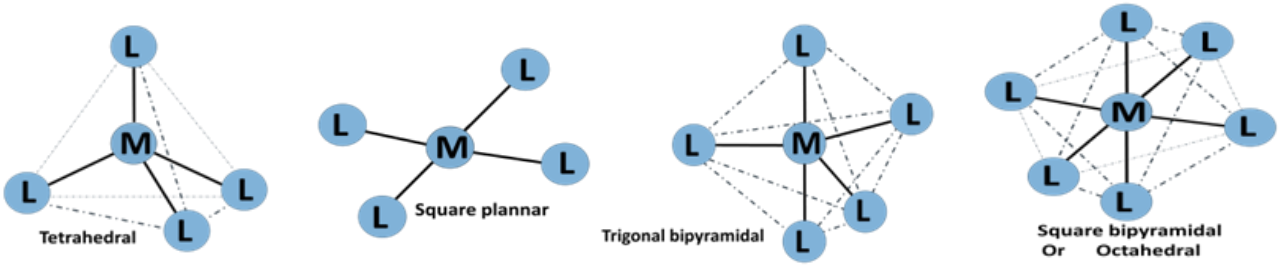
- The **oxidation state** of the **central metal atom/ion** in a coordination compound is **the charge** it would have if **all the ligands were removed** along with their shared electron pairs.
- **Example:**
  - In complex, $[Fe(CN)_6]^{-4}$, the oxidation state of Fe is **+2**.
  - In complex, $[Co(NH_3)_6]Cl_3$, the oxidation state of Co is **+3**.

Counter Ion

- A **counter ion** is the **ion present outside the coordination sphere** that balances the overall charge of the coordination entity.
- Counter ions are **ionizable** in solution, while the coordination entity remains intact.
- **Examples:**
  - In **$[Co(NH_3)_6]Cl_3$** Complex ion = $[Co(NH_3)_6]^{+3}$ Counter ion = $3Cl^{-1}$
  - In **$K_4[Fe(CN)_6]$** Complex ion = $[Fe(CN)_6]^{-4}$ Counter ion = $4K^{+}$
- Counter ions are important in determining the **electrolytic nature**, **conductivity**, and **chemical reactivity** of coordination compounds.

Coordination Polyhedron or Coordination Geometry

- The **coordination polyhedron** represents the **three-dimensional spatial arrangement** of donor ligands around the central metal atom/ion.
- Common coordination polyhedral are:
  - **Octahedral** (Coordination number = 6) : **$[Co(NH_3)_6]^{+3}$**
  - **Trigonal bipyramidal** (Coordination number = 5) : **$[Fe(CO)_5]$**
  - **Square planar** (Coordination number = 4) : **$[PtCl_4]^{-2}$**
  - **Tetrahedral** (Coordination number = 4) : **$[Ni(CO)_4]$**



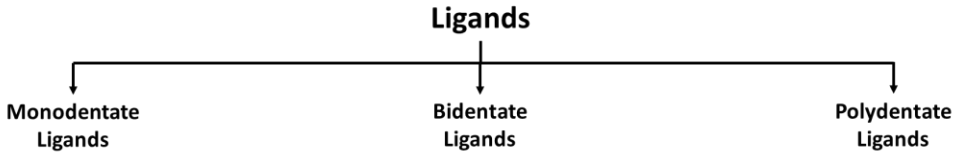
Homoleptic and Heteroleptic Complexes

- **Homoleptic Complexes:**
  - Complexes in which a metal is bound to **only one type of ligand**.
  - **Example:** $[Co(NH_3)_6]^{+3}$, $[Fe(CN)_6]^{-3}$
- **Heteroleptic Complexes:**
  - Complexes in which a metal is bound to **two or more different types of ligands**.
  - **Example:** $[CoCl_2(NH_3)_4]^{+1}$, $[CrCl_2(en)_2]^{+1}$

Ligands

- A **ligand** is an atom, ion, or molecule that can **donate a lone pair of electrons** to a central metal atom/ion to form a **coordinate (dative) bond**.
- **Ligands** act as **Lewis bases** (lone pair donor), while the **central metal atom/ion** acts as a **Lewis acid** (lone pair acceptor).
- Ligands can range from **simple ions** (i.e., CN^{-1}, OH^{-1} etc.) and **small molecules** (i.e., H_2O, NH_3 etc.) to **complex macromolecules** (i.e., $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$ (ethylenediamine), proteins etc.).

Types of Ligands



Monodentate Ligands

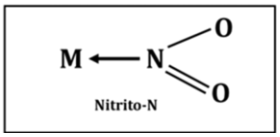
- Ligands that can coordinate to the central metal ion through **only one donor atom** are called **monodentate (unidentate)** ligands.
- Each ligand donates **one lone pair of electrons** to form a single coordinate bond.

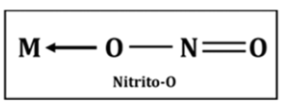
Neutral Ligands			
Name of Ligands	**Formula**	**Donor Atom**	**Name Given in Complex**
Ammonia	NH_3	N	ammine
Water	H_2O	O	aqua
Methyl amine	CH_3NH_2	N	methylamine
Nitric oxide	NO	N	nitrosyl
Carbon monoxide	CO	O	carbonyl
Thiocarbonyl	CS	S	thiocarbonyl
Phosphine	PH_3	P	phosphine
Triphenyl phosphine	$(C_6H_5)_3P$	P	triphenylphosphine
Thiourea (tu)	$H_2N\text{-}CS\text{-}NH_2$	S	thiourea
Pyridine (py)	C_5H_5N	N	Pyridine

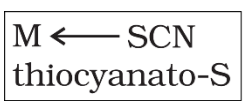
Negative Ligands (ends in -o)			
Name of Ligands	**Formula**	**Donor Atom**	**Name Given in Complex**
Cyanide ion	CN^-	C	cyano
Halide ion	X^- (F, Cl, Br, I)	X	halido (fluorido/chlorido)
Hydride ion	H^-	H	hydrido
Nitrite-N ion	NO_2^-	N	nitrito-N
Nitrite-O ion	ONO^-	O	nitrito-O
Nitrate ion	NO_3^-	N	nitrato
Hydroxide ion	OH^-	O	hydroxo
Amide ion	NH_2^-	N	amido
Imide ion	NH^{2-}	N	imido
Acetate ion	CH_3COO^-	O	acetato
Sulphate ion	SO_4^{2-}	S	sulphato
Sulphite ion	SO_3^{2-}	S	sulphito
Sulphide ion	S^{2-}	S	sulphido
Carbonate ion	CO_3^{2-}	O	carbonato
Thiocyanate ion	SCN^-	S	thiocyanato
Isothiocyanate ion	NCS^-	N	isothiocyanato
Oxide ion	O^{2-}	O	oxo
Peroxide ion	O_2^{2-}	O	peroxo
Nitride ion	N^{3-}	N	nitrido
Phosphide ion	P^{3-}	P	phosphido
Azide ion	N_3^-	N	azido
Bicarbonate ion	HCO_3^-	O	bicarbonato
Chlorate ion	ClO_3^-	O	chlorato

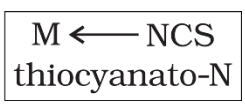
Positive Ligands (ends in -ium)			
Name of Ligands	**Formula**	**Donor Atom**	**Name Given in Complex**
Nitrosonium ion	NO^+	N	nitrosonium
Nitronium ion	NO_2^+	N	nitronium
Hydrazinium ion	$NH_2 - NH_3^+$	N	hydrazinium

- **Ambidentate Ligands**
  - These are **monodentate ligands** that can coordinate through **more than one possible donor atom**, but use **only one donor atom** at a time.





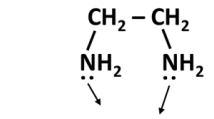
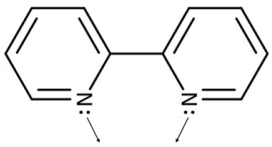
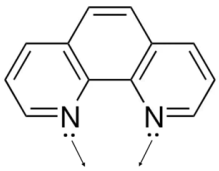


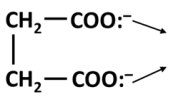
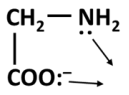
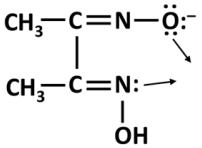
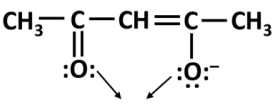


- **Examples:**
  - **NO_2^-** ⟶ can coordinate through **N** (as nitro/nitrito-N) or **O** (as nitrito-O).
  - **CN^-** ⟶ can coordinate through **C** (as cyano) or **N** (as isocyano).
- They contain **two or more potential donor atoms**, giving rise to **linkage isomerism** when they coordinate through **different atoms**.

Bidentate or Didentate Ligands:

- Ligands that have **two donor atoms** and can coordinate to the central metal ion **at two distinct positions** are called bidentate or didentate ligands.

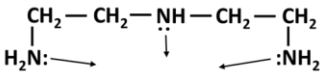
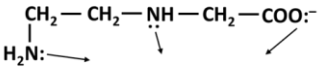
Neutral Bidentate Ligands			
Name of Ligands	**Formula**	**Abbreviation**	**Name Given in Complex**
Ethylene diamine (Ethane-1,2-diamine)		en	Ethylene diamine (Ethane-1,2-diamine)
2,2-Dipyridyl		dipy	2,2-Dipyridyl
Ortho-Phenanthroline		phen	phenanthroline

Negative Bidentate Ligands (ends in –o)			
Name of Ligands	**Formula**	**Abbreviation**	**Name Given in Complex**
Oxalate ion		ox	oxalato
Glycinate ion		gly	glycinato
Dimethyl glyoxime ion		dmg	dimethylglyoximato
Acetyl acetonate ion		acac	acetylacetonato

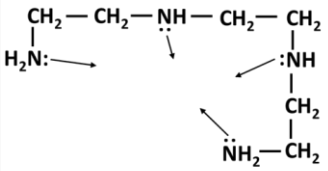
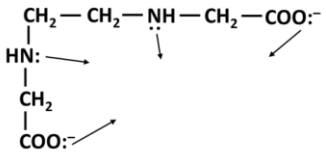
Polydentate Ligands

- Ligands that have **more than two donor atoms** are called polydentate ligands.
- These are further classified as: (a) **Tridentate** (b) **Tetradentate** (c) **Pentadentate** and (d) **Hexadentate**

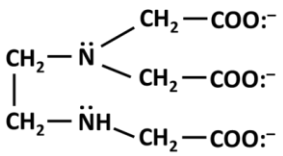
Tridentate Ligands

Name of Ligands	Formula	Abbreviation	Name Given in Complex
Diethylene triamine		dien	diethylenetriamine
Ethylenediamine monoacetate		EDMA	ethylenediaminemono acetato

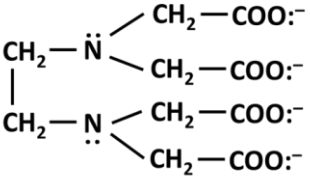
Tetradentate Ligands

Name of Ligands	Formula	Abbreviation	Name Given in Complex
Triethylene tetraamine		trien	triethylenetetraamine
Ethylenediamine diacetate ion		EDDA	ethylenediamine-diacetato

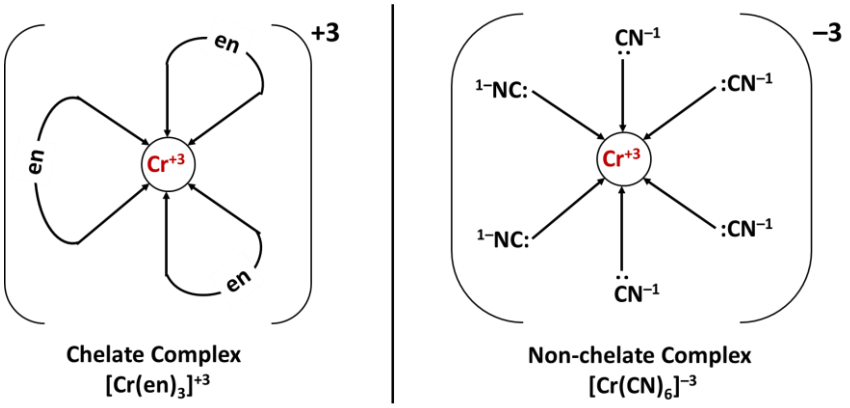
Pentadentate Ligands

Name of Ligands	Formula	Abbreviation	Name Given in Complex
Ethylenediamine triacetate ion		$EDTA^{-3}$	ethylenediamine-triacetato

Hexadentate Ligands

Name of Ligands	Formula	Abbreviation	Name Given in Complex
Ethylenediamine tetraacetate ion		$EDTA^{-4}$	ethylenediamine-tetraacetato

- **Chelation:**
  - When a **bidentate or polydentate** ligand uses **two or more donor atoms** to bind to the **same central metal ion**, it results in the formation of a **cyclic ring structure** around the central metal ion. This phenomenon is called **Chelation**.
  - The ligand involved in chelation is called a **chelate ligand**.



  - **<u>Chelate Effect:</u>**
    - Complexes containing **chelate rings** are significantly **more thermodynamically stable** than non-chelate complexes (those containing only monodentate ligands).
    - The **stability** of the complex **increases** with the **number of rings** formed.

  - **<u>Importance and Applications of Chelation:</u>**
    - Chelating agents like **EDTA** are used in the **softening of hard water**.
    - Chelate ligands are used in the **separation of Lanthanoids and Actinoids**.
    - Chelate ligand are used in **analytical chemistry**.
      - **Dimethylglyoxime** forms a **bright red** chelate complex with Ni^{+2}, confirming its presence.
    - Chelating agents like **EDTA** are injected to **treat heavy metal poisoning** (caused by **lead**, **mercury**, etc.). This process is called **chelation therapy**.

IUPAC Rules for Writing Formulas of Mononuclear Coordination Entities

$$\left[\text{C.M.I} + \text{Ligands}\right]^{\pm \text{ Charge}}$$

- **<u>Rule 1:</u>**
  The **coordination sphere** (central metal ion and its attached ligands) is enclosed in **square brackets [ ]**.

- **<u>Rule 2:</u>**
  Within the coordination sphere, the symbol of the **central metal atom/ion** is always **written first**, followed by the **ligands**.
  Example: If Co^{+3} is central metal ion and NH_3 is the ligand, then:
  Correct: $[Co(NH_3)_6]^{+3}$
  Incorrect: $[(NH_3)_6Co]^{+3}$

- **Rule 3:**
  In **heteroleptic complexes** (complexes with **more than one type of ligand**), the ligands are listed in **alphabetical order** based on the **first symbol of their chemical name**.
  Example:
  If **Co^{+3}** is central metal ion while **NH_3 (ammine) and Cl^{-1} (chlorido)** are the ligands, then: **$[Co(NH_3)_4Cl_2]^{+1}$**

- **Rule 4:**
  Parentheses ( ) are used to **enclosed the ligands** in the following situations:
  - **Polyatomic Ligands**: Ligands containing more than one atom (e.g., NH_3 , CN^{-1}, H_2O).
    Example: **$[Co(NH_3)_6]^{+3}$** , **$[Fe(CN)_6]^{-4}$**
  - **Abbreviations**: If an abbreviation is used for a ligand (e.g., ox, en, py , acac, dmg etc.)
    Example: **$[Co(en)_3]^{+3}$** , **$[Fe(ox)_3]^{-3}$**

- **Rule 5:**
  If the coordination entity is **an ion** (charged), the **net charge** is written outside the square brackets as a **right superscript**.
  Example:
  - **$[Co(NH_3)_6]^{+3}$** ; the net charge is +3
  - **$[Fe(CN)_6]^{-4}$** ; the net charge is –4

- **Rule 6:**
  When **writing the formula** for the **complete ionic compound** (containing counter ions), the **Cationic part** is always **written first**, followed by the **anionic part**.
  Example:
  - **Case-A:** If **coordination entity is positive** and **counter ion is negative**.
    $[Co(NH_3)_6]$ Cl_3 ; $[Co(NH_3)_6]^{+3}$ is the **cation** while Cl^{-1} is the **anion**.
  - **Case-B:** If **coordination entity is negative** and **counter ion is positive**.
    K_4 **$[Fe(CN)_6]$** ; $[Fe(CN)_6]^{-4}$ is the **anion** while K^+ is the **cation**.

