THE TRANSITION METALS

Transition Elements

When studying the periodic table, we come across a very important block in the center known as the **transition elements**. These elements possess unique chemical and physical properties, making them vital in everyday life.

- **Copper** is used in electrical wiring, coins, and plumbing.
- **Iron** is essential for bridges, vehicles, and construction.
- **Chromium** gives strength and shine to plumbing fixtures.
- **Gold and silver** are valuable in jewelry and electronics.
- **Platinum** is used in catalytic converters.
- **Titanium** finds applications in bicycles, aircraft, and artificial joints.
- **Nickel, vanadium, molybdenum, and tantalum** serve important industrial and medical purposes.

Transition elements also form **alloys**, such as:

- **Brass** (copper + zinc)
- **Bronze** (copper + tin)

Definition

Transition elements are those elements which have an **incomplete d-subshell** in their most stable ionic states. They are called "transition" elements because they represent a gradual change in properties, from the highly reactive **Group 2 elements** (like calcium) to the much less reactive **Group 13 elements** (like gallium).

First Transition Series

The **first row of transition elements** starts from **scandium (Sc)** and goes up to **zinc (Zn)**.

- **Zinc (Zn)** does not strictly qualify as a transition element because it forms only one ion (Zn^{2+}) with a **complete 3d subshell**, which shows none of the typical variable oxidation states or colored compounds.
  - Hence, zinc is a **d-block element but not a transition element**.
- **Scandium (Sc)** was initially debated for inclusion because its common **+3 oxidation state (Sc^{3+})** has an empty d-subshell. However, after the discovery of compounds in +1 and +2 oxidation states (such as $CsScCl_3$), IUPAC included it in the transition metals.

Focus of Study

In this chapter, we will mainly focus on the **first transition series**, the elements from **titanium (Ti)** through to **copper (Cu)**. To fully understand their distinct properties, we must first examine their **electronic configurations**, which form the foundation for their behavior.

Electronic Configurations of the d-Block Elements

The **electronic configuration** of transition metals generally follows the **Aufbau principle**, but there are a few important exceptions.

- **Chromium (Cr)** and **Copper (Cu)** do not follow the expected order.
  - Instead of $4s^2 3d^4$, chromium has **$4s^1 3d^5$**.
  - Instead of $4s^2 3d^9$, copper has **$4s^1 3d^{10}$**.

Reason: Atoms or ions with **half-filled ($3d^5$)** or **completely filled ($3d^{10}$)** d-subshells are relatively more stable.

- This happens because:
  - The electron cloud is **symmetrical**, giving better shielding.
  - It reduces **electron–electron repulsion** in the 4s orbital.

Key Information

- When forming **cations**, electrons are always removed **first from the 4s orbital** (higher energy) before the 3d orbital.

Electronic Configurations of First-Row Transition Metals

Element	Ground State Configuration	Common Ion(s)	Ion Configuration
Scandium (Sc)	[Ar] $3d^1\ 4s^2$	Sc^+	[Ar] $3d^1\ 4s^1$
		Sc^{2+}	[Ar] $3d^1$
Titanium (Ti)	[Ar] $3d^2\ 4s^2$	Ti^{2+}	[Ar] $3d^2$
Vanadium (V)	[Ar] $3d^3\ 4s^2$	V^{4+}	[Ar] $3d^1$
Chromium (Cr)	[Ar] $3d^5\ 4s^1$	Cr^{2+}	[Ar] $3d^4$
		Cr^{3+}	[Ar] $3d^3$
Manganese (Mn)	[Ar] $3d^5\ 4s^2$	Mn^{2+}	[Ar] $3d^5$
Iron (Fe)	[Ar] $3d^6\ 4s^2$	Fe^{2+}	[Ar] $3d^6$
		Fe^{3+}	[Ar] $3d^5$
Cobalt (Co)	[Ar] $3d^7\ 4s^2$	Co^{2+}	[Ar] $3d^7$
Nickel (Ni)	[Ar] $3d^8\ 4s^2$	Ni^{2+}	[Ar] $3d^8$
Copper (Cu)	[Ar] $3d^{10}\ 4s^1$	Cu^+	[Ar] $3d^{10}$
		Cu^{2+}	[Ar] $3d^9$
Zinc (Zn)	[Ar] $3d^{10}\ 4s^2$	Zn^{2+}	[Ar] $3d^{10}$

Notice:

- **Scandium (Sc^{3+})** → loses all outer electrons → no d-electrons left.
- **Zinc (Zn^{2+})** → full 3d subshell → does not show transition metal properties.
- **Cr and Cu** → exceptions due to stability of half-filled or full-filled d orbitals.

Physical Properties of Transition Elements

Transition metals exhibit several unique physical properties that distinguish them from other elements of the periodic table.

Key Properties

1. **High Melting and Boiling Points**
   - Due to strong **metallic bonding** (delocalized electrons strongly attracted to positive metal ions).
2. **High Density**
   - Atoms are **closely packed** in metallic lattices, leading to heavy and compact structures.
3. **Good Conductors of Electricity**
   - Presence of **mobile (delocalized) electrons** allows easy flow of electric current.
4. **Good Thermal Conductors**
   - Free electrons also transfer heat efficiently.
5. **Metallic Luster**
   - Shiny appearance, especially when freshly polished.
6. **Malleable and Ductile**
   - Can be hammered into thin sheets or drawn into wires without breaking.
7. **Hard and Strong**
   - This makes them suitable for **construction, tools, machinery, and manufacturing**.
8. **Magnetic Properties**
   - Many transition metals show **paramagnetism** (weakly attracted by a magnetic field) due to unpaired d-electrons.
   - Some (like Fe, Co, Ni) show **ferromagnetism** (strong permanent magnetism).

Physical Characteristics of First-Row Transition Metals

Transition metals (Sc → Zn) exhibit unique physical properties due to their **partially filled d-orbitals**, strong **metallic bonding**, and ability to form **alloys**.

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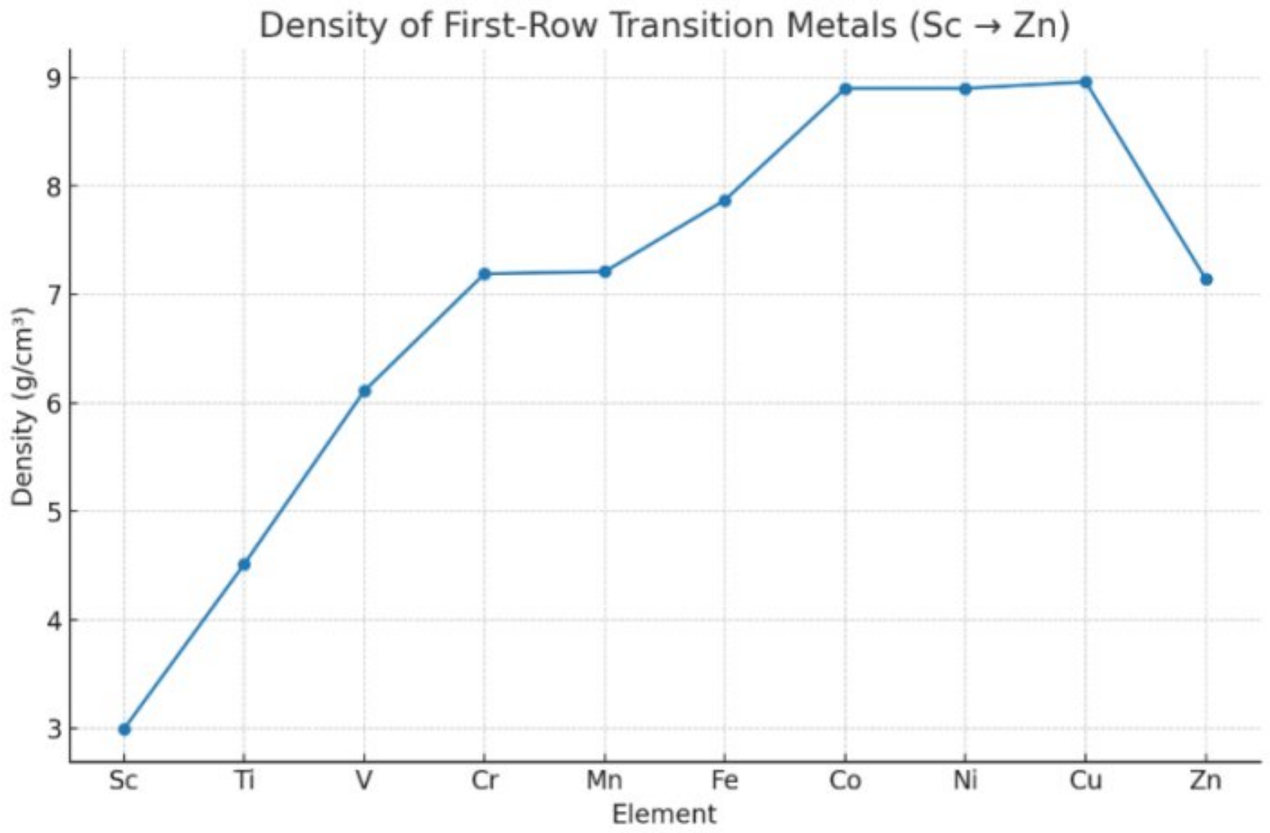
1. Density

- **Definition:** Density is the mass per unit volume, expressed in **g/cm^3**.
- **Trend across Sc → Cu:**
  - **Density increases** across the series because:
    1. **Atomic mass increases** → nuclei become heavier.

2. **Atomic radius decreases** → due to increasing nuclear charge pulling electrons closer.
   - Since density = mass ÷ volume, both factors combine to give higher densities.

- **Exceptions:**
  - **Manganese (Mn)** and **Copper (Cu)** show irregular densities due to electronic stability.
  - **Zinc (Zn)** has **larger atomic radius** (due to completely filled $3d^{10}$ subshell and less tight packing), leading to **reduced density** compared to copper.



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2. Atomic Radii

- **General trend:** Radii **decrease** across Sc → Ni due to increasing nuclear charge.
- **Special notes:**
  - Decrease is **less steep** than in main group elements, because added 3d electrons **do not shield each other effectively**.
  - At the **middle of the series**: nuclear attraction and shielding balance out → atomic radius remains nearly **constant**.
  - From **Ni → Cu → Zn**: radii **increase slightly**.
    - **Copper**: 3d subshell becomes full, increasing shielding of 4s orbital.
    - **Zinc**: extra electron in 4s increases shielding, so its radius is **larger than Cu**.

