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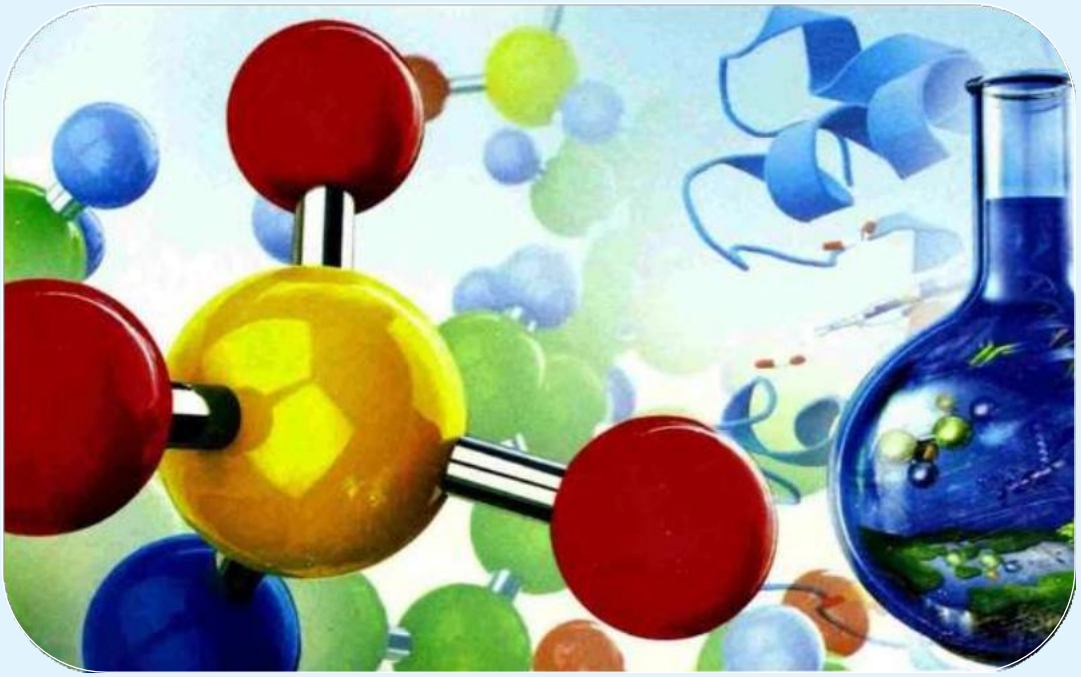
## Inorganic Chemistry II

Master of Science (M.Sc.)
Semester - 2



SELF LEARNING MATERIAL

# MASTER OF SCIENCE

# (M.Sc)

# Inorganic Chemistry

# CODE: ODL/MSS/MSCCH/201

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# BLOCK 1

# THEORIES OF METAL COMPLEXES

## Unit 1 Introduction to Metal Complex Theories

**Structure**



## 1.1 Introduction

Metals and their compounds have fascinated chemists for centuries due to their remarkable structural diversity and chemical behavior. Among these, metal complexes—also known as coordination compounds—represent one of the most significant classes of substances in inorganic chemistry. These compounds are formed when metal atoms or ions bond with neutral molecules or anionic species, collectively termed ligands. The study of these complexes has been central to the development of coordination chemistry, a discipline that has profound implications across catalysis, bioinorganic chemistry, material science, and industrial processes.

Historically, the field began to take shape in the late 19th century with the pioneering work of Alfred Werner, who proposed the coordination theory to explain the structures and bonding in metal complexes. Before Werner's work, the bonding and geometry of these compounds were poorly understood, as traditional valency concepts failed to explain phenomena such as isomerism and color. Werner's coordination model introduced the concept of coordination number and distinguished between primary (ionic) and secondary (coordinate) valencies, laying the foundation for modern coordination chemistry.

As the field evolved, theoretical models such as the Crystal Field Theory (CFT) and the Molecular Orbital Theory (MOT) emerged to explain the electronic structures, magnetic properties, and color of metal complexes. These theories remain crucial for understanding reactivity and stability patterns in coordination compounds and for designing new materials with tailored electronic properties.

## 1.2 Objectives

**After completing this unit, learners should be able to:**

1. Understand the historical development and fundamental concepts of metal complex theories.
2. Define and describe coordination compounds, ligands, and coordination numbers.
3. Apply theoretical models to predict magnetic, spectroscopic, and chemical properties of metal complexes.

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## 1.3 Core Principles in Coordination Chemistry

Coordination chemistry revolves around the interaction between a metal center and surrounding ligands. These interactions dictate the structure, stability, and reactivity of the resulting complex. Several key principles define this field:

### (a) Coordination Number and Geometry

The coordination number is the number of ligand donor atoms directly bonded to the central metal atom or ion. Typical coordination numbers are 2, 4, and 6, leading to geometries such as linear, tetrahedral, square planar, and octahedral. The geometry often depends on the size, charge, and electronic configuration of the central metal ion as well as the nature of the ligands.

Common geometries include:

- CN = 2 → Linear (e.g., $[Ag(NH_3)_2]^+$)
- CN = 4 → Tetrahedral or Square planar (e.g., $[NiCl_4]^{2-}$, $[PtCl_4]^{2-}$)
- CN = 6 → Octahedral (e.g., $[Co(NH_3)_6]^{3+}$)

The geometry depends on the size and charge of the metal ion and the steric and electronic properties of ligands.

### (b) Ligands and Chelation

Ligands can be monodentate (donating one electron pair) or polydentate (donating multiple pairs). When a ligand forms multiple bonds with a single metal ion, a chelate is formed—significantly increasing the stability of the complex through the chelate effect. Examples include ethylenediamine (en) and ethylenediaminetetraacetate (EDTA).

### (c) Oxidation State and Coordination Sphere

The oxidation state of the metal determines its electronic configuration and bonding capacity. The coordination sphere encompasses the central metal and its directly attached ligands, while any ions outside this sphere constitute the ionization sphere. Understanding this distinction is critical for predicting chemical behavior and reactions of coordination compounds.

### (d) Isomerism in Metal Complexes

Coordination compounds can exhibit structural and stereoisomerism, analogous to organic compounds. Common types include linkage isomerism, geometrical isomerism, and optical isomerism, which are often dictated by ligand arrangement and bonding flexibility.

These principles serve as the foundation for theoretical models like CFT and MOT, which provide deeper insights into the electronic and spectroscopic behavior of coordination complexes.

## 1.4 Crystal Field Theory: Fundamentals and Applications

Crystal Field Theory (CFT), developed in the early 20th century, provides a model to understand the electronic structures of transition metal complexes. The theory assumes that ligands act as point charges (or dipoles) that create an electrostatic field around the central metal ion, leading to splitting of the metal's degenerate d-orbitals.

### (a) The Origin of d-Orbital Splitting

In an isolated metal ion, all five d-orbitals are degenerate (equal in energy). When ligands approach, their negative charges repel the electrons in the metal d-orbitals unequally depending on their spatial orientation.

- In an octahedral field, orbitals dx2−y2d_{x^2-y^2}dx2−y2 and dz2d_{z^2}dz2 (collectively called ege_geg) experience greater repulsion and are raised in energy, while dxyd_{xy}dxy , dxzd_{xz}dxz, and dyzd_{yz}dyz (the t2gt_{2g}t2g set) are stabilized.
- The energy difference between these sets, called the crystal field splitting energy ($\Delta_o$), is key to predicting magnetic and spectroscopic behavior.

### (b) High Spin and Low Spin Complexes

Depending on the magnitude of $\Delta_o$ and the pairing energy (P), complexes may adopt high-spin or low-spin configurations:

- If $\Delta_o < P$, electrons occupy higher energy orbitals (high-spin).

- If $\Delta_o$ > P, electrons pair in lower energy orbitals (low-spin). This principle explains the variation in magnetic moments among complexes with the same metal ion but different ligands.

**(c) Applications of CFT**

Crystal Field Theory successfully explains:

1. The colors of transition metal complexes through d–d transitions.
2. The magnetic properties, using unpaired electron counts.
3. The stability and spectrochemical series of ligands, ranking them from weak to strong field donors.

However, CFT is a purely electrostatic model and does not account for covalent character in bonding. To address these limitations, Molecular Orbital Theory (MOT) was developed.

## 1.5 Metal Complexes: Molecular Orbital Theory

Molecular Orbital Theory (MOT) offers a quantum mechanical approach to metal–ligand bonding by considering the overlap of metal atomic orbitals with ligand orbitals to form molecular orbitals. This model extends beyond the electrostatic assumptions of CFT and provides a more accurate picture of bonding and reactivity.

**(a) σ and π Bonding in Complexes**

In MOT, ligands contribute orbitals (usually lone pairs) that overlap with the metal's vacant orbitals to form σ-bonds. Additionally, π-interactions may arise through ligand orbitals that can either donate electron density to or accept it from the metal:

- π-donor ligands (e.g., halides) donate electron density from filled p-orbitals.
- π-acceptor ligands (e.g., CO, $CN^-$) accept electron density from metal d-orbitals into their vacant π* orbitals, stabilizing low oxidation states.

**(b) Molecular Orbital Diagrams**

MOT describes bonding using energy-level diagrams that combine ligand group orbitals (LGOs) with metal orbitals of matching symmetry. For octahedral complexes, the resulting molecular orbitals are classified as bonding ($t_1u$, e_g), nonbonding ($t_2g$), and **antibonding (e_g)*. This framework explains the covalent character in metal–

ligand interactions and accounts for properties like back-bonding in metal carbonyls.

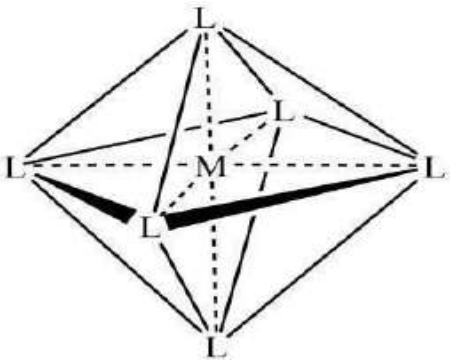


*Fig- 1.The octahedral coordination and corresponding σ-basis set for ligand orbitals in octahedral complexes.*

**(c) Advantages of MOT**

MOT provides a unified explanation for:

- The strength and nature of metal–ligand bonds.
- The observed spectroscopic and magnetic behavior.
- The synergic bonding in organometallic compounds.

While more complex than CFT, Molecular Orbital Theory represents a significant advancement in understanding coordination chemistry at an electronic level.

**Check Your Progress**

1. Define the terms coordination number and coordination sphere with examples.
   ---
   ---
   ---
   ---
2. What is meant by **crystal field splitting energy ($\Delta_o$)** in an octahedral complex?
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## 1.6 Summary

In this chapter, we explored the evolution and theoretical frameworks that underpin **metal complex chemistry**. Beginning with Werner's coordination theory, the field advanced through electrostatic and

quantum mechanical models such as **Crystal Field Theory (CFT)** and **Molecular Orbital Theory (MOT)**.

CFT provides a simplified yet powerful model for understanding d-orbital splitting, magnetic properties, and color, while MOT offers a more comprehensive explanation of bonding through orbital interactions. Together, these theories form the backbone of modern coordination chemistry, guiding research in catalysis, bioinorganic systems, and advanced materials.

### 1.7 Exercises

### Multiple Choice Questions (MCQs)

**1.** The primary contribution of Alfred Werner to coordination chemistry was:
A) Discovery of metal–ligand π bonding
B) Explanation of color in transition metal complexes
C) Distinction between primary and secondary valencies
D) Introduction of Molecular Orbital Theory
Answer: C) Distinction between primary and secondary valencies

**2.** In an octahedral complex, the d-orbitals split into:
A) ege_geg and t2gt_{2g}t2g sets
B) dxyd_{xy}dxy and dz2d_{z^2}dz2 orbitals
C) Three orbitals of higher and two of lower energy
D) Two orbitals of lower and three of higher energy
Answer: A) ege_geg and t2gt_{2g}t2g sets

**3**. The color of a transition metal complex is mainly due to:
A) Charge transfer between ligands
B) d–d electronic transitions
C) Ionic bonding between metal and ligand
D) Metal–metal bonding
Answer: B) d–d electronic transitions

**4.** Which of the following ligands is a strong field ligand according to the spectrochemical series?
A) $Cl^-$
B) $H_2O$
C) $CN^-$
D) $OH^-$
Answer: C) $CN^-$

**5.** In Molecular Orbital Theory, π-acceptor ligands such as CO stabilize the complex by:
A) σ-donation only
B) π back-donation from metal to ligand
C) Ionic attraction

D) Ligand–ligand repulsion
Answer: B) π back-donation from metal to ligand

**Short Answer Type Questions**

1. Differentiate between **high-spin** and **low-spin** complexes with suitable examples.
2. What are **π-donor** and **π-acceptor** ligands? Give one example of each.
3. Explain the importance of the **spectrochemical series** in predicting the properties of metal complexes.

**Long Answer Type Questions**

1. Discuss in detail the assumptions, orbital splitting pattern, and applications of Crystal Field Theory (CFT)
2. Explain the fundamentals of Molecular Orbital Theory (MOT)
3. Compare and contrast the features, assumptions, and predictive abilities of Crystal Field Theory (CFT) and Molecular Orbital Theory (MOT).

## 1.8 References and Suggested Readings


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# Unit 2 Valence Bond Theory (VBT)

**Structure**



## 2.1 Introduction

The behavior of transition-metal complexes—particularly their geometry, magnetic properties, and bonding patterns—cannot be fully explained by classical valency concepts. To bridge this gap, Valence Bond Theory (VBT) was introduced by Linus Pauling (1931) as an extension of the covalent bonding concept to coordination compounds.

VBT treats the formation of coordination compounds as a result of coordinate covalent bond formation between the central metal ion and surrounding ligands. Each ligand donates a lone pair of electrons into a vacant orbital of the metal atom or ion, leading to bond formation and predictable geometry.

Although later replaced by more advanced models such as Crystal Field Theory (CFT) and Molecular Orbital Theory (MOT), VBT remains fundamental because it provides a simple, qualitative picture of bonding in complexes and helps explain shapes and magnetic behavior using the concept of orbital hybridization.

## 2.2 Objectives

After completing this unit, learners should be able to:

1. Explain the basic idea of Valence Bond Theory and its historical background.
2. Describe the **assumptions and postulates** of VBT as applied to coordination compounds.
3. Relate the **hybridization** of metal orbitals to the geometry of complexes.

## 2.3 Basic Principles & Assumptions

Valence Bond Theory extends the classical covalent bond model to coordination compounds. The theory assumes that the metal–ligand

bond arises from the **overlap** between the vacant orbitals of the central metal ion and the filled orbitals (lone pairs) of the ligands.

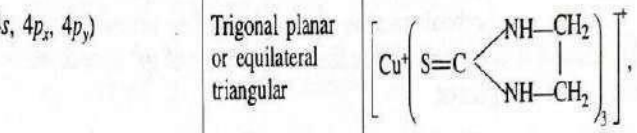
**(a) Fundamental Assumptions of VBT**

1. **Hybridization of Orbitals:** The central metal ion undergoes hybridization of suitable orbitals (s, p, d) to produce a set of equivalent hybrid orbitals directed toward the ligands.
2. **Coordinate Bond Formation:** Each ligand donates an electron pair to one of these hybrid orbitals, forming a **coordinate covalent bond**.
3. **Geometry of Complex:** The spatial arrangement of hybrid orbitals determines the **geometry** of the complex.
4. **Magnetic Behavior:** The number of unpaired electrons remaining on the metal ion after hybridization determines whether the complex is **paramagnetic** or **diamagnetic**.
5. **Inner and Outer Orbital Complexes:**
    - **Inner-orbital (low-spin) complexes** use (n − 1)d orbitals for hybridization ($d^2sp^3$).
    - **Outer-orbital (high-spin) complexes** use nd orbitals ($sp^3d^2$).

| Coordination Number | Type of Hybridisation | Distribution of Hybrid Orbitals in Space |
|---|---|---|
| 4 | $sp^3$ | Tetrahedral |
| 4 | $dsp^2$ | Square planar |
| 5 | $sp^3d$ | Trigonal bipyramidal |
| 6 | $sp^3d^2$ | Octahedral |
| 6 | $d^2sp^3$ | Octahedral |

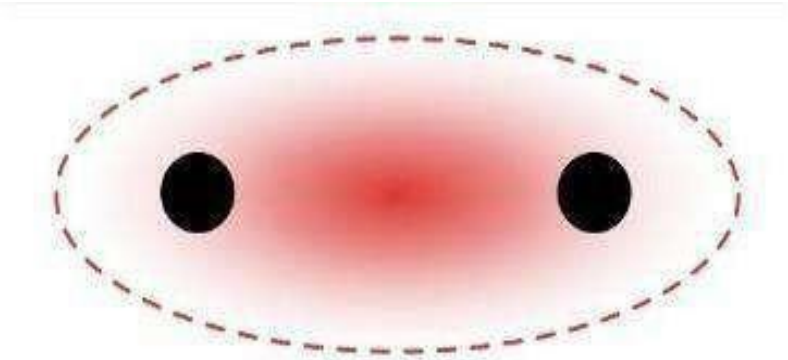
**(b) Types of Hybridization and Resulting Geometries**

**Table: 1 Important types of hybridisations found in the first row transition metal complexes and the geometry of the complexes**