IUPAC Rules for Naming Coordination Compounds

- **Rule 1: (Naming the Coordination Sphere)**
  - When naming the complex entity, **follow this specific sequence**:

    Name of Ligands + Name of Central metal ion + (Oxidation state in Roman Numerals)

  - **Name of Ligands:**
    - Use **prefixes (di, tri, tetra)** to indicate the **number of simple ligands**.
    - Use **complex prefixes (bis, tris)** to indicate the number ligands that **already contain** numerical prefixes (e.g., **di, tri, tetra**) in their names (**e.g., ethylenediamine**).
    - If **multiple types of ligands** are present, list them in **alphabetical order** based on their **name**, not their chemical formula.

- **Central Metal Ion name:**
  - If complex is **cationic or neutral** the central metal retains its **common English name**:
    Example: Cobalt, Platinum, Chromium, Iron etc.
  - If complex is **anionic**, the **suffix –ate** is added to the **name of the central metal**.
    Example:

Metal Symbol	English Name	Name in Anionic complex (–ate)
Zn	Zinc	**Zincate**
Co	Cobalt	**Cobaltate**
Ni	Nickel	**Nickelate**
Pt	Platinum	**Platinate**
Fe	Iron	**Ferrate**
Cu	Copper	**Cuprate**
Ag	Silver	**Argentate**
Au	Gold	**Aurate**
Pb	Lead	**Plumbate**
Sn	Tin	**Stannate**

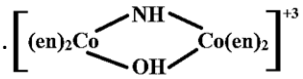
- **Indicating Oxidation State:**
  - The oxidation state of the **central metal** is indicated by a **Roman Numeral** (0, I, II, III, IV) enclosed in **parentheses ( )** immediately following the **central metal name** without a space.

- **Rule 2: (Naming the Counter Ion)**
  - **Do not** use the **prefixes (di, tri, tetra)** to indicate the **number of counter ion**. Their number is inferred from the charge balance.

- **Rule 3: (Order of Complex and Counter ion Names)**
  - **For Cationic or Anionic Complex:**
    Similar to simple salts (e.g., Sodium Chloride), the **Cation** is always named **first**, followed by **Anion**.
    - If the counter ion is a **cation**, it is written **before** the **anionic complex** name.
    - If the counter ion is an **anion**, it is written **after** the **cationic complex** name.
  - **For Neutral Complex:**
    If the complex has **no charge**, it is written as a **single**, continuous **one-word name** without spaces.

Coordination Compounds and Their Names:

1. $[Co(NH_3)_4Cl_2]Cl$: teraamminedichloridocobalt(III) chloride
2. $K_3[Fe(CN)_6]$: Potassium hexacyanidoferrate(III)
3. $[Cr(NH_3)_3(H_2O)_3]Cl_3$: triamminetriaquachromium(III) chloride
4. $[Co(en)_3]_2(SO_4)_3$: tris(ethane-1,2-diamine)cobalt(III) sulphate
5. $[Ag(NH_3)_2][Ag(CN)_2]$: diamminesilver(I) dicyanidoargentate(I)
6. $[Co(NH_3)_4(H_2O)Cl]Cl_2$: tetraammineaquachloridocobalt(III) chloride
7. $K_2[Zn(OH)_4]$: Potassium tetrahydroxidozincate(II)

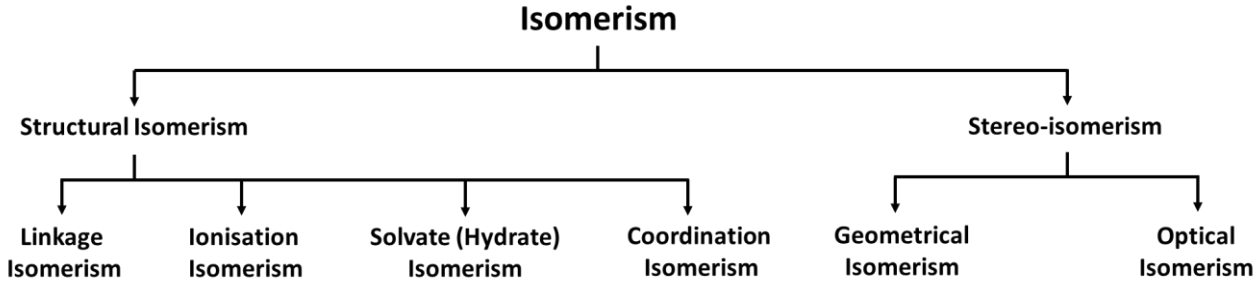
8. $K_3[Al(C_2O_4)_3]$: Potassium trioxalatoaluminate(III)
9. $[CoCl_2(en)_2]^+$: Dichloridobis(ethane-1,2-diamine)cobalt(III)
10. $[Ni(CO)_4]$: Tetracarbonylnickel(0)
11. $K_3[Fe(CN)_5NO]$: Potassium pentacyanidonitrosylferrate(II)
12. $[Pt(NH_3)_4][PtCl_4]$: tetraammineplatinum(II) tetrachloridoplatinate(II)
13.  : bis(ethane-1,2-diamine)cobalt(III)-μ-imido-μ-hydroxobis(ethane-1,2-diamine)cobalt(III) ion

Practice Problems

1. Write the IUPAC names of the following coordination compounds:
   (a) $[Pt(NH_3)_2Cl(NO_2)]$ (b) $K_3[Cr(C_2O_4)_3]$ (c) $[CoCl_2(en)_2]Cl$
   (d) $[Co(NH_3)_5(CO_3)]Cl$ (e) $Hg[Co(SCN)_4]$ (f) $[Co(NH_3)_6]Cl_3$
   (g) $[Co(NH_3)_5Cl]Cl_2$ (h) $K_3[Fe(CN)_6]$ (i) $K_3[Fe(C_2O_4)_3]$
   (j) $K_2[PdCl_4]$ (k) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$ (l) $[Pt(NH_3)_2Cl_2]$
2. Write the formulas for the following coordination compounds:
   (a) Tetraamminediaquacobalt(III) chloride
   (b) Potassium tetracyanidonickelate(II)
   (c) Tris(ethane–1,2–diamine)chromium(III) chloride
   (d) Amminebromidochloridonitrito-N-platinate(II)
   (e) Dichloridobis(ethane–1,2–diamine)platinum(IV) nitrate
   (f) Iron(III) hexacyanidoferrate(II)
   (g) Dichloridobis(ethane-1,2-diamine)cobalt(III)
   (h) Mercury(I) tetrathiocyanato-S-cobaltate(III)
3. What is meant by the chelate effect? Discuss its applications.
4. What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.
5. Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic complexes.

Isomerism

- Isomers are **two or more compounds** that have the **same chemical formula** but **different structures (or arrangements of atoms)**; therefore, **they differ** in one or more physical or chemical properties. This phenomenon is called **Isomerism**.



Structural Isomerism

- The isomers that have **same molecular formula** but **different chemical bonds of ligands** around the central metal ion. This phenomenon is called **Structural Isomerism**.

Linkage Isomerism

- Linkage isomerism arises in coordination compounds that contain **ambidentate ligands**.
- These isomers have the **same molecular formula** but **differ in attachment of specific atom of the ligand** to the central metal ion.
- Examples:
  - $[Co(NH_3)_5(NO_2)]Cl_2$: Bonded via **N** (Nitro form) → Yellow
  - $[Co(NH_3)_5(ONO)]Cl_2$: Bonded via **O** (Nitrito form) → Red

Ionisation Isomerism

- Ionisation isomerism arises when **the counter ion** in a coordination compound is **itself a potential ligand** and can **displace a ligand of coordination entity** which can then become the counter ion.
- This form of isomerism involves the **exchange of ions** between **coordination sphere** and **ionisation sphere**.
- This isomerism is mainly **found in cationic complexes**.
- Example:
  - The compound **$Co(NH_3)_5BrSO_4$** exists in **two** isomeric forms:
    - $[Co(NH_3)_5SO_4]Br \longrightarrow [Co(NH_3)_5SO_4]^{+1} + Br^{-1}$
      Presence of **Br^{-1} can be confirmed** by adding **$AgNO_3$ solution** result in formation of **yellow** precipitate of AgBr.
    - $[Co(NH_3)_5Br]SO_4 \longrightarrow [Co(NH_3)_5Br]^{+2} + SO_4^{-2}$
      Presence of **SO_4^{-2} can be confirmed** by adding **$BaCl_2$ solution** result in formation of **white** precipitate of $BaSO_4$.

Solvate (Hydrate) Isomerism

- Solvate isomerism arises in coordination compounds where **water acts as both a ligand and a solvent**.
- These isomers **differ** in the number of water molecules **directly bonded to the central metal** versus those **present as free water of crystallization** in the crystal lattice.
- Example:
  - The compound **$CrCl_3.6H_2O$** exists in **three** distinct isomeric forms:
    - $[Cr(H_2O)_6]Cl_3$: Violet
    - $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$: Grey-green
    - $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$: Dark green

Coordination Isomerism

- Coordination isomerism arises in compounds containing **both cationic and anionic complex entities**.
- This isomerism involves in **interchange of ligands** between the cationic and anionic entities (usually containing different central metal atoms/ions).

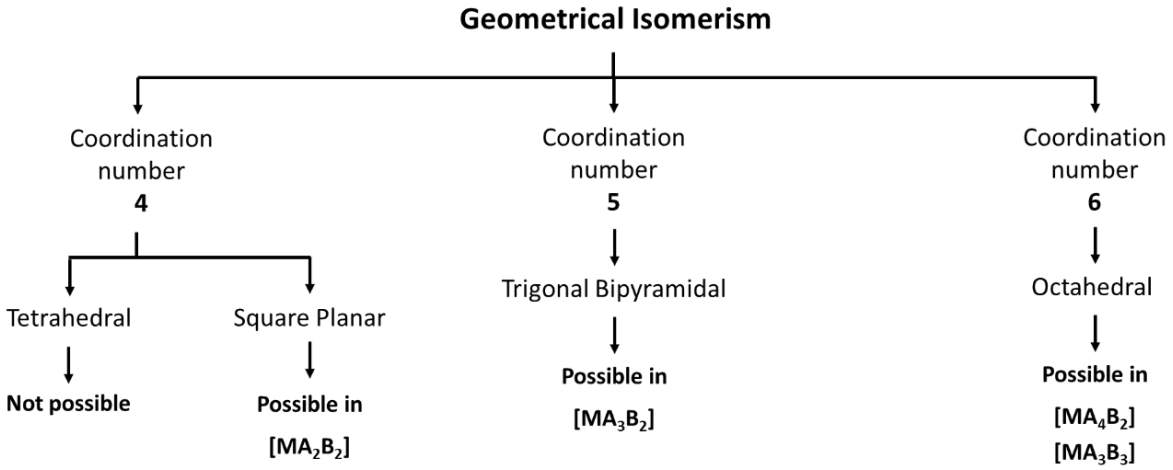
- Example:
  - **Complete Interchange:**
    - $[Co(NH_3)_6][Cr(CN)_6]$ Vs $[Cr(NH_3)_6][Co(CN)_6]$
  - **Partial Interchange:**
    - $[Co(NH_3)_6][Cr(CN)_6]$ Vs $[Co(NH_3)_4(CN)_2][Cr(NH_3)_2(CN)_4]$

Stereo-isomerism

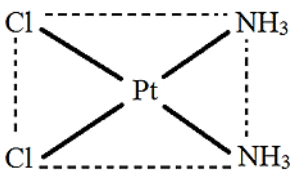
- In stereo-isomerism the isomers have the **same chemical formula** and **same chemical bonds** (connectivity of ligands to central metal ion) but **differ in the spatial arrangement of atoms** in 3D space.

Geometrical Isomerism (Cis-Trans)

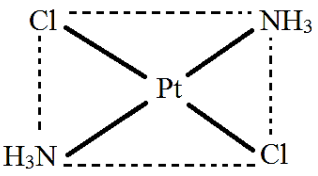
- This isomerism is **found in heteroleptic complexes** (complexes with different types of ligands) and arises due to **different possible geometric arrangements** of the ligands around the central metal atom/ion in 3D space.
  - **Cis–Isomer:** When **similar ligands** occupy **adjacent positions** in the coordination geometry.
  - **Trans–isomer:** When **similar ligands** occupy **opposite positions** in the coordination geometry.



- **Square Planar Complexes (Coordination Number = 4)**
  - Geometrical isomerism is found in coordination complexes having the **general formula: $[MA_2B_2]$**
  - Example: **$[Pt(NH_3)_2Cl_2]$**

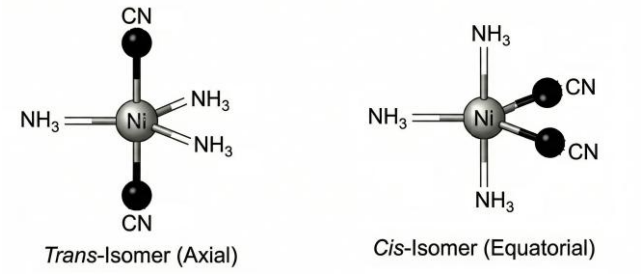


Cis-Platin
(Used in cancer therapy)

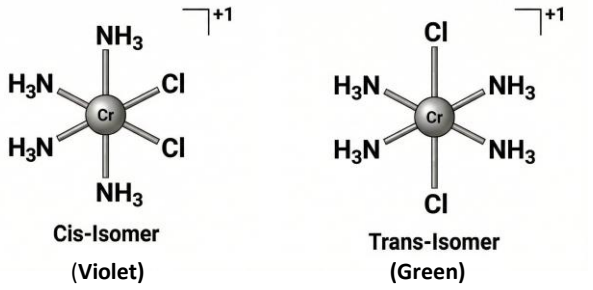


Trans-Platin

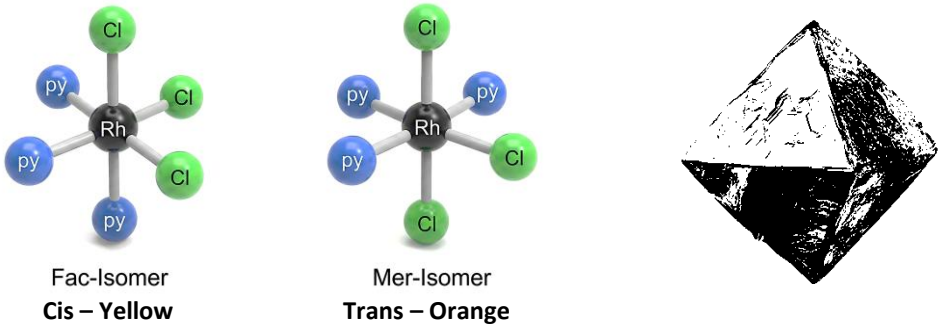
- **Trigonal Bipyramidal Complexes (Coordination Number = 5)**
  - Geometrical isomerism is found in coordination complexes having the **general formula: $[MA_3B_2]$**
  - Example: **$[Ni(NH_3)_3(CN)_2]$**