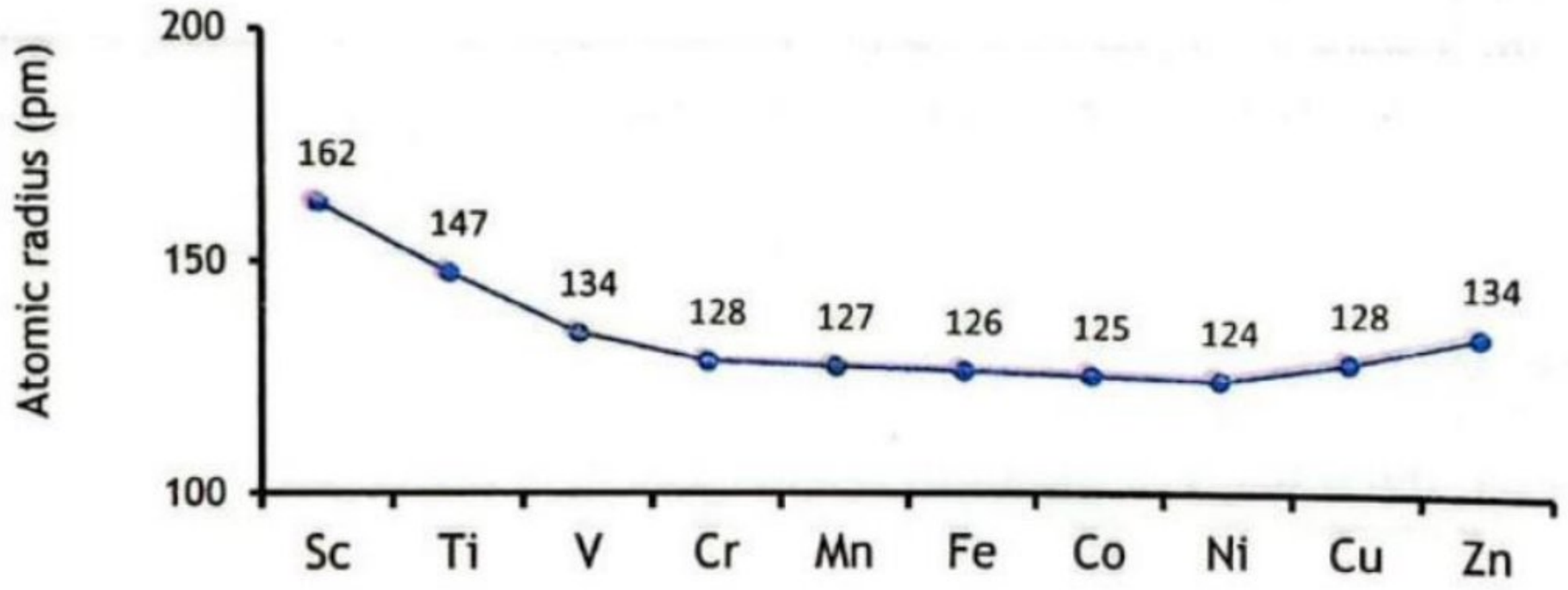

Fig 6.1: Atomic radii of first row transition metals

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3. Melting and Boiling Points

- Transition metals have **very high melting and boiling points** compared to s- and p-block elements.
- **Reason:** Strong metallic bonding, involving both **3d and 4s electrons**.
- **Trend across the series:**
  - Increases initially as metallic bonding strengthens.
  - **Manganese (Mn):** shows a **minimum** due to half-filled stability ($3d^5$, $4s^2$ → fewer electrons available for bonding).
  - **Zinc (Zn):** lowest melting and boiling points because its **full $3d^{10}$ and $4s^2$ subshells** cannot contribute to metallic bonding.
  - **Mercury (Hg):** in zinc's family → extremely weak bonding → liquid at room temperature.

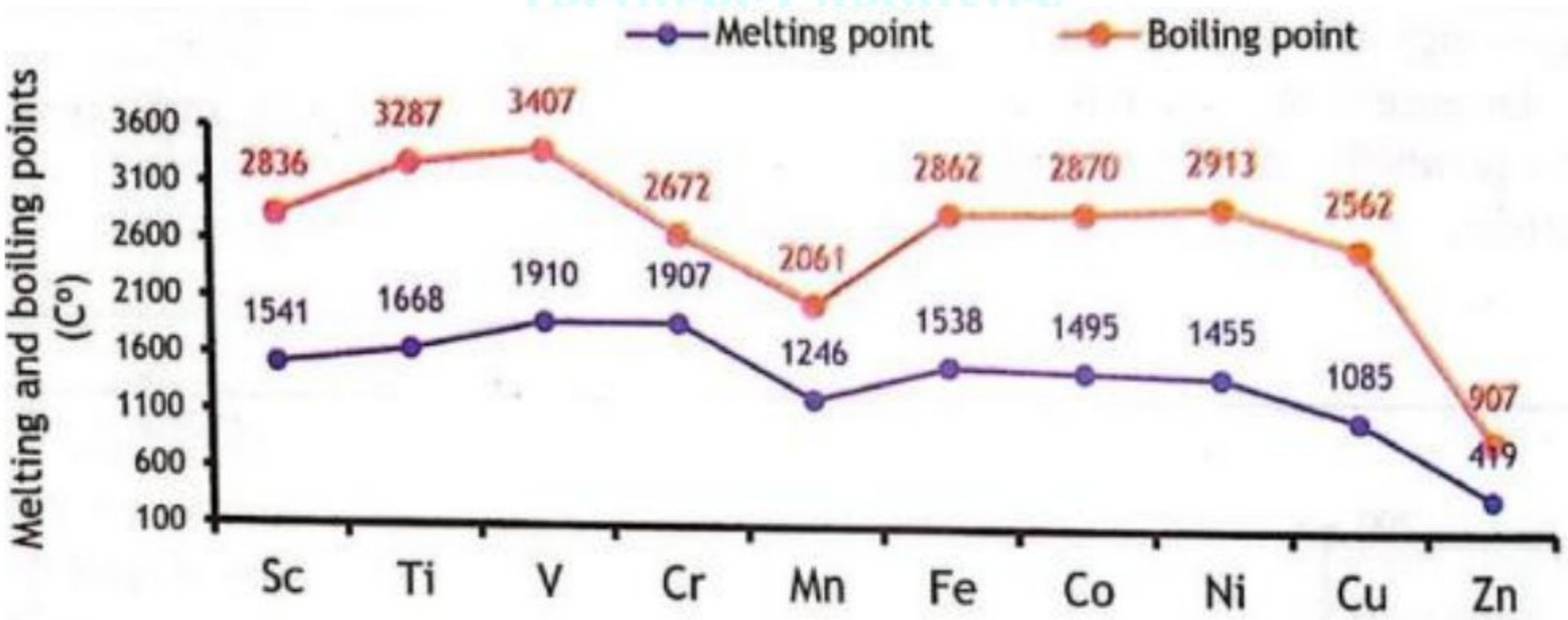

Fig 6.2: Melting and boiling points of transition metals

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4. Magnetic Properties

Transition metals show three types of magnetism depending on their electron configurations:

- **(a) Paramagnetism**
  - Weak attraction in a magnetic field.
  - Caused by **unpaired electrons** with random alignment.
  - Example: Mn^{2+}, Fe^{2+}.
  - Effect disappears when the field is removed.
- **(b) Ferromagnetism**
  - **Very strong attraction** (up to a million times stronger than paramagnetism).
  - Unpaired electrons are **aligned in the same direction** due to interactions with neighboring atoms.
  - Permanent magnets retain magnetism even after field removal.
  - Examples: **Fe, Co, Ni**.
- **(c) Diamagnetism**
  - Weak repulsion by a magnet.
  - Occurs in atoms/ions with **all paired electrons**.
  - Example: **Cu, Zn**.

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5. Alloy Formation

- **Reason:** Transition metals have **similar atomic radii** → atoms can substitute for one another in metallic lattices.
- **Result:** Alloys often have **improved hardness, resistance to corrosion, and durability** compared to pure metals.

Examples:

- **Steel** = alloy of Fe, Cr, Ni, Mn (strong, corrosion-resistant).
- **Brass** = Cu + Zn (hard, shiny, corrosion-resistant).
- **Bronze** = Cu + Sn (tough, used historically for weapons and tools).

Chemical Properties of First Row Transition Metals

Unlike their **physical properties**, the **chemical properties** of transition metals do not show a simple uniform pattern across the series. Some of the most important chemical properties are given below:

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1. Variable Oxidation States

- A **characteristic feature** of transition metals is the exhibition of **variable oxidation states**.
- **Reason:** Both 4s and 3d electrons have comparable energies and can participate in bonding.

- The **common oxidation state** for most first-row transition metals is **+2**, arising from the loss of two 4s electrons ($M \rightarrow M^{2+}$).
- The **maximum stable oxidation state** generally corresponds to the total number of available valence (3d + 4s) electrons.
    - Example: **Manganese** ([Ar] $3d^5 4s^2$) can achieve a maximum oxidation state of **+7** (as in MnO_4^-).

Did You Know?

- Simple ions of transition metals (e.g., Mn^{2+}) usually exist in **lower oxidation states**.
- Complex ions (e.g., MnO_4^-) are often more stable in **higher oxidation states**.

Oxidation States of First Row Transition Metals

Element	Common Oxidation States
Scandium (Sc)	+3
Titanium (Ti)	+2, +3, +4
Vanadium (V)	+2, +3, +4, +5
Chromium (Cr)	+2, +3, +6
Manganese (Mn)	+2, +3, +4, +6, +7
Iron (Fe)	+2, +3
Cobalt (Co)	+2, +3
Nickel (Ni)	+2, +3
Copper (Cu)	+1, +2
Zinc (Zn)	+2 (only)

Trends in Oxidation State Stability

- **+2 state stability increases** across the series from Sc → Zn
  → because removal of 3d electrons becomes progressively more difficult.
- **Higher oxidation states stability decreases** from left → right
  → due to increasing nuclear charge and reluctance of later elements to lose 3d electrons.
- **Special cases:**
    - Mn^{2+} is more stable than Mn^{3+} due to **half-filled $3d^5$ stability**.
    - Fe^{3+} is more stable than Fe^{2+} due to the same reason (half-filled $3d^5$ subshell).

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2. Catalytic Activity

Transition metals and their compounds act as **excellent catalysts** in many chemical reactions.

Reasons for Catalytic Activity

1. They can exist in **multiple oxidation states**, allowing them to gain/lose electrons during reactions.

2. They have **vacant d-orbitals** that can form **temporary dative bonds** with reactant molecules (ligands).

This enables:

- **Adsorption** of reactants on the catalyst surface.
- **Weakening of reactant bonds** → easier bond breaking.
- **Product formation** on the surface, which is then released.
- The metal is regenerated, ready to catalyze another cycle.