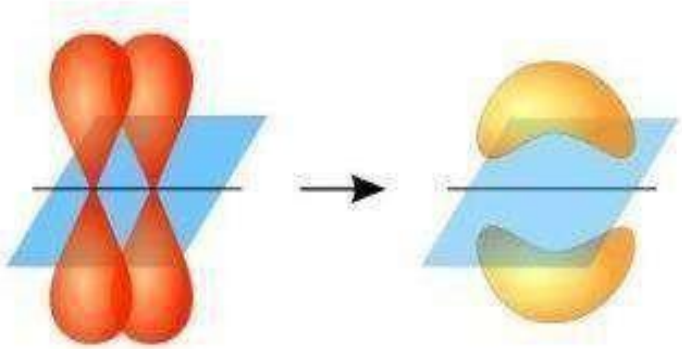
| *Coordination number of the central metal atom/ion* | *Type of hybridisation undergone by the central metal atom/ion* | *Geometry of the complex* | *Examples of complexes* |
|---|---|---|---|
| 2 | $sp(4s, 4p_x)$ | Linear or diagonal | $[CuCl_2]^-$, $[Cu(NH_3)_2]^+$ etc. |
| 3 | $sp^2(4s, 4p_x, 4p_y)$ | Trigonal planar or equilateral triangular |  $[Cu^+Cl(tu)_2]^0$ (distorted trigonal planar) etc. |
| 4 | $dsp^2(3d_{x^2-y^2}, 4s, 4p_x, 4p_y)$ | Square planar | $[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$ |
| 4 | $sp^2d(4s, 4p_x, 4p_y, 4d_{x^2-y^2})$ | Square planar | $[Cu(NH_3)_4]^{2+}$ $[Pt(NH_3)_4]^{2+}$ etc. |
| 4 | $sp^3(4s, 4p_x, 4p_y, 4p_z)$ | Tetrahedral | $[NiCl_4]^{2-}$, $[Cu(CN)_4]^{3-}$, $Ni(CO)_4$ etc. |
| 5 | $dsp^3(3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$ | Trigonal bipyramidal | $Fe(CO)_5$, $[CuCl_5]^{3-}$, $[Ni^{2+}(triars)\ Br_2]^0$ |
| 5 | $dsp^3(3d_{x^2-y^2}, 4s, 4p_x, 4p_y, 4p_z)$ | Square pyramidal | $[Co^{2+}(triars)\ I_2]^0$, $[Ni(CN)_5]^{3-}$ etc. |
| 6 | $d^2sp^3(3d_{x^2-y^2}, 3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$ | Inner-orbital octahedral | $[Ti(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$ etc. |
| 6 | $sp^3d^2(4s, 4p_x, 4p_y, 4p_z, 4d_{x^2-y^2}, 4d_{z^2})$ | Outer-orbital octahedral | $[Fe^*(NO^+)(H_2O)_5]^{2+}$, $[CoF_6]^{3-}$ etc. |

| **Geometry** | **Hybridization** | **Example** | **Magnetic Property** |
|---|---|---|---|
| Linear | sp | $[Ag(NH_3)_2]^+$ | Diamagnetic |
| Tetrahedral | $sp^3$ | $[NiCl_4]^{2-}$ | Paramagnetic |
| Square Planar | $dsp^2$ | $[PtCl_4]^{2-}$ | Diamagnetic |
| Octahedral (inner-orbital) | $d^2sp^3$ | $[Co(NH_3)_6]^{3+}$ | Diamagnetic |

| Geometry | Hybridization | Example | Magnetic Property |
|---|---|---|---|
| Octahedral (outer-orbital) | $sp^3d^2$ | $[FeF_6]^{3-}$ | Paramagnetic |



σ bond between two atoms: localization of electron density



Two p-orbitals forming a π-bond.

**(c) Illustrative Examples**

**(i) $[Co(NH_3)_6]^{3+}$ (Octahedral, Inner Orbital Complex)** Cobalt(III) has the electronic configuration [Ar] $3d^6$. In the presence of the strong-field ligand $NH_3$, two 3d electrons pair up, leaving two vacant 3d orbitals. These combine with one 4s and three 4p orbitals to form **$d^2sp^3$** hybrid orbitals directed toward the six ligands, giving an **octahedral** geometry. All electrons are paired → **diamagnetic**.

**(ii) $[FeF_6]^{3-}$ (Octahedral, Outer Orbital Complex)** $Fe^{3+}$ has [Ar] $3d^5$ configuration. The weak-field ligand $F^-$ does not cause pairing, so 3d orbitals remain half-filled. Hybridization involves one

4s, three 4p, and two 4d orbitals → **$sp^3d^2$** hybridization. The complex has five unpaired electrons → **paramagnetic**.

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**(d) Merits of VBT**

- Provides a qualitative explanation for the **geometry** of complexes.
- Predicts **magnetic properties** (paramagnetism or diamagnetism).
- Relates bonding conceptually to **hybridization** and **electron pairing**.
- Offers an intuitive framework for beginners before moving to CFT or MOT.

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## 2.4 Limitations of VBT

Despite its usefulness, Valence Bond Theory has several major limitations:

1. **No Explanation for Color:** VBT cannot explain the characteristic colors of transition metal complexes arising from **d–d electronic transitions**.
2. **No Quantitative Prediction:** The theory gives **qualitative** results only; it does not provide quantitative data on bond energies or stability.
3. **Neglect of Ligand Field Strength:** VBT cannot explain why some ligands cause **high-spin** and others **low-spin** configurations.
4. **No Account of Spectra and Thermodynamics:** It fails to predict spectral bands, magnetic susceptibilities accurately, or thermodynamic stabilities.
5. **Assumes Fixed Hybridization:** The hybridization model sometimes contradicts observed geometries and electronic spectra, especially for complexes with π-bonding ligands.

Because of these shortcomings, **Crystal Field Theory** and later **Molecular Orbital Theory** were developed to provide a more comprehensive and quantitative understanding of metal–ligand interactions.

**Check Your Progress**

1. What is meant by a **coordinate covalent bond** in the context of metal complexes?

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2. Explain the difference between **inner-orbital** and **outer-orbital** complexes.

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## 2.5 Summary

Valence Bond Theory describes coordination compound formation through the overlap of ligand lone-pair orbitals with the hybrid orbitals of the metal ion. The type of hybridization determines the shape and magnetic behavior of the complex.

Although VBT successfully explains geometries and magnetism, it cannot account for the colors, spectral features, or ligand field effects observed experimentally. Therefore, it serves as an essential introductory model that paved the way for more advanced bonding theories such as CFT and MOT.

## 2.6 Exercises

### A. Multiple Choice Questions (MCQs)

**1.** According to VBT, the geometry of $[Ni(CN)_4]^{2-}$ is:

A) Tetrahedral
B) Square planar
C) Octahedral
D) Trigonal bipyramidal

**Answer:** B) Square planar

**2.** Which of the following is an outer-orbital complex?

A) $[Fe(CN)_6]^{4-}$
B) $[FeF_6]^{3-}$
C) $[Co(NH_3)_6]^{3+}$
D) $[Ni(CN)_4]^{2-}$

**Answer:** B) $[FeF_6]^{3-}$

**3.** Hybridization type in $[Co(NH_3)_6]^{3+}$ is:

A) $sp^3d^2$
B) $d^2sp^3$
C) $sp^3$
D) $dsp^2$

**Answer:** B) $d^2sp^3$

**4.** VBT cannot explain:

A) Magnetic properties
B) Geometry
C) Color
D) Bond formation

**Answer:** C) Color

**5.** An inner-orbital complex uses which orbitals in hybridization?

A) (n − 1)d
B) nd
C) np
D) ns only

**Answer:** A) (n − 1)d

**B. Short Answer Questions**

1. What is meant by a **coordinate covalent bond** in the context of metal complexes?
2. Explain the difference between **inner-orbital** and **outer-orbital** complexes.
3. State two key assumptions of Valence Bond Theory.
4. Describe the type of hybridization and geometry expected for $[PtCl_4]^{2-}$.
5. Mention any two limitations of VBT.

**C. Long Answer Questions**

1. Explain the main postulates of Valence Bond Theory and discuss how it accounts for the geometry and magnetism of transition-metal complexes with examples.

2. Describe the formation and properties of $[Co(NH_3)_6]^{3+}$ and $[FeF_6]^{3-}$ according to VBT, highlighting the concept of inner- and outer-orbital complexes.
3. Discuss the major limitations of Valence Bond Theory and explain how these led to the development of Crystal Field Theory.

## 2.7 References and Suggested Readings

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## Unit 3 Ligand Field Theory

**Structure**



### 3.1 Introduction

**Ligand Field Theory (LFT)** is a powerful model developed to provide a more comprehensive understanding of bonding, structure, color, and magnetism in coordination compounds. It evolved as an extension and unification of **Crystal Field Theory (CFT)** and **Molecular Orbital Theory (MOT)**.

While **CFT** treated metal–ligand interactions as purely electrostatic (ionic) and **MOT** emphasized covalent bonding, **LFT** combines the best features of both. It considers both **electrostatic interactions** and **orbital overlap** between metal and ligand orbitals to explain a wide range of experimental observations.

LFT effectively accounts for the **d-orbital splitting**, **spectroscopic transitions**, **magnetic properties**, **bonding covalency**, and phenomena such as the **Jahn–Teller effect** in transition metal complexes. It thus provides a bridge between simple electrostatic and full quantum mechanical models.

### 3.2 Objectives

After completing this unit, learners should be able to:

1. Understand the conceptual foundation and purpose of Ligand Field Theory.
2. Explain how d-orbitals split differently in various ligand geometries.
3. Describe the influence of metal–ligand orbital overlap on bonding.
4. Explain the **Jahn–Teller effect** and its implications for molecular geometry and stability.

5. Relate LFT predictions to observable properties such as color, magnetism, and structure.

### 3.3 Differential Splitting of d-Orbitals in Different Ligand Fields

One of the central features of Ligand Field Theory is its explanation of **d-orbital splitting** under the influence of ligands surrounding a metal ion. The magnitude and pattern of this splitting depend on the **geometry** and **symmetry** of the ligand field.

#### (a) Octahedral Field

In an **octahedral complex**, six ligands approach the metal ion along the Cartesian axes. The five degenerate d-orbitals split into two sets:

- **$t_2g$ (lower energy)**: dxy,dxz,dyzd_{xy}, d_{xz}, d_{yz}dxy ,dxz,dyz — experience less repulsion.
- **e_g (higher energy)**: dx2−y2,dz2d_{x^2−y^2}, d_{z^2}dx2−y2,dz2 — directly face ligand approach and experience more repulsion.

The energy gap between these two sets is called **$\Delta_0$ (crystal field splitting energy)**. The relative filling of these orbitals determines whether the complex is **high-spin** or **low-spin**, depending on the strength of the ligand field.

#### (b) Tetrahedral Field

In a **tetrahedral complex**, four ligands approach between the axes, not along them. As a result, the splitting pattern reverses:

- **e (lower energy)**: dx2−y2,dz2d_{x^2−y^2}, d_{z^2}dx2−y2 ,dz2
- **$t_2$ (higher energy)**: dxy,dxz,dyzd_{xy}, d_{xz}, d_{yz}dxy ,dxz,dyz

The splitting energy ($\Delta_t$) is smaller than in octahedral fields and follows the approximate relationship:

$\Delta t \approx 49\Delta 0\Delta_t \approx \frac{4}{9}\ \Delta_0\Delta t \approx 94\Delta 0$

Because $\Delta_t$ is small, tetrahedral complexes are generally **high-spin**.

#### (c) Square Planar Field

Square planar complexes arise mainly for **$d^8$ metal ions** (e.g., $Ni^{2+}$, $Pd^{2+}$, $Pt^{2+}$). The splitting pattern here is more complex due to the removal of two ligands along the z-axis.

The general order of orbital energies is:

dx2−y2>dxy>dz2>dxz,dyzd_{x^2−y^2} > d_{xy} > d_{z^2} > d_{xz}, d_{yz}dx2−y2>dxy>dz2>dxz,dyz

The high energy of dx2−y2d_{x^2−y^2}dx2−y2 explains why square planar complexes are usually **low-spin** and **diamagnetic**, as all electrons pair in lower energy orbitals (e.g., $[Ni(CN)_4]^{2-}$).

**(d) Linear Field**

In a **linear complex**, such as $[Ag(NH_3)_2]^+$, the metal ion is coordinated by two ligands along the z-axis. The dz2d_{z^2}dz2 orbital faces the ligands directly and thus becomes highest in energy, while dxyd_{xy}dxy, dxzd_{xz}dxz, and dyzd_{yz}dyz remain degenerate at lower energy levels.

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**(e) Factors Affecting d-Orbital Splitting**

1. **Nature of the Metal Ion:** Higher oxidation states produce larger Δ values due to stronger metal–ligand electrostatic attraction.
2. **Nature of Ligand:** Strong-field ligands (like $CN^-$, CO) cause larger splitting compared to weak-field ligands (like $Cl^-$, $H_2O$).
3. **Geometry:** Octahedral > Square planar > Tetrahedral in splitting magnitude.
4. **Metal–Ligand Distance:** Shorter distances lead to greater splitting.

**3.4 Metal Complexes Molecular Orbital Theory**

Within the framework of LFT, **Molecular Orbital (MO) Theory** provides a detailed description of how metal and ligand orbitals interact to form bonding, nonbonding, and antibonding orbitals.

**(a) σ-Bonding**

Ligands with lone pairs on donor atoms (e.g., N, O, Cl) overlap with vacant metal orbitals (s, p, d) to form **σ-bonds**. These interactions determine the basic geometry and strength of the metal–ligand framework.

**(b) π-Bonding**

In addition to σ-bonding, π-type interactions can occur:

- **π-Donor ligands** (e.g., $Cl^-$, $OH^-$) donate electrons from filled p orbitals to metal $t_2g$ orbitals, reducing Δ.

- **π-Acceptor ligands** (e.g., CO, $CN^-$) accept electron density from metal $t_{2g}$ orbitals into their vacant π* orbitals, increasing Δ.

This synergic interaction (σ donation + π back-donation) strengthens bonding and stabilizes low oxidation states.

**(c) MO Diagram for Octahedral Complexes**

The interaction of metal and ligand orbitals generates three sets of molecular orbitals:

1. **Bonding MOs** (mainly ligand in character)
2. **Nonbonding MOs** (mainly metal $t_{2g}$ orbitals)
3. **Antibonding MOs** (metal e_g* orbitals)

Electrons occupy the lowest energy orbitals first, and transitions between these levels explain **color** and **spectroscopic behavior**.

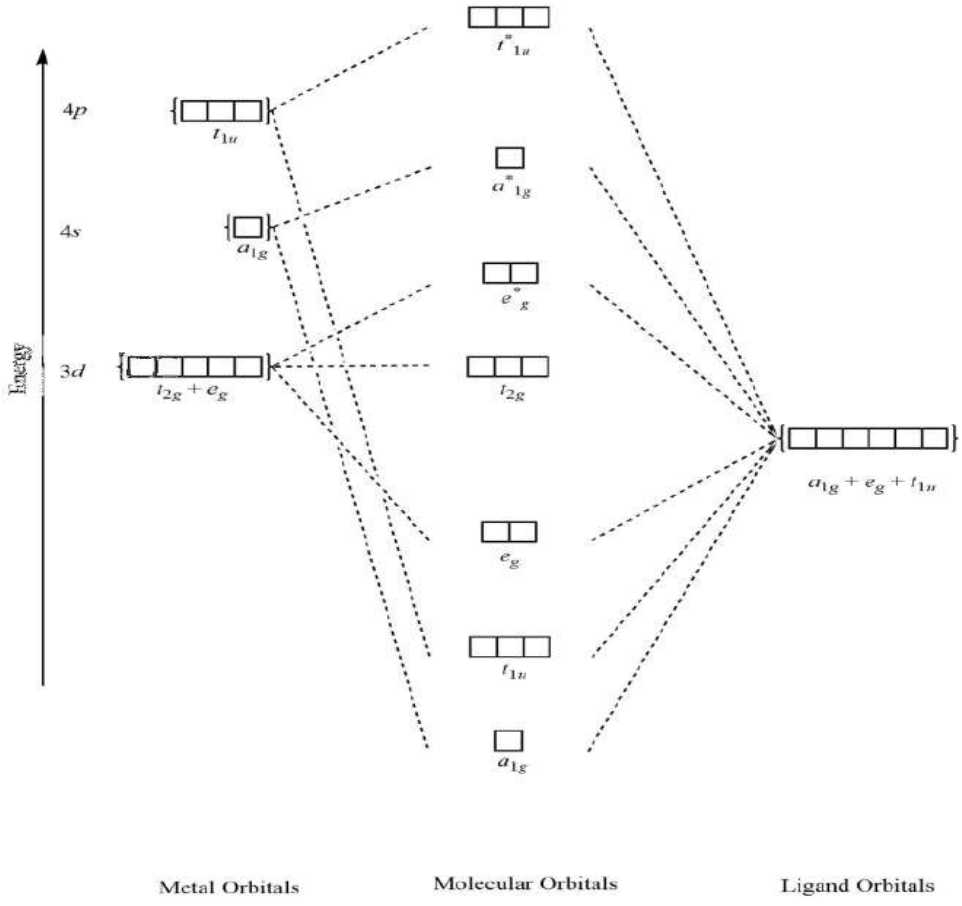


*Figure - The formation of σ-molecular orbitals (bonding, antibonding and non-bonding) in octahedral complexes of transition metals.*