- **Octahedral Complexes (Coordination Number = 6)**
  - Geometrical isomerism is found in complexes having the **general formulas: $[MA_4B_2]$** and **$[MA_3B_3]$**
  - **<u>Type – 1: $[MA_4B_2]$</u>**
    - Example: **$[Cr(NH_3)_4Cl_2]^{+1}$** ; tertraamminedichloridochromium(III) ion



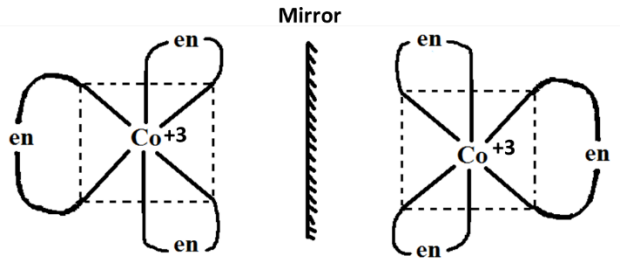
  - **<u>Type – 2: $[MA_3B_3]$</u> : (Facial-Meridional Isomerism)**
    - Example: **$[RhCl_3(py)_3]$** ; trichloridotripyridinerhodium(III)



Optical Isomerism

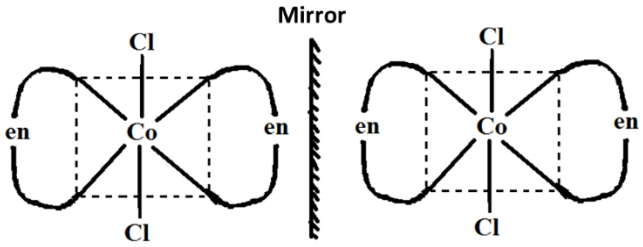
- Optical isomers are **non-superimposable mirror images** of each other. They have the **ability to rotate the plane of polarized light** in opposite directions. These pairs of isomers are called **Enantiomers**.
  - **Dextrorotatory (*d* or +):**
    The enantiomer that **rotates** the plane of polarised light to the **right angle** (clockwise).
  - **Laevorotatory (*l* or –):**
    The enantiomer that **rotates** the plane of polarised light to the **left angle** (counter-clockwise).

- **Racemic Mixture:** A **1:1 equimolar mixture** of dextro- and laevo- isomers that has **zero net optical rotation**.
- To show optical isomerism, the molecule must be **chiral** (i.e., it must **lack a plane of symmetry**).
- Example:
  - **$[Co(en)_3]^{+3}$**



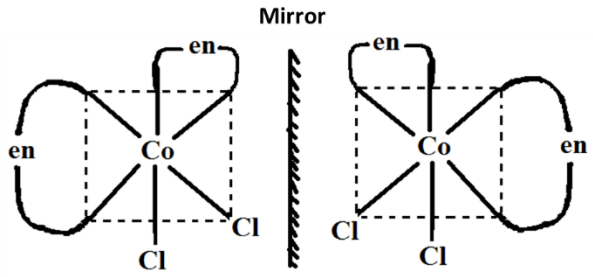
Non-superimposable mirror images (optically active)

  - **$[CoCl_2(en)_2]^{+1}$**
    - **Trans – $[CoCl_2(en)_2]^{+1}$**



Superimposable mirror images (optically inactive)

    - **Cis – $[CoCl_2(en)_2]^{+1}$**



Non-superimposable mirror images (optically active)

Practice Problems

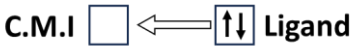
1. Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion?
2. Out of the following two coordination entities which is chiral (optically active)?
   (a) cis-$[CrCl_2(ox)_2]^{3-}$ (b) trans-$[CrCl_2(ox)_2]^{3-}$
3. Draw structures of geometrical isomers of $[Fe(CN)_4(NH_3)_2]^{-1}$ and $[CoCl_3(H_2O)_3]$.
4. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

(a) $K[Cr(H_2O)_2(C_2O_4)_2]$ (b) $[Co(NH_3)_5(NO_2)](NO_3)_2$
(c) $[Co(en)_3]Cl_3$ (d) $[Pt(NH_3)(H_2O)Cl_2]$

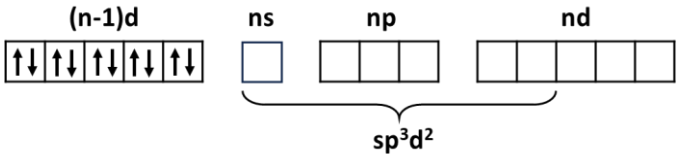
5. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionisation isomers.
6. What type of isomerism is shown by the complex $[Co(NH_3)_6][Cr(CN)_6]$?
7. Out of cis and trans $[Pt(NH_3)_2Cl_2]$, which one is polar?
8. Write the formula of a complex that is a linkage isomer of $[Pd(dipy)(SCN)_2]$.
9. Out of $[Co(ox)_3]^{-3}$ and $[CoCl_6]^{-3}$, which one is expected to be chiral?
10. What is the specific name given to the isomer where three identical ligands are in the equatorial position of an octahedron?
11. The complex $[Co(NH_3)_5(NO_2)]Cl_2$ is red in color. Give the IUPAC name of its linkage isomer.
12. Draw structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^{-1}$.

Valence Bond Theory (VBT)

- The **main postulates** of Valence Bond Theory are:
  - **Availability of Empty Orbitals:**
    - The central metal atom/ion provides a **specific number of empty atomic orbitals** (s, p, and d) equal to its **coordination number**.
    - These empty orbitals **accept electron pairs** from ligands to form coordinate (dative) bonds.

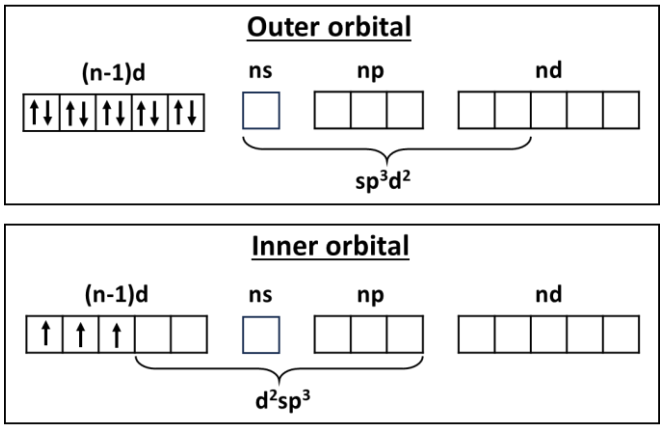


  - **Hybridization:**
    - These **empty atomic orbitals**, which may have slightly different energies, **mix to form a new set of hybrid orbitals**.

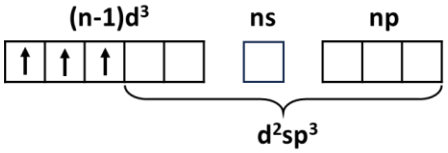


  - **Geometry Determination:**
    - The **type of hybridization determines** the spatial arrangement (**geometry**) of the ligands around the metal, such as **tetrahedral**, **square planar**, or **octahedral**.

Coordination Number	Type of Hybridization	Geometry
4	sp^3	Tetrahedral
	d^1sp^2	Square Planar
5	d^1sp^3	Trigonal bipyramidal (Inner Orbital)
	sp^3d^1	Trigonal bipyramidal (Outer Orbital)
6	d^2sp^3	Octahedral (Inner Orbital)
	sp^3d^2	Octahedral (Outer orbital)



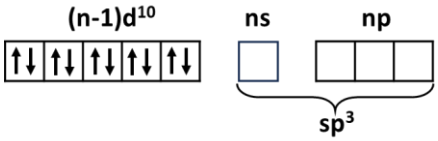
- **Magnetic Properties:**
  - **Paramagnetic**: If complex contains **unpaired electrons**, it is **attracted** by a magnetic field.



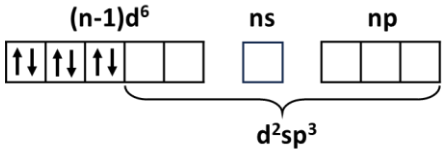
The "**Spin Only**" **magnetic moment (μ)** is calculated using the **number of unpaired electrons (n).**

$$\mu = \sqrt{n(n+2)} \quad \text{B.M. (Bohr Magnetons)}$$

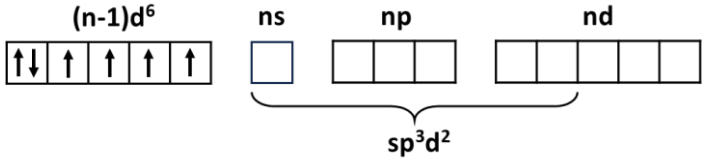
  - **Diamagnetic:** If all electrons are **paired**, it is **repelled** by a magnetic field.



- **Role of Ligands (Strong vs. Weak):**
  - **Strong Field Ligands (e.g., CN^{-1}, CO, NH_3):**
    These **can force electrons** in the metal's d-orbitals **to pair up against Hund's Rule**.



  - **Weak Field Ligands (e.g., F^{-1}, Cl^{-1}, H_2O):**
    These **cannot force pairing**, leaving electrons unpaired.

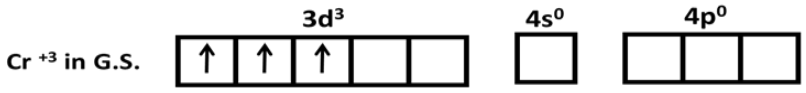


Octahedral Complexes (Coordination number - 6)

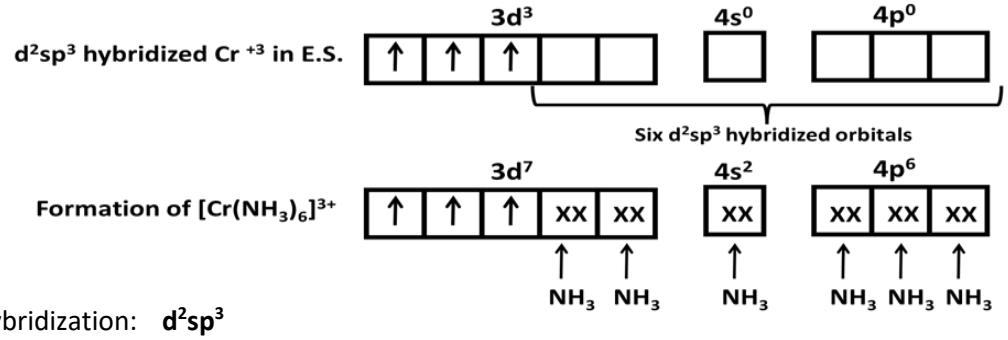
- **$[Cr(NH_3)_6]^{+3}$ Complex :**
  - Oxidation State of Chromium (Cr) in the complex is: **+3**

    $x + 6(0) = +3$

    $x = +3$
  - Electronic Configuration of **Cr^{+3}** ion is: **[Ar] $3d^3$ $4s^0$**



  - In this complex, **coordination number** of chromium is **6**.
    Therefore, **six empty orbitals** of the Cr^{+3} ion are required for hybridization.



  - Hybridization: **d^2sp^3**
  - Geometry: **Octahedral**
  - Nature of complex: **Inner orbital**
  - Number of unpaired electrons: **3**
  - Magnetic behavior: **Paramagnetic**
  - Spin only magnetic moment (B.M.): $\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} =$ **3.87**
  - Effective Atomic Number (EAN) = (At. No. – Oxidation state) + (2 × Coordination No.)

    = (24 – 3) + (2 × 6)

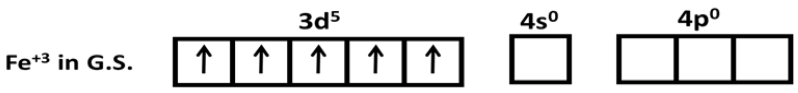
    = 21 + 12 = **33**

- **$[Fe(CN)_6]^{-3}$ Complex :**

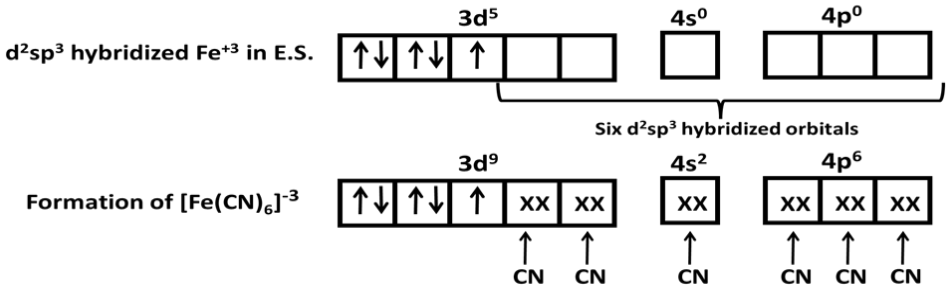
  - Oxidation State of Iron (Fe) in the complex is: **+3**

    $x + 6(-1) = -3$

    $x = -3 + 6 = +3$
  - Electronic Configuration of **Fe^{+3}** ion is: **[Ar] $3d^5$ $4s^0$**



  - In this complex, **coordination number** of Iron is **6**.
    Therefore, **six empty orbitals** of the Fe^{+3} ion are required for hybridization.
    Since, the **CN^{-1}** is a **strong field ligand**, it forces the electrons to **pair up against Hund's Rule** in the inner **(n-1)d** subshell.

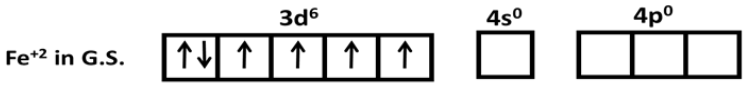


- Hybridization: **d^2sp^3**
- Geometry: **Octahedral**
- Nature of complex: **Inner orbital (Low spin)**
- Number of unpaired electrons: **1**
- Magnetic behavior: **Weakly Paramagnetic**
- Spin only magnetic moment (B.M.): $\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3}$ = **1.73**
- Effective Atomic Number (EAN) = (At. No. – Oxidation state) + (2 × Coordination No.)
  = (26 – 3) + (2 × 6) = **35**

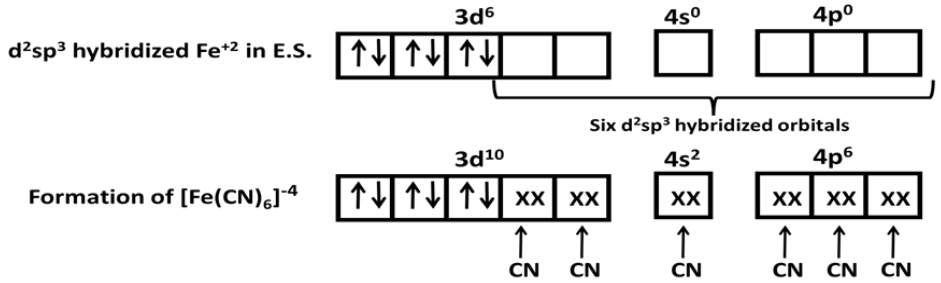
- **$[Fe(CN)_6]^{-4}$ Complex :**
  - Oxidation State of Iron (Fe) in the complex is: **+2**

    $x + 6(-1) = -4$

    $x = -4 + 6 = +2$
  - Electronic Configuration of **Fe^{+2}** ion is: **[Ar] $3d^6$ $4s^0$**



  - In this complex, **coordination number** of Iron is **6**.
    Therefore, **six empty orbitals** of the Fe^{+2} ion are required for hybridization.
    Since, the **CN^{-1}** is a **strong field ligand**, it forces the electrons to **pair up against Hund's Rule** in the inner **(n-1)d** subshell.