Examples of Catalysis

Heterogeneous Catalysis

(catalyst and reactants in different phases)

- **Haber Process:** Iron (Fe) catalyst → adsorbs N_2 and H_2, speeding up ammonia formation.
- **Contact Process:** Vanadium(V) oxide (V_2O_5) catalyst → undergoes reversible change between V^{5+} and V^{4+} in SO_2 oxidation to SO_3.

Homogeneous Catalysis

(catalyst and reactants in the same phase)

- Example: **Oxidation of iodide (I^-)** by peroxodisulphate ($S_2O_8^{2-}$):

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

  - Slow because both are negatively charged ions (repulsion).
  - Addition of Fe^{2+} catalyst speeds up the reaction:

Step 1:

$$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$$

Step 2:

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$

  - Here $Fe^{2+} \rightleftharpoons Fe^{3+}$ cycle provides a **fast-alternate pathway** involving attraction between oppositely charged ions.

Ligands

- Definition:
  A ligand is an atom, ion, or molecule that is electron-rich and can donate a lone pair of electrons to a transition metal ion.
- Bonding:
  The bond formed is a coordinate (dative covalent) bond.
- Nature:
  - Act as Lewis bases (electron-pair donors).
  - Also called nucleophiles.

Key Concept

- When ligands approach a transition metal ion, they cause splitting of the d-orbitals of the metal atom.

Types of Ligands

1. **Monodentate Ligands (one-toothed)**
   - Can form only one coordinate bond with the central metal atom/ion.
   - Even if they have more than one lone pair, they can donate only one pair at a time.
   - Examples:
     - Aqua (H_2O)
     - Ammine (NH_3)
     - Hydroxo (OH^-)
     - Halo (Cl^-, Br^-, I^-, F^-)
     - Cyano (CN^-)

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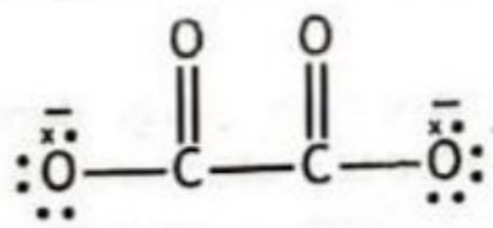
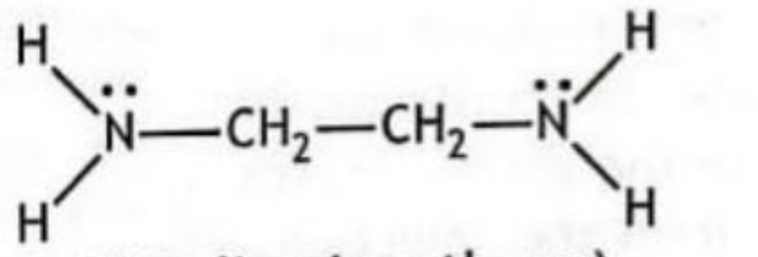
2. **Polydentate Ligands (many-toothed)**
   - Can form two or more coordinate bonds with the central metal ion at the same time.
   - Bidentate Ligands (two-toothed):
     - Can form two bonds with the metal ion.
     - Examples:
       - Ethane-1,2-diamine ($NH_2–CH_2–CH_2–NH_2$)
       - Oxalate ion ($C_2O_4^{2-}$ or $(COO)_2^{2-}$)

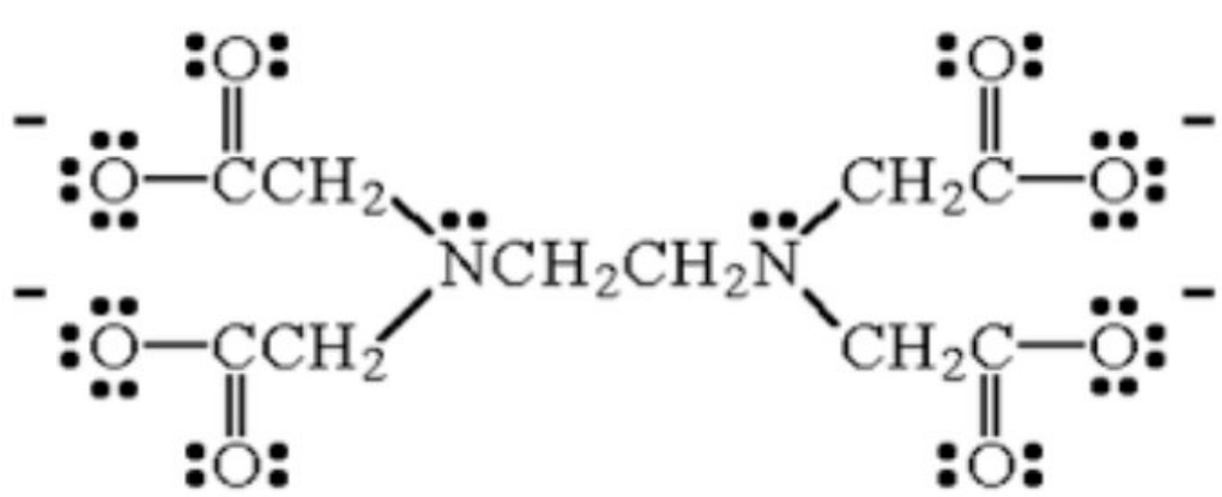


(ethanedioate)
oxalato



(1,2-diaminoethane)
ethylenediammine (en)

- Hexadentate Ligand (six-toothed):
  - Can donate six lone pairs to the central metal ion.
  - Example:
    - EDTA (ethylenediaminetetraacetic acid)



Formation of Complex Compounds

A complex compound (or coordination compound) is formed when transition metals bond with ligands.

- Ligands are ions or molecules that donate a lone pair of electrons to the central transition metal ion.
- The transition metal ion accepts the electron pair into its vacant orbitals.
- Thus:
  - **Ligand** = *Lewis base* (electron pair donor)
  - **Transition metal ion** = *Lewis acid* (electron pair acceptor)

Complex compounds may be positive, negative, or neutral.

Why Transition Metals Form Complexes

1. Small size and high charge density → They strongly attract ligands.
2. Presence of 3d sub-shell → It has relatively low energy and can overlap with the p-orbitals of ligands easily.

Process of Complex Formation

1. Transition metals lose electrons → They become cations.
2. The metal ion has vacant d-orbitals that undergo hybridization to form new orbitals of equal energy.
3. Ligands donate electron pairs into these hybridized vacant orbitals → forming coordinate covalent bonds (dative bonds).
4. The first-row transition metals (Sc to Cu) have accessible, low-energy 3d orbitals → ligands can easily donate their lone pairs, resulting in stable complex ions.

i. Complexes of Copper(II) with Water and Chloride Ligands

- **Copper(II) ion (Cu^{2+})**
  Electronic configuration:

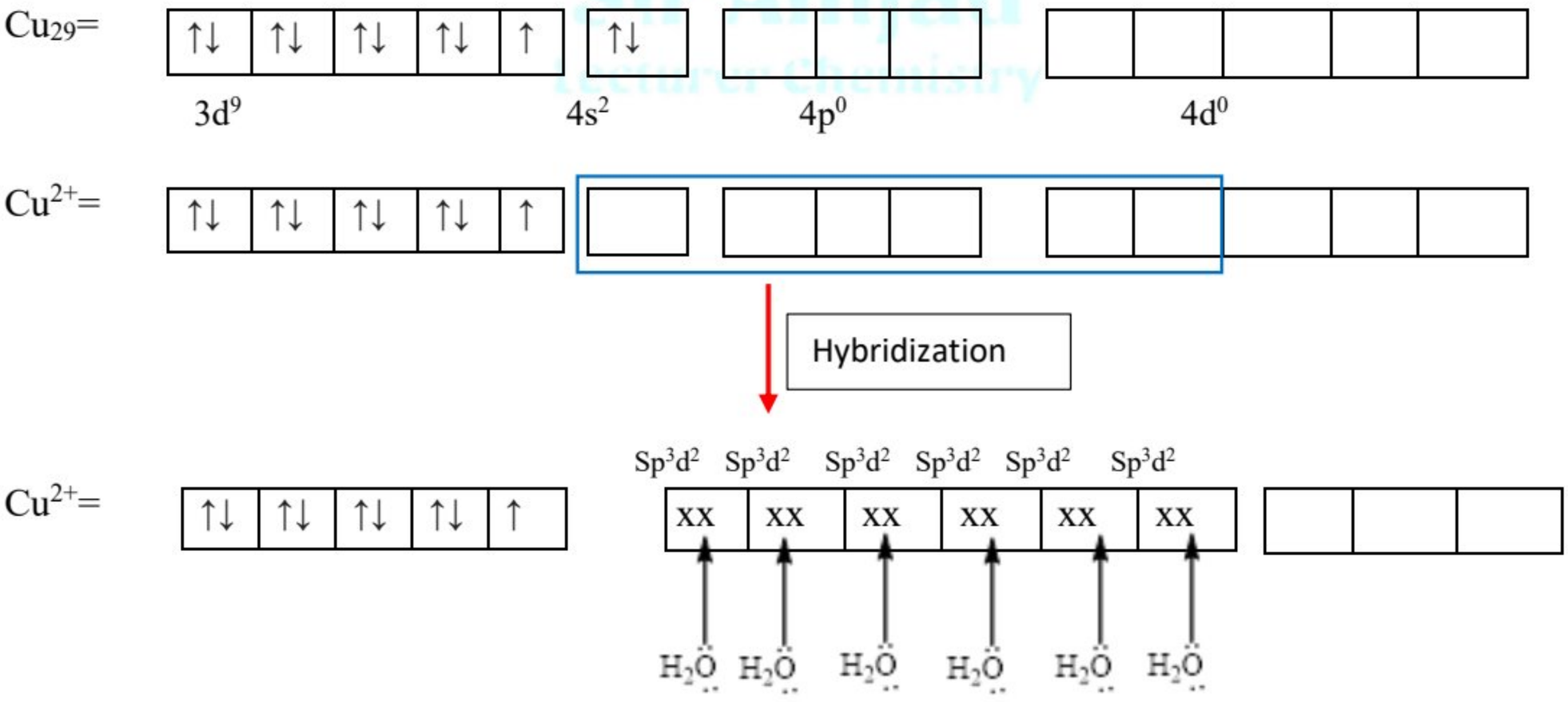
$$\text{Cu atom: [Ar] } 3d^{10}4s^{1}$$

After losing 2 electrons (to form Cu^{2+}):

$$Cu^{2+}: [Ar]3d^{9}$$

Formation with Water Ligands

1. In aqueous solution, six water molecules (H_2O) approach the Cu^{2+} ion.
2. Each water molecule donates a lone pair of electrons from its oxygen atom to Cu^{2+}.
3. Before bonding, the copper ion undergoes hybridization:
   - It mixes one 4s orbital, three 4p orbitals, and two 4d orbitals.
   - This gives six sp^3d^2 hybrid orbitals of equal energy.
4. Each of the six hybrid orbitals accepts one lone pair from six water molecules → forming $[Cu(H_2O)_6]^{2+}$, an octahedral complex.