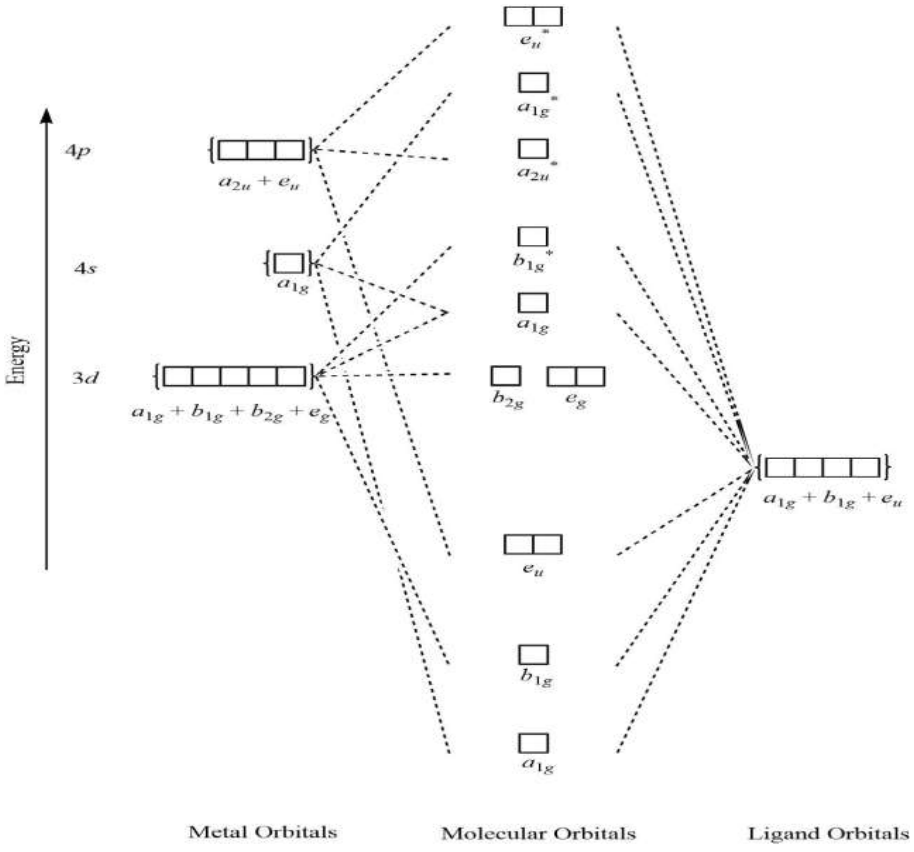


*Figure -. The generation of σ-molecular orbitals in square-planar complexes*

### 3.5 Jahn–Teller Effect

The **Jahn–Teller effect** describes the geometrical distortion observed in certain coordination complexes with unevenly filled degenerate orbitals. According to the **Jahn–Teller theorem**, any non-linear molecule with a degenerate electronic ground state will undergo a distortion that removes the degeneracy and lowers the overall energy.

#### (a) Origin

When degenerate orbitals (like e_g or $t_2g$) are asymmetrically occupied, the electron–ligand repulsion becomes unbalanced, causing the complex to distort (usually elongate or compress along one axis).

#### (b) Common Examples

The most pronounced Jahn–Teller distortions occur in **octahedral $d^9$** (e.g., $Cu^{2+}$) and **high-spin $d^4$** (e.g., $Mn^{3+}$) systems. For instance, in $[Cu(H_2O)_6]^{2+}$, elongation along the z-axis leads to longer Cu–O bonds in the axial positions, creating a slightly tetragonally distorted geometry.

**(c) Consequences**

- Alters bond lengths and geometry.
- Affects electronic spectra and magnetic properties.
- Influences reactivity and stability of complexes.

The Jahn–Teller effect thus helps explain deviations from ideal symmetry in many transition metal compounds.

**Check Your Progress**

1. What is Ligand Field Theory and how does it differ from Crystal Field Theory?

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2. Explain why tetrahedral complexes are usually high-spin.

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## 3.6 Summary

Ligand Field Theory integrates electrostatic and covalent perspectives to explain the bonding and properties of transition metal complexes.

- It refines Crystal Field Theory by incorporating metal–ligand orbital overlap and covalent contributions.
- The d-orbital splitting pattern depends on the geometry (octahedral, tetrahedral, square planar, linear) and ligand field strength.
- Incorporating Molecular Orbital Theory allows LFT to explain both σ and π bonding, color, and magnetic behavior.
- The Jahn–Teller effect accounts for structural distortions in complexes with unevenly occupied degenerate orbitals.

Overall, LFT provides a more accurate and unified description of coordination compounds, connecting structural, electronic, and spectroscopic aspects.

## 3.7 Exercises

**Multiple Choice Questions (MCQs)**

1. In an octahedral field, which d-orbitals experience greater repulsion?
   A) $d_{xy}$, $d_{xz}$, $d_{yz}$

B) $d_{x2-y2}$, $d_{z2d}$
C) $d_{xz}$, $d_{z2}$
D) All five equally
Answer: B) $d_{x2-y2}$, $d_{z2d}$

2. The splitting energy in tetrahedral complexes ($\Delta_t$) is approximately:
A) Equal to $\Delta_o$
B) Twice $\Delta_o$
C) 4/9 of $\Delta_o$
D) Half of $\Delta_o$
Answer: C) 4/9 of $\Delta_o$

3. The Jahn–Teller effect is most significant in which electronic configuration?
A) $d^3$
B) $d^6$
C) $d^9$
D) $d^8$
Answer: C) $d^9$

4. A π-acceptor ligand like CO tends to:
A) Decrease $\Delta_o$
B) Increase $\Delta_o$
C) Have no effect on $\Delta_o$
D) Eliminate splitting
Answer: B) Increase $\Delta_o$

5. In a square planar field, the orbital of highest energy is:
A) $d_{z2d}$
B) $d_{xy}$
C) $d_{x2-y2}$
D) $d_{xz}$
Answer: C) $d_{x2-y2}$

**Short Answer Type Questions**

1. Describe the effect of π-acceptor ligands on the crystal field splitting energy.
2. What is the Jahn–Teller effect? Give an example.
3. Explain the role of Molecular Orbital Theory in understanding metal–ligand bonding.

**Long Answer Type Questions**

1. Describe the splitting of d-orbitals in octahedral, tetrahedral, and square planar ligand fields using diagrams.

2. Discuss the principles of Ligand Field Theory, emphasizing how it integrates electrostatic and covalent bonding models.
3. Explain the Jahn–Teller effect in detail and discuss its significance in transition metal complexes.

## 3.8 References and Suggested Readings


- Miessler, G. L., Fischer, P. J., & Tarr, D. A**.** (2014). *Inorganic Chemistry* (5th Edition). Pearson Education Inc., 221 River Street, Hoboken, NJ 07030, USA.
- Housecroft, C. E., & Sharpe, A. G. (2018). *Inorganic Chemistry* (5th Edition). Pearson Education Limited, 80 Strand, London WC2R 0RL, United Kingdom.
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# Unit 4 LIGAND FIELD STABILIZATION ENERGY (LFSE)

**Structure**



## 4.1 Introduction

The **Ligand Field Stabilization Energy (LFSE)** is one of the most significant concepts derived from **Ligand Field Theory (LFT)**. It provides a quantitative measure of the stabilization a metal ion experiences when surrounded by ligands that cause a splitting of its degenerate d-orbitals.

When a free transition metal ion interacts with ligands, the **degenerate (equal-energy) d-orbitals** split into sets of orbitals with different energies depending on the geometry of the complex (octahedral, tetrahedral, square planar, etc.). The distribution of d-electrons among these orbitals leads to a net stabilization or destabilization energy — termed **LFSE**.

LFSE helps explain many observable properties of coordination compounds, such as:

- **Color** and **absorption spectra**
- **Magnetic behavior** (high-spin vs. low-spin)
- **Thermodynamic stability** of complexes
- **Preference for specific geometries**

In short, LFSE provides a bridge between theoretical orbital splitting and experimental chemical behavior.

## 4.2 Objectives

After completing this unit, learners should be able to:

1. Define and derive the concept of **Ligand Field Stabilization Energy (LFSE)**.

2. Calculate LFSE values for different d-electron configurations.

3. Distinguish between **high-spin** and **low-spin** complexes in terms of LFSE.
4. Explain the **factors affecting the splitting parameter (Δ)**.
5. Relate LFSE to **complex stability, color, and magnetic properties**.

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### 4.3 Factors Affecting the Splitting Parameter (Δ)

The magnitude of the **crystal-field or ligand-field splitting parameter (Δ)** plays a vital role in determining the LFSE of a complex. Δ represents the energy difference between the higher-energy and lower-energy sets of d-orbitals created when ligands approach a central metal ion.

The **greater** the Δ value, the **larger** the LFSE, leading to more stable complexes. Several factors influence Δ:

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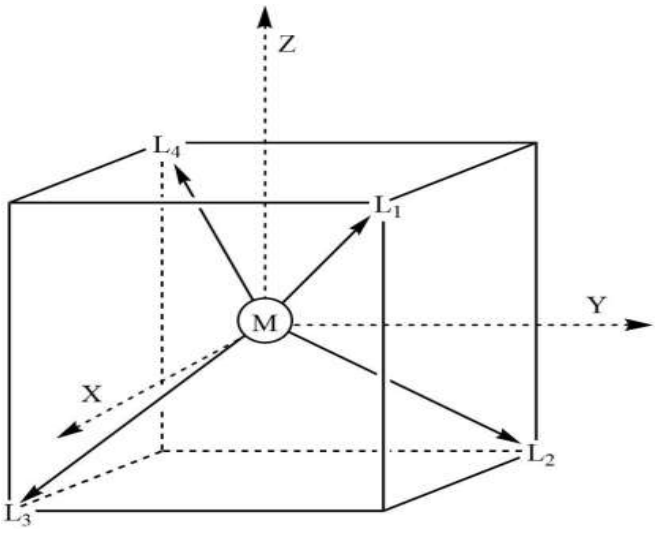
#### (a) Nature of the Metal Ion

1. **Oxidation State:** Higher oxidation states of metal ions result in larger Δ values because the increased positive charge pulls ligands closer, enhancing electrostatic interaction.
   Example:

$$\Delta_{oct}(Co^{3+}) > \Delta_{oct}(Co^{2+})$$

2. **Principal Quantum Number (n):**
   For ions of the same oxidation state, Δ increases down a group as the metal d-orbitals become more diffuse.

$$\Delta_{oct}(Fe^{3+}) < \Delta_{oct}(Ru^{3+}) < \Delta_{oct}(Os^{3+})$$




**(b) Nature of the Ligands**

Different ligands cause different degrees of d-orbital splitting depending on their ability to interact with the metal orbitals. This trend is represented by the **Spectrochemical Series**, where ligands are arranged in order of increasing field strength (Δ):

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

Strong-field ligands such as **$CN^-$** and **CO** cause large Δ values, often leading to **low-spin** complexes. Weak-field ligands such as **$Cl^-$** and **$H_2O$** give small Δ values, favoring **high-spin** configurations.

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**(c) Geometry of the Complex**

The splitting pattern and magnitude differ with geometry:

- **Octahedral ($\Delta_o$):** Greatest splitting; ligands approach directly along axes.
- **Tetrahedral ($\Delta_t$):** Smaller splitting; ligands approach between axes.

$$\Delta t \approx \frac{4}{9}\Delta_o$$

- **Square Planar (Δ_{sp}):** Very large splitting, often leading to diamagnetic low-spin complexes.

### (d) Nature of Metal–Ligand Bonding

The extent of covalency between the metal and ligands affects Δ.

- **π-donor ligands** decrease Δ because they donate electron density into metal d-orbitals.
- **π-acceptor ligands** increase Δ due to back-bonding interactions that stabilize $t_{2g}$ orbitals.

### (e) Coordination Number and Ligand Arrangement

An increase in coordination number (more ligands) generally increases total repulsion and can slightly increase Δ. Likewise, distortions from ideal geometry (e.g., Jahn–Teller effects) can modify orbital energies and thus the splitting parameter.

### Check Your Progress

1. Define Ligand Field Stabilization Energy (LFSE) with an example.

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2. Explain why the LFSE for high-spin $d^5$ octahedral complexes is zero.

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## 4.4 Summary

- **Ligand Field Stabilization Energy (LFSE)** represents the extra stabilization a metal ion experiences due to uneven filling of split d-orbitals in a ligand field.
- LFSE depends on **the number of d-electrons**, **their arrangement**, and **the strength of the ligand field (Δ)**.

- Strong-field ligands increase Δ, causing electrons to pair in lower orbitals (low-spin). Weak-field ligands reduce Δ, giving high-spin arrangements.
- The splitting parameter Δ is influenced by **metal oxidation state**, **ligand nature**, **geometry**, and **metal–ligand covalency**.
- LFSE helps rationalize experimental properties such as **complex color**, **magnetic moment**, and **relative stability**.

**4.5 Exercises**

**A. Multiple Choice Questions (MCQs)**

**1.** LFSE arises due to:
A) Equal distribution of electrons among d-orbitals
B) Unequal occupancy of split d-orbitals in a ligand field
C) Covalent bond formation
D) Metal ion polarization

**Answer:** B) Unequal occupancy of split d-orbitals in a ligand field

**2.** The LFSE for a high-spin $d^5$ octahedral complex is:
A) 0
B) $-2.0\ \Delta_o$
C) $-0.4\ \Delta_o$
D) $-1.2\ \Delta_o$

**Answer:** A) 0

**3.** The splitting energy ($\Delta_o$) increases with:
A) Decreasing metal oxidation state
B) Stronger field ligands
C) Weaker ligand–metal interactions
D) Larger metal–ligand distance

**Answer:** B) Stronger field ligands

**4.** The relation between octahedral and tetrahedral splitting is approximately:
A) $\Delta_t = 2\Delta_o$
B) $\Delta_t = \Delta_o$
C) $\Delta_t = (4/9)\Delta_o$
D) $\Delta_t = (9/4)\Delta_o$

**Answer:** C) $\Delta_t = (4/9)\Delta_o$

**5.** Among the following, which ligand produces the highest splitting?
A) $H_2O$
B) $NH_3$
C) $CN^-$
D) $Cl^-$

**Answer:** C) $CN^-$

**B. Short Answer Questions (SAQs)**

1. How does oxidation state of a metal ion affect Δ?

2. Write the spectrochemical series and indicate which ligands produce high-spin vs. low-spin complexes.

3. Compare the splitting energies of octahedral, tetrahedral, and square planar complexes.

**C. Long Answer Questions (LAQs)**

1. Derive an expression for LFSE in octahedral complexes and calculate the LFSE for $d^4$, $d^6$, and $d^8$ configurations (high-spin and low-spin).

2. Discuss in detail the factors affecting the splitting parameter (Δ) and how they determine the geometry and magnetic properties of complexes.

3. Explain how LFSE influences the color, stability, and reactivity of coordination compounds.

## 4.6 References and Suggested Readings

1. Miessler, G. L., Fischer, P. J., & Tarr, D. A**.** (2014). *Inorganic Chemistry* (5th Edition). Publisher: Pearson Education Inc., 221 River Street, Hoboken, NJ 07030, USA.

2. Housecroft, C. E., & Sharpe, A. G. (2018). *Inorganic Chemistry* (5th Edition). Publisher: Pearson Education Ltd., 80 Strand, London WC2R 0RL, United Kingdom.

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# Unit 5 METAL COMPLEXES

**Structure**



## 5.1 Introduction

Metal complexes—also known as coordination compounds—are chemical species consisting of a **central metal ion** bonded to one or more **ligands** through coordinate covalent bonds. These compounds form the basis of **coordination chemistry**, a cornerstone of inorganic chemistry that connects theory with numerous real-world applications.

The study of metal complexes began with **Alfred Werner's Coordination Theory (1893)**, which introduced the concepts of **coordination number**, **primary valency**, and **secondary valency**. Werner's pioneering work explained the structures of many cobalt–ammonia complexes and earned him the **Nobel Prize in Chemistry (1913)**.

Over time, more advanced theories evolved to describe the nature of metal–ligand bonding:

- **Valence Bond Theory (VBT):** describes bond formation via orbital hybridization.
- **Crystal Field Theory (CFT):** explains the electrostatic interactions and d-orbital splitting.
- **Ligand Field Theory (LFT):** integrates covalent and electrostatic perspectives.
- **Molecular Orbital Theory (MOT):** provides a quantum mechanical framework for metal–ligand bonding.

These theories collectively help explain **color, magnetism, geometry, reactivity, and stability** of coordination compounds,

enabling chemists to design complexes for medicine, catalysis, materials, and biological systems.

## 5.2 Objectives

After completing this unit, learners should be able to:

1. Understand the general structure and bonding in metal complexes.
2. Explain the major theoretical frameworks used to describe metal–ligand bonding.
3. Identify and describe important applications of metal complexes in daily life.
4. Connect the theoretical background with practical uses in medicine, industry, and environment.
5. Evaluate the role of coordination chemistry in modern technology and biochemistry.

## 5.3 Metal Complexes: Applications in Our Daily Lives

Metal complexes are not merely academic curiosities; they are **integral to modern life**. From biological systems to industrial catalysts, their roles are both diverse and essential.

### (a) Biological Systems

1. **Hemoglobin ($Fe^{2+}$ complex):** The iron(II) center in hemoglobin binds reversibly to oxygen in the blood, allowing oxygen transport from lungs to tissues.
2. **Chlorophyll ($Mg^{2+}$ complex):** The magnesium ion in chlorophyll is responsible for capturing light energy during photosynthesis.
3. **Vitamin $B_{12}$ ($Co^{3+}$ complex):** Contains a cobalt center essential for red blood cell formation and metabolic processes.
4. **Cytochromes:** Iron–porphyrin complexes that facilitate electron transfer in respiration and photosynthesis.

