

UNIT 1 - INORGANIC CHEMISTRY

TRANSITION ELEMENTS AND COORDINATION COMPOUNDS

1. Transition Elements – General Features

Definition:

- Elements with **partially filled d-orbitals** in ground or excited states.
- Found in **groups 3–12**.

General Characteristics:

- Variable oxidation states.
- Form coloured ions and complexes.
- Exhibit catalytic activity.
- Often paramagnetic (unpaired d-electrons).
- High melting & boiling points, densities.

2. Oxidation States & Stability

- Multiple oxidation states due to close energy of (n-1) d and ns orbitals.
- **Stability trend:** Middle elements show more stable higher oxidation states.
e.g. Mn (+2 to +7), Fe (+2, +3).
- **+2 oxidation state** common for most (due to loss of 4s electrons).
- Higher oxidation states stabilize with electronegative ligands (O, F).

3. Comparison: 1st, 2nd, and 3rd Transition Series

Property	1st Series (3d)	2nd Series (4d)	3rd Series (5d)
Atomic size	Smallest	Larger	Largest
Density	Moderate	Higher	Highest
Oxidation states	More variable	Fewer but stable	Similar to 4d
Complex formation	Strong tendency	Stronger	Very strong
Magnetic properties	Spin-only	Spin-orbit coupling	Spin-orbit coupling strong
Example	Fe, Co, Ni	Ru, Rh, Pd	Os, Ir, Pt

4. Bonding Theories in Coordination Compounds

(a) Valence Bond Theory (VBT):

- Bonding via **hybridization** of metal orbitals.
- Explains geometry & magnetic properties.
- Limitations: can't explain color or spectra.

(b) Crystal Field Theory (CFT):

- Ligands create **electrostatic field** splitting d-orbitals.
- Δ (crystal field splitting energy) decides:
 - **High spin / Low spin.**
 - **Color (due to d-d transitions).**
- **Order of splitting strength:**
 $\text{CN}^- > \text{NO}_2^- > \text{en} > \text{NH}_3 > \text{H}_2\text{O} > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

(c) Ligand Field Theory (LFT):

- Combines CFT + MO theory; explains spectra and magnetism better.

5. Spectral & Magnetic Properties

Magnetic Moment (μ):

$$\mu = \sqrt{n(n+2)} \text{ BM}$$

where n = number of unpaired electrons.

Used to identify oxidation state and geometry.

Color:

- Due to **d–d transitions** and **charge-transfer transitions**.
- Intensity depends on **Laporte & spin selection rules**.

6. Reaction Mechanisms in Complexes

Type	Mechanism	Example
Substitution (ligand exchange)	Dissociative (D), Associative (A), Interchange (I)	$[\text{Co}(\text{NH}_3)_6]^{3+}$ + H_2O
Electron transfer	Inner-sphere / Outer-sphere	$[\text{Fe}(\text{CN})_6]^{3-}$ / $[\text{Fe}(\text{CN})_6]^{4-}$
Isomerization / Racemization	Rearrangement within complex	$[\text{Co}(\text{en})_3]^{3+}$

7. Electronic Transitions & Selection Rules

Types of Transitions:

- **d–d transitions** – within metal d-orbitals.
- **Charge Transfer (CT):**
 - MLCT (Metal → Ligand)
 - LMCT (Ligand → Metal)
→ usually more intense than d–d transitions.

Selection Rules:

1. Laporte Rule:

- Forbidden if no change in parity ($g \rightarrow g$ or $u \rightarrow u$ not allowed).
- Allowed in tetrahedral complexes (no center of symmetry).

2. Spin Rule:

- $\Delta S = 0$ (no change in spin state).

8. Ground States & Correlation Diagrams

- Ground state term symbols found from **Hund's rules**.
- **Correlation diagrams**: show how terms split with increasing field strength from weak \rightarrow strong ligand field (CF splitting).

9. Orgel Diagrams (Qualitative):

- Explain **d–d transitions** for **high-spin** octahedral/tetrahedral complexes.
- Show allowed transitions & relative energies.
- Simple, but only for d^1 – d^9 (not low-spin).

10. Tanabe–Sugano Diagrams (Quantitative):

- Plot energy of terms vs. crystal field strength (Δ/B).
- Applicable for both **high-spin and low-spin** complexes.
- Helps estimate:

- Racah parameters (B)
- Transition energies
- Spin-pairing energy

11. Quick Summary Table

Concept	Key Point
Transition Metal Property	Variable oxidation, colored ions, catalysis
CFT Splitting	Octahedral: t_{2g} – e_g ; Tetrahedral: e – t_2
Color	d–d or CT transitions
Selection Rules	Laporte & spin-forbidden transitions weak
VBT	Explains geometry & magnetism
CFT/LFT	Explains spectra & stability
Orgel Diagram	Qualitative, high-spin only
Tanabe–Sugano Diagram	Quantitative, both spins

COORDINATION COMPOUNDS

1. Crystal Field Theory (CFT)

- Proposed by Hans Bethe & Van Vleck.
- Treats metal–ligand bond as purely electrostatic.
- Ligands = point charges (anions) or dipoles (neutral molecules).