Formation with Chloride Ligands

- If chloride ions (Cl^-) replace some water ligands:
  - 4 Cl^- ions can coordinate with Cu^{2+}, forming $[CuCl_4]^{2-}$.
  - Here the hybridization is sp^3 → giving a tetrahedral complex.
- This shows that copper(II) can form complexes of different shapes depending on the nature of the ligands.
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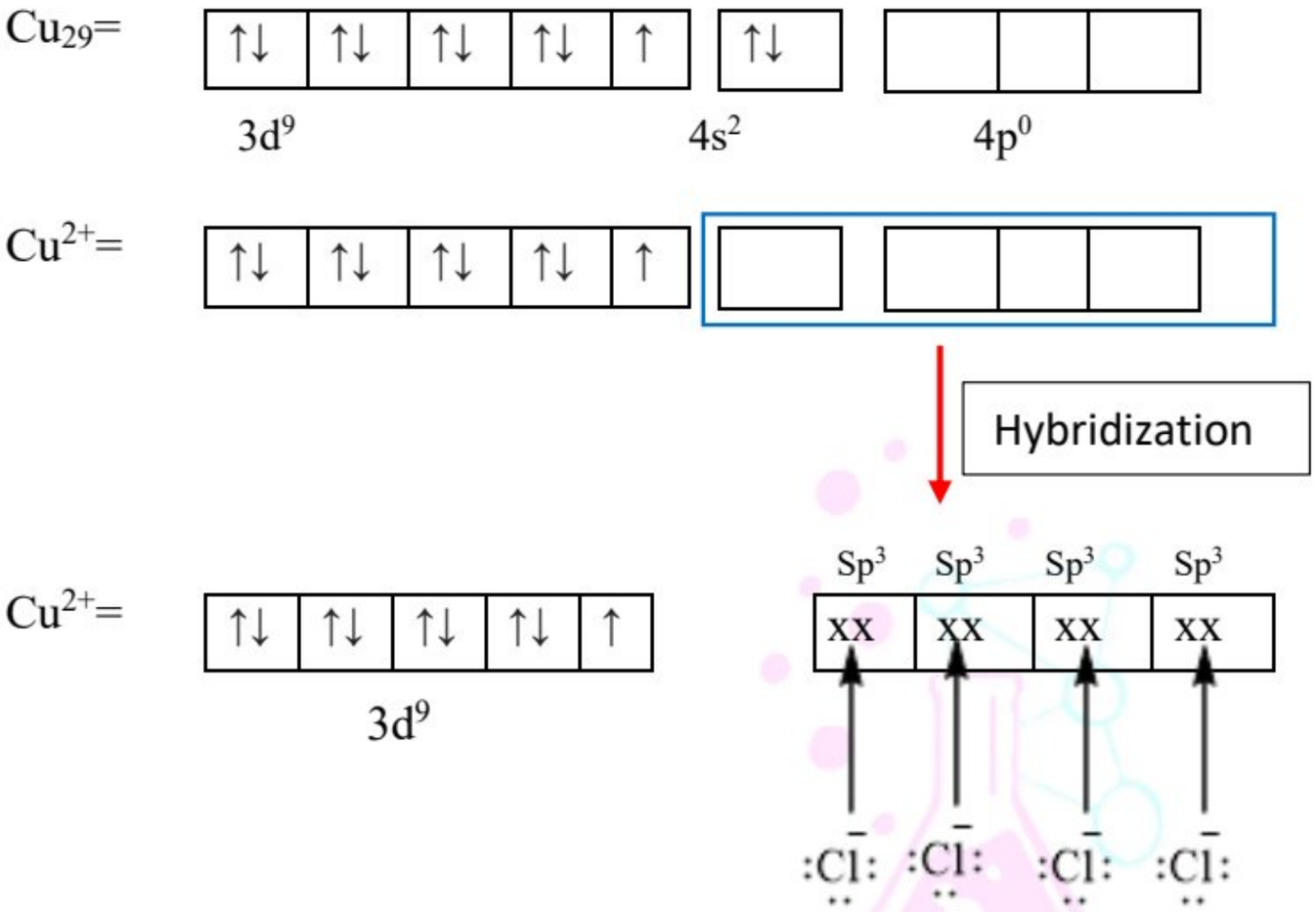

With chloride ligands, copper(II) forms tetrahedral complex, tetrachlorocuprate(II) ion, because chloride is a big ligands and six chloride ligands cannot surround a small copper(Il) ion.

Do You Know?

- Transition metal ions like **Cu^{2+}** have **small size** and **high charge density**.
- This makes them **highly polarizing** compared to s-block cations (like Na^+, K^+, Ca^{2+}).
- Because of this, ligands are strongly attracted, and stable complexes are easily formed.

ii. Complexes of Cobalt(II) Ion with Water and Chloride Ligands

- **Cobalt atom (Co):**
  Electronic configuration = [Ar] $3d^7$ $4s^2$
- **Cobalt(II) ion (Co^{2+}):**
  After losing two 4s electrons:

$$Co^{2+}: [Ar]3d^7$$

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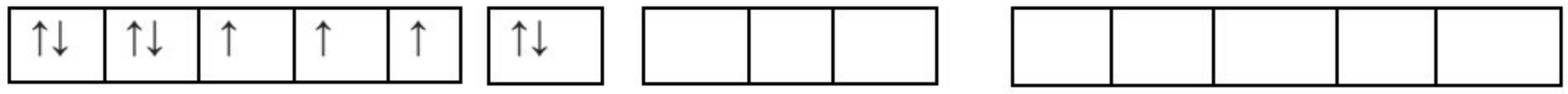
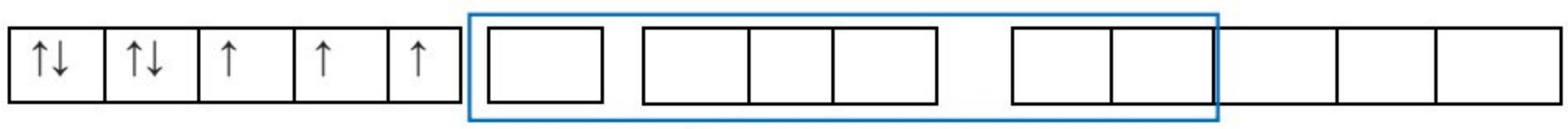
1. Complex with Water Ligands

- In aqueous solution, **six water molecules (H_2O)** approach the **Co^{2+} ion**.
- Each water ligand donates a **lone pair of electrons** from oxygen to vacant orbitals of Co^{2+}.
- Before bonding, the metal ion undergoes **hybridization**:
  - It mixes **one 4s orbital, three 4p orbitals, and two 4d orbitals**.
  - This produces **six sp^3d^2 hybrid orbitals**.
- The six orbitals then accept electron pairs from six H_2O ligands, forming the **$[Co(H_2O)_6]^{2+}$** complex.
- Geometry: **Octahedral**

Co_{29}=

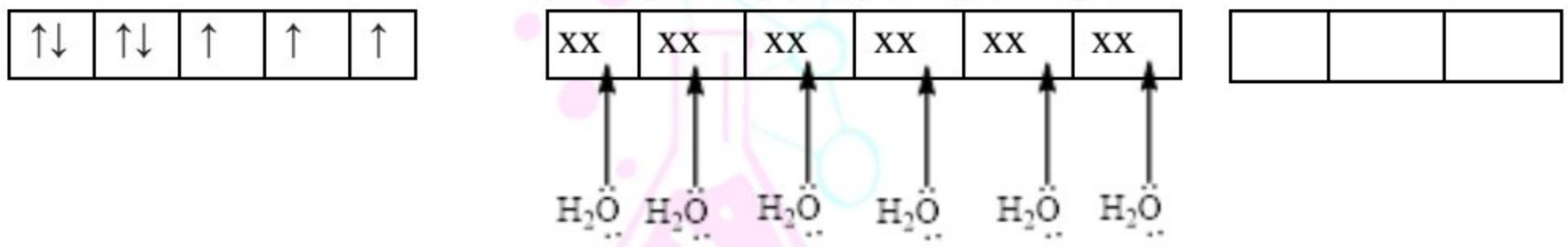


Co^{2+}=



Hybridization

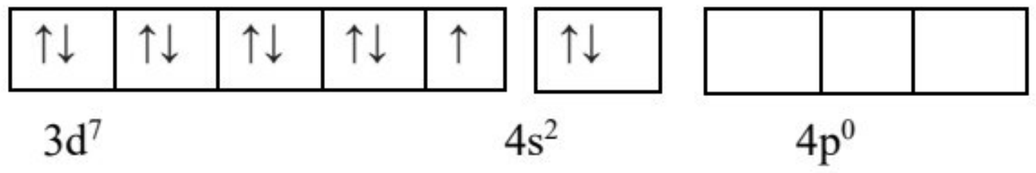
Co^{2+}=



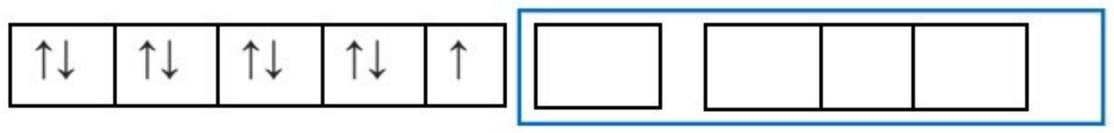
2. Complex with Chloride Ligands

- Chloride ions (Cl^-) are larger ligands compared to water molecules.
- Due to **steric hindrance**, only **four chloride ligands** coordinate with Co^{2+}.
- Hybridization: **sp^3** → forms **$[CoCl_4]^{2-}$**
- Geometry: **Tetrahedral**

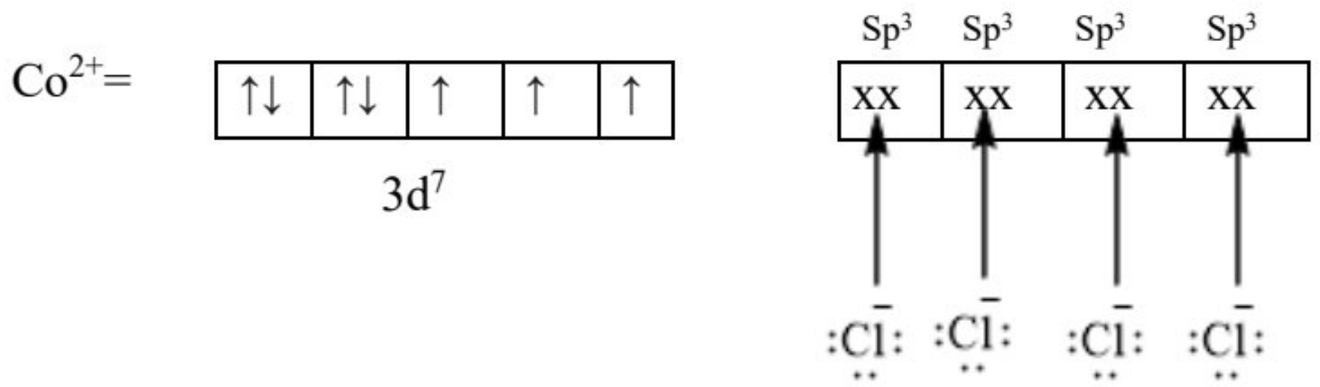
Cu_{29}=



Co^{2+}=



Hybridization



Terminology of Complex Compounds

1. Coordination Number

- **Definition:** The number of **coordinate covalent bonds** formed between the central metal ion and ligands.
- Common coordination numbers = **4 and 6** (but 2 also exists).