### (b) Medicinal Applications

1. **Cisplatin [$Pt(NH_3)_2Cl_2$]:** A platinum-based anticancer drug used to treat testicular, ovarian, and bladder cancers. It acts by binding to DNA and disrupting replication.

2. **Silver complexes:** Possess antimicrobial properties and are used in wound dressings and coatings for medical instruments.

3. **Gold complexes:** Employed in the treatment of rheumatoid arthritis and as imaging agents.

4. **Technetium and gadolinium complexes:** Used as contrast agents in nuclear and magnetic resonance imaging (MRI).

**(c) Industrial and Environmental Applications**

1. **Catalysis:** Transition metal complexes act as catalysts in many chemical processes:

    - **Wilkinson's catalyst [$RhCl(PPh_3)_3$]:** hydrogenation of alkenes.

    - **Ziegler–Natta catalysts ($TiCl_4$ with $AlEt_3$):** polymerization of alkenes.

    - **Hydroformylation catalysts:** convert alkenes into aldehydes using CO and $H_2$.

2. **Electroplating and Pigments:** Complexes of Cr, Ni, and Co are used in coatings and coloring materials.

3. **Water Treatment:** Metal chelates (like EDTA complexes) are used to remove metal ions from wastewater.

4. **Sensors and Electronics:** Ruthenium and iridium complexes are used in OLEDs (organic light-emitting diodes) and chemical sensors.

**(d) Environmental and Agricultural Uses**

1. **Chelates in fertilizers:** Metal–EDTA complexes supply essential micronutrients (Fe, Zn, Cu) to plants in bioavailable forms.

2. **Pollution control:** Complexes help capture harmful gases (like CO and NO) or sequester heavy metals from the environment.

3. **Photocatalytic reactions:** Metal complexes aid in solar energy conversion and pollutant degradation.

## 5.4 Theoretical Frameworks for Metal Complexes: Practical Applications

The understanding of metal complexes relies on several interrelated theoretical models.

### (a) Werner's Coordination Theory

Proposed the existence of **primary** (ionic) and **secondary** (coordination) valencies. It successfully explained complex stoichiometry and isomerism, forming the foundation of coordination chemistry.

### (b) Crystal Field Theory (CFT)

Explains the color and magnetism of complexes based on **electrostatic interactions** between metal ions and ligands, leading to **d-orbital splitting**. For example, the deep blue color of $[Cu(H_2O)_6]^{2+}$ arises from d–d transitions between split orbitals.

### (c) Ligand Field Theory (LFT)

Builds upon CFT by including covalent aspects of metal–ligand bonding. It explains phenomena like **$\pi$ back-bonding**, **Jahn–Teller distortions**, and **spectrochemical series**.

### (d) Molecular Orbital Theory (MOT)

Provides the most detailed quantum description, showing how metal and ligand orbitals combine to form bonding, nonbonding, and antibonding molecular orbitals. MOT helps design metal complexes for specific optical and electronic properties.

### (e) Ligand Field Stabilization Energy (LFSE)

Quantifies the energetic stabilization achieved by particular d-electron arrangements. LFSE explains why some geometries or spin states are more stable and helps predict magnetic behavior and thermodynamic preference.

By integrating these theoretical models, chemists can **design complexes with targeted reactivity**, predict stability, and optimize industrial and biological functions.

**Check Your Progress**

1. Define a coordination complex and give two examples.

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2. Explain the role of ligands in determining the geometry of metal complexes.

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## 5.5 Summary

- **Metal complexes** are formed by coordinate bonds between a central metal ion and surrounding ligands.
- Theoretical models—**Werner's theory, VBT, CFT, LFT, MOT, and LFSE**—collectively explain bonding, geometry, and properties.
- Metal complexes play essential roles in **biology, medicine, catalysis, materials, and environmental science**.
- Understanding their theoretical background enables the **rational design** of new catalysts, drugs, and functional materials.
- Coordination chemistry thus serves as a bridge between theory and practical innovation.

## 5.6 Exercises

### A. Multiple Choice Questions (MCQs)

**1.** The central metal atom in a coordination complex act as:
A) Electron donor
B) Electron acceptor
C) Free radical generator
D) Neutral species

**Answer:** B) Electron acceptor

**2.** The active center in hemoglobin is:
A) $Mg^{2+}$
B) $Fe^{2+}$
C) $Co^{3+}$
D) $Cu^{2+}$

**Answer:** B) $Fe^{2+}$

**3.** Which of the following is used as an anticancer drug?
A) $[Fe(CN)_6]^{3-}$
B) $[Pt(NH_3)_2Cl_2]$
C) $[Co(NH_3)_6]^{3+}$
D) $[Ni(CO)_4]$

**Answer:** B) $[Pt(NH_3)_2Cl_2]$

**4.** Which of the following theories explains the color of transition metal complexes?
A) Valence Bond Theory
B) Crystal Field Theory
C) Werner's Theory
D) Ionic Theory

**Answer:** B) Crystal Field Theory

**5.** The geometry of $[Ni(CN)_4]^{2-}$ complex is:
A) Tetrahedral
B) Octahedral
C) Square planar
D) Trigonal bipyramidal

**Answer:** C) Square planar

**B. Short Answer Questions (SAQs)**

1. Mention two biological functions of metal complexes.

2. What is the importance of Crystal Field Theory in understanding metal complexes?

3. Name two industrial processes that employ metal complex catalysts.

**C. Long Answer Questions (LAQs)**

1. Discuss the applications of metal complexes in biological and medicinal systems.

2. Explain the major theoretical frameworks that describe bonding and properties in metal complexes.

3. Describe at least four industrial and environmental applications of metal complexes with suitable examples.

## 5.7 References and Suggested Readings

1. Housecroft, C. E., & Sharpe, A. G. (2018). *Inorganic Chemistry* (5th Edition). Pearson Education Ltd., 80 Strand, London WC2R 0RL, United Kingdom.

2. Miessler, G. L., Fischer, P. J., & Tarr, D. A. (2014). *Inorganic Chemistry* (5th Edition). Publisher: Pearson Education Inc., 221 River Street, Hoboken, NJ 07030, USA.

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**BLOCK 2**

**SPECTRAL & MAGNETIC CHARACTERISTICS OF METAL COMPLEX**

**Unit 6 Introduction to Reaction Mechanisms**

**Structure**



## 6.1 Introduction

Transition metal complexes exhibit a wide range of **colors** and **magnetic behaviors**, which arise from the presence of **partially filled d-orbitals** and their interactions with surrounding ligands. The **spectral characteristics** of these complexes are primarily due to **electronic transitions** between split d-orbitals or between metal and ligand orbitals, while **magnetic characteristics** depend on the number of unpaired electrons present.

These properties not only define the visual appearance and magnetic response of a compound but also provide valuable insights into its **structure, oxidation state, coordination environment, and bonding nature**.

Spectroscopic and magnetic data together allow chemists to deduce the **geometry**, **spin state**, and **electronic configuration** of metal complexes, thus bridging theoretical coordination chemistry with experimental observations.

## 6.2 Objectives

After completing this unit, learners should be able to:

1. Understand the origin of color and magnetism in transition metal complexes.

2. Describe the types of electronic transitions responsible for absorption spectra.

### 6.3 Theoretical Background for Electronic Transitions

The color of a coordination compound arises from the **absorption of light** in the visible region, which promotes an electron from a lower-energy d-orbital to a higher-energy one. The **energy difference (Δ)** between these orbitals corresponds to the wavelength of absorbed light.

#### (a) d–d Transitions

In transition metal complexes, **d–d transitions** occur when an electron is excited between split d-orbitals (e.g., from $t_2g$ to e_g in an octahedral field).

- The energy required corresponds to the **crystal field splitting energy (Δ)**.
- These transitions are **Laporte-forbidden** in centrosymmetric molecules, but they occur weakly due to vibronic coupling.
- Example: The pale blue color of $[Ti(H_2O)_6]^{3+}$ results from a single d–d transition.

#### (b) Charge Transfer Transitions

These are generally more intense than d–d transitions and occur due to electron movement between the metal and ligands.

1. **Ligand-to-Metal Charge Transfer (LMCT):** Electrons move from filled ligand orbitals to empty metal orbitals. Example: $[Fe(SCN)]^{2+}$ complex shows a deep red color.
2. **Metal-to-Ligand Charge Transfer (MLCT):** Electrons move from filled metal d-orbitals to empty ligand π* orbitals. Example: $[Ru(bpy)_3]^{2+}$ complex displays intense orange-red color.

#### (c) Selection Rules

Two key rules govern the probability of electronic transitions:

1. **Laporte Selection Rule:** In centrosymmetric molecules, transitions between orbitals of the same parity (g → g or u → u) are forbidden. However, in complexes without inversion centers (like tetrahedral), such transitions are allowed.

2. **Spin Selection Rule:** Transitions that involve a change in spin multiplicity (e.g., from singlet to triplet) are forbidden. Complexes with paired electrons often show weak absorption due to this restriction.

These rules help explain why some complexes are **intensely colored**, while others appear **pale or colorless**.

### 6.4 Electromagnetic Spectrum and Its Regions

The **electromagnetic spectrum** covers all wavelengths of radiation, from gamma rays to radio waves. The visible region (approximately 400–700 nm) is particularly important in the study of metal complexes.

| Region | Wavelength (nm) | Type of Transition / Application |
|---|---|---|
| Ultraviolet (UV) | 200–400 | $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, charge transfer |
| Visible | 400–700 | d–d and charge transfer transitions |
| Infrared (IR) | 700–2500 | Vibrational transitions, ligand identification |
| Microwave | $10^5$–$10^7$ | Rotational transitions, ESR spectroscopy |

**UV–Vis spectroscopy** is primarily used to investigate d–d and charge transfer transitions, whereas **IR spectroscopy** provides information about ligand environments and bonding.

The **color observed** in a complex corresponds to the **complementary color** of the absorbed wavelength. For example, if a complex absorbs red light (around 650 nm), it appears green to the eye.

### 6.5 Electronic Structure and Magnetic Characteristics Relationship

The magnetic behavior of metal complexes is a direct result of the number of **unpaired electrons** in the metal's d-orbitals.

#### (a) Origin of Magnetism

Electrons possess both **spin** and **orbital angular momentum**. The overall magnetic moment (μ) of a complex is mainly due to unpaired electron spins and is expressed as:

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

where:

- $\mu$ = magnetic moment (Bohr Magneton, BM)
- n = number of unpaired electrons

For example:

- $d^5$ high-spin ($Fe^{3+}$) → 5 unpaired electrons → $\mu$ = 5.92 BM
- $d^6$ low-spin ($Fe^{2+}$ in $[Fe(CN)_6]^{4-}$) → 0 unpaired electrons → diamagnetic ($\mu$ = 0 BM)

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**(b) Types of Magnetic Behavior**

1. **Paramagnetic Complexes:** Contain unpaired electrons; attracted to magnetic fields (e.g., $[Fe(H_2O)_6]^{2+}$).
2. **Diamagnetic Complexes:** Contain all paired electrons; weakly repelled by magnetic fields (e.g., $[Ni(CN)_4]^{2-}$).
3. **Ferromagnetic and Antiferromagnetic Materials:** Occur in solid-state complexes where magnetic moments interact collectively.

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**(c) Factors Affecting Magnetic Properties**

1. **Oxidation State of Metal Ion:** Higher oxidation states often reduce the number of unpaired electrons.
2. **Ligand Field Strength:** Strong-field ligands cause electron pairing (low-spin), decreasing magnetic moment.
3. **Geometry and Symmetry:** Octahedral and tetrahedral environments influence the d-orbital splitting and spin state.
4. **Temperature:** In some cases (like spin-crossover complexes), magnetic behavior changes with temperature.

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**(d) Experimental Measurement**

Magnetic susceptibility can be measured using instruments like:

- **Gouy Balance** (classical method)
- **Vibrating Sample Magnetometer (VSM)**
- **Evans NMR method** (solution-state magnetism)

These techniques provide experimental magnetic moments that confirm theoretical predictions about electronic configuration and geometry.

**Check Your Progress**

1. Explain why most transition metal complexes are colored.

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1. Differentiate between d–d and charge transfer transitions.

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## 6.6 Summary

- Spectral properties of metal complexes arise from **electronic transitions** (mainly d–d and charge transfer).
- The **color** of a complex corresponds to the **energy difference** (Δ) between split d-orbitals.
- **Selection rules** (Laporte and spin) determine transition intensities.
- The **electromagnetic spectrum** provides the basis for UV–Vis and IR spectroscopy used in complex characterization.
- **Magnetic properties** depend on the number of unpaired electrons and are expressed in **Bohr Magnetons (BM)**.
- Spectroscopic and magnetic analyses together reveal the **geometry, oxidation state, and spin configuration** of transition metal complexes.

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## 6.7 Exercises

### A. Multiple Choice Questions (MCQs)

**1.** The color of a coordination compound is due to:
A) σ-bonding
B) d–d electronic transitions
C) Ligand vibrations
D) Proton transfer

**Answer:** B) d–d electronic transitions

**2.** A complex that shows strong absorption in the visible region is likely to involve:
A) d–d transitions only
B) Charge transfer transitions
C) Ionic transitions
D) Lattice vibrations

**Answer:** B) Charge transfer transitions

**3.** The magnetic moment (μ) of a complex with two unpaired electrons is approximately:
A) 1.73 BM
B) 2.83 BM
C) 3.87 BM
D) 4.90 BM

**Answer:** B) 2.83 BM

**4.** The Laporte rule forbids transitions between orbitals of:
A) Different parity
B) Same parity
C) s and p orbitals
D) p and d orbitals

**Answer:** B) Same parity

**5.** $[Fe(CN)_6]^{4-}$ is diamagnetic because:
A) It has no ligands
B) It is a high-spin complex
C) It is a low-spin complex
D) It contains delocalized electrons

**Answer:** C) It is a low-spin complex

**B. Short Answer Questions (SAQs)**

2. Define magnetic moment and give its unit.
3. Why is $[Cu(H_2O)_6]^{2+}$ paramagnetic while $[Cu(CN)_4]^{3-}$ is diamagnetic?
4. Mention two instruments used to measure magnetic susceptibility.

### C. Long Answer Questions (LAQs)

1. Discuss the types of electronic transitions observed in coordination compounds and the factors affecting their intensities.
2. Explain the relationship between electronic configuration, ligand field strength, and magnetic properties in transition metal complexes.
3. Describe how UV–Vis spectroscopy and magnetic measurements can be used to determine the geometry and spin state of a metal complex.

## 6.8 References and Suggested Readings

1. Miessler, G. L., Fischer, P. J., & Tarr, D. A. (2014). *Inorganic Chemistry* (5th Edition). Publisher**:** Pearson Education Inc., 221 River Street, Hoboken, NJ 07030, USA.
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# Unit 7 Electronic Transitions in Metal Complexes

**Structure**



## 7.1 Introduction

The unique **colors and spectral properties** of transition metal complexes arise from **electronic transitions** within their d-orbitals or between metal and ligand orbitals. These transitions are influenced by **ligand field strength, geometry, and the oxidation state** of the metal center.

The study of these transitions allows chemists to determine important parameters such as **crystal field splitting energy (Δ)**, **geometry**, and **spin state** of complexes.

In particular, **d–d transitions**, **charge transfer transitions**, and related spectral diagrams such as **Orgel** and **Tanabe–Sugano diagrams** help to explain the observed absorption spectra and predict the behavior of metal complexes under electromagnetic radiation.

Understanding electronic transitions is essential for interpreting **UV–Visible spectra**, which are key tools for analyzing complex structure, bonding, and reactivity.

## 7.2 Objectives

After completing this unit, students will be able to:

1. Explain the nature and origin of electronic transitions in transition metal complexes.
2. Describe the characteristics and rules governing **d–d transitions**.

3. Understand the **spin selection rule** and its significance in spectroscopy.
4. Interpret **Orgel diagrams** for simple systems.
5. Utilize **Tanabe–Sugano diagrams** to predict spectral transitions and spin states.
6. Relate observed colors and spectra to electronic configurations and ligand field strengths.

### 7.3 Characteristics of d–d Transitions

The **d–d transition** involves the promotion of an electron from a lower-energy d-orbital to a higher-energy d-orbital within the same metal ion under the influence of the ligand field.

These transitions are responsible for the **color** observed in many coordination compounds. For example, $[Ti(H_2O)_6]^{3+}$ appears violet due to the absorption of yellow-green light (around 500 nm).

**Key Features of d–d Transitions:**

1. **Intra-ionic Transitions:** The transition occurs within the same metal ion, between crystal field–split d-levels (e.g., $t_2g \rightarrow e\_g$).
2. **Dependence on Geometry:** The energy difference between d-orbitals varies for octahedral, tetrahedral, and square planar geometries, influencing the wavelength absorbed.
3. **Weak Intensity:** Because d–d transitions are **Laporte-forbidden** ($\Delta l = 0$), they have low molar absorptivities ($\varepsilon < 100$ $M^{-1}cm^{-1}$). However, distortions in symmetry allow weak transitions via **vibronic coupling**.
4. **Multiplicity of Transitions:** Ions with several d-electrons (e.g., $d^2$, $d^5$, $d^6$) can exhibit multiple transitions, each corresponding to promotion between different electronic states.
5. **Color and Complementary Absorption:** The color of the complex corresponds to the **complementary color** of the absorbed light (e.g., absorption of red → appearance of green).

### 7.4 Spin Selection Rule

In addition to symmetry considerations, **spin multiplicity** also governs the allowedness of transitions.