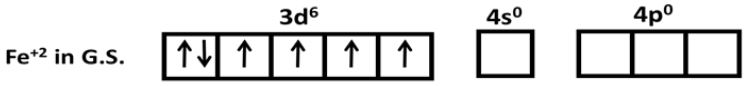


  - Hybridization: **d^2sp^3**
  - Geometry: **Octahedral**
  - Nature of complex: **Inner orbital (Low spin)**
  - Number of unpaired electrons: **0**
  - Magnetic behavior: **Diamagnetic**
  - Effective Atomic Number (EAN) = (At. No. – Oxidation state) + (2 × Coordination No.)
    = (26 – 2) + (2 × 6) = **36**

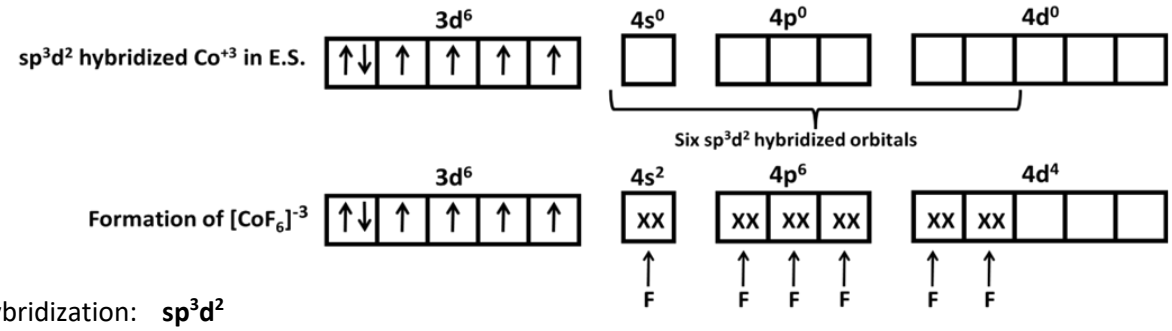
- **$[CoF_6]^{-3}$ Complex :**
  - Oxidation State of Cobalt (Co) in the complex is: **+3**

    $x + 6(-1) = -3$

    $x = -3 + 6 = +3$
  - Electronic Configuration of Co^{+3} ion is: **[Ar] $3d^6$ $4s^0$**



  - In this complex, **coordination number** of Cobalt is **6**.
    Therefore, **six empty orbitals** of the Co^{+3} ion are required for hybridization.
    Since, F^{-1} is a **weak field ligand**, it **does not** force the electrons to **pair up** in the **(n-1)d** subshell. As a result, the outer **nd** subshell is involved in hybridisation.



  - Hybridization: **sp^3d^2**
  - Geometry: **Octahedral**
  - Nature of complex: **Outer orbital (High spin)**
  - Number of unpaired electrons: **4**

  - Magnetic behavior: **Highly Paramagnetic**
  - Spin only magnetic moment (B.M.): $\mu = \sqrt{n(n+2)}$

    $= \sqrt{4(4+2)} = \sqrt{24} =$ **4.89**
  - Effective Atomic Number (EAN) = (At. No. – Oxidation state) + (2 × Coordination No.)

    = (27 – 3) + (2 × 6)

    = 24 + 12 = **36**

Note: High Spin and Low Spin Complexes

- **High Spin Complex:**
  - When the formation of a complex involves the **outer 'nd'–orbitals** for hybridization (**sp^3d^2**), it is called an **outer orbital complex** or **hypo-ligated (weak field ligand) complex**.
  - These complexes have a **large number of unpaired electrons**.
  - They exhibit **strong paramagnetic** behaviour and are therefore referred to as **high spin complexes**.
  - Examples: $[CoF_6]^{-3}$, $[MnCl_6]^{-3}$, $[FeF_6]^{-3}$, $[Ni(H_2O)_6]^{+2}$, $[Fe(H_2O)_6]^{+2}$, $[Fe(H_2O)_6]^{+3}$ etc.

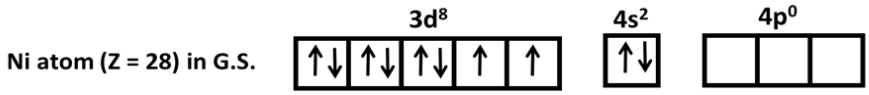
- **Low Spin Complex:**
  - When the formation of a complex involves the **inner '(n-1)d'–orbitals** for hybridization (d^2sp^3), it is called an **inner orbital complex** or **hyper-ligated (strong field ligand) complex**.
  - These complexes have a **lower number of unpaired electrons**.
  - They exhibit **diamagnetic or low paramagnetic** behaviour and are referred to as **low spin complexes**.
  - Examples: $[Cr(NH_3)_6]^{+3}$, $[Fe(CN)_6]^{-3}$, $[Fe(CN)_6]^{-4}$, $[Co(NH_3)_6]^{+3}$, $[Co(CN)_6]^{-3}$, $[Co(CN)_6]^{-4}$ etc.

Tetrahedral Complexes (Coordination number - 4)

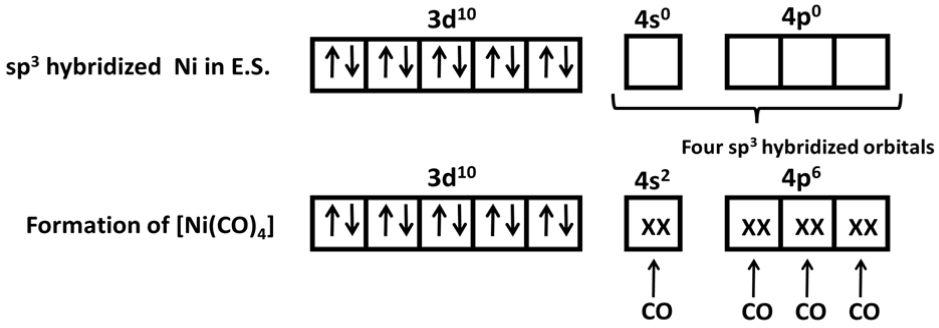
- **$[Ni(CO)_4]$ Complex :**
  - Oxidation State of Nickel (Ni) in the complex is: **0**

    $x + 4(0) = 0$

    $x = 0$
  - Electronic Configuration of **Ni atom** is: **[Ar] $3d^8$ $4s^2$**



  - In this complex, **coordination number** of Nickel is **4**.
    Therefore, **four empty orbitals** of the Ni atom are required for hybridization.
    Since, the **CO** is a **very strong field ligand**, it forces the two electrons from the 4s orbital to shift into the 3d orbital to **pair up with existing electrons**.



  - Hybridization: **sp^3**
  - Geometry: **Tetrahedral**
  - Number of unpaired electrons: **0**
  - Magnetic behavior: **Diamagnetic**
  - Effective Atomic Number (EAN) = (At. No. – Oxidation state) + (2 × Coordination No.)

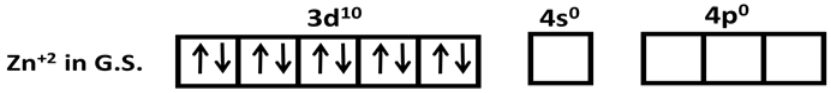
    = (28 – 0) + (2 × 4) = **36**

- **$[Zn(NH_3)_4]^{+2}$ Complex :**
  - Oxidation State of Zinc (Zn) in the complex is: **+2**

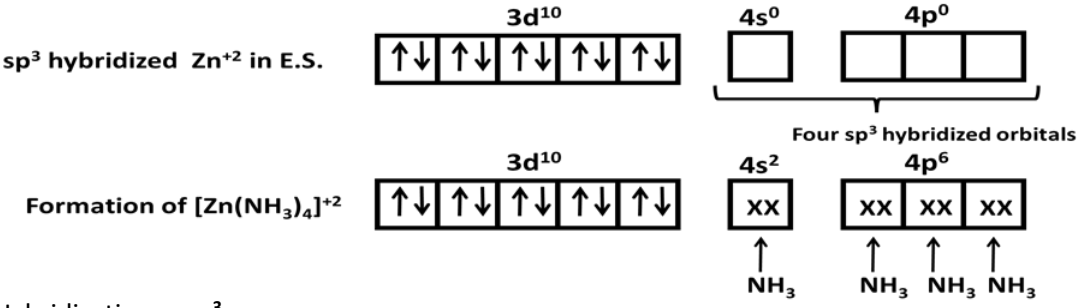
    $x + 4(0) = +2$

    $x = +2$

- Electronic Configuration of **Zn^{+2} ion** is: **[Ar] $3d^{10}$ $4s^0$**



- In this complex, **coordination number** of Zinc is **4**.
  Therefore, **four empty orbitals** of the Zinc ion are required for hybridization.

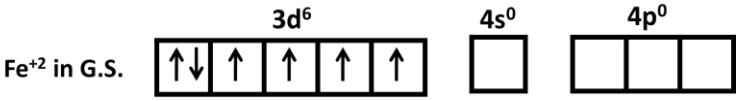


- Hybridization: **sp^3**
- Geometry: **Tetrahedral**
- Number of unpaired electrons: **0**
- Magnetic behavior: **Diamagnetic**
- Effective Atomic Number (EAN) = (At. No. – Oxidation state) + (2 × Coordination No.)
  = (30 – 2) + (2 × 4) = **36**

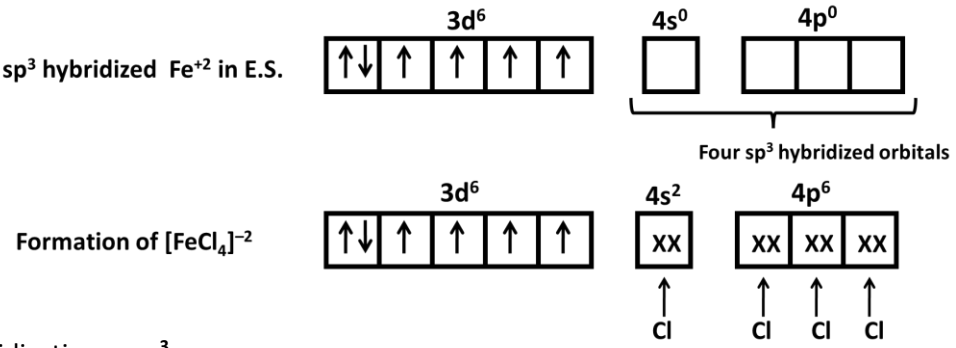
- **$[FeCl_4]^{-2}$ Complex :**
  - Oxidation State of Iron (Fe) in the complex is: **+2**

    $x + 4(-1) = -2$

    $x = -2 + 4 = +2$
  - Electronic Configuration of **Fe^{+2} ion** is: **[Ar] $3d^6$ $4s^0$**



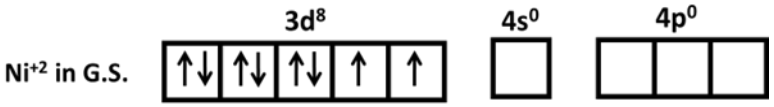
  - In this complex, **coordination number** of Iron is **4**.
    Therefore, **four empty orbitals** of the Ferrous ion (Fe^{+2}) are required for hybridization.
    Since, **Cl^{-1}** is a **weak field ligand**, it **does not** force the electrons to **pair up** in the **(n-1)d** subshell.



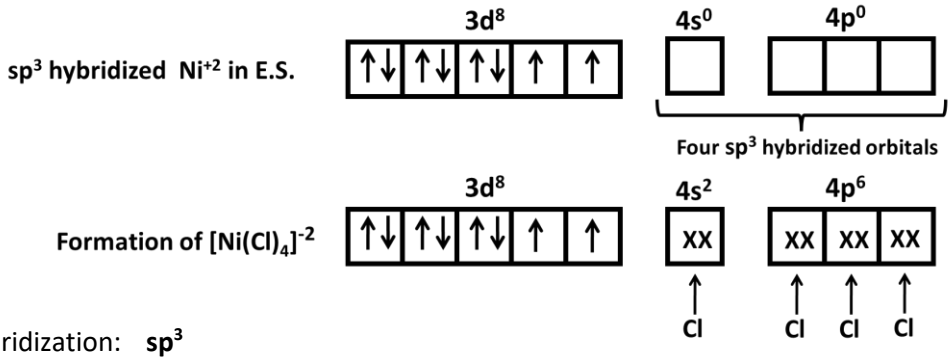
  - Hybridization: **sp^3**
  - Geometry: **Tetrahedral**
  - Number of unpaired electrons: **4**

- Magnetic behavior: **Paramagnetic**
- Spin only magnetic moment (B.M.): $\mu = \sqrt{n(n+2)}$
  $= \sqrt{4(4+2)} = \sqrt{24} =$ **4.89**
- Effective Atomic Number (EAN) = (At. No. – Oxidation state) + (2 × Coordination No.)
  = (26 – 2) + (2 × 4) = **32**

- **$[NiCl_4]^{-2}$ Complex :**
  - Oxidation State of Nickel (Ni) in the complex is: **+2**
    $x + 4(-1) = -2$
    $x = -2 + 4 = +2$
  - Electronic Configuration of **Ni^{+2} ion** is: **[Ar] $3d^8$ $4s^0$**



  - In this complex, **coordination number** of Iron is **4**.
    Therefore, **four empty orbitals** of the Nickel ion (Ni^{+2}) are required for hybridization.
    Since, **Cl^{-1}** is a **weak field ligand**, it **does not** force the electrons to **pair up** in the **(n-1)d** subshell.

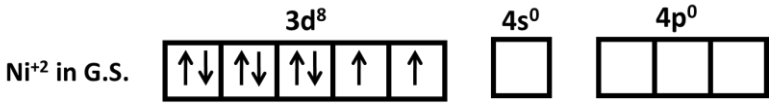


  - Hybridization: **sp^3**
  - Geometry: **Tetrahedral**
  - Number of unpaired electrons: **2**
  - Magnetic behavior: **Paramagnetic**
  - Spin only magnetic moment (B.M.): $\mu = \sqrt{n(n+2)}$
    $= \sqrt{2(2+2)} = \sqrt{8} =$ **2.83**
  - Effective Atomic Number (EAN) = (At. No. – Oxidation state) + (2 × Coordination No.)
    = (28 – 2) + (2 × 4) = **34**

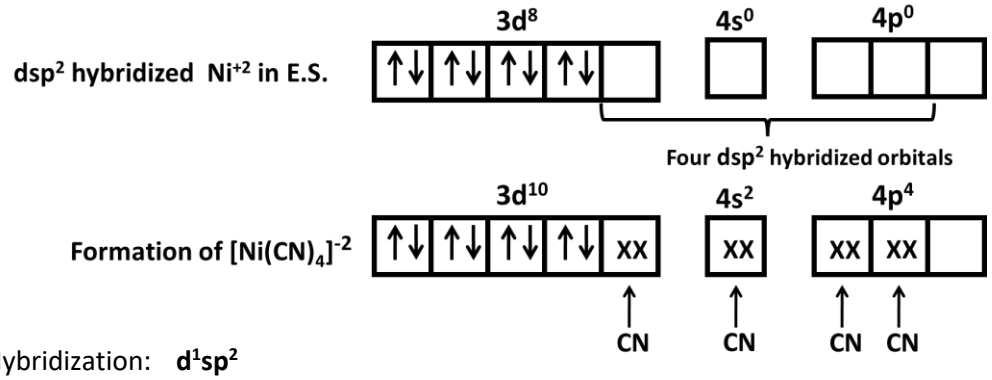
Square Planar Complexes (Coordination number - 4)

- **$[Ni(CN)_4]^{-2}$ Complex :**
  - Oxidation State of Nickel (Ni) in the complex is: **+2**
    $x + 4(-1) = -2$
    $x = -2 + 4 = +2$

- Electronic Configuration of **Ni^{+2} ion** is: **[Ar] $3d^8$ $4s^0$**

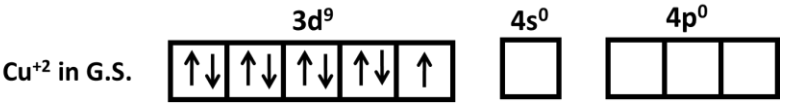


- In this complex, **coordination number** of Nickel is **4**.
  Therefore, **four empty orbitals** of the Zinc ion are required for hybridization.
  Since, the **CN^{-1}** is a **strong field ligand**, it forces the electrons to **pair up against Hund's Rule** in the inner **(n-1)d** subshell.