Examples:

- $[Cu(NH3)4]2+ \rightarrow$ coordination number = **4**
- $[Ni(CO)_4] \rightarrow$ coordination number = **4**
- $Na_4[Fe(CN)_6] \rightarrow$ coordination number = **6**
- $[Co(NO^2)^3(NH^3)^3] \rightarrow$ coordination number = **6**

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2. Coordination Sphere

- **Definition:** The central atom/ion **together with its attached ligands**, written inside **square brackets [ ]**.
- The coordination sphere may be:
  - **Anionic** (overall negative)
  - **Cationic** (overall positive)
  - **Neutral** (no overall charge)

Examples:

- $K4[Fe(CN)6] \rightarrow$ anionic coordination sphere
- $[Fe(CN)_6]^{4-}$
- $[Cu(NH3)4]SO4 \rightarrow$ cationic coordination sphere
- $[Cu(NH3)4]2+$
- $[Ni(CO)_4] \rightarrow$ neutral coordination sphere

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3. Charge on Coordination Sphere

- **Definition:** The algebraic sum of:

- Charge on central transition metal ion
- Charges on all ligands

Examples:

i. $Na_4[Fe(CN)_6]$

- Oxidation state of Fe = **+2**
- Charge on 6 cyanide ligands = $6 \times -1 = -6$
- Charge on coordination sphere = $+2+(-6)=-4$

ii. $[Cu(NH_3)_4]SO_4$

- Oxidation state of Cu = **+2**
- Charge on 4 NH_3 ligands = 0 (neutral ligand)
- Charge on coordination sphere = $+2+0=+2$

Rules for Naming Complex Compounds (IUPAC)

1. **Cation before Anion**
   - Name the cation first, then the anion, whether simple or complex.
   - Example: $[Cr(H_2O)_6]Cl_3$ → *Hexaaquachromium(III) chloride*
2. **Inside the Coordination Sphere**
   - Ligands are named **before** the central metal atom.
   - Ligands are listed in **alphabetical order**, ignoring prefixes like di-, tri-, etc.
   - Example: $[Pt(NH_3)_4BrCl]Cl_2$ → *Tetraamminebromochloroplatinum(IV) chloride*
3. **Suffix for Metals**
   - If the complex ion is **anionic**, add suffix **"-ate"** to the metal name.
   - Special names: Iron → *ferrate*, Copper → *cuprate*, Silver → *argentate*.
   - Example: $K_4[Fe(CN)_6]$ → *Potassium hexacyanoferrate(II)*
4. **Prefixes for Number of Ligands**
   - Mono, di, tri, tetra, penta, hexa… (for simple ligands).
   - For **polydentate ligands** or ligands with prefixes, use **bis, tris, tetrakis** etc.
   - Example: $[Cr(en)_2Cl_2]Cl$ → *Dichlorobis(ethylenediamine)chromium(III) chloride*
5. **Anionic Ligands**
   - End with **"-o"**:
     - Cl^- → chloro,
     - OH^- → hydroxo,
     - CO_3^{2-} → carbonato,
     - CN^- → cyano.
6. **Neutral Ligands**
   - Usually keep their names:
     - H_2O → *aqua*,
     - NH_3 → *ammine*,
     - CO → *carbonyl*.
7. **Oxidation State**
   - Written in **Roman numerals** in brackets after the metal.

- Example: $[Ni(CO)_4]$ → *Tetracarbonylnickel(0)*

8. **Counter Ions**
   - Counter ions (outside the square bracket) are named **normally** and **not counted as ligands**.

Worked Examples

1. **$[Pt(NH_3)_4BrCl]Cl_2$**
   - Ligands: 4 × NH_3 (*tetraammine*), Br (*bromo*), Cl (*chloro*)
   - Central metal: Pt (oxidation state +4)
   - Anion outside: Cl– → "chloride"

   Tetraamminebromochloroplatinum(IV) chloride
2. **$[Cu(NH_3)_2]^{2+}$**
   - Ligands: 2 × NH_3 (*diammine*)
   - Metal: Copper (oxidation state +2)

   Diamminecopper(II) ion
3. **$K_4[Fe(CN)_6]$**
   - Metal in anionic complex → "ferrate"
   - Ligands: 6 × CN (*hexacyano*)
   - Metal oxidation: Fe = +2

   Potassium hexacyanoferrate(II)
4. **$[Cr(H_2O)_6]Cl_3$**
   - Ligands: 6 × H2O (*hexaaqua*)
   - Metal: Chromium (oxidation +3)

   Hexaaquachromium(III) chloride
5. **$[Ni(CO)_4]$**
   - Ligands: 4 × CO (*tetracarbonyl*)
   - Metal: Ni (oxidation 0)

   Tetracarbonylnickel(0)
6. **$[Co(NO_2)_3(NH_3)_3]$**
   - Ligands: 3 × NO_2 (*trinitro*), 3 × NH_3 (*triamine*)
   - Metal: Co (+3)

   Triamminetrinitrocobalt(III)
7. **$[Cr(en)_2Cl_2]Cl$**
   - Ligands: 2 × en (ethylenediamine → *bis(ethylenediamine)*), 2 × Cl (*dichloro*)
   - Metal: Cr (+3)

   Dichlorobis(ethylenediamine)chromium(III) chloride
8. **$K_2[PtCl_6]$**
   - Metal: Pt in anionic complex → *platinate*
   - Ligands: 6 × Cl (*hexachloro*)
   - Oxidation: Pt = +4

   Potassium hexachloroplatinate(IV)

Coloured Complexes

1. Absorption of White Light

- When **white light** passes through a transition metal complex (in solid or solution):
  - If **all light is absorbed** → compound looks **black**.
  - If **some light is absorbed, some transmitted** → compound looks **coloured**.
  - If **all light is reflected** → compound looks **white**.

---

2. Role of d-Orbitals

- Transition metal ions are coloured because they **absorb part of visible light**.
- **Condition:** The metal ion must have an **incomplete 3d sub-shell**.
  - Example: **Cu^{2+}** ($[Ar]3d^9$) → coloured (incomplete d-orbital).
  - Example: **Zn^{2+}** ($[Ar]3d^{10}$) → colourless (complete d-orbital).

---

3. Degeneracy of d-Orbitals

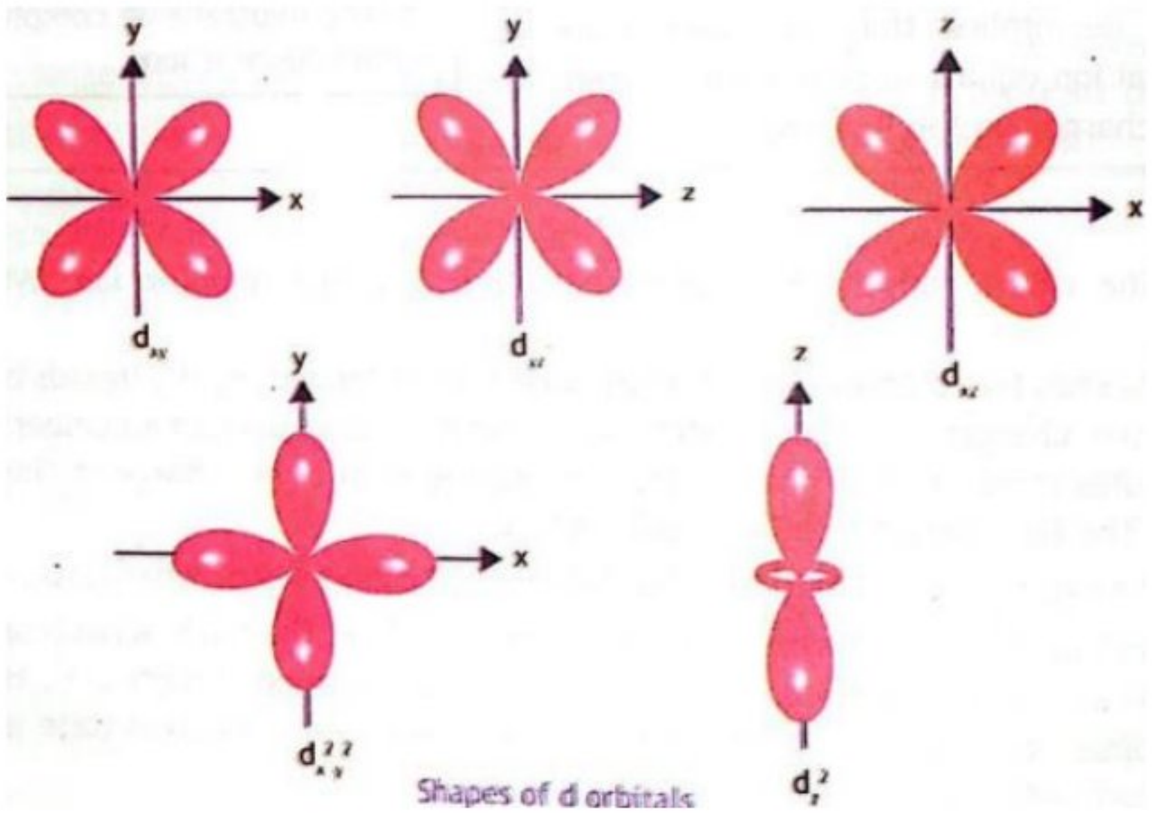
- In a free ion (without ligands), **all 5 d-orbitals** have the **same energy** (degenerate).
- In an **octahedral complex**:
  - 6 ligands approach along **x, y, z axes**.
  - This causes **splitting of d-orbitals** into two sets due to repulsion:

a. Higher energy (e_g set):