2. Splitting of d Orbitals

(a) Octahedral Field

Five d orbitals split into two sets:

t_{2g} (lower energy): d_{xy} , d_{yz} , d_{zx}

e_g (higher energy): $d_{x^2-y^2}$, d_{z^2}

Crystal Field Splitting Energy (Δ_o or $10Dq$): Energy difference between e_g and t_{2g} orbitals.

(b) Tetrahedral Field

Reverse of octahedral:

e (lower): $d_{x^2-y^2}$, d_{z^2}

t_2 (higher): d_{xy} , d_{yz} , d_{zx}

Splitting is smaller: $\Delta_t = 4/9 \Delta_o$.

(c) Square Planar Field

Derived from octahedral by removing two ligands on z-axis.

Order: $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz} \approx d_{yz}$.

3. Crystal Field Stabilization Energy (CFSE)

Electron Configuration	CFSE (Octahedral)
d^1	$0.4\Delta_o$
d^2	$0.8\Delta_o$
d^3	$1.2\Delta_o$
d^4 (high spin)	$0.6\Delta_o$
d^4 (low spin)	$1.6\Delta_o + P$
d^5 (low spin)	$2.0\Delta_o + 2P$

P = Pairing energy

High-spin complex: Weak-field ligands \rightarrow small Δ_o

Low-spin complex: Strong-field ligands \rightarrow large Δ_o

4. Spectrochemical Series

(Increasing ligand field strength)

$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < en < NO_2^- <$

$CN^- < CO$

Weak-field \rightarrow High-spin

Strong-field \rightarrow Low-spin

5. Jahn–Teller Distortion

Occurs when degenerate orbitals are unevenly occupied, leading to geometrical distortion to remove degeneracy.

Common in: Octahedral d^9 (Cu^{2+}), d^4 (Mn^{3+}) complexes.

Causes elongation or compression along one axis.

6. Limitations of CFT

- Considers bonds as purely ionic, ignores covalent character.
- Cannot explain π -bonding or color intensity accurately.
- Fails to justify magnetic moments in some complexes.

7. Molecular Orbital (MO) Theory of Complexes

Sigma Bonding

Ligand orbitals (usually lone pairs) overlap with metal d, s, p orbitals to form σ -bonds.

Explains metal–ligand covalency.

Pi Bonding

Ligand π -orbitals interact with metal d-orbitals:

π -donor ligands (e.g., F^- , Cl^-) \rightarrow donate e^- to metal (reduce Δ).

π -acceptor ligands (e.g., CO , CN^-) \rightarrow accept e^- from metal (increase Δ).

MO theory explains spectrochemical series and magnetic properties better than CFT.

INNER TRANSITION ELEMENTS (F-BLOCK)

Inner Transition Elements (f-block)

Definition:

- Elements where differentiating electron enters **4f (lanthanides)** or **5f (actinides)**.
- Lanthanides: Ce–Lu, Actinides: Th–Lr.

1. Spectral Properties

- **Lanthanides:** $f \rightarrow f$ transitions \rightarrow weak, sharp lines \rightarrow characteristic colors.
- **Actinides:** $f \rightarrow f$ & $f \rightarrow d$ transitions \rightarrow broad, intense \rightarrow more colored.
- 4f electrons are well shielded \rightarrow spectra less affected by ligands.

2. Magnetic Properties

- **Lanthanides:** Paramagnetic, depends on unpaired 4f electrons (spin + orbital contribution).
- **Actinides:** Paramagnetic, stronger spin–orbit coupling, higher magnetic moments.

3. Redox Properties

- **Lanthanides:** Mostly +3; exceptions: Ce(IV), Eu(II), Yb(II).
- Reducing power **increases down the series**.
- **Actinides:** Multiple oxidation states (+3 to +6); higher states more stable than lanthanides.

4. Applications

- Lanthanides: Phosphors (TV, LEDs), lasers, magnets
- Ce: Catalyst (CeO_2).
- Gd: MRI contrast agent.
- Actinides (U, Pu): Nuclear fuels & weapons.
- Th: Thorium reactors
- Sm, Eu: Magnets, phosphors.

Quick Tips

- Lanthanides: mostly +3, sharp spectra, paramagnetic.
- Actinides: multiple oxidation states, more colored, reactive.
- Spectral intensity: Actinides > Lanthanides.

Professor Academy