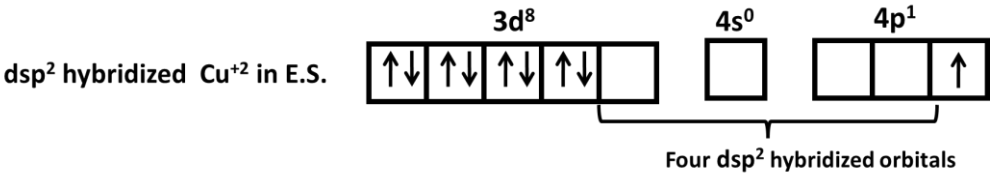


- Hybridization: **d^1sp^2**
- Geometry: **Square Planar**
- Nature of complex: **Inner orbital (Low spin)**
- Number of unpaired electrons: **0**
- Magnetic behavior: **Diamagnetic**
- Effective Atomic Number (EAN) = (At. No. – Oxidation state) + (2 × Coordination No.)
  = (28 – 2) + (2 × 4) = **34**

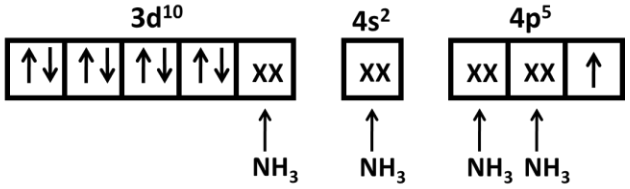
- **$[Cu(NH_3)_4]^{+2}$ Complex :**
  - Oxidation State of Copper (Cu) in the complex is: **+2**
    $x + 4(0) = +2$
    $x = +2$
  - Electronic Configuration of **Cu^{+2} ion** is: **[Ar] $3d^9$ $4s^0$**



  - In this complex, **coordination number** of Copper is **4**.
    Therefore, **four empty orbitals** of the Copper ion (Cu^{+2}) are required for hybridization.
    While one might **expect sp^3 hybridization,** but **experimental evidence** confirms that the complex undergoes **d^1sp^2 hybridization**.



Formation of $[Cu(NH_3)_4]^{+2}$



- Hybridization: d^1sp^2
- Geometry: **Square Planar**
- Number of unpaired electrons: **1**
- Magnetic behavior: **Paramagnetic**
- Spin only magnetic moment (B.M.): $\mu = \sqrt{n(n+2)}$
  $= \sqrt{1(1+2)} = \sqrt{3} =$ **1.73**
- Effective Atomic Number (EAN) = (At. No. – Oxidation state) + (2 × Coordination No.)
  = (29 – 2) + (2 × 4) = **35**

NOTE:

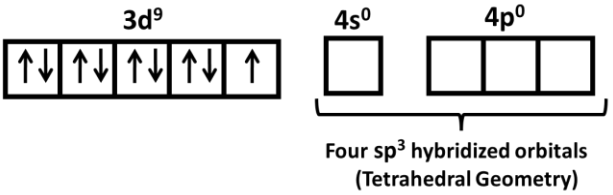
Why is $[Cu(NH_3)_4]^{+2}$ Square Planar and not Tetrahedral?

(The Failure of the Magnetic Criterion)

In many complexes, the magnetic behaviour alone is enough to predict the geometry. However, this complex is a notable exception:

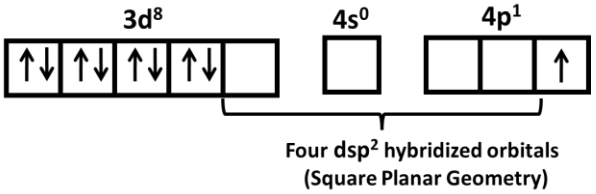
1. **The sp^3 Expectation:** Based on the **$3d^9$** electronic configuration **Cu^{+2} ion**, if **sp^3 hybridization** occurred, the **unpaired electron** would **remain in the 3d orbital**. This would result in a **paramagnetic** complex with a **tetrahedral geometry**.

Expected sp^3 hybridization of Cu^{+2} in E.S.



2. **The d^1sp^2 Reality:** In d^1sp^2 hybridization, the **unpaired electron** from the 3d orbital **is promoted to** an empty **4p orbital**, leaving one 3d orbital empty for the ligands. In this case, the complex also remains **paramagnetic** with a **square planar geometry**.

Experimentally proved dsp^2 hybridized of Cu^{+2} in E.S.



3. **The Conflict:** Because both the **sp^3 and d^1sp^2** models result in exactly **one unpaired electron**, and hence, **magnetic behaviour cannot be used to distinguish between the two geometries.**

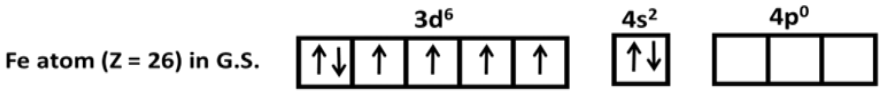
4. **X-Ray Evidence:** The definitive **proof** for the **square planar geometry** comes from **X-ray diffraction studies**, which show that the **four ligands are co-planar** (in the same plane). This arrangement is only possible with **d^1sp^2 hybridization**.

Trigonal bipyramidal Complexes (Coordination number - 5)

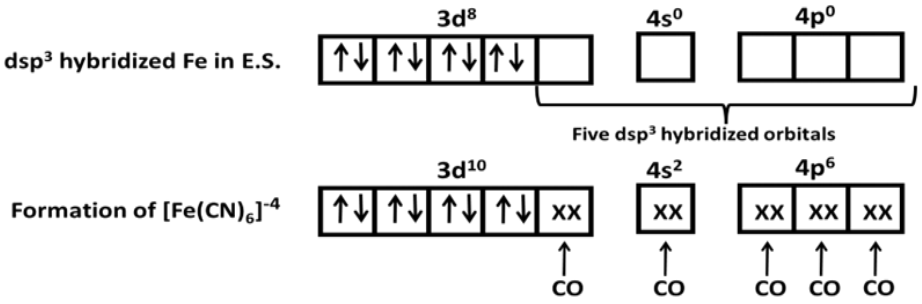
- **$[Fe(CO)_5]$ Complex :**
  - Oxidation State of Iron (Fe) in the complex is: **0**

    $x + 5(0) = 0$

    $x = 0$
  - Electronic Configuration of **Fe atom** is: **[Ar] $3d^6$ $4s^2$**



  - In this complex, **coordination number** of Iron is **5**.
    Therefore, **five empty orbitals** of the Fe atom are required for hybridization.
    Since, the **CO** is a **very strong field ligand**, it forces the two electrons from the 4s orbital to shift into the 3d orbital to **pair up with existing electrons against Hund's rule**.



  - Hybridization: **d^1sp^3**
  - Geometry: **Trigonal bipyramidal**
  - Number of unpaired electrons: **0**
  - Magnetic behavior: **Diamagnetic**
  - Effective Atomic Number (EAN) = (At. No. – Oxidation state) + (2 × Coordination No.)
    = (26 – 0) + (2 × 5) = **36**

Limitations/Drawbacks of Valence Bond Theory (VBT)

- The **magnetic behaviour** predicted by VBT can sometimes be **misleading** or **fail to align** with experimental results (e.g., the $[Cu(NH_3)_4]^{+2}$ paradox).
- It **cannot** explain **why a metal ion in a particular oxidation state** forms a **low spin** complex with certain ligands but a **high spin** complex with others.
- VBT **does not distinguish** between **weak field ligands** and **strong field ligands**, a gap later filled by the Spectrochemical Series in Crystal Field Theory.
- It **cannot** explain the **color** exhibited by coordination complexes, as it **lacks** an explanation for **d-d electron transitions**.

- For complexes with a **coordination number of 4**, Valence Bond Theory **does not make exact or reliable predictions** to distinguish between **tetrahedral** (sp^3) and **square planar** (dsp^2) geometries without prior experimental data.
- It provides **no information** regarding the **quantitative** and **thermodynamic stability** of complexes; it remains a qualitative model rather than a mathematical one.
- It **fails** to explain the **kinetic stabilities** or **the rates of reaction** of coordination compounds.

Practice Problems

1. Explain why $[Fe(H_2O)_6]^{+3}$ has magnetic moment of 5.92 BM whereas $[Fe(CN)_6]^{-3}$ has a value of only 1.74 BM.
2. Why do compounds having similar geometry have different magnetic moment?
3. Using valence bond theory, explain the following in relation to the complexes given below:
   $[Mn(CN)_6]^{-3}$, $[Co(NH_3)_6]^{+3}$, $[Cr(H_2O)_6]^{+3}$, $[FeCl_6]^{-4}$
   (i) Type of hybridisation. (ii) Inner or outer orbital complex.
   (iii) Magnetic behaviour. (iv) Spin only magnetic moment value.
4. Explain why $[Ni(CO)_4]$ is diamagnetic whereas $[NiCl_4]^{-2}$ is paramagnetic.
5. Differentiate between weak field and strong field ligands. How does the strength of the ligand influence the spin of the complex ?
6. Answer the following about the complexes: $[FeF_6]^{-3}$ and $[Fe(CN)_6]^{-4}$
   a. Write the hybridisation involved in each case.
   b. Which of them is the outer orbital complex and which one is the inner orbital complex?
   c. Compare the magnetic behaviour.
7. Write the hybridization of $[Ni(CN)_4]^{-2}$ and predict its magnetic behaviour.
8. $[Cr(NH_3)_6]^{+3}$ is paramagnetic while $[Ni(CN)_4]^{-2}$ is diamagnetic. Explain why. [At.No.: Cr=24, Ni=28]
9. Out of $[CoF_6]^{-3}$ and $[Co(C_2O_4)_3]^{-3}$, which one complex is:
   (i) More stable ? (ii) The high spin complex ?
10. Using valence bond theory, deduce the shape and hybridization of $[Ni(NH_3)_6]^{+2}$.
11. $[Ni(CO)_4]$ has tetrahedral geometry while $[Ni(CN)_4^{-2}$ has square planar yet both exhibit diamagnetism. Explain.
12. Spin only magnetic moment of $[MnBr_4]^{-2}$ is 5.9 BM. Predict the geometry and hybridization of the complex.

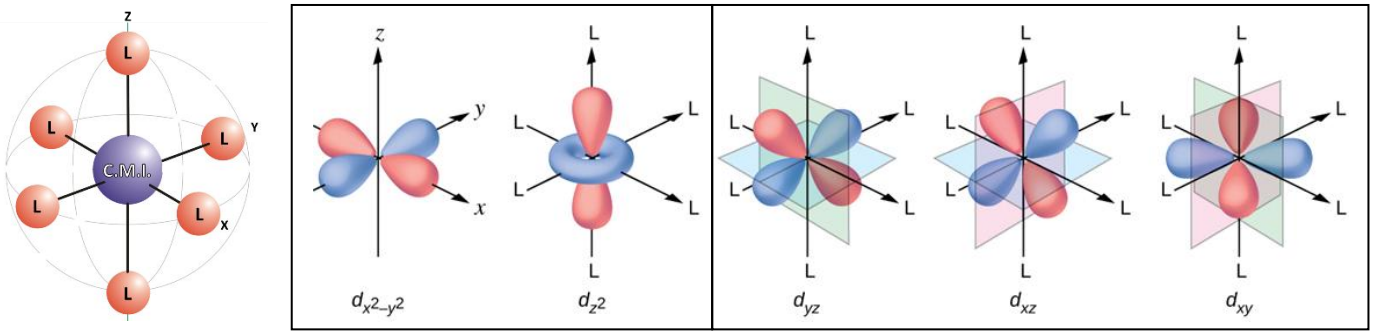
Crystal Field Splitting Theory (CFST)

- This theory was developed by **Hans Bethe** and **J.H. Van Vleck**. The main postulates are as follows:
  - It considers the **metal-ligand bond** to be **purely ionic** (unlike Valence Bond Theory, which considers the bond to be covalent).
  - If the ligand is a **negative ion (anion)**, the force of attraction is due to **opposite charges** (**ionic attraction or electrostatic attraction**).
  - If the ligand is a **neutral molecule** (e.g., NH_3, H_2O), the **partial negative end of its dipole** is attracted toward the central metal ion (**ion-dipole attraction**).

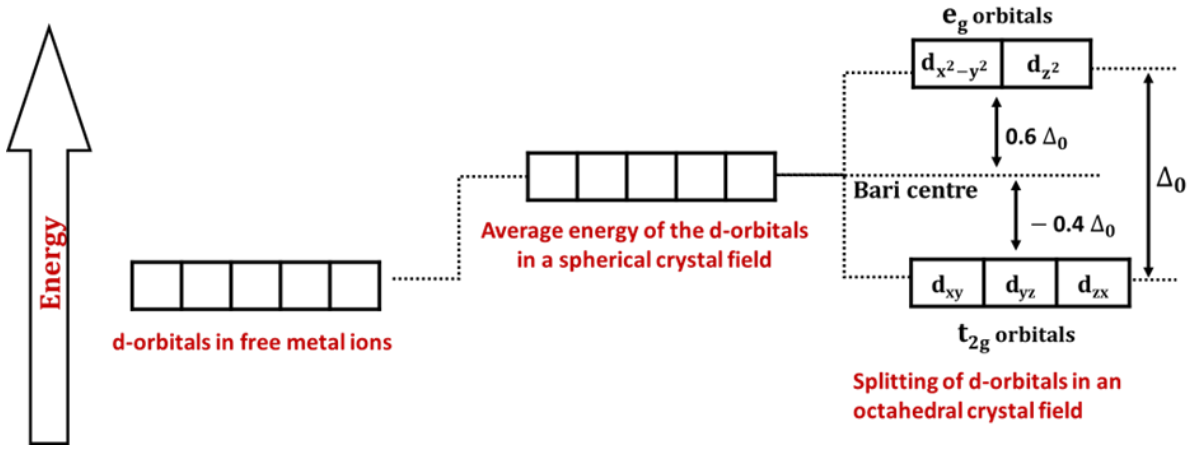
- **Each ligand** is considered a **point of negative charge**. They **arrange themselves** around the metal ion to **minimize repulsions**.
- In a **free metal ion**, all five d-orbitals are **degenerate** (equal in energy).
  - When ligands approach, they create an electric field. If the field is **spherically symmetrical**, the orbitals **remain degenerate**.
  - However, in **actual complexes**, the **field is asymmetrical**, causing the d-orbitals to **split into different energy levels**. This is called **Crystal Field Splitting**.
  - The type of splitting depends upon the nature of crystal field.