  - $d_{x^2-y^2}, d_{z^2}$ → lie along axes → **more repulsion**.

b. Lower energy (t_{2g} set):

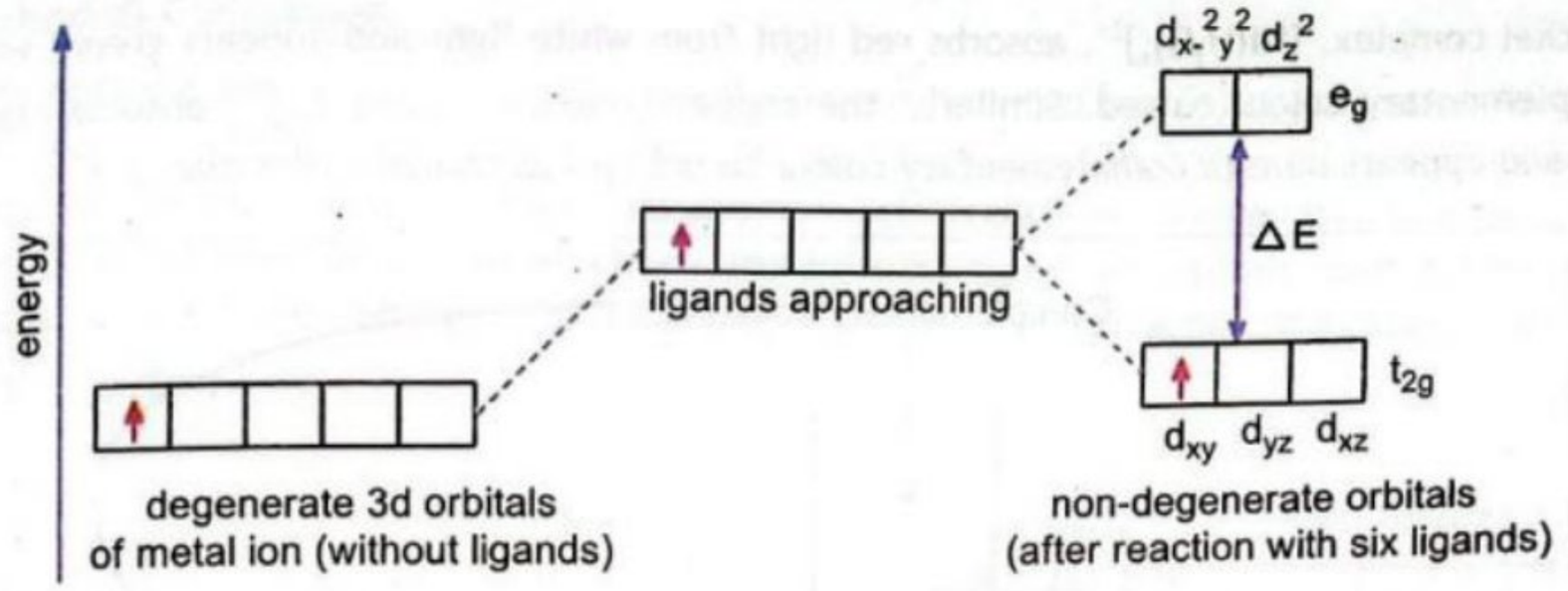
  - d_{xy}, d_{xz}, d_{yz} → between axes → **less repulsion**.
- The **energy gap (ΔE)** between e_g and t_{2g} orbitals depends on the nature of metal ion and ligands.



Shapes of d orbitals

4. d–d Electronic Transition

- When white light strikes the complex:
  - A photon of matching energy is absorbed.
  - An electron jumps from lower t_{2g} to higher e_g orbital.
  - This is called a d–d transition.
- The absorbed photon corresponds to a specific colour of visible light.
- The remaining (unabsorbed) colours mix to give the complementary colour, which we observe.



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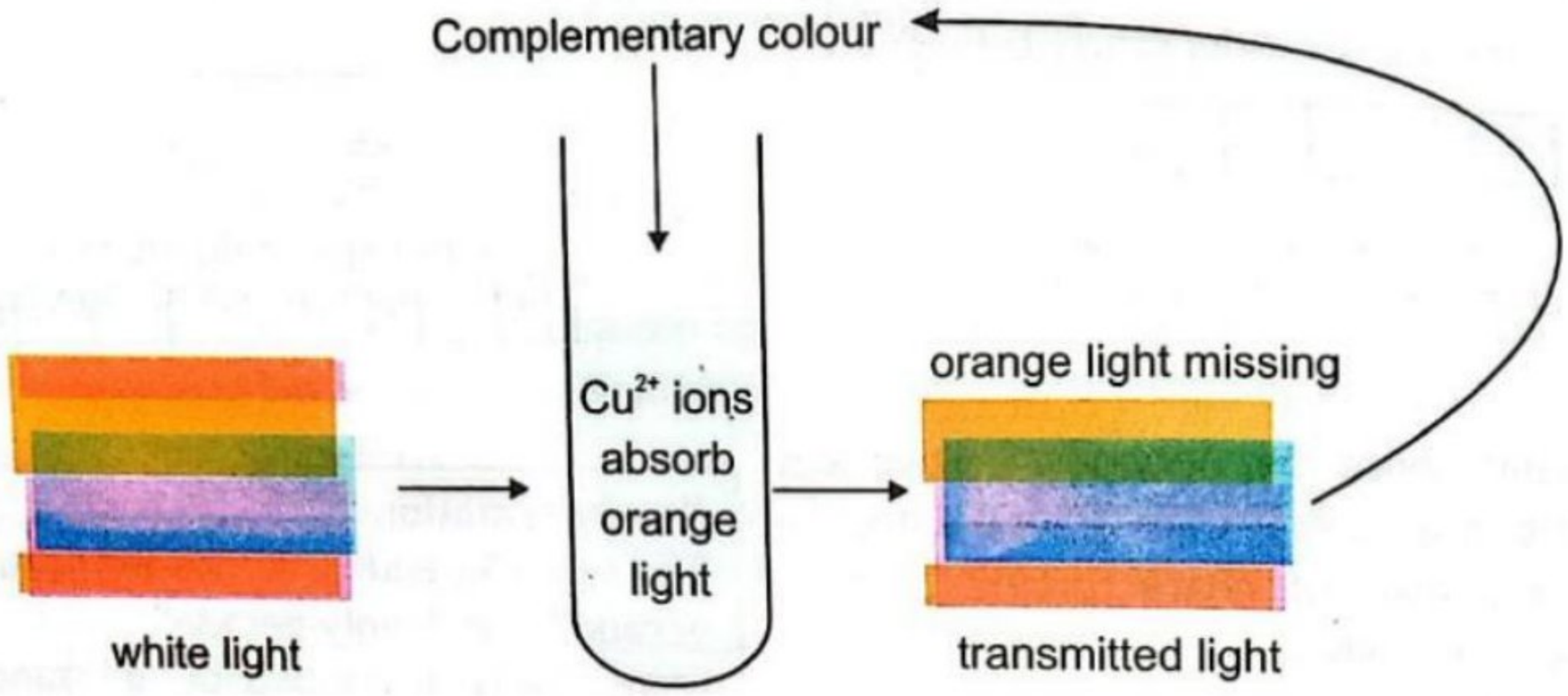
5. Complementary Colours

- **Example 1:** $[Ni(H_2O)_6]^{2+}$ absorbs **red** → appears **green** (complementary to red).
- **Example 2:** $[Cu(H_2O)_6]^{2+}$ absorbs **orange** → appears **blue** (complementary to orange).

(This is explained using the colour wheel — absorbed colour is opposite to the observed colour.)



How complexes Get Colours?

The d–d Splitting Pattern in Octahedral and Tetrahedral Complexes

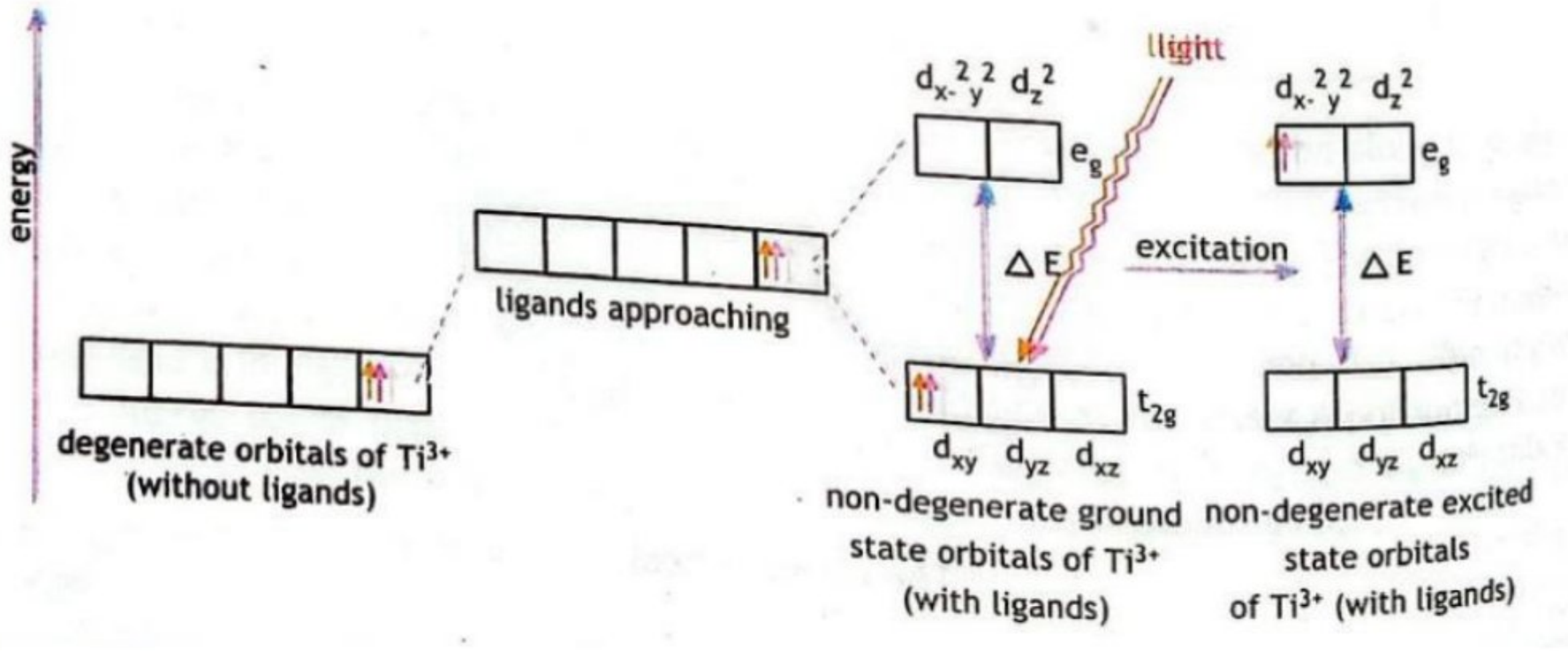
Octahedral Complexes

- In an **octahedral field**, six ligands surround the central metal ion along the x, y, and z axes.
- The **eg orbitals** $(d_{z^2}, d_{x^2-y^2})$ point directly toward the ligands, so they experience **greater repulsion** and have **higher energy**.
- The **t2g orbitals** (d_{xy}, d_{xz}, d_{yz}) lie between the axes, experiencing **less repulsion**, so they have **lower energy**.