The **Spin Selection Rule** states that:

"Electronic transitions that involve a change in spin multiplicity ($\Delta S \neq 0$) are forbidden."

**Explanation:**

- If the number of unpaired electrons changes during excitation, the transition is spin-forbidden.
- For example:
    - Allowed transition: triplet → triplet ($\Delta S = 0$)
    - Forbidden transition: singlet → triplet ($\Delta S \neq 0$)

**Consequences:**

- **High-spin complexes** often exhibit multiple weak bands due to partial relaxation of this rule.
- **Low-spin complexes**, with all paired electrons, show fewer but often more intense bands due to greater orbital overlap and spin–orbit coupling.

**Relaxation of the Rule:**

Although spin-forbidden transitions are weak, they can occur due to:

- **Spin–orbit coupling**, which mixes states of different spin multiplicities.
- **Asymmetry or distortion** in the complex geometry, reducing symmetry restrictions.

Thus, while selection rules provide guidance, real spectra often show weak bands corresponding to formally forbidden transitions.

**7.5 Orgel Diagrams**

**Orgel diagrams** are simple qualitative tools used to correlate the **electronic configuration** of a metal ion with its **spectral transitions** in weak ligand fields (typically for high-spin complexes).

They are especially useful for predicting the number and relative energy of **spin-allowed** transitions for octahedral and tetrahedral complexes of configurations $d^1$ to $d^9$ (except $d^0$ and $d^{10}$, which have no d–d transitions).

**Construction and Features:**

1. Each diagram represents transitions between terms of the same spin multiplicity (e.g., ^4F → ^4P).
2. The vertical axis denotes the **relative energy** of the electronic states.
3. The splitting patterns for **octahedral (Oh)** and **tetrahedral (Td)** fields are shown separately.

4. Lines between states indicate possible **spin-allowed transitions** observable in the UV–Vis spectrum.

**Example:**

- **$d^2$ configuration ($V^{3+}$, $Cr^{4+}$):**
  - Ground state term: ^3F
  - Excited state term: ^3P
  - In octahedral field, ^3F splits into $^3T_1g$, $^3T_2g$, and $^3A_2g$ levels.
  - The most intense absorption corresponds to the transition $^3T_1g(F) \rightarrow {}^3T_1g(P)$.

**Utility:**

- Orgel diagrams provide **qualitative** understanding of electronic spectra.
- They help identify **number of bands**, **relative energy separations**, and **electronic configurations**.
- However, they cannot predict **exact transition energies** or handle low-spin systems effectively — for that, **Tanabe–Sugano diagrams** are used.

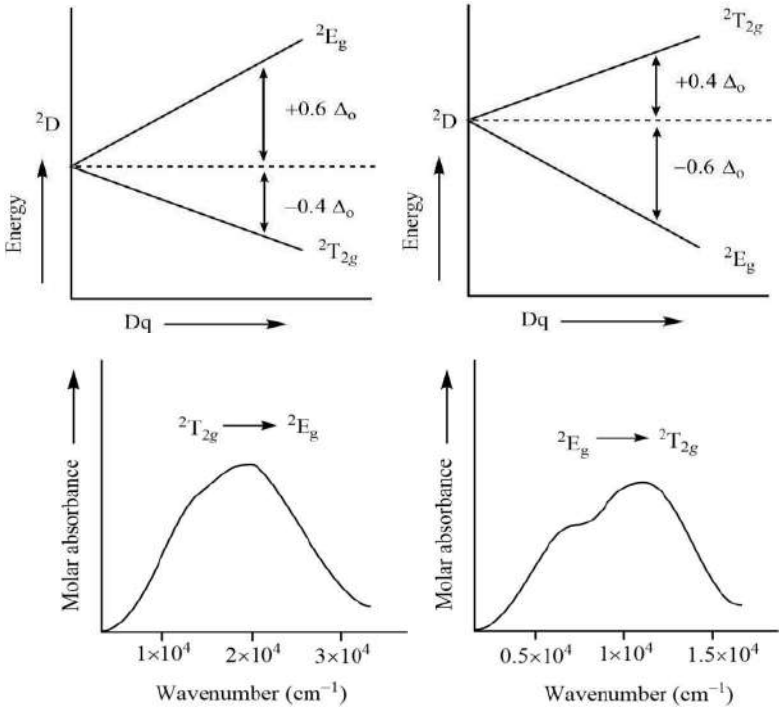


*Figure –2. 1 The splitting pattern of 2D state in octahedral complexes with (a) d1-configuration and (b) d9- configuration; and the corresponding electronic spectra of (c) $[Ti(H_2O)_6]^{3+}$ and (d) $[Cu(H_2O)_6]^{2+}$.*

## 7.6 Tanabe–Sugano Diagrams

**Tanabe–Sugano diagrams** are more quantitative representations that show how the energy of electronic states varies with **ligand field strength (Δ/B)** for all possible spin states of a $d^n$ configuration.

**Key Features:**

1. The x-axis represents **ligand field strength** in terms of Δ/B, where **B** is the Racah parameter (measuring electron–electron repulsion).
2. The y-axis represents **energy** (E/B) of various electronic states.
3. Each line corresponds to a different electronic term (^3T₁g, ^3T₂g, etc.).
4. The **ground state** and possible **excited states** are plotted as Δ increases, indicating **high-spin to low-spin crossover** points.

**Uses:**

1. To determine the **crystal field splitting energy (Δ)** from experimental absorption spectra.
2. To distinguish between **high-spin** and **low-spin** configurations.
3. To estimate **Racah parameter (B)** and assess the **degree of covalency**.
4. To explain **spectral band positions and intensities** quantitatively.

**Example:**

For a **$d^3$ ion** like $Cr^{3+}$ (in $[Cr(H_2O)_6]^{3+}$), three spin-allowed transitions are observed:

- ^4A₂g → ^4T₂g
- ^4A₂g → ^4T₁g(F)
- ^4A₂g → ^4T₁g(P)

From these transitions, Δ and B can be calculated, and the observed spectral data can be matched with the Tanabe–Sugano diagram for the $d^3$ system.

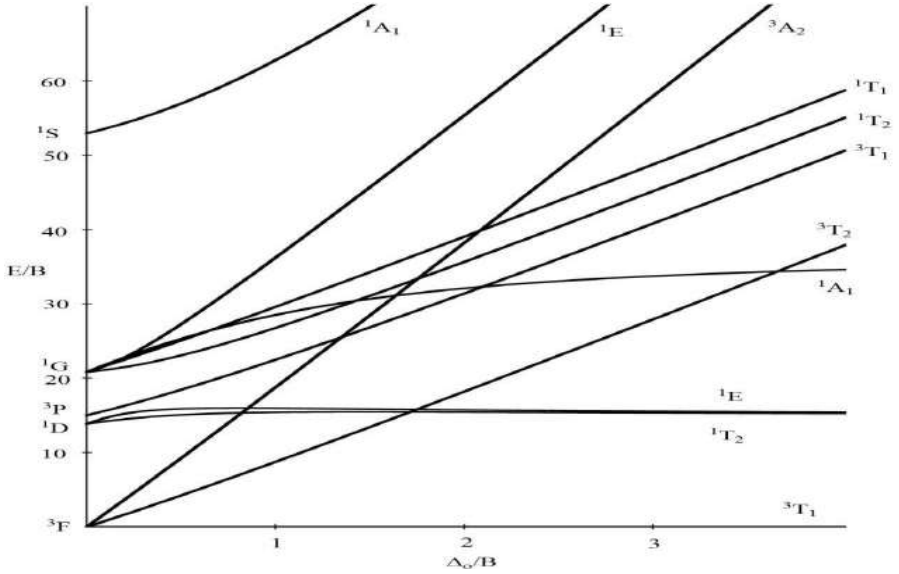


*Figure Splitting of free ion terms for d2 complexes in the octahedral crystal field.*

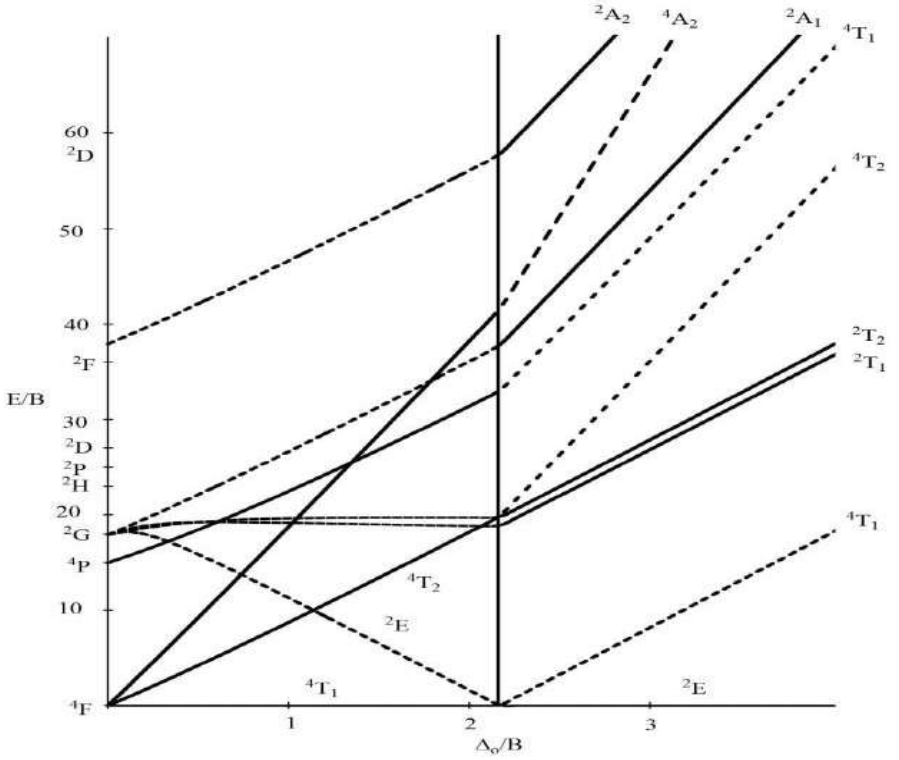


*Figure : Splitting of free ion terms for d7 complexes in the octahedral crystal field*

**Check Your Progress**

1. Define d–d transition and explain why it is weak in intensity.

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2. State the spin selection rule and give one example of a spin-forbidden transition.

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## 7.7 Summary

- Electronic transitions in metal complexes are primarily **d–d** or **charge transfer** in nature.
- **d–d transitions** depend on metal ion configuration and ligand field geometry.
- **Selection rules** (Laporte and spin) determine the intensity and number of observed bands.
- **Orgel diagrams** give a **qualitative picture** of electronic transitions in high-spin complexes.
- **Tanabe–Sugano diagrams** provide a **quantitative relationship** between electronic energy levels and ligand field strength, allowing calculation of Δ and B values.
- Together, these diagrams form the foundation of **electronic spectroscopy** of coordination compounds.

## 7.8 Exercises

### A. Multiple Choice Questions (MCQs)

**1.** d–d transitions are responsible for:
A) Magnetic properties
B) Color in transition metal complexes
C) Bonding strength
D) Melting point

**Answer:** B) Color in transition metal complexes

**2.** The spin selection rule forbids transitions where:
A) $\Delta S = 0$

B) $\Delta S \neq 0$
C) $\Delta L = \pm 1$
D) $\Delta J = 0$

**Answer:** B) $\Delta S \neq 0$

**3.** Orgel diagrams are not applicable to:
A) High-spin complexes
B) Low-spin complexes
C) Octahedral complexes
D) Tetrahedral complexes

**Answer:** B) Low-spin complexes

**4.** In a Tanabe–Sugano diagram, the x-axis represents:
A) Energy (E/B)
B) Ligand field strength (Δ/B)
C) Wavelength (nm)
D) Racah parameter (B)

**Answer:** B) Ligand field strength (Δ/B)

**5.** The ground state for a $d^3$ octahedral complex is:
A) $^4A_2g$
B) $^4T_1g$
C) $^3T_1g$
D) $^1A_1g$

**Answer:** A) $^4A_2g$

**B. Short Answer Questions (SAQs)**

1. What is the main limitation of Orgel diagrams?
2. How can Tanabe–Sugano diagrams be used to determine crystal field splitting energy?
3. Differentiate between high-spin and low-spin complexes with reference to electronic transitions.

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**C. Long Answer Questions (LAQs)**

1. Explain the theory of d–d transitions in coordination complexes and discuss the factors affecting their intensity.
2. Describe the construction and application of Orgel diagrams with suitable examples.
3. Discuss the principles, interpretation, and importance of Tanabe–Sugano diagrams in determining electronic structures of metal complexes.

## 7.9 References and Suggested Readings

1. Greenwood, N. N., & Earnshaw, A. (2012). *Chemistry of the Elements* (2nd ed.). Butterworth-Heinemann. Publisher address: Butterworth-Heinemann (Elsevier), 125 London Wall, London EC2Y 5AS, United Kingdom.
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# Unit 8 Effects on Spectra

**Structure**



## 8.1 Introduction

The **spectra of transition metal complexes** provide a window into their **electronic structure, geometry, and bonding interactions**. While the basic electronic transitions—such as d–d and charge transfer transitions—determine the principal absorption bands, several effects can **modulate the energy, intensity, and pattern of these spectra**.

Among these effects, **Jahn-Teller distortions** and other **structural deviations from ideal geometry** are especially significant. These perturbations lead to **splitting of degenerate energy levels**, changes in absorption wavelength, and shifts in color, making the spectral features sensitive indicators of complex geometry.

Understanding these effects is essential for interpreting **UV–Vis spectra**, assigning **electronic transitions**, and predicting **chemical reactivity**.

## 8.2 Objectives

After completing this unit, students should be able to:

1. Explain the origin and significance of **Jahn-Teller distortions** in transition metal complexes.
2. Understand how molecular orbital theory describes deviations in spectra.

## 8.3 Jahn-Teller Distortion in Spectra

The **Jahn-Teller effect** occurs when a **degenerate electronic state** in a non-linear molecule leads to **spontaneous geometric distortion** to remove degeneracy and lower the overall energy.

**Key Features:**

1. **Occurrence:**
    - Most pronounced in **octahedral $d^9$, high-spin $d^4$, and low-spin $d^7$ configurations**.
    - Typically observed in **Cu(II), Mn(III), and Cr(II) complexes**.
2. **Effect on Geometry:**
    - In octahedral complexes, the distortion often manifests as **elongation or compression along one axis** (usually the z-axis).
    - Tetrahedral and square planar geometries may also exhibit minor distortions.
3. **Impact on Spectra:**
    - Splitting of degenerate orbitals leads to **additional absorption bands**.
    - The **position, number, and intensity of d–d transitions** are modified.
    - Often, one observes **shifts in λ_max** and the **appearance of fine structure** in UV–Vis spectra.

**1. Static Jahn-Teller Distortion:**

- Occurs when the **distortion is permanent**, and the molecule adopts a **fixed, lower-symmetry geometry**.
- Typical in complexes with **strong Jahn-Teller ions** (e.g., $Cu^{2+}$ in octahedral geometry).
- **Spectral consequences:**
    - Clear splitting of d-orbitals.
    - Well-resolved additional bands in the UV–Vis spectrum.
    - Distinct differences from ideal octahedral patterns.

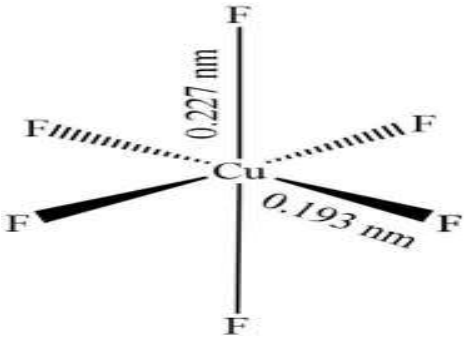
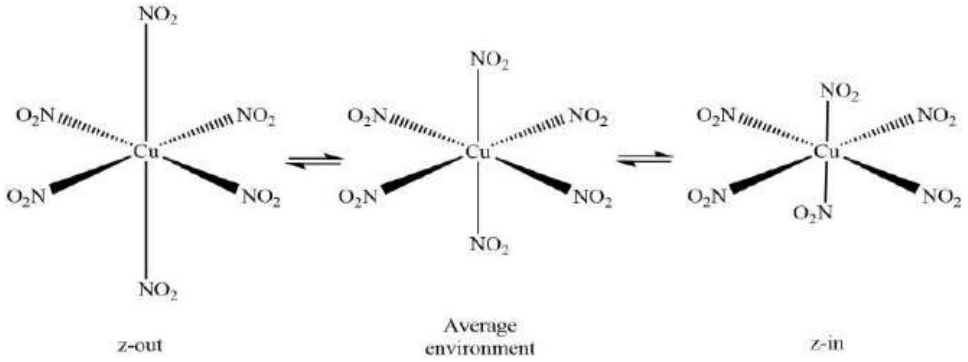



**Fig Static Jahn-Teller distortion in CuF2 lattice.**

**2. Dynamic Jahn-Teller Distortion:**

- Occurs when the complex **rapidly oscillates between degenerate geometries** due to thermal motion.
- No permanent distortion; instead, the molecule exists as a **time-averaged symmetrical structure**.
- Common in weaker Jahn-Teller ions (e.g., low-spin $d^7$ complexes at room temperature).
- **Spectral consequences:**
    - Partial or smeared splitting of d-orbitals.
    - Broadened absorption bands.
    - Sometimes only subtle spectral deviations from the ideal geometry.