Crystal Field for Octahedral Complexes

- In octahedral complexes, **six ligands** approach the central metal ion **along the x, y, and z axes**.



- The $\mathbf{d_{x^2-y^2}}$ **and** $\mathbf{d_{z^2}}$ **orbitals** have lobes **along the axes**. They **point directly** at the approaching ligands, experience **higher repulsion**, and are raised to a **higher energy level**. These orbitals are called $\mathbf{e_g}$ **orbitals**.
- The $\mathbf{d_{xy}}$**,** $\mathbf{d_{yz}}$**, and** $\mathbf{d_{zx}}$ **orbitals** have lobes **between the axes**. They experience **less repulsion** and remain at a **lower energy level**. These orbitals are called $\mathbf{t_{2g}}$ **orbitals**.
- The **energy difference** between $\mathbf{e_g}$ **and** $\mathbf{t_{2g}}$ is the **Crystal Field Splitting Energy** (**Δo**, where 'o' stands for octahedral).
  - $\mathbf{e_g}$ **energy** increases by **+0.6 Δo** (or +6 Dq) from the **barycenter**.
  - $\mathbf{t_{2g}}$ **energy** decreases by **–0.4 Δo** (or –4 Dq) from the **barycenter**.



Factors Affecting the Magnitude of Crystal Field Splitting Energy (i.e., Δ_O)

- **Nature of the Ligand**
  - The magnitude of splitting depends on the **field strength of the ligand**.
  - Some ligands produce **strong fields**, resulting in **large splitting**, while others produce **weak fields**, resulting in **small splitting**.
  - **The Spectrochemical Series:**
    The arrangement of **ligands** in **increasing order of their crystal field splitting energy (Δ_O)**, is known as the Spectrochemical Series.

Spectrochemical Series

$$I^{-1} < Br^{-1} < SCN^{-1} < Cl^{-1} < S^{-2} < F^{-1} < OH^{-1} < C_2O_4^{-2} < H_2O < NCS^{-1} < EDTA^{-4} < NH_3 < en < NO_2^{-1} < CN^{-1} < CO$$

Weak Field Ligands ⟶ Strong Field Ligands

Increasing Order of CFSE (Δ_O)

  - **Applications of the Spectrochemical Series:**
    - **Predicting Spin States (High spin vs. Low spin):**
      By comparing the **splitting energy (Δ_O)** with the **pairing energy (P)** we can determine the spin state or electronic configuration.

> **NOTE:**
> **Pairing Energy (P)** is the energy required to pair **two electrons** into the **same d-orbital** of the central metal.

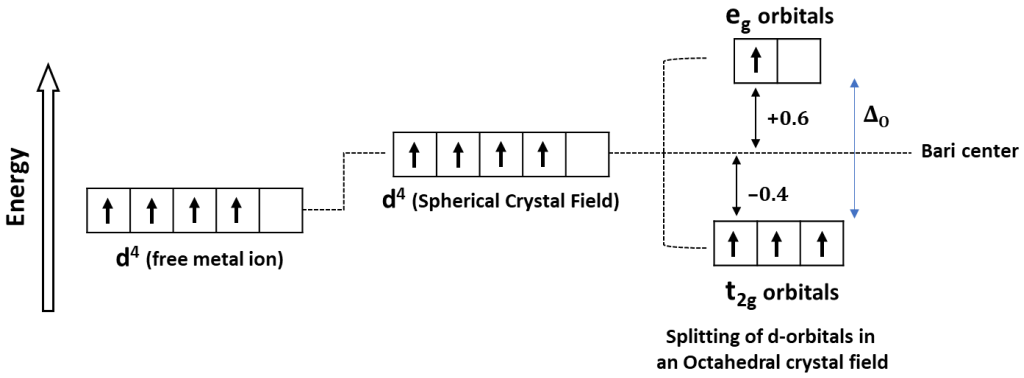
      - If $\Delta_O > P$: Splitting is **large**; electrons pair up in the **lower energy orbitals**, forming a **low spin** complex.
      - If $\Delta_O < P$: Splitting is **small;** electrons remain unpaired and occupy **higher energy orbitals**, forming a **high spin** complex.
    - **Explaining Magnetic Properties:**
      - Complexes with **weak field ligands** often have **more unpaired electrons**, resulting in **stronger paramagnetic** behaviour.
      - Complexes with **strong field ligands** often have **fewer or no unpaired electrons**, resulting in **diamagnetic or weakly paramagnetic** behaviour.
    - **Explaining Colour in Coordination Complexes:**
      - The colour of complex depends on the **energy gap (Δ)** between the **split d-orbitals**.
      - A complex **absorbs light** with energy equal to **energy gap (Δ)** to promote an electron from **lower to higher energy level** (**d-d transition**).
      - The **colour we observe** is **complementary** to the **wavelength of light absorbed**.
    - **Determining Thermodynamic Stability:**
      - Generally, complexes formed with ligands **higher** in the **spectrochemical series** (Strong Field Ligand) are **more stable** than those formed with ligands **lower** in the **series** (Weak Field Ligand).
      - This is because higher splitting leads to higher **Crystal Field Stabilization Energy (CFSE)**.

- **Oxidation State of the Metal ion**
  - A **higher oxidation state** of the central metal ion **increases the electrostatic attraction** between the central metal ion and the ligands.
  - This increased attraction pulls the ligands closer to the central metal ion, leading to **greater repulsion of the d-electrons**.
  - This increased repulsion results in a **larger splitting of the d-orbitals**, leading to a **higher value Δ_O**.

Calculation of Crystal Field Splitting Energy (i.e., Δ_O)

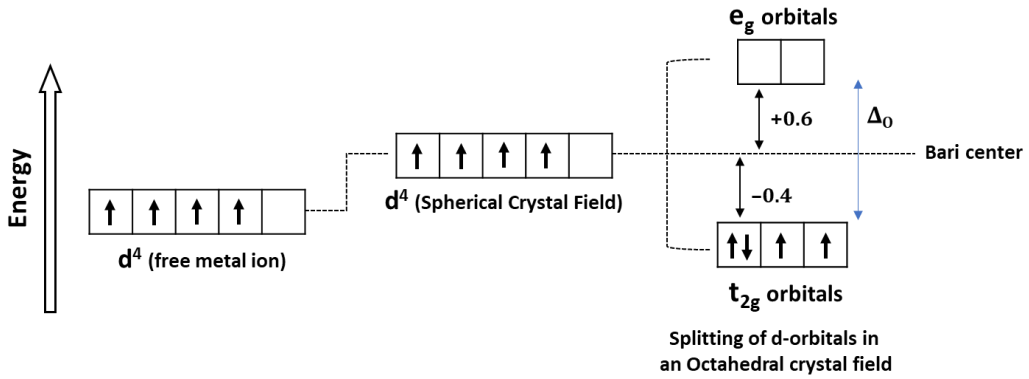
- The Δ_O of a complex is determined by the **distribution of electrons** between the **t_{2g} and e_g orbitals**.
  - **Each electron** occupying a **t_{2g} orbital** results in the **lowering** of energy by **–0.4 Δ_O** (or **–4 Dq**).
  - **Each electron** occupying an **e_g orbital** results in an **increase** of energy by **+0.6 Δ_O** (or **+6 Dq**).

- **Example 1: Calculation for d^4 system**
  - For **High Spin** Complex (Weak Field; **$\Delta_O < P$**)



    - Electronic Configuration: $t_{2g}^3\ e_g^1$
    - Crystal Field Splitting energy (Δ_O) = [3 × (–0.4)] + [1 × (+0.6)]
      = –1.2 + 0.6
      = **–0.6 Δ_O (or –6 Dq)**

  - For **Low Spin** Complex (Weak Field; **$\Delta_O > P$**)

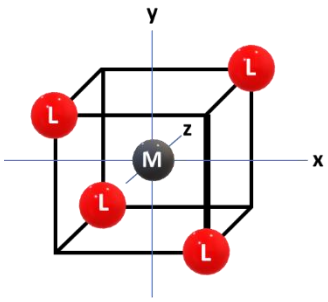


    - Electronic Configuration: $t_{2g}^4\ e_g^0$
    - Crystal Field Splitting energy (Δ_O) = 4 × (–0.4)
      = **–1.6 Δ_O (or –16 Dq)**

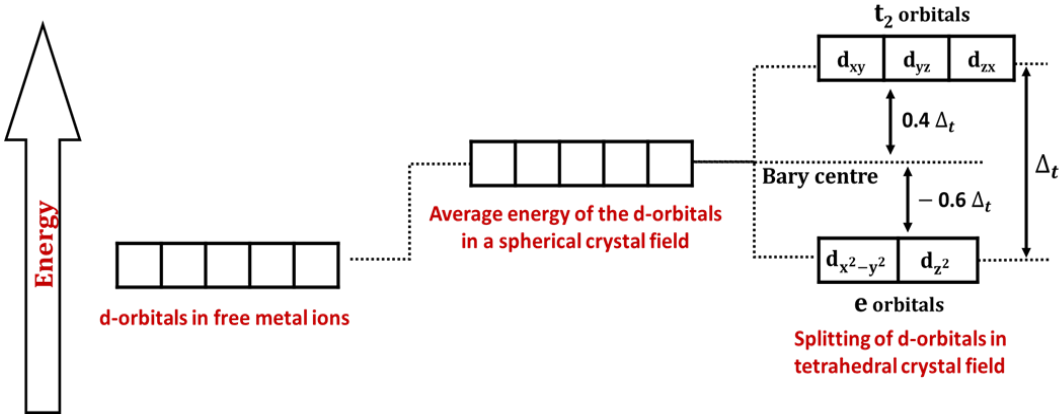
NOTE:
Crystal field **stabilization** Energy (**CFSE**) = $\Delta_O + nP$
Where,
Δ_O = Crystal field splitting energy.
nP =Total pairing energy for any **additional electron pairs formed** in the complex that were **not present** in the **free metal ion**.

Crystal Field for Tetrahedral Complexes (The Inverted Splitting)

- The splitting pattern for **tetrahedral complexes** is the **inverse** of the splitting pattern for **octahedral complexes.** This occurs because the **four ligands** approach the central metal ion from **between the x, y, and z axes** instead of along them.



  - The **d_{xy}, d_{yz}, and d_{zx} orbitals** have lobes **between the axes**. They **point directly** at the approaching ligands, experience **higher repulsion**, and are raised to a **higher energy level**. These orbitals are called **t_2 orbitals**.
  - The **$d_{x^2-y^2}$ and d_{z^2} orbitals** have lobes **along the axes**. They experience **less repulsion** and remain at a **lower energy level**. These orbitals are called **e orbitals**.
  - The **energy difference** between **t_2 and e** is the **Crystal Field Splitting Energy** (**Δt**, where 't' stands for tetrahedral).
    - **t_2 energy** increases by **+0.4 Δt** (or +4 Dq) from the **barycenter**.
    - **e energy** decreases by **–0.6 Δt** (or –6 Dq) from the **barycenter**.



The Mathematical Relationship between Δ_t and Δ_O

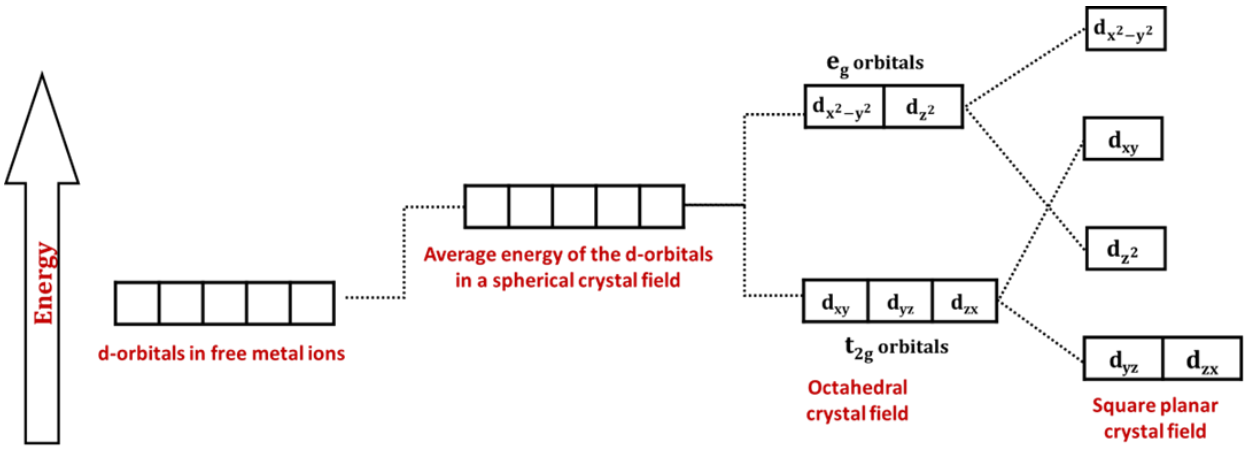
- The tetrahedral splitting is much weaker than octahedral splitting. The mathematical relationship is:

$$\Delta_t \approx \frac{4}{9}\Delta_O$$

- Because Δ_t is less than half of the Δ_O, it is not sufficient to force the pairing of electrons. Therefore, $\Delta_t < P$. Hence, tetrahedral complexes have high-spin configuration.

Crystal Field for Square Planar Complexes

- The **Square Planar** geometry can be **derived from an octahedral** geometry by imagining the **two ligands** on the **z-axis** being **removed**.
- As these ligands move away, all d-orbitals with a **z-component** (dz^2, dyz , and dxz) become significantly **more stable** (**lower in energy**) because they experience **less repulsion**.



- **Energy Level Explanation:**
  - **$dx^2 – y^2$ (Highest Energy):**
    - Lobes of this orbital **point directly** at the four ligands approaching **along the x- and y-axes**.
    - It experiences the **maximum repulsion** and therefore has the **highest energy**.
  - **dxy (Second Highest):**
    - Lobes of this orbital lie in the same plane as the ligands (xy–plane) but point between them.
    - While the repulsion is high, it is less than that of the $dx^2 – y^2$ orbital.
  - **dz^2 (Third Highest):**
    - Although the main lobes point along the z-axis, where ligands have been removed, the central "donut" or ring of the dz^2 orbital lies in the xy-plane.
    - It still feels some repulsion from the four ligands, placing it below dxy.
  - **dyz and dxz (Lowest Energy):**
    - These two orbitals are **degenerate** (equal in energy). Their lobes **point out** of the **xy-plane** and have **no components pointing toward the ligands**.
    - They are the **least affected** by the electrostatic field and thus have the **lowest energy**.

Explanation for the Colour of Gemstones

- The colour in gemstones is mainly due to **d-d transitions** of transition metal ions.
- **Small amounts of transition metal ions** (impurities) occupy **octahedral sites** in a colourless crystal lattice. This environment **splits the metal's d-orbitals**, allowing them to **absorb** specific wavelengths of **visible light**.
- The **unique colour** we **observe** is the **complementary colour** to the wavelength of **light absorbed**.

Ruby

- **Composition:**
  - Primarily Aluminium Oxide (**Al_2O_3**), also called **corundum**.
  - A small percentage (0.5 to 1%) of **Al^{+3} ions** are **replaced by Cr^{+3} ions**.

- **Mechanism:**
  - The **Cr^{+3} ions** occupy **octahedral sites** where the crystal field causes **d-orbital splitting**.
  - When **white light** hits the **ruby**, electrons of **Cr^{+3}** undergo d-d transitions, **absorbing green-yellow light** and reflecting the **deep red colour** we see.