Thus, in octahedral complexes:

$$t_{2g} < e_g$$

- Example: **$[Ti(H_2O)_6]^{3+}$**
  - Titanium (III) has one electron in the 3d orbital.
  - When white light passes through, the complex absorbs **yellow-green light** to promote the electron from $t_{2g} \rightarrow e_g$.
  - The complementary color seen is **red-violet**.



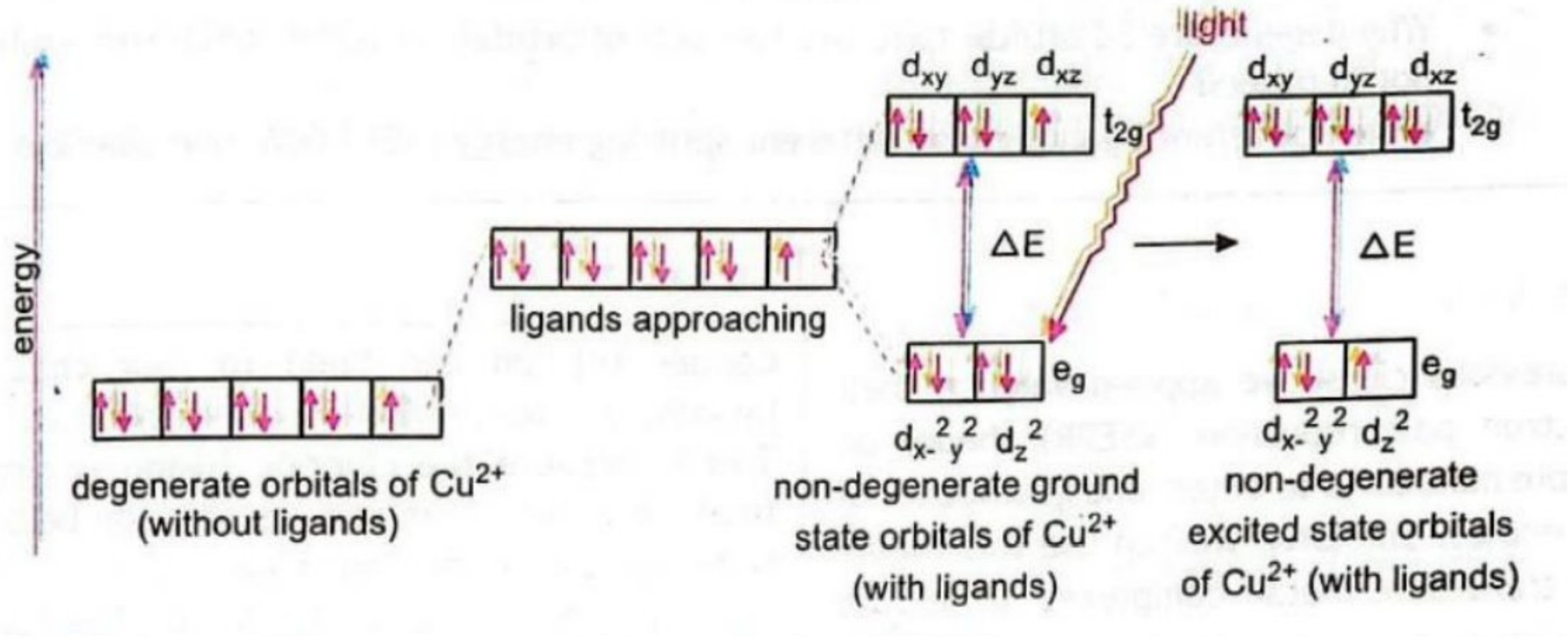
Tetrahedral Complexes

- In a **tetrahedral field**, four ligands are positioned between the axes.
- The **t2g orbitals** (d_{xy}, d_{xz}, d_{yz}) point closer to ligand positions, so they experience **greater repulsion** and have **higher energy**.
- The **eg orbitals** $(d_{z^2}, d_{x^2-y^2})$ point between the ligands, so they experience **less repulsion** and have **lower energy**.

Thus, in tetrahedral complexes:

$$e < t_{2g}$$

- Example: **$[CuCl_4]^{2-}$**
  - The complex absorbs certain wavelengths in the visible spectrum due to d-d transition, and the transmitted color is observed.



Key Differences

- **Octahedral**: t_{2g} lower, e_g higher.
- **Tetrahedral:** e_g lower, t_{2g} higher.
- **Splitting energy (Δ_t)** for tetrahedral complexes is **smaller** than that for octahedral complexes (Δ_o):

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

Effect of Ligands on Colour of Complexes

1. Cause of Colour

- Transition metal complexes appear coloured due to **d–d transitions**.
- When ligands approach a transition metal ion, their electric fields interact with the metal's ddd-orbitals, causing them to split into two energy levels.
- The **energy difference** (Δ) depends on the **nature of the ligands**.
- If visible light is absorbed to excite an electron from the lower to the higher set of orbitals, the **complementary colour** of the absorbed light is observed.

---

2. Ligand Field Strength

- Ligands differ in their ability to split the d-orbitals.
- This order of field strength is known as the **Spectrochemical Series**:

$$CN^- > NH_3 > H_2O > OH^- > Cl^- > Br^-$$

- **Strong field ligands** → cause **large splitting** (Δ)
- **Weak field ligands** → cause **small splitting** (Δ)

---

3. Example: Copper (II) Complex

- Aqueous copper (II) ions exist as:

$$[Cu(H_2O)_6]^{2+}(blue\ solution)$$

- When ammonia is added, since **NH_3 is a stronger field ligand than H_2O**, it partially replaces water molecules:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

- The new complex, $[Cu(NH_3)_4(H_2O)_2]^{2+}$ has **greater splitting energy** because NH_3 is stronger than H_2O.
- This shifts the absorption of light to **higher energy (shorter wavelength)**.
- Hence, the colour changes from **blue → violet-blue**.

Geometries of Complexes

In the previous class, we applied the **Valence Shell Electron Pair Repulsion (VSEPR) theory** to simple molecules in order to determine their geometries. Similarly, this theory can also be applied to **transition metal complexes**. It helps to arrange ligands in such a way that there is **maximum distance** and **minimum repulsion** among the coordinate (dative) bond pairs.

---

1. Complexes with Coordination Number 6

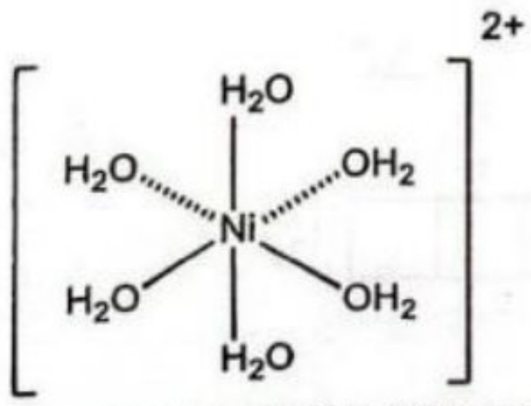
- The **coordination number** of a complex is the number of donor atoms directly bonded to the central metal ion.
- Example: The **copper (II) ion (Cu^{2+})** can bond with different ligands:
  - With **chloride ions (Cl^-)** → only **4 ligands** can attach.
  - With **water (H_2O)** → **6 ligands** can attach.
  - With **ammonia (NH_3)** → **6 ligands** can attach.

Reason:

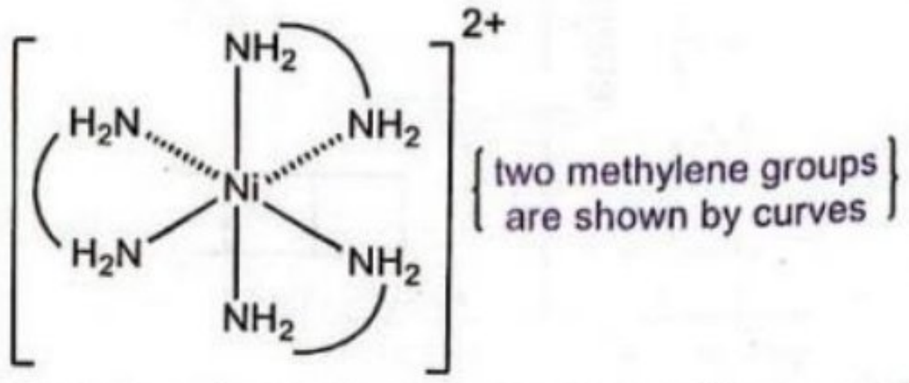
- The chloride ion (Cl^-) is relatively **large** in size (chlorine belongs to **Period 3**).
- Oxygen in water and nitrogen in ammonia are **smaller atoms** (both from **Period 2**).
- Therefore, the limited space around the Cu^{2+} ion cannot accommodate **six bulky chloride ions**, but it can easily fit **six smaller water or ammonia ligands**.

Octahedral Shape

- Complexes with coordination number **6** generally adopt an **octahedral geometry**.
- In this arrangement, six donor atoms of ligands (monodentate or polydentate) are placed at the **vertices of an octahedron**.
- The word **"octahedron"** comes from *octa* (eight) and *hedron* (faces).
- According to **VSEPR theory**, this three-dimensional geometry provides **minimum repulsion** among the ligands.
- The angle between any two adjacent ligands is **90°**.