**Dynamic Jahn -Teller distortion in $K_2Pb\ [Cu(NO_2)_6]$.**

4. **Example:**
    - In $[Cu(H_2O)_6]^{2+}$, an octahedral $d^9$ complex, the Jahn-Teller elongation along the z-axis splits the e_g orbitals (d_$z^2$ and d_$x^2$–$y^2$), producing multiple absorption bands instead of a single peak.
5. **Significance:**
    - Provides insight into **electronic configuration** and **ligand-metal interactions**.
    - Helps to **distinguish high-spin and low-spin states**.
    - Explains deviations from **ideal octahedral spectral patterns**.

## 8.4 Metal Complexes Molecular Orbital Theory and Spectra

**Molecular Orbital Theory (MOT)** extends the understanding of spectral features by considering the **mixing of metal d-orbitals with ligand orbitals**.

1. **Ligand field splitting** is explained through **σ- and π-bonding interactions**, which determine the **energy levels** of molecular orbitals.
2. Distortions such as Jahn-Teller or low-symmetry coordination affect the **degeneracy of orbitals**, altering spectral transitions.
3. MOT allows prediction of:
    - **Shift in absorption maxima** (bathochromic or hypsochromic shifts).
    - **Changes in intensity** of spin-allowed or spin-forbidden transitions.
    - **Splitting patterns** of orbitals in non-ideal geometries.

Thus, MOT provides a **quantitative and qualitative framework** to relate observed spectra to molecular structure, complementing **crystal field theory (CFT)** and **ligand field theory (LFT)**.

**Check Your Progress**

**1.** Explain the occurrence of Jahn-Teller effect

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**2.** Explain the effect of geometry on Jahn-Teller effect.

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## 8.5 Summary

- The spectra of metal complexes are influenced not only by **d–d and charge transfer transitions** but also by **structural distortions**.
- **Jahn-Teller distortions** remove degeneracy in octahedral $d^9$, high-spin $d^4$, and low-spin $d^7$ complexes, leading to additional spectral bands.

- **Molecular orbital theory** explains changes in spectral patterns due to bonding interactions and geometrical distortions.
- Understanding these effects is crucial for **interpreting UV–Vis spectra**, **assigning transitions**, and analyzing **electronic structure** of complexes.

## 8.6 Exercises

### A. Multiple Choice Questions (MCQs)

**1.** Jahn-Teller distortion primarily affects which type of metal complex?
A) $d^0$ complexes
B) $d^9$ octahedral complexes
C) $d^{10}$ tetrahedral complexes
D) s-block metal complexes

**Answer:** B) $d^9$ octahedral complexes

**2.** The main spectral consequence of Jahn-Teller distortion is:
A) Decreased absorption intensity only
B) Splitting of degenerate energy levels
C) Complete disappearance of d–d transitions
D) Formation of charge transfer bands

**Answer:** B) Splitting of degenerate energy levels

**3.** Molecular Orbital Theory explains spectral shifts in complexes by considering:
A) Only nuclear positions
B) Metal-ligand orbital interactions
C) Temperature effects
D) Solvent viscosity

**Answer:** B) Metal-ligand orbital interactions

**4.** Jahn-Teller distortions usually lead to:
A) Increased symmetry
B) Elongation or compression along an axis
C) Complete loss of color
D) Conversion to tetrahedral geometry

**Answer:** B) Elongation or compression along an axis

**5.** Which metal ion is commonly associated with Jahn-Teller distortions?
A) $Mg^{2+}$
B) $Cu^{2+}$
C) $Zn^{2+}$
D) $Na^{+}$

**Answer:** B) $Cu^{2+}$

**B. Short Answer Questions (SAQs)**

1. Describe the role of molecular orbital theory in understanding spectral effects.
2. Give an example of a metal complex that exhibits Jahn-Teller distortion.
3. Explain why $d^0$ and $d^{10}$ complexes do not show Jahn-Teller distortions.

**C. Long Answer Questions (LAQs)**

1. Discuss the Jahn-Teller effect in octahedral complexes, including its impact on orbital splitting and electronic spectra.
2. Explain how molecular orbital theory accounts for spectral changes due to geometric distortions in metal complexes.
3. Analyze the combined effects of Jahn-Teller distortion and ligand field interactions on the UV–Vis spectra of a $d^9$ transition metal complex.

## 8.7 References and Suggested Readings

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# Unit 9 Magnetic Characteristics of Metal Complexes

**Structure**



## 9.1 Introduction

ransition metal complexes exhibit fascinating **magnetic properties** arising from the presence of **unpaired electrons in their d-orbitals**. Unlike s- or p-block elements, the partially filled d-orbitals in transition metals allow for **paramagnetism, ferromagnetism, antiferromagnetism, and diamagnetism**. Understanding these magnetic behaviors provides critical insights into the **electronic structure, bonding, geometry, and reactivity** of metal complexes.

Magnetic measurements complement spectroscopic techniques such as **UV–Vis and IR spectroscopy**, helping chemists to determine **spin states, ligand field strengths, and electronic configurations**. The study of magnetic properties is not only theoretically significant but also practically relevant in areas such as **catalysis, material science, and bioinorganic chemistry**.

## 9.2 Objectives

By the end of this chapter, students should be able to:

1. Explain the **types of magnetism** observed in transition metal complexes.
2. Relate the **number of unpaired electrons** and **spin states** to magnetic moments.
3. Understand how magnetic measurements can be used to infer **geometry, electronic configuration, and ligand field effects**.

## 9.3 Magnetic Characteristics of Metal Complexes

### 1. Origin of Magnetism

Magnetism in metal complexes primarily arises from **unpaired electrons** in the d-orbitals. The interaction of these electrons with an **external magnetic field** determines the type of magnetism exhibited. Magnetic behavior is quantified in terms of **magnetic susceptibility** (χ) and **magnetic moment** (μ), usually expressed in **Bohr magnetons (B.M.)**.

For complexes with unpaired electrons, the **spin-only formula** can be used to calculate the magnetic moment:

μso=n(n+2) B.M.\mu_{so} = \sqrt{n(n+2)} \, \text{B.M.}μso=n(n+2) B.M.

Where **n** is the number of unpaired electrons.

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## 2. Types of Magnetism

### A. Diamagnetism

- Occurs in complexes with **all paired electrons**.
- Weakly repelled by a magnetic field.
- Examples: $Zn^{2+}$ ($d^{10}$), $Cd^{2+}$ ($d^{10}$).
- Magnetic moment: 0 B.M.

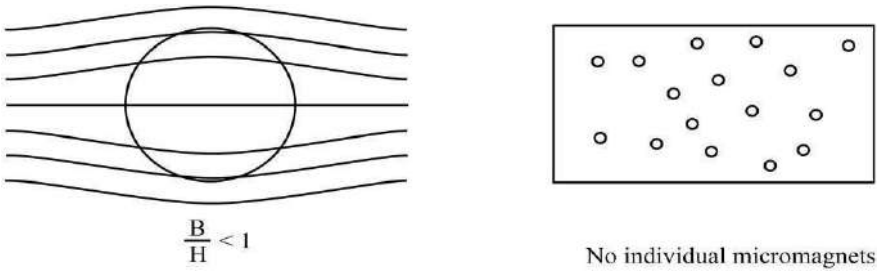


*Figure -The behavior of a diamagnetic body in the externally applied magnetic field and corresponding magnetic domain.*

### B. Paramagnetism

- Caused by **one or more unpaired electrons**.
- Attracted to a magnetic field.
- Examples: High-spin $Fe^{3+}$ ($d^5$), $Mn^{2+}$ ($d^5$).
- Magnetic moment calculated using spin-only formula.

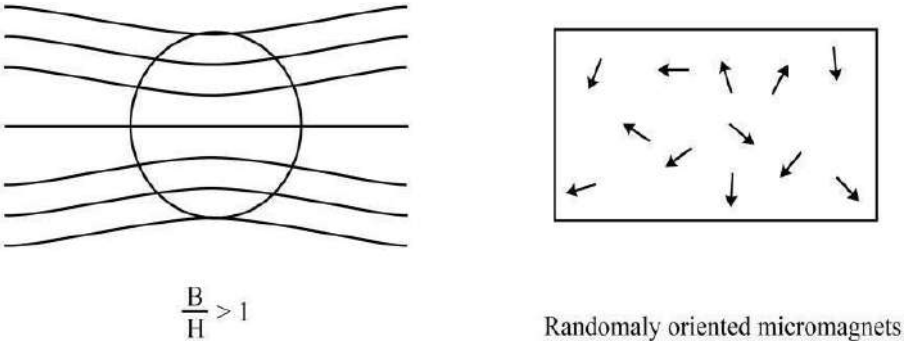


*Figure - The behaviorof a paramagnetic body in the externally applied magnetic field and corresponding magnetic domain*

**C. Ferromagnetism**

- Parallel alignment of magnetic moments leads to **spontaneous magnetization**.
- Observed in some solid-state metal complexes (e.g., Fe, Co, Ni complexes).

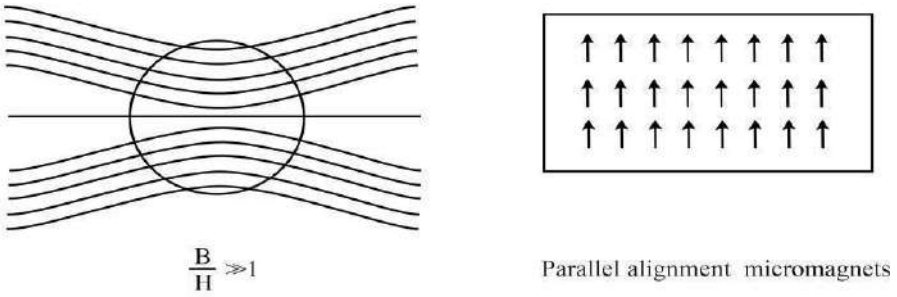


Figure -The behavior of a ferromagnetic body in an externally applied magnetic field and corresponding magnetic domain.

**D. Antiferromagnetism**

- Magnetic moments of adjacent ions align **antiparallel**, canceling each other.
- Observed in solids like MnO and some $Cr^{2+}$ complexes.

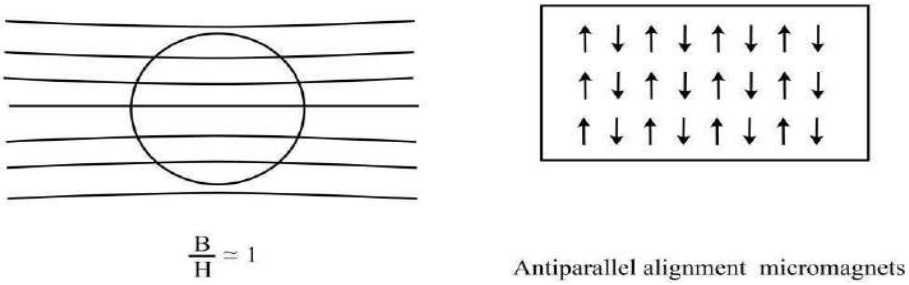


*Figure 4 . The behavior of an antiferromagnetic body in an externally applied magnetic field and corresponding magnetic domain*.

**E. Ferrimagnetism**

- Unequal antiparallel alignment leads to **partial magnetization**.
- Examples: Mixed metal oxides such as $Fe_3O_4$.

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**3. High-Spin and Low-Spin Complexes**

- In **octahedral complexes**, the **ligand field strength** determines the distribution of electrons among d-orbitals.
- **High-spin complexes**: Weak-field ligands → more unpaired electrons → higher magnetic moments.
- **Low-spin complexes**: Strong-field ligands → fewer unpaired electrons → lower magnetic moments.
- Example: $[Fe(H_2O)_6]^{3+}$ (high-spin) vs $[Fe(CN)_6]^{3-}$ (low-spin).

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**4. Magnetic Measurements and Applications**

- **Magnetic susceptibility measurements** help determine the **number of unpaired electrons**.
- Magnetic data can validate theoretical predictions of **geometry and electronic configuration**.
- Practical applications:
    - Characterization of **catalysts**
    - Study of **bioinorganic systems** like hemoglobin and cytochromes
    - Development of **magnetic materials** for electronics

**Check Your Progress**

1. Define paramagnetism and give an example.

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2. Differentiate between diamagnetism and paramagnetism.

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## 9.4 Summary

Magnetism in metal complexes is a powerful tool for understanding **electronic structure and bonding**. Complexes can be **diamagnetic or paramagnetic**, depending on the presence of **unpaired electrons**, and may also exhibit **ferromagnetic, antiferromagnetic, or ferrimagnetic behavior** in the solid state. The distinction between **high-spin and low-spin complexes** explains variations in magnetic moments, which can be measured experimentally to infer **geometry, ligand field effects, and spin states**. Overall, the study of magnetic characteristics bridges theory and experiment in transition metal chemistry.

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## 9.5 Exercises

### A. Multiple Choice Questions (MCQs)

1. Diamagnetic complexes have:
   A) One or more unpaired electrons
   B) All electrons paired
   C) Ferromagnetic alignment
   D) Antiferromagnetic alignment

**Answer:** B) All electrons paired

2. The spin-only formula for magnetic moment is:
   A) $\mu = \sqrt{(n^2 + 2)}$
   B) $\mu = \sqrt{(n(n+2))}$
   C) $\mu = n(n+1)$
   D) $\mu = 2n$

**Answer:** B) $\mu = \sqrt{(n(n+2))}$

3. Which of the following is an example of a low-spin complex?
   A) $[Fe(H_2O)_6]^{3+}$
   B) $[Fe(CN)_6]^{3-}$
   C) $[Mn(H_2O)_6]^{2+}$
   D) $[Co(H_2O)_6]^{2+}$

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

4. Antiferromagnetism occurs when:
   A) Magnetic moments align parallel
   B) Magnetic moments align antiparallel
   C) All electrons are paired
   D) Magnetic moments are unequal

**Answer:** B) Magnetic moments align antiparallel

5. A high-spin $Fe^{3+}$ ($d^5$) octahedral complex has approximately:
   A) 0 B.M.

B) 5.92 B.M.
C) 3.87 B.M.
D) 1.73 B.M.

**Answer:** B) 5.92 B.M.

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**B. Short Answer Questions (SAQs)**

1. What is the significance of magnetic moment measurements?
2. Explain high-spin and low-spin complexes in octahedral geometry.
3. Give an example of a ferromagnetic complex and explain its magnetic behavior.

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**C. Long Answer Questions (LAQs)**

1. Discuss the different types of magnetism observed in transition metal complexes and explain the origin of each type.
2. Explain how ligand field strength affects the magnetic properties of octahedral complexes, using examples.
3. Describe how magnetic susceptibility and magnetic moment measurements can be used to determine the spin state and geometry of a metal complex.

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# Unit 10 Advanced Magnetic Concepts

**Structure**



## 10.1 Introduction

While basic magnetism in metal complexes can often be explained by **unpaired electrons** and the **spin-only formula**, real systems frequently exhibit more complex behavior. **Advanced magnetic concepts** account for factors beyond spin-only considerations, including:

- **Orbital contributions** to magnetic moments
- **Spin-orbit coupling** in transition metal and lanthanide complexes
- **Exchange interactions** between metal centers
- **Temperature-dependent magnetic behavior**

These phenomena provide deeper insights into **electronic structure, bonding, and cooperative effects** in complexes. Understanding advanced magnetic behavior is essential in **magnetic materials, molecular magnetism, spintronics, and bioinorganic chemistry**.

## 10.2 Objectives

After completing this unit, the learners will be able to:

1. Understand the **limitations of the spin-only approach** and the importance of orbital contributions.
2. Explain **spin-orbit coupling** and its effect on magnetic properties.
3. Analyze **temperature-dependent magnetism** and exchange interactions in polynuclear metal complexes.

## 10.3 Orbital Contribution to Magnetic Moments

- In many **first-row transition metal complexes**, the orbital angular momentum is **partially quenched** by the ligand field, so the **spin-only formula** works reasonably well.
- In **heavier transition metals and lanthanides**, orbital contributions are significant.
- Example: Octahedral $Co^{2+}$ ($d^7$) complexes often show **observed μ > spin-only value**, due to orbital contribution.

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**2. Spin-Orbit Coupling**

- **Spin-orbit coupling** arises from the interaction between the electron's **spin** and its **orbital angular momentum**.
- In complexes of **heavy transition metals and lanthanides**, this interaction significantly **modifies magnetic behavior**, producing **anisotropy** in the magnetic response.
- It explains why some complexes exhibit **temperature-dependent magnetic moments** or **directional dependence** in magnetic susceptibility.

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**3. Temperature Effects on Magnetism**

- Magnetic moments are **not always constant**; they can vary with temperature.
- **Curie's Law** describes paramagnetic behavior:
- **Deviations from Curie's Law** occur due to:
    - Zero-field splitting
    - Spin-orbit coupling
    - Antiferromagnetic or ferromagnetic interactions
- **Example:** In $Fe^{3+}$ polynuclear complexes, **antiferromagnetic coupling** lowers the effective magnetic moment at low temperatures.

---

**4. Exchange Interactions in Polynuclear Complexes**

- **Exchange interactions** occur when unpaired electrons in adjacent metal centers interact via bridging ligands.
- Can be:

  - **Ferromagnetic** (parallel spin alignment → enhanced μ)
  - **Antiferromagnetic** (antiparallel spin alignment → reduced μ)
- The **Heisenberg exchange Hamiltonian** is used to describe interactions:
- Positive J → ferromagnetic, Negative J → antiferromagnetic.
- Applications: Molecular magnets, magnetic clusters, and spin-crossover materials.