Topaz (Yellow Sapphire)

- **Composition:**
  - Primarily Aluminium Oxide (**Al_2O_3**) or **corundum**.
  - A small percentage of **Al^{+3} ions** are **replaced by Fe^{+3} ions**.
- **Mechanism:**
  - The **Fe^{+3} ions** occupy **octahedral sites** leading to specific **d-orbital splitting**.
  - When **white light** hits the **stone**, electrons of **Fe^{+3}** undergo d-d transitions, **absorbing blue-violet light** and reflecting the **yellow-golden colour** we see.

Amethyst

- **Composition:**
  - Primarily **Quartz** (SiO_2).
  - A small percentage of **Si^{+4} ions** are **replaced by Mn^{+3}** (or sometimes **Fe^{+3}**) ions.
- **Mechanism:**
  - When **white light** hits the **amethyst**, the electrons of **Mn^{+3}** undergo d-d transition, absorbing **yellow-green** light and reflecting **purple-violet colour** we see.

Emerald

- **Composition:**
  - Primarily the mineral called **Beryl** (**$Be_3Al_2Si_6O_{18}$**).
  - A small percentage of **Cr^{+3} ions** occupy **octahedral sites** within the beryl lattice.
- **Mechanism:**
  - Although it contains the same Cr^{+3} ions as Ruby, the different crystal lattice (Beryl) changes the splitting energy (Δ_O)
  - When **white light** hits the **stone**, electrons of **Cr^{+3}** undergo d-d transition, **absorbing red-yellow light** and reflecting **green colour** we see.

Influence of Ligands on Colour

- In the **absence of ligands**, crystal field splitting **does not** occur, and the d-orbitals **remain degenerate**. Without splitting, **d-d transitions cannot happen**, and the substance remains **colourless**.
  Example:
  - When **purple**-coloured **$[Ti(H_2O)_6]Cl_3$** is heated, it loses its water ligands. The resulting **anhydrous $TiCl_3$** is **colourless (white)**.
  - **Blue**-coloured **$CuSO_4 \cdot 5H_2O$** loses its water ligands upon heating, The resulting **anhydrous $CuSO_4$** is **white** because the crystal field disappears.

Nature of Ligand

- The colour of a complex depends on the **strength of the ligand**.
- According to the **Spectrochemical Series**, as the strength of the ligand **increases** the degrees of splitting (Δ_O) also **increases**. A **larger Δ_O** requires **higher energy** (shorter wavelength) light for the d-d transition.
- Consider these **Co^{+3} complexes**: As you move from **$H_2O < NH_3 < CN^{-1}$**, the energy gap (**Δ_O**) **widens** and the **absorbed wavelength** shifts **toward the violet end** of the spectrum.

Complex	$[Co(H_2O)_6]^{+3}$	$[Co(NH_3)_6]^{+3}$	$[Co(CN)_6]^{-3}$
Colour Absorbed	Orange	Blue	Violet (or Purple)
Colour Transmitted	Blue	Yellow orange	Yellow

- **Case Study: $[Ni(H_2O)_6]^{+2}$ and Ethane-1,2-diamine**
  - When the stronger bidentate ligand **ethane-1,2-diamine (en)** is added to a **green solution** of **$[Ni(H_2O)_6]^{+2}$**, the water molecules are progressively replaced.
  - This increases the splitting (Δ_O), causing the complex to **absorb shorter wavelengths** (higher energy), shifting the observed colour across the spectrum.

$$[Ni(H_2O)_6]^{+2}_{(aq.)} + en \longrightarrow [Ni(H_2O)_4(en)]^{+2}_{(aq.)} + 2\,H_2O$$
Green → Pale Blue

$$[Ni(H_2O)_4(en)]^{+2}_{(aq.)} + en \longrightarrow [Ni(H_2O)_2(en)_2]^{+2}_{(aq.)} + 2\,H_2O$$
Pale Blue → Blue/Purple

$$[Ni(H_2O)_2(en)_2]^{+2}_{(aq.)} + en \longrightarrow [Ni(en)_3]^{+2}_{(aq.)} + 2\,H_2O$$
Blue/Purple → Purple

Complex	Δ_O (Splitting)	Absorbed Light	Transmitted Light
$[Ni(H_2O)_6]^{+2}$	Lowest	Red	Green
$[Ni(H_2O)_4(en)]^{+2}$	Higher	Orange-Yellow	Pale Blue
$[Ni(H_2O)_2(en)_2]^{+2}$	Even Higher	Yellow-Green	Blue-Purple
$[Ni(en)_3]^{+2}$	Highest	Green-Blue	Violet-Purple

Limitations of Crystal Field Theory

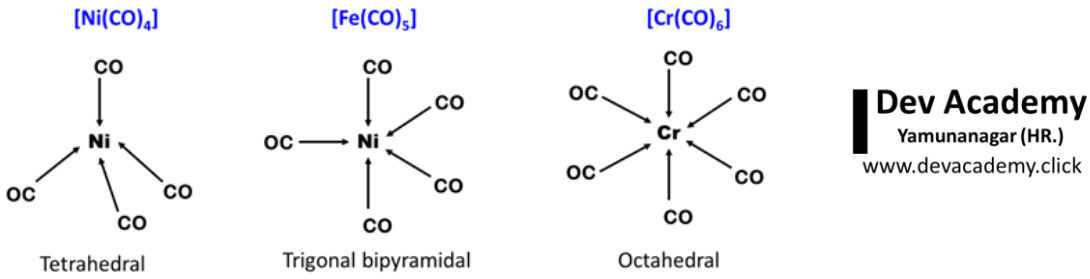
- While Crystal Field Theory successfully explains the colour and magnetic properties of many complexes, it has several key limitations:
  - The theory treats the metal-ligand bond as **purely ionic** (electrostatic). It completely ignores any **covalent character** or orbital overlapping between the metal and the ligands.
  - CFT assumes ligands are **point charges**. Logically, this means **anionic ligands** (like OH^{-1} or Cl^{-1}), which have a **full negative charge**, should cause a **very large** splitting effect.
    However, in the **spectrochemical series**, these **anions** are mostly at the **bottom** and cause the **smallest** splitting effect.
  - CFT only **focuses on the d-orbitals** of the central metal ion. It **does not consider** the involvement of **s- and p-orbitals** of the metal, nor the **π-bonding** between metal and ligands.
- The limitations of CFT are addressed by more advanced theories:
  - Ligand Field Theory (**LFT**)
  - Molecular Orbital Theory (**MOT**)

Practice Problems

1. Low spin tetrahedral complexes are not known. Why?
2. Co^{+2} is easily oxidized to Co^{+3} in the presence of a strong ligand. Why?
3. The hexaaquamanganese(II) ion contains five unpaired electrons, while the hexacyanomanganate(II) ion contains only one unpaired electron. Explain using Crystal Field Theory.
4. On the basis of crystal field theory explain why Co^{+3} forms paramagnetic octahedral complex with weak field ligands whereas it forms diamagnetic octahedral complex with strong field ligands.
5. Give the electronic configuration of the following complexes on the basis of Crystal Field Splitting theory.
   (a.) $[CoF_6]^{-3}$ (b.) $[Fe(CN)_6]^{-4}$, and (c.) $[Cu(NH_3)_6]^{+2}$
6. $CuSO_4 .5H_2O$ is blue in colour while $CuSO_4$ is colourless. Why?
7. Using Crystal Field theory, write the number of unpaired electrons in octahedral complexes of Fe^{+3} in the presence of: (a) Strong field ligand, and (b) Weak field ligand
8. What is meant by crystal field splitting energy ? For a d^4 ion, write the configuration if:
   (i) $\Delta_O < P$ (ii) $\Delta_O > P$
9. What happens to the colour of complex $[Ti(H_2O)_6]^{+3}$ when heated gradually ?
10. Write the electronic configuration for d^5 ion if (a) $\Delta_O < P$, and (b) $\Delta_O > P$
11. On the basis of Δ_O and P, how can you differentiate between a strong field ligand and a weak field ligand ?
12. How is the crystal field splitting energy for octahedral complex (Δ_O) related to that of tetrahedral complex (Δ_t)?
13. Solution of $[Ni(H_2O)_6]^{+2}$ is green in colour wheras $[Ni(CN)_4]^{-2}$ is colourless. Give reason.
14. If the crystal field splitting energy for an octahedral complex (Δ_O) is 18,000 cm^{-1}, what is the approximate value of the splitting energy for the same metal ion in a tetrahedral complex (Δ_t)?
15. If Δ_O for a complex is x, and the corresponding Δ_t is observed to be 16 units, what is the value of x?

Metal Carbonyl

- Metal carbonyls are coordination compounds formed by the combination of **carbon monoxide (CO)** with **transition metals**.
- In **homoleptic metal carbonyls** (where only CO ligands are present), the **carbonyl ligands** are linked to the **metal atom** via coordinate (dative) bonds.
- In these complexes, the **central metal atom** is typically in a **zero-oxidation state**.
- Metal carbonyls are **classified based on the number of metal-centers** present in the complex:
  - **Mononuclear Complexes (Single Metal Center):**



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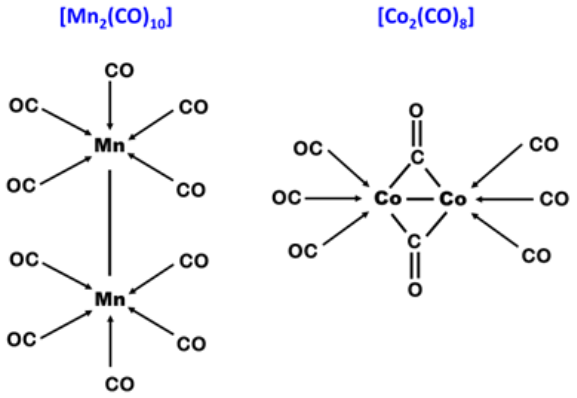
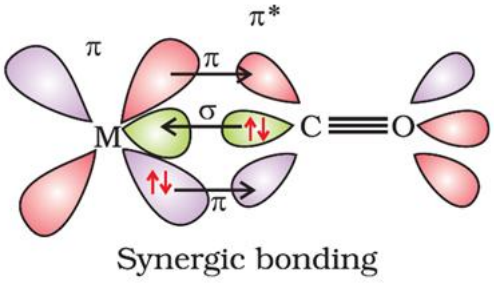
- **Polynuclear Complexes (Multiple Metal Centers):**



Bonding in Metal Carbonyls: The Synergic Effect

- The **metal-carbon (M-C) bond** in carbonyls is unique because it possesses both ***σ* and π character**.
  - ***σ* Bond** is formed by the donation of a lone pair of electrons from the **carbon atom of CO** into a **vacant d-orbital** of the metal.
  - **π Bond (Back-bonding)** is formed by the donation of a pair of electrons from a **filled d-orbital** of the metal into the **vacant antibonding π orbital** of the carbon monoxide molecule.
    - Since **CO accepts** a lone pair of electrons from the metal into its **vacant π*2p orbitals**, it is called a **π-acid or π-acceptor ligand**. This behavior explains why CO is a strong-field ligand.
  - **Synergic effect:** It is **self-strengthening** bonding mechanism in metal carbonyls where **the *σ*-bond** (ligand-to-metal donation) is **strengthened** by the formation of a **π-back bond** (metal-to-ligand donation), and vice versa.



Synergic bonding

Properties of Metal Carbonyls

- **Physical State:**
  - Most are **solids** at room temperature.
  - However, **Iron pentacarbonyl** and **Nickel tetracarbonyl** are liquids.
- **Volatility & Toxicity:**
  - Mononuclear carbonyls are generally **volatile and highly toxic**.
- **Colour:**
  - Mononuclear carbonyls are typically **colourless or light-coloured**, whereas polynuclear carbonyls generally have **deep colours**.

Preparation of Metal Carbonyls

- Metal carbonyls are prepared by the **direct combination** of finely divided metal and carbon monoxide under specific conditions. Most were first synthesized by **Ludwig Mond** in 1890.
- **Mond's Process for Nickel**
  - Nickel tetracarbonyl **[$Ni(CO)_4$]** is a **highly volatile** compound that **decomposes easily** upon heating (450 – 470 K) to **yield pure nickel**.
  - This property is utilized in the **purification of nickel** via Mond's Process.

$$Ni + 4\,CO \xrightarrow{\text{Room temp.}} \underset{\text{Nickel tetracarbonyl}}{[Ni(CO)_4]}$$

$$Fe + 5\,CO \xrightarrow[\text{Pressure}]{\text{Heat \&}} \underset{\text{Iron pentacarbonyl}}{[Fe(CO)_5]}$$

Organometallic Compounds **(Not Included in NCERT)**

- They are chemical compounds that contain at least one **direct metal-to-carbon (M–C) bond**.
- Examples:
  - **Metal carbonyls**: $[Ni(CO)_4]$, $[Fe(CO)_5]$
  - **Grignard reagent**: CH_3CH_2–Mg–Br
  - **Tetraethyl lead**: $Pb(C_2H_5)_4$ (Note: Historically used as an **anti-knock agent** in petrol.)
  - **Diethyl Zinc**: $Zn(C_2H_5)_2$ (Note: Also known as **Frankland's reagent**)
- Exclusions:
  - **Sodium ethoxide (C_2H_5ONa)** is **not organometallic** because sodium is bonded to oxygen, not carbon.
  - **Metal carbides** (e.g., CaC_2), **cyanides** (e.g., KCN), and **carbonates** (e.g., Na_2CO_3) are generally **excluded** because their properties are **more similar to inorganic salts** than organic complexes.
- Classification of organometallic compounds:
  - σ bonded organometallic compounds
  - π bonded organometallic compounds

Stability of Coordination Compounds

- Stability in coordination chemistry refers to **the resistance of a complex to dissociation** into its constituent metal ion and ligands in a specific medium.
- **Thermodynamic Stability:**
  - The **degree of dissociation** depends on the **strength** of the metal–ligand bond.
  - **Stronger** metal–ligand bond leads to **greater thermodynamic stability**, resulting in **less dissociation**.
- **Stability Vs. Instability Constants:**
  - **Instability/Dissociation Constant (K_i):** This represents the equilibrium for the dissociation of a complex.

$$[Co(NH_3)_6]^{+3} \rightleftarrows Co^{+3} + 6\,NH_3$$

Instability constant, $K_i = \frac{[Co^{+3}]\,[NH_3]^6}{[Co(NH_3)_6]^{+3}}$

- **Stability/Formation Constant (K_β):** This represents the equilibrium for the formation of a complex from its components.

$$Co^{+3} + 6\,NH_3 \rightleftarrows [Co(NH_3)_6]^{+3}$$

Stability constant, $K_\beta = \frac{[Co(NH_3)_6]^{+3}}{[Co^{+3}]\,[NH_3]^6}$

- **Relationship:** The stability constant is the reciprocal of the instability constant:

$$K_\beta = \frac{1}{K_i}$$

Factors Affecting the Stability of Complexes:

- **Charge on Metal Ion:**
  - A **higher** positive charge on the metal ion **increases** the electrostatic attraction for ligands, leading to **greater thermodynamic stability**.
  - Example: Fe^{+3} complexes ($[Fe(CN)_6]^{-3}$) are generally **more stable** than Fe^{+2} complexes ($[Fe(CN)_6]^{-4}$).
- **Size of Metal Ion:**
  - For metal ions with the same charge, **smaller ions** have a **higher charge-to-radius ratio (charge density)**, allowing them to bind ligands **more tightly** and form **more stable** complexes.
    - **Irving-Williams Order:** For divalent metal ions (M^{+2}) of the 3d-series, the stability follows this specific trend regardless of the ligand:

$$Cr^{+2} < Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$$

      Note: Stability increases as ionic radius decreases towards Copper.
- **Basic Strength of Ligands:**
  - Ligands that are **stronger Lewis bases** (better electron pair donors) form **more stable** complexes.
  - Example: NH_3 typically form **more stable** complexes than H_2O because it is a stronger base.
- **Chelate Effect:**
  - Ligands that form **ring structures** (**chelates**), such as ethylenediamine (en) or EDTA, significantly **increase the stability** of a complex.