Hexaaquanickel(II) ion, $[Ni(H_2O)_6]^{2+}$



Tris(1,2-diaminoethane)nickel(II) ion, $[Ni(en)_3]^{2+}$

2. Complexes with Coordination Number 4

Complexes with coordination number **4** can have two possible geometries depending on the nature of the metal ion and the ligands:

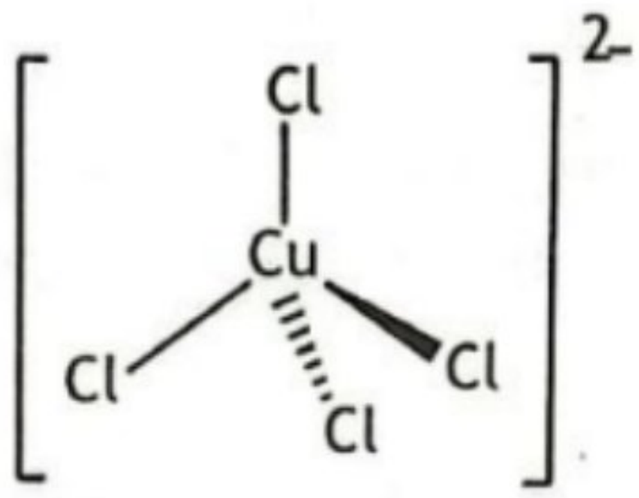
1. **Tetrahedral Geometry** – supported by VSEPR theory.
2. **Square Planar Geometry** – not explained by VSEPR, but observed in certain transition metals.

Let's discuss both in detail.

---

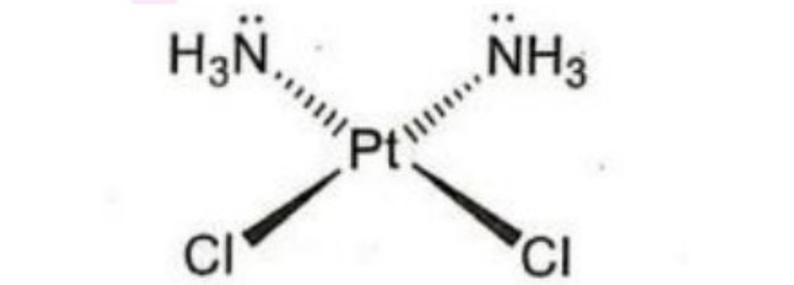
i. Tetrahedral Complexes

- These complexes are **less common than octahedral ones**, but are frequently found with larger ligands, such as chloride.
- Example: **Tetrachlorocuprate(II), $[CuCl_4]^{2-}$**
  - The four chloride ligands arrange themselves at the corners of a **tetrahedron**.
  - Bond angle between ligands = **109.5°** (as predicted by VSEPR).
- Tetrahedral complexes are mostly formed by **metal ions with d^{10} electronic configuration**, such as **Cu^+** and **Zn^{2+}**.
- **Examples:**
  - $[CuCl_4]^{2-}$
  - $[Cu(CN)_4]^{3-}$
  - $[Zn(NH_3)_4]^{2+}$



ii. Square Planar Complexes

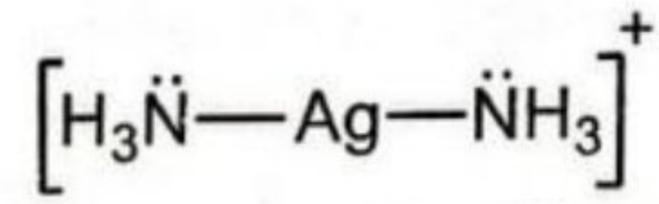
- In these complexes, the four ligands occupy the **corners of a square** around the central metal ion.
- Bond angles between ligands = **90°**.
- This geometry **cannot be explained by VSEPR** (which predicts tetrahedral for 4 ligands). Instead, it is explained by **Crystal Field Theory (CFT)** and the strong splitting of d-orbitals in certain cases.
- Square planar geometry is **less common than tetrahedral**, but very important.
- Typically formed by **transition metal ions with d^8 electronic configuration**, such as **Ni^{2+}, Pd^{2+}, Pt^{2+}, and Au^{3+}**.
- **Examples:**
  - $[Ni(CN)_4]^{2-}$
  - $[Pt(NH_3)_4]^{2+}$
  - $[AuCl_4]^-$
  - Cisplatin: $[Pt(NH_3)_2Cl_2]$ (an anticancer drug).



cis-diaaminedichloroplatinum(II)

3. Complexes with Coordination Number 2

- Complexes with coordination number **2** have **linear geometry**.
- The two ligands are arranged **opposite to each other** at **180°** angle.
- These complexes are generally **less stable** and occur with some transition metals.
- **Examples:**
  - $[Ag(NH_3)_2]^+$
  - $[Au(CN)_2]^-$
  - $[CuCl_2]^-$



Diamminesilver(I) ion

Stability of Complexes and Stability Constant (K_{stab})

Definition

The **stability constant (K_{stab})** is the equilibrium constant obtained from **ligand exchange reactions** in a solvent. It expresses the **stability of a complex** in terms of the equilibrium constant for the replacement of one ligand by another.

Since ligand exchange reactions are **reversible**, the stability constant can be derived in the same way as we derived the **equilibrium constant (Kc)** in chemical equilibrium.

Example: Cobalt(II) Complexes

Consider the equilibrium:

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

- The **pink solution** corresponds to **hexaaquacobalt(II)** $[Co(H_2O)_6]^{2+}$.
- The **blue solution** corresponds to **tetrachlorocobaltate(II)** $[CoCl_4]^{2-}$

The **position of equilibrium** shows which complex is **more stable**.

- A **strong field ligand** always replaces a **weak field ligand**.

Effect of Adding Reagents

- **Adding water**: pushes the equilibrium **backward** → the **pink colour** of $[Co(H_2O)_6]^{2+}$ reappears.
- **Adding concentrated HCl**: increases $[Cl^-]$ concentration, shifting equilibrium **forward** → the **blue colour** of $[CoCl_4]^{2-}$ appears.

Thus, **chloride ions** and **water molecules** are in competition to bond with the central Co^{2+} ion.

Deriving the Stability Constant Expression

From the equilibrium law:

$$K_c = \frac{[CoCl_4]^{2-}\,[H_2O]^6}{[Co(H_2O)_6]^{2+}\,[Cl^-]^4}$$

But since **water is the solvent** (present in large excess), its concentration is **constant** and not included in the expression.

Therefore, the **stability constant (Kstab)** is:

$$K_{stab} = \frac{[CoCl_4]^{2-}}{[Co(H_2O)_6]^{2+}\,[Cl^-]^4}$$

This shows how firmly the chloride ligands are bonded compared to water ligands.

Units of Stability Constant

The **units of Kstab** depend on the overall expression, just like **Kc** in chemical equilibrium.
For the above reaction:

- Numerator → mol dm^{-3}
- Denominator → (mol dm^{-3}) × (mol dm^{-3})^4 = (mol dm^{-3})^5

So, units of Kstab = (mol dm^{-3})$^{-4}$ = dm^{12} mol^{-4}

Significance of Stability Constant

- **Large Kstab value** → ligand forms a strong, stable complex with the metal ion.
- **Small Kstab value** → ligand binds weakly → less stable complex.

General rule:

- Ligands with **donor atoms of lower electronegativity** bond **more strongly** with central metal ions than ligands with higher electronegativity atoms.
- Example:
  - **Ammonia (NH_3)**: nitrogen is less electronegative → bonds strongly → higher Kstab.
  - **Water (H_2O)**: oxygen is more electronegative → bonds weakly → lower Kstab.

Example: Stability Constants of Copper(II) Complexes

The stability constants of some copper(II) complexes show the trend clearly:

Complex	Relative Kstab	Explanation
$[Cu(NH_3)_4]^{2+}$	High	NH_3 forms strong coordinate bonds with Cu^{2+}
$[Cu(H_2O)_6]^{2+}$	Lower	H_2O forms weaker bonds with Cu^{2+}

This demonstrates that **NH_3 ligands** stabilize the Cu^{2+} complex more than **H_2O ligands**.

Worked Example 1

Problem:
We get a mixture of aqueous solutions of **tetrachlorocuprate(II)** and **hexaaquacopper(II)** ions after adding concentrated hydrochloric acid to an aqueous solution of copper(II) sulfate.

i. Write the expression for the stability constant of $[CuCl_4]^{2-}$.

Reaction:

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$$

Since water is the solvent (constant), we exclude it:

$$K_{stab} = \frac{[CuCl_4]^{2-}}{[Cu(H_2O)_6]^{2+}\,[Cl^-]^4}$$

---

ii. What are the units of the stability constant?

- Numerator: mol dm^{-3}
- Denominator: (mol dm^{-3}) × (mol dm^{-3})^4 = (mol dm^{-3})^5

So:

$$K_{stab} = (mol\,dm^{-3})^{-4} = dm^{12}\,mol^{-4}$$

Redox Reactions

Transition elements can exist in multiple oxidation states. In redox reactions, these oxidation states change due to the transfer of electrons between reacting species.

- **Oxidation**: Increase in oxidation state (loss of electrons).
- **Reduction**: Decrease in oxidation state (gain of electrons).
- **Oxidizing agent**: Accepts electrons and undergoes reduction.
- **Reducing agent**: Donates electrons and undergoes oxidation.

To understand this better, let us consider the redox reaction between **copper(II) ions** and **iodide ions**.

Reaction Between Copper(II) Ions and Iodide Ions

When aqueous **copper(II) sulfate solution** is treated with excess **potassium iodide solution**, the following reaction takes place:

$$2Cu^{2+}(aq) + 4I^{-}(aq) \longrightarrow 2CuI(s) + I_2(aq)$$

- A **white precipitate** of copper(I) iodide (**CuI**) is formed.
- The solution turns **red-brown** due to the liberation of iodine.

Splitting into Half-Reactions

The overall redox reaction can be divided into two half-equations:

Oxidation half-reaction (iodide oxidized):

$$2I^{-}(aq) \longrightarrow I_2(aq) + 2e^{-}$$

Standard electrode potential:

$$E^{\circ}(I_2/I^{-}) = +0.54\,V$$

Reduction half-reaction (copper reduced):

$$Cu^{2+}(aq) + e^{-} \longrightarrow Cu^{+}(aq)$$

Standard electrode potential:

$$E^{\circ}(Cu^{2+}/Cu^{+}) = +0.15\,V$$

Feasibility of the Reaction

- The **higher potential** of the I_2/I^{-} couple indicates that the oxidation of iodide to iodine is favorable.
- The **lower potential** of the Cu^{2+}/Cu^{+} couple shows that reduction of copper(II) ions to copper(I) is less favorable.
- Calculating overall cell potential:

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

$$= (+0.15) - (+0.54) = -0.39\,V$$

Since the overall standard electrode potential is **negative**, the reaction appears to be non-spontaneous.

However, in practice, the reaction proceeds forward because the insoluble **CuI continuously precipitates out**, driving the reaction to completion by removing the product from the equilibrium system.

Determination of Iodine Formed

The amount of liberated iodine in solution can be quantitatively determined by **titration with sodium thiosulphate solution**:

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

This allows accurate measurement of iodine formed during the redox reaction.