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**5. Magnetic Anisotropy and Single-Molecule Magnets**

- **Magnetic anisotropy** arises when a molecule exhibits **direction-dependent magnetic behavior**, often due to **spin-orbit coupling**.
- **Single-molecule magnets (SMMs)** retain magnetization below a **blocking temperature**, displaying hysteresis like bulk magnets.
- Example: $Mn_{12}$-acetate cluster, Fe-based SMMs.
- Importance: Quantum computing, molecular memory devices, and spintronics.

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**6. Spin-Crossover Phenomena**

- Certain octahedral $Fe^{2+}$ and $Co^{3+}$ complexes can **switch between high-spin and low-spin states** depending on:
  - Temperature
  - Pressure
  - Light irradiation (LIESST effect)
- Spin crossover causes **large changes in magnetic moment**, which can be observed using magnetic susceptibility measurements.

**Check Your Progress**

1. Define spin-orbit coupling and explain its effect on magnetic properties.

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2. What is magnetic anisotropy and why is it important?

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### 10.4 Summary

Advanced magnetic behavior in metal complexes extends beyond **spin-only considerations**. Key factors include **orbital contributions, spin-orbit coupling, temperature-dependent behavior, exchange interactions, and anisotropy**. These effects explain deviations from simple models, enable the design of **molecular magnets**, and have practical applications in **material science, electronics, and bioinorganic systems**. Understanding these concepts is crucial for interpreting experimental data in modern inorganic chemistry.

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### 10.5 Exercises

**MCQs**

1. Which factor is responsible for deviations from the spin-only magnetic moment?
   A) Only unpaired electrons
   B) Orbital contribution and spin-orbit coupling
   C) Temperature alone
   D) Molecular weight

**Answer:** B) Orbital contribution and spin-orbit coupling

2. Exchange interactions in polynuclear complexes can lead to:
   A) Diamagnetism only
   B) Ferromagnetism or antiferromagnetism
   C) Paramagnetism only
   D) Spin-only behavior

**Answer:** B) Ferromagnetism or antiferromagnetism

3. Single-molecule magnets (SMMs) retain magnetization below:
   A) Curie temperature
   B) Blocking temperature
   C) Room temperature
   D) Melting point

**Answer:** B) Blocking temperature

4. Spin-orbit coupling arises due to interaction between:
   A) Two unpaired electrons
   B) Electron spin and orbital motion
   C) Nuclear spin and electron spin
   D) Ligand field only

**Answer:** B) Electron spin and orbital motion

5. Spin-crossover complexes change spin states in response to:
   A) Only temperature
   B) Temperature, pressure, or light
   C) Ligand field only
   D) Magnetic anisotropy only

**Answer:** B) Temperature, pressure, or light

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**SAQs**

1. Explain the difference between ferromagnetic and antiferromagnetic exchange interactions.
2. How does temperature affect the magnetic moment of a polynuclear complex?
3. Give an example of a spin-crossover complex and describe its behavior.

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**LAQs**

1. Discuss orbital contributions to magnetic moments and give examples where spin-only formula fails.
2. Explain single-molecule magnets (SMMs) and their potential applications in technology.
3. Describe the effect of exchange interactions in polynuclear metal complexes and how they are quantified using the Heisenberg Hamiltonian.

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**BLOCK 3**

**REACTION MECHANISM OF TRANISTION METAL COMPLAEX – PART I**

**Unit 11:** Introduction to reaction mechanisms

**Structure**



## 11.1 Introduction to Metal Complex Theories

Coordination chemistry is one of the most fascinating and extensive branches of inorganic chemistry. It deals with the study of **complex compounds** or **coordination compounds** formed by the combination of metal ions with neutral molecules or anions known as **ligands**. These compounds have widespread applications in catalysis, biological systems, analytical chemistry, and materials science.

The concept of metal complexes originated in the late 19th century, when **Alfred Werner (1893)** proposed his revolutionary **Coordination Theory**, explaining the structures of cobalt–ammine complexes. This theory introduced the ideas of **primary valency** (oxidation state) and **secondary valency** (coordination number) of metals, marking the beginning of modern coordination chemistry. Werner's work earned him the Nobel Prize in Chemistry in 1913 and provided the foundation for understanding the geometric and bonding characteristics of metal–ligand systems.

Over time, several advanced models have evolved to explain the bonding, electronic structure, color, magnetism, and reactivity of metal complexes. These include:

- **Crystal Field Theory (CFT):** Explains the effect of ligand electric fields on the d-orbitals of the central metal ion, helping predict magnetic and optical properties.
- **Ligand Field Theory (LFT):** A refinement of CFT incorporating covalent effects between metal and ligands.

- **Molecular Orbital Theory (MOT):** Describes bonding in metal complexes in terms of orbital overlap and delocalized molecular orbitals, giving a deeper understanding of covalency and electronic transitions.

These theories collectively help explain why certain complexes are **colored**, **paramagnetic**, or **highly reactive**, and why they adopt particular **geometries** (octahedral, tetrahedral, square planar, etc.).

Thus, the study of metal complex theories forms the backbone of coordination chemistry, bridging classical ionic views with quantum-mechanical explanations of metal–ligand bonding.

## 11.2 Objectives

After studying this unit, learners will be able to:

1. Understand the fundamental concepts of coordination compounds and metal–ligand bonding.
2. Explain the structural principles governing metal complexes.
3. Discuss the crystal field splitting of d-orbitals in different geometries.
4. Interpret the magnetic and electronic behavior of transition metal complexes using crystal field theory.
5. Describe the bonding in coordination compounds using molecular orbital theory.
6. Relate theoretical models to experimental observations such as color, magnetism, and reactivity.
7. Develop a comparative understanding of CFT, LFT, and MOT in explaining coordination chemistry.

## 11.3 Core Principles in Coordination Chemistry

Coordination chemistry revolves around the study of **coordination compounds**—substances that contain a central metal atom or ion surrounded by a set of molecules or anions called **ligands**. These ligands are attached to the metal through **coordinate covalent bonds**, where both electrons in the shared pair are contributed by the ligand. Understanding the fundamental principles of coordination chemistry helps explain the **structure, bonding, reactivity, and properties** of metal complexes.

### Coordination Compounds and Complexes

A **coordination compound** consists of a central metal ion surrounded by ligands within a definite geometry. The portion enclosed in square brackets represents the **coordination sphere**.

**Example:**

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

Here, the complex ion $[Cu(NH_3)_4]^{2+}$ is the coordination entity, and $SO_4^{2-}$ is the counter ion.

**Central Metal Atom or Ion**

The **metal center** acts as a Lewis acid (electron pair acceptor) and provides empty orbitals for coordination. Common transition metals forming complexes include **Fe, Co, Ni, Cu, Zn, Pt, and Cr.**

**Example:**
In $[Fe(CN)_6]^{3-}$, $Fe^{3+}$ is the central metal ion.

The ability of metals to form complexes depends on:

- Availability of vacant orbitals.
- Oxidation state of the metal.
- Nature of the ligands (donor atoms and charge).

**Ligands**

**Ligands** are ions or molecules that donate a lone pair of electrons to the metal to form a coordinate bond. They act as **Lewis bases**.

**Types of Ligands:**

1. **Monodentate:** Bind through one donor atom (e.g., $NH_3$, $H_2O$, $Cl^-$).
2. **Bidentate:** Have two donor atoms (e.g., ethylenediamine, $C_2H_8N_2$).
3. **Polydentate:** Contain multiple donor sites (e.g., $EDTA^{4-}$).
4. **Ambidentate:** Can coordinate through two different atoms (e.g., $NO_2^-$ via N or O).
5. **Chelating Ligands:** Form ring structures with the metal, enhancing stability.

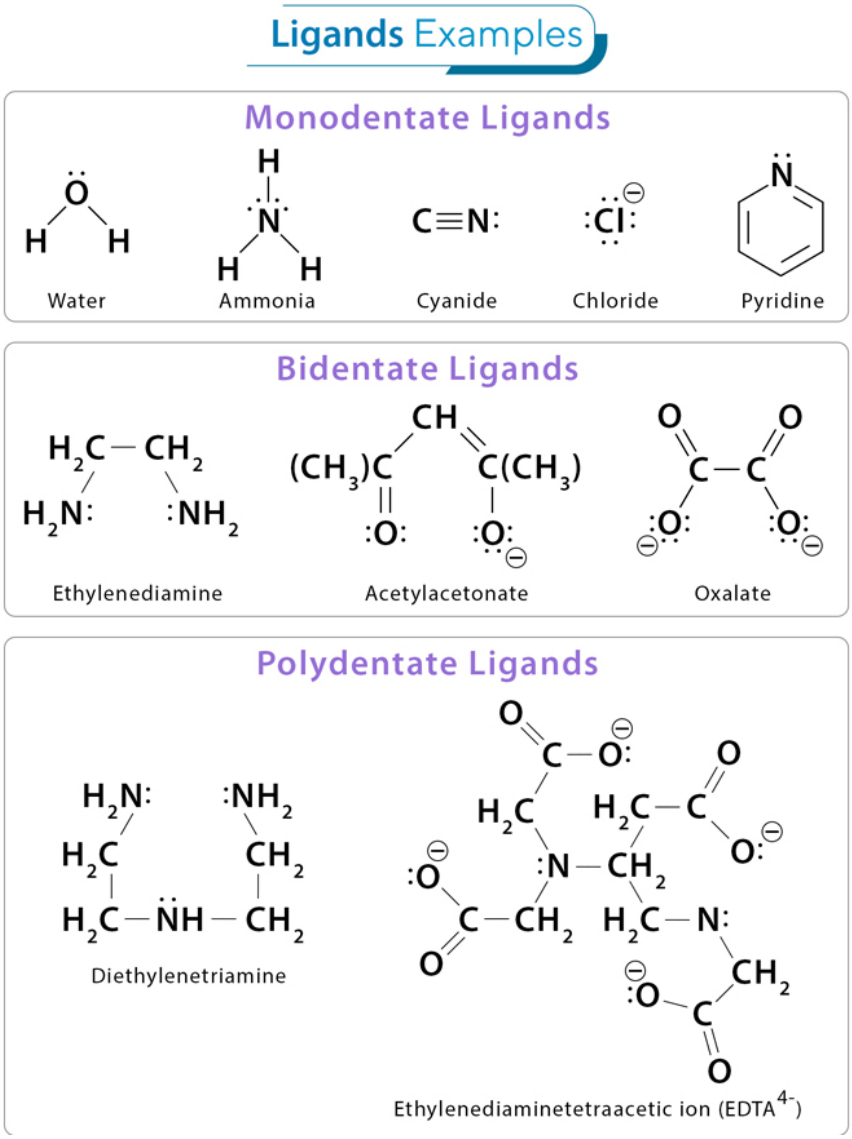



**Fig: Types of ligands**

**Chelate Effect:**Chelating ligands increase the thermodynamic stability of complexes due to the formation of cyclic structures, reducing entropy loss upon coordination.

## Coordination Number and Geometry

The **coordination number (C.N.)** is the number of ligand donor atoms directly bonded to the central metal ion.
It determines the **geometry** of the complex.

| Coordination Number | Common Geometry | Example |
|---|---|---|
| 2 | Linear | $[Ag(NH_3)_2]^+$ |
| 4 | Tetrahedral or Square planar | $[NiCl_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$ |
| 6 | Octahedral | $[Fe(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$ |

| Coordination number | Name | Geometry | Polyhedron | Example |
|---|---|---|---|---|
| 2 | Linear | M | | $AuCl(PPh_3)$ |
| 3 | Trigonal planar | M | | $Pt(PPh_3)_3$ |
| 4 | Square planar | M | | $RhCl(PPh_3)_3$ |
| 4 | Tetrahedral | M | | $Ni(CO)_4$ |
| 5 | Trigonal bipyramidal | M | | $Fe(CO)_5$ |
| 5 | Square pyramidal | M | | $[VOCl_4]^{2-}$ |
| 6 | Octahedral | M | | $Mo(CO)_6$ |
| 6 | Trigonal prismatic | M | | $W(CH_3)_6$ |

## Oxidation Number

The **oxidation number** of a metal in a complex is the apparent charge on the metal ion when all ligands and counterions are removed according to their normal charges.

**Example:**
In $[Fe(CN)_6]^{4-}$, each $CN^-$ = –1
Let oxidation number of Fe = x
Then, $x + 6(-1) = -4 \rightarrow$ **x = +2**

Hence, Fe is in the +2 oxidation state.

## Werner's Coordination Theory

Alfred Werner proposed the first modern explanation for coordination compounds (1893).

**Postulates:**

1. Metals exhibit **primary valency** (oxidation state) and **secondary valency** (coordination number).
2. Primary valency is ionizable; secondary valency is non-ionizable.
3. Secondary valencies are directed in space and give the geometry of the complex.
4. Complexes can exist in **isomeric forms** (linkage, coordination, and geometrical isomerism).

**Example:**

For $[Co(NH_3)_6]Cl_3$:

- Primary valency = 3 (ionizable $Cl^-$).
- Secondary valency = 6 ($NH_3$ ligands forming octahedral geometry).

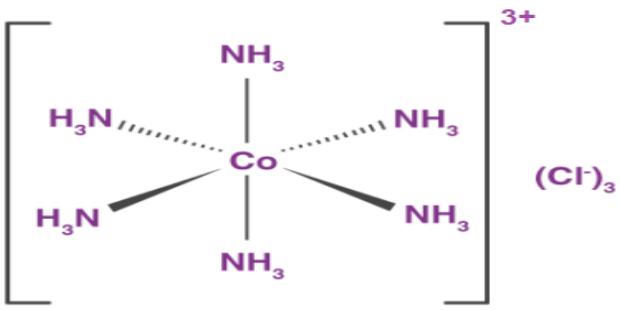



**Fig: General structure of a coordination compound**

## Isomerism in Coordination Compounds

Coordination compounds can exhibit **isomerism**, similar to organic compounds.

**Types of Isomerism:**

1. **Structural Isomerism:**
    - *Ionization isomerism*: Exchange of ligands between coordination sphere and counter ions.
      Example: $[Co(NH_3)_5Br]SO_4$and $[Co(NH_3)_5SO_4]Br$.

- *Linkage isomerism*: Ambidentate ligands bind through different donor atoms.
  Example: $[Co(NH_3)_5NO_2]^{2+}$(nitro) and $[Co(NH_3)_5ONO]^{2+}$(nitrito).

2. **Stereoisomerism:**
   - *Geometrical isomerism*: Ligands occupy different positions (cis/trans forms).
     Example: $[Pt(NH_3)_2Cl_2]$— cis and trans isomers.
   - *Optical isomerism*: Mirror-image (non-superimposable) forms of chiral complexes, such as $[Co(en)_3]^{3+}$.

**Stability of Complexes**

The stability of metal complexes depends on:

- **Nature of the metal ion:** Higher charge and smaller size increase stability.
- **Nature of the ligand:** Chelating ligands and those with π-acceptor properties stabilize complexes.
- **Solvent effects and temperature:** Aqueous solutions and temperature changes affect complex stability constants.

**Applications of Coordination Compounds**

1. **Biological systems:** Hemoglobin, chlorophyll, and vitamin $B_{12}$ are coordination complexes.
2. **Catalysis:** Zeise's salt and Wilkinson's catalyst are used in hydrogenation and polymerization.
3. **Analytical chemistry:** EDTA complexes in titrations for hardness of water.
4. **Medicinal chemistry:** Cisplatin $[Pt(NH_3)_2Cl_2]$used in cancer therapy.
5. **Industrial chemistry:** Used in electroplating, pigment formation, and extraction of metals.

## 11.4 Crystal Field Theory: Fundamentals and Applications

### Introduction

**Crystal Field Theory (CFT)** was developed in the 1930s by physicists Hans Bethe and John Hasbrouck Van Vleck to explain the electronic structures, colors, and magnetic properties of transition metal complexes.
It describes the interaction between a **central metal ion** (bearing positive charge) and surrounding **negative ligands** (or negative ends of polar ligands) as purely **electrostatic in nature**.

The theory assumes that:

- The metal ion acts as a point positive charge.
- The ligands are point negative charges (anions) or dipoles (neutral molecules like $NH_3$, $H_2O$).
- The attraction between the metal and ligands affects the energy of the metal's **d-orbitals**, causing **splitting** into groups of different energies.

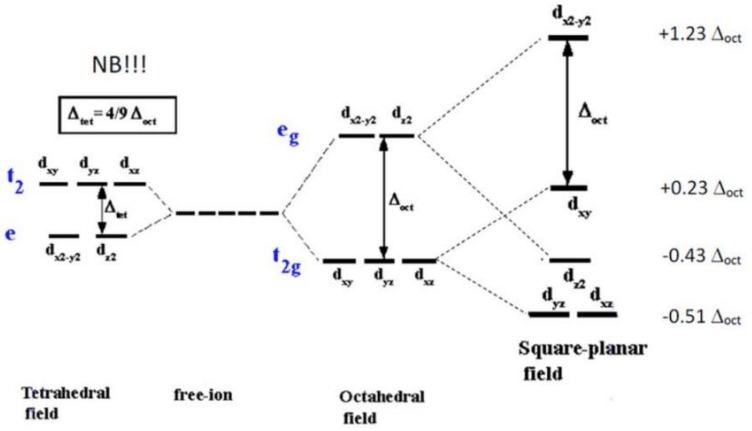



**Fig: Crystal Field Theory**

Although CFT neglects covalent bonding, it successfully explains important physical properties such as:

- **Color** of complexes
- **Magnetic behavior**
- **Spectral transitions**
- **Stability and geometry** of metal–ligand systems

**Assumptions of Crystal Field Theory**

1. Metal–ligand interactions are **electrostatic** (ionic).
2. Ligands are treated as point charges or dipoles.
3. Metal ion's d-orbitals are degenerate in a free ion but split in an electric field created by ligands.
4. The difference in energy between the split d-orbitals is called **Crystal Field Splitting Energy (Δ)**.
5. Electrons fill the orbitals according to Hund's rule and the pairing energy.