Importance and Applications of Coordination Compounds

- **In Analytical Chemistry**
  - Coordination compounds are vital for the **qualitative and quantitative estimation** of metal ions through **specific colour reactions**.
    - **Dimethylglyoxime (DMG):**
      - Used to detect and estimate **Ni^{+2}**.
      - **Ni^{+2}** forms **insoluble rosy-red precipitate** with DMG in an alkaline medium.
    - **EDTA:**
      - Used in complexometric titrations to determine the **hardness of water** (by estimating **Ca^{+2} and Mg^{+2} ions**.
    - **Ammonium Thiocyanate (NH_4SCN):**
      - Used for the detection of **Co^{+2} ions**, as it produces a **deep blue colour** due to the formation of $[Co(SCN)_4]^{-2}$.

- **Extraction and Purification of Metals**
  - **Cyanide Process (or MacArthur-Forrest process):**
    - Metals like **Au and Ag** are extracted and purified from their ores by forming **soluble cyanide complexes**. The precious metal is recovered from the clear solution by adding Zinc dust.
      - Step-1 : $Ag_2S + 4\,NaCN \longrightarrow 2\,Na[Ag(CN)_2] + Na_2S$
        Step-2 : $2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag$
  - **Mond's Process:**
    - Purification of **Nickel** by forming the volatile **Nickel tetracarbonyl** $[Ni(CO)_4]$ complex, which **decomposes easily** upon heating (450 – 470 K) to **yield pure nickel**.
      - Step-1 : $Ni/Impurity + 4CO \longrightarrow [Ni(CO)_4] + Impurity$
        Step-2 : $[Ni(CO)_4] \xrightarrow{450-470\ K} Ni + 4CO$

- **In Biological Systems**
  - Coordination complexes are the backbone of many vital life processes:
    - **Chlorophyll:**
      - The green pigment in plants responsible for photosynthesis; it is a coordination complex of **Magnesium (Mg^{+2})**.
    - **Haemoglobin:**
      - The oxygen-carrier in red blood cells; it is a coordination complex of **Iron (Fe^{+2})**.
    - **Vitamin B_{12} (Cyanocobalamin):**
      - The anti-pernicious anaemia factor; it is a coordination complex of **Cobalt (Co^{+3})**.
    - **Enzymes**
      - **Carboxypeptidase A** contains a **Zn^{+2}** center and is essential for protein digestion.
      - **Carbonic Anhydrase** contains a **Zn^{+2}** center that catalyzes the rapid interconversion of CO_2 and water in the blood.

- **As Industrial Catalysts**
  - **Wilkinson's Catalyst:** $[RhCl(PPh_3)_3]$ – Chloridotris(triphenylphosphine)rhodium(I)
    - It is used as a homogeneous catalyst for the **hydrogenation of alkenes**.

- **In Electroplating**
  - Complexes like **$Na[Ag(CN)_2]$** and **$Na[Au(CN)_2]$** are used in electroplating baths.
  - They provide a **controlled, slow supply** of metal ions, resulting in a **smoother and more even coating** of silver or gold compared to using simple metal salts.

- **In Photography**
  - In black-and-white photography, the "**fixing**" step involves removing unexposed **silver bromide** (**AgBr**) from the film using **Sodium thiosulfate**.
    - $AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

- **In the Medical Field (Chelation Therapy)**
  - **EDTA:**
    - Used to treat **lead poisoning** by forming a stable, soluble complex with lead that is excreted from the body.
  - **Cis-platin ($cis–[Pt(NH_3)_2Cl_2]$):**
    - A highly effective drug used in **chemotherapy** to inhibit the growth of **tumors** (**cancer**).
  - **Specific Chelators:**
    - **D-penicillamine:** Used to remove excess **Copper** (**Wilson's disease**).
    - **Desferrioxamine B:** Used to remove excess **Iron** from the system.

NCERT : Intext Questions

1. Write the formulas for the following coordination compounds:
   a. Tetraamminediaquacobalt(III) chloride
   b. Potassium tetracyanidonickelate(II)
   c. Tris(ethane–1,2–diamine) chromium(III) chloride
   d. Amminebromidochloridonitrito-N-platinate(II)
   e. Dichloridobis(ethane–1,2–diamine)platinum(IV) nitrate
   f. Iron(III) hexacyanidoferrate(II)
2. Write the IUPAC names of the following coordination compounds:
   a. $[Co(NH_3)_6]Cl_3$
   b. $[Co(NH_3)_5Cl]Cl_2$
   c. $K_3[Fe(CN)_6]$
   d. $K_3[Fe(C_2O_4)_3]$
   e. $K_2[PdCl_4]$
   f. $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$
3. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:
   a. $K[Cr(H_2O)_2(C_2O_4)_2$
   b. $[Co(en)_3]Cl_3$
   c. $[Co(NH_3)_5(NO_2)](NO_3)_2$
   d. $[Pt(NH_3)(H_2O)Cl_2]$
4. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$ are ionisation isomers.
5. Explain on the basis of valence bond theory that $[Ni(CN)_4]^{-2}$ ion with square planar structure is diamagnetic and the $[NiCl_4]^{-2}$ ion with tetrahedral geometry is paramagnetic.
6. $[NiCl_4]^{-2}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?
7. $[Fe(H_2O)_6]^{+3}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{-3}$ is weakly paramagnetic. Explain.
8. Explain $[Co(NH_3)_6]^{+3}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{+2}$ is an outer orbital complex.
9. Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{-2}$ ion.
10. The hexaquamanganese(II) ion contains five unpaired electrons, while the hexacyanoion contains only one unpaired electron. Explain using Crystal Field Theory.

NCERT : Exercise Questions

1. Explain the bonding in coordination compounds in terms of Werner's postulates.
2. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{+2} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu^{+2} ion. Explain why?
3. Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.
4. What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.
5. Specify the oxidation numbers of the metals in the following coordination entities:
   a. $[Co(H_2O)(CN)(en)_2]^{+2}$
   b. $[PtCl_4]^{-2}$
   c. $[Cr(NH_3)_3Cl_3]$
   d. $[CoBr_2(en)_2]^{+1}$
   e. $K_3[Fe(CN)_6]$
6. Using IUPAC norms write the formulas for the following:
   a. Hexaamminecobalt(III) sulphate
   b. Potassium tetrachloridopalladate(II)
   c. Potassium tri(oxalato)chromate(III)
   d. Tetrahydroxidozincate(II)
   e. Diamminedichloridoplatinum(II)
   f. Hexaammineplatinum(IV)

g. Potassium tetracyanidonickelate(II)
h. Tetrabromidocuprate(II)
i. Pentaamminenitrito-O-cobalt(III)
j. Pentaamminenitrito-N-cobalt(III

7. Using IUPAC norms write the systematic names of the following:
   a. $[Co(NH_3)_6]Cl_3$
   b. $[Co(NH_3)_4Cl(NO_2)]Cl$
   c. $[Ni(NH_3)_6]Cl_2$
   d. $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$
   e. $[Mn(H_2O)_6]^{+2}$
   f. $[Co(en)_3]^{+3}$
   g. $[Ti(H_2O)_6]^{+3}$
   h. $[NiCl_4]^{-2}$
   i. $[Ni(CO)_4]$
8. List various types of isomerism possible for coordination compounds, giving an example of each.
9. How many geometrical isomers are possible in the following coordination entities?
   (i) $[Cr(C_2O_4)_3]^{-3}$ (ii) $[Co(NH_3)_3Cl_3]$
10. Draw the structures of optical isomers of:
    (i) $[Cr(C_2O_4)_3]^{-3}$ (ii) $[PtCl_2(en)_2]^{+2}$ (iii) $[Cr(NH_3)_2Cl_2(en)]^{+1}$
11. Draw all the isomers (geometrical and optical) of:
    (i) $[CoCl_2(en)_2]^{+2}$ (ii) $[Co(NH_3)Cl(en)_2]^{+2}$ (iii) $[Co(NH_3)_2Cl_2(en)]^{+1}$
12. Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?
13. Aqueous copper sulphate solution (blue in colour) gives:
    (i) a green precipitate with aqueous potassium fluoride and
    (ii) a bright green solution with aqueous potassium chloride. Explain these experimental results.
14. What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S_{(g)}$ is passed through this solution?
15. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:
    (i) $[Fe(CN)_6]^{-4}$ (ii) $[FeF_6]^{-3}$ (iii) $[Co(C_2O_4)_3]^{-3}$ (iv) $[CoF_6]^{-3}$
16. Draw figure to show the splitting of d orbitals in an octahedral crystal field.
17. What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.
18. What is crystal field splitting energy? How does the magnitude of Δo decide the actual configuration of d-orbitals in a coordination entity?
19. $[Cr(NH_3)_6]^{+3}$ is paramagnetic while $[Ni(CN)_4]^{-2}$ is diamagnetic. Explain why?
20. A solution of $[Ni(H_2O)_6]^{+2}$ is green but a solution of $[Ni(CN)_4]^{-2}$ is colourless. Explain.
21. $[Fe(CN)_6]^{-4}$ and $[Fe(H_2O)_6]^{+2}$ are of different colours in dilute solutions. Why?
22. Discuss the nature of bonding in metal carbonyls.
23. Give the oxidation state, d orbital occupation and coordination number of the central metal ion in the following complexes:
    a. $K_3[Co(C_2O_4)_3]$
    b. $(NH_4)_2[CoF_4]$
    c. cis-$[CrCl_2(en)_2]Cl$
    d. $[Mn(H_2O)_6]SO_4$
24. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:
    a. $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$
    b. $[CrCl_3(py)_3]$
    c. $K_4[Mn(CN)_6]$
    d. $[Co(NH_3)_5Cl]Cl_2$
    e. $Cs[FeCl_4]$
25. Explain the violet colour of the complex $[Ti(H_2O)_6]^{+3}$ on the basis of crystal field theory.
26. What is meant by the chelate effect? Give an example.

27. Discuss briefly giving an example in each case the role of coordination compounds in:
    a. biological systems
    b. analytical chemistry
    c. medicinal chemistry and
    d. extraction/metallurgy of metals.
28. How many ions are produced from the complex Co(NH3)6Cl2 in solution?
    (i) 6 (ii) 4 (iii) 3 (iv) 2
29. Amongst the following ions which one has the highest magnetic moment value?
    (i) $[Cr(H_2O)_6]^{+3}$ (ii) $[Fe(H_2O)_6]^{+2}$ (iii) $[Zn(H_2O)_6]^{+2}$
30. Amongst the following, the most stable complex is:
    (i) $[Fe(H_2O)6]^{+3}$ (ii) $[Fe(NH_3)_6]^{+3}$ (iii) $[Fe(C_2O_4)_3]^{-3}$ (iv) $[FeCl_6]^{-3}$
31. What will be the correct order for the wavelengths of absorption in the visible region for the following:
    (i) $[Ni(NO_2)_6]^{-4}$ (ii) $[Ni(NH_3)_6]^{+2}$ (iii) $[Ni(H_2O)_6]^{+2}$

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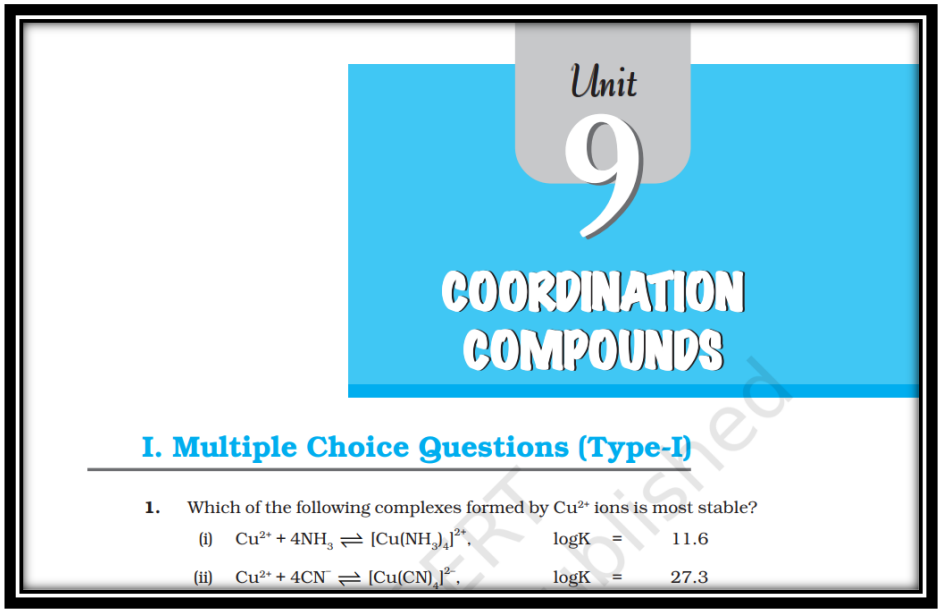
Unit
9
COORDINATION COMPOUNDS

I. Multiple Choice Questions (Type-I)

1. Which of the following complexes formed by Cu^{2+} ions is most stable?
(i) $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$, logK = 11.6
(ii) $Cu^{2+} + 4CN^- \rightleftharpoons [Cu(CN)_4]^{2-}$, logK = 27.3

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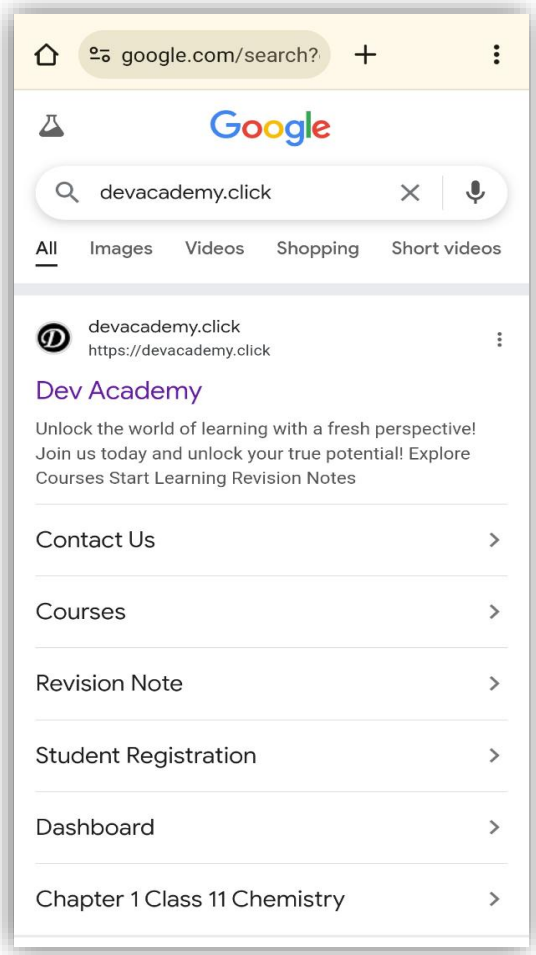

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