**Crystal Field Splitting in Octahedral Complexes**

In a **free transition metal ion**, the five d-orbitals ($d_xy$, $d_xz$, d_yz, $d_x^2$–$y^2$, d_$z^2$) are degenerate (same energy).
When ligands approach along the **x, y, and z axes** in an **octahedral field**, the repulsion between ligand electrons and d-electrons on the metal ion is not uniform.

- The orbitals pointing directly along the axes (**$d_x^2$–$y^2$, d_$z^2$**) experience **greater repulsion** and thus are **raised in energy**.
- The orbitals oriented between axes (**$d_xy$, $d_xz$, d_yz**) experience **less repulsion** and are **lowered in energy**.

This results in the splitting of d-orbitals into two sets:

| Set | Orbitals | Energy Level |
|---|---|---|
| **$t_2g$** | $d_xy$, $d_xz$, d_yz | Lower energy |
| **e_g** | $d_x^2$–$y^2$, d_$z^2$ | Higher energy |

The energy difference between these two sets is called the **Crystal Field Splitting Energy ($\Delta_o$)** or **10Dq** for octahedral complexes.

**Crystal Field Stabilization Energy (CFSE)**

The **Crystal Field Stabilization Energy (CFSE)** is the energy gained by a complex due to the arrangement of d-electrons in the split orbitals.

For an octahedral complex:

- Each electron in a $t_2g$ orbital gains **$-0.4\Delta_o$** energy.
- Each electron in an e_g orbital loses **$+0.6\Delta_o$** energy.

**Example:**
For a $d^4$ low-spin octahedral complex:
CFSE = $(4 \times -0.4\Delta_o) + P$ (pairing energy) = $-1.6\Delta_o + P$

The magnitude of CFSE influences:

- Complex stability
- Color intensity
- Magnetic moment

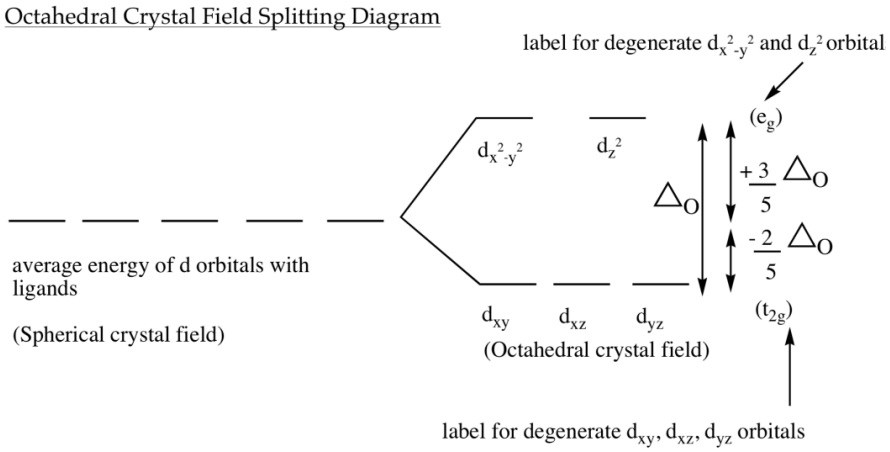



**Fig: Splitting of d-orbitals in an Octahedral Field**

### High-Spin and Low-Spin Complexes

The arrangement of d-electrons in $t_{2g}$ and e_g orbitals depends on the relative magnitudes of **crystal field splitting energy ($\Delta_o$)** and **pairing energy (P)**.

| Condition | Type of Complex | Electronic Configuration | Magnetic Behavior |
|---|---|---|---|
| $\Delta_o < P$ | **High-spin** | Maximum unpaired electrons | Paramagnetic |
| $\Delta_o > P$ | **Low-spin** | Electrons pair in $t_{2g}$ first | Diamagnetic or weakly magnetic |

**Example:**

- $[Fe(H_2O)_6]^{2+}$ → Weak field, high-spin (4 unpaired $e^-$)
- $[Fe(CN)_6]^{4-}$ → Strong field, low-spin (0 unpaired $e^-$)

**Crystal Field Splitting in Tetrahedral Complexes**

In **tetrahedral geometry**, four ligands surround the metal ion at the corners of a tetrahedron.

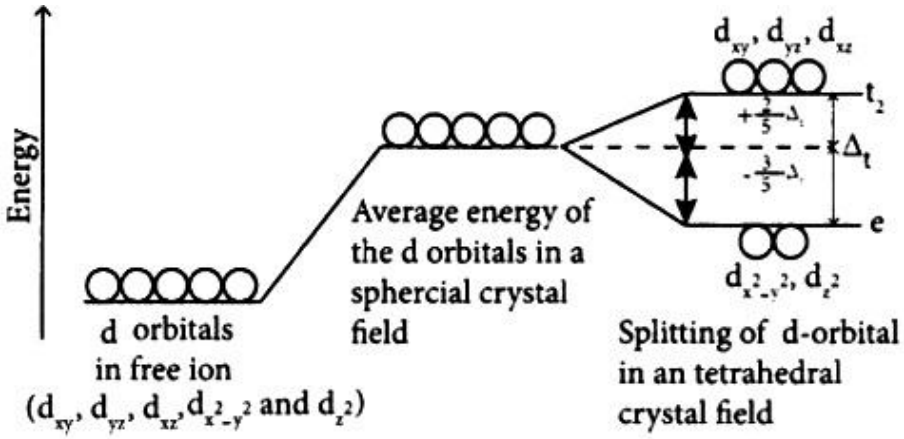
- There is **no direct overlap** with $d_x^2$–$y^2$ and d_$z^2$ orbitals, so they experience **less repulsion**.
- The **$t_2$ orbitals** ($d_x$y, $d_x$z, d_yz) are raised in energy, and **e orbitals** ($d_x^2$–$y^2$, d_$z^2$) are lowered.

Thus, the splitting pattern is **reversed** compared to octahedral complexes.

**Relation between splitting energies:**

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

Since Δ_t is smaller, tetrahedral complexes are usually **high-spin** (pairing is unfavorable).




Crystal field splitting in tetrahedral field

**Fig: splitting of d-orbitals in a Tetrahedral Field**

**Square Planar Complexes**

A **square planar field** can be considered as a distorted octahedral field where the two ligands along the z-axis are removed.

**Order of d-orbital energy:**

$$d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz} = d_{yz}$$

This geometry is common for **$d^8$ metal ions** like $Ni^{2+}$, $Pd^{2+}$, $Pt^{2+}$.

**Example:** $[Ni(CN)_4]^{2-}$ → diamagnetic square planar
$[NiCl_4]^{2-}$ → paramagnetic tetrahedral

**Factors Affecting Crystal Field Splitting (Δ)**

1. **Nature of the metal ion:**
   Higher oxidation state → greater attraction → larger $\Delta_o$.
   Example: $\Delta_o(Fe^{3+}) > \Delta_o(Fe^{2+})$
2. **Nature of the ligand:**
   Strong-field ligands produce larger splitting.
   (Explained by **Spectrochemical Series** below.)
3. **Geometry of the complex:**
   Octahedral > Square planar > Tetrahedral in Δ magnitude.
4. **Nature of the metal (period):**
   4d and 5d transition metals exhibit greater $\Delta_o$ than 3d metals due to larger orbitals.

**Spectrochemical Series**

An experimentally determined order of ligands based on increasing field strength ($\Delta_o$):

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

- **Left-side ligands:** Weak-field → small $\Delta_o$ → high-spin complexes.
- **Right-side ligands:** Strong-field → large $\Delta_o$ → low-spin complexes.

**Applications of Crystal Field Theory**

1. **Explains Color of Complexes:**
   Color arises due to **d–d electronic transitions** between split d-orbitals absorbing visible light.
   Example: $[Ti(H_2O)_6]^{3+}$ appears purple due to absorption in the green region.

2. **Explains Magnetic Behavior:**
   Predicts number of unpaired electrons → helps calculate **magnetic moment**:

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

where $n$ = number of unpaired electrons.

3. **Predicts Geometry:**
   Explains whether a complex is tetrahedral, octahedral, or square planar.
4. **Stability and Reactivity:**
   Larger CFSE leads to higher thermodynamic stability.

**Limitations of Crystal Field Theory**

- Assumes purely ionic bonding; ignores covalent interactions.
- Fails to explain π-bonding and back donation.
- Cannot justify spectra and stability trends completely.
- Improved by **Ligand Field Theory** and **Molecular Orbital Theory (MOT)**.

## 11.5 Metal Complexes: Molecular Orbital Theory (MOT)

**Introduction**

While **Crystal Field Theory (CFT)** explains many properties of coordination compounds using an **electrostatic model**, it does not account for **covalent bonding interactions** between the metal and ligands. To overcome this limitation, the **Molecular Orbital Theory (MOT)** for coordination compounds was developed.

This theory treats metal–ligand bonding as a result of the **overlap of atomic orbitals** of the metal ion and the ligands to form **molecular orbitals** that extend over the entire complex. MOT therefore combines both **ionic and covalent** character, offering a more comprehensive description of bonding, magnetism, and spectra in metal complexes.

The theory forms the foundation of **Ligand Field Theory**, which merges ideas from both Crystal Field and Molecular Orbital approaches.

**Basic Concepts of Molecular Orbital Theory**

1. **Orbital Overlap:**
   Covalent bonding results from the overlap of suitable orbitals of the metal and ligands.
2. **Formation of Molecular Orbitals:**
   When atomic orbitals (AOs) combine, they form:
   - **Bonding molecular orbitals (MOs)** — lower in energy.
   - **Antibonding molecular orbitals (MOs)** — higher in energy.
   - **Non-bonding orbitals** — unchanged in energy.
3. **σ and π Interactions:**
   - **σ-bonding** occurs through the direct overlap of orbitals along the internuclear axis.
   - **π-bonding** involves sidewise overlap of orbitals (p or d orbitals) perpendicular to the axis.
4. **Hybridization of Metal Orbitals:**
   Depending on geometry, the metal orbitals hybridize to provide appropriate bonding orientations:
   - Octahedral: **$d^2sp^3$**
   - Tetrahedral: **$sp^3$**
   - Square planar: **$dsp^2$**
5. **Bonding Type:**
   - **σ-donation**: Ligands donate lone pairs into vacant metal orbitals.
   - **π-back bonding**: Metal donates electron density from its filled d-orbitals into ligand π* (antibonding) orbitals.

**σ-Bonding in Octahedral Complexes**

In an **octahedral complex** [$ML_6$], six ligands donate electron pairs to the central metal ion through **σ-type interactions**.

- The six **σ-donor orbitals** from ligands (directed along Cartesian axes) interact with the metal's six suitable orbitals:
  $$d_{x^2-y^2}, d_{z^2}, s, p_x, p_y, p_z$$
- The resulting molecular orbitals form bonding and antibonding sets with **octahedral ($O_h$)** symmetry.

**Energy order:**

$$\sigma^*(e_g) > nonbonding(t_{2g}) > \sigma(a_{1g}, t_{1u})$$

Here:

- **Bonding orbitals** = lower energy (ligand → metal donation)
- **Nonbonding orbitals** = primarily metal $t_2g$ orbitals ($d_xy$, $d_xz$, d_yz)
- **Antibonding orbitals** = higher energy σ* orbitals with e_g symmetry ($d_x^2$-$y^2$, d_$z^2$)

Thus, CFT's **$t_2g$–e_g splitting** corresponds closely to MOT's energy diagram, but MOT provides the **bonding rationale** behind it.

### π-Bonding in Complexes

π-bonding can occur **in addition to σ-bonding**, depending on the type of ligands:

1. **π-Donor Ligands:**
   Ligands such as $Cl^-$, $F^-$, or $OH^-$ have filled p-orbitals that can overlap with empty $t_2g$ orbitals of the metal.
   → This **reduces** **$\Delta_0$** (weaker field).
   → Example: $[Fe(H_2O)_6]^{2+}$, $[TiCl_6]^{3-}$.
2. **π-Acceptor (π-Acid) Ligands:**
   Ligands like CO, $CN^-$, and $NO^+$ have empty π* orbitals that can accept electron density from filled metal $t_2g$ orbitals.
   → This **increases** **$\Delta_0$** (stronger field).
   → Example: $[Fe(CO)_6]^{2+}$, $[Cr(CO)_6]$.

**Effect on Bond Strength:** π-acceptor interaction strengthens the metal–ligand bond and stabilizes low oxidation states of the metal (as in carbonyl complexes).

### Molecular Orbital Diagram for $[ML_6]$ Complex

A qualitative energy-level scheme for an octahedral complex includes:

- **Ligand group orbitals (LGOs):** Combination of ligand donor orbitals according to symmetry.
- **Metal orbitals:** s, p, and d orbitals of compatible symmetry mix with LGOs.
- **Molecular orbitals:** Resulting from bonding interactions.

**Order of energy levels (approximate):**

$$\sigma^*(e_g) > \pi^*(t_{2g}) > nonbonding > \pi(t_{2g}) > \sigma(a_{1g}, t_{1u})$$

This diagram explains the **electronic transitions** observed in UV–visible spectra as **d–d transitions** and **charge-transfer transitions** (ligand-to-metal or metal-to-ligand).

**Molecular Orbital Considerations in Other Geometries**

**(a) Tetrahedral Complexes [$ML_4$]:**
The metal orbitals involved are:

$$s + p_x + p_y + p_z + d_{xy} + d_{yz} + d_{zx}$$

Hybridization: **$sp^3$ or $sd^3$**

- Ligand orbitals form combinations that interact with metal orbitals of the same symmetry.
- The splitting pattern is **reverse of octahedral** (e orbitals lower than $t_2$).

**(b) Square Planar Complexes [$ML_4$]:**

- Hybridization: **$dsp^2$** (uses one $d_{x^2-y^2}$, one s, and two p orbitals).
- The **$d_{x^2-y^2}$** orbital has the highest energy due to direct interaction with ligands in the xy-plane.
- These complexes are common for **$d^8$ systems** ($Ni^{2+}$, $Pd^{2+}$, $Pt^{2+}$).

**Comparison: Crystal Field Theory vs. Molecular Orbital Theory**

| Feature | Crystal Field Theory | Molecular Orbital Theory |
|---|---|---|
| Nature of Bonding | Purely electrostatic | Includes covalent (σ, π) character |
| Orbitals considered | Only metal d-orbitals | Metal s, p, and d + ligand orbitals |
| Explains | Magnetic and spectral properties | Bonding, charge transfer, π-effects |
| π-bonding | Not considered | Fully explained |

| Feature | Crystal Field Theory | Molecular Orbital Theory |
|---|---|---|
| Accuracy | Qualitative | More quantitative and realistic |

**Applications of Molecular Orbital Theory**

1. **Explains Spectra and Color:** Electronic transitions between MOs account for the absorption of specific wavelengths, explaining the observed color.
2. **Predicts Magnetic Properties:** Depending on electron occupancy of MOs, the number of unpaired electrons (paramagnetism or diamagnetism) can be predicted accurately.
3. **Describes Bonding in Complexes with π-Interaction:** Explains synergic bonding in metal carbonyls and nitrosyl complexes (π-back bonding).
4. **Accounts for Stability of Complexes:** Strong σ + π bonding results in more stable complexes.
5. **Explains Low Oxidation States of Metals:** π-back bonding stabilizes low oxidation states by metal-to-ligand charge transfer (MLCT).

**Limitations of Molecular Orbital Theory**

- Requires complex mathematical treatment.
- Difficult to construct exact MO diagrams for large complexes.
- Overemphasizes delocalization and may overlook ionic contributions.
- Needs experimental data (spectra, magnetism) for confirmation.

**Check Your Progress**

1. Define coordination compound and give one example.

_____

_____

_____

_____

2. What is meant by the term *ligand*? Give examples of bidentate and ambidentate ligands.

_____
_____
_____
_____
_____

## 11.6 Summary

Metal complex theories form the foundation of coordination chemistry, explaining how transition metals form stable compounds with ligands through coordinate covalent bonds. Werner's Coordination Theory laid the structural basis by introducing primary and secondary valencies. Crystal Field Theory (CFT) expanded this by explaining the splitting of metal d-orbitals in the presence of ligands, influencing color, magnetic, and stability properties of complexes. Molecular Orbital Theory (MOT) further refined our understanding by integrating covalency into bonding, accounting for both σ and π interactions between metal and ligand orbitals. These combined models provide a unified picture of bonding, geometry, and electronic behavior in metal complexes and form the core for advanced theories such as Ligand Field Theory. The study of coordination compounds is crucial to diverse fields including catalysis, bioinorganic chemistry, and materials science.

## 11.7 Exercises

### 11.7.1 Multiple Choice Questions

1. **In $[Co(NH_3)_6]Cl_3$, the coordination number of cobalt is:**
   a) 3
   b) 4
   c) 6
   d) 2
   **Answer:** c) 6

2. **According to Crystal Field Theory, in an octahedral field the d-orbitals split into:**
   a) $t_1g$ and $e_1g$
   b) e_g and $t_2g$
   c) $a_1g$ and $t_2g$

d) e_g and $t_1u$
**Answer:** b) e_g and $t_2g$

3. **Which of the following ligands can act as a π-acceptor?**
   a) $Cl^-$
   b) $H_2O$
   c) $CN^-$
   d) $NH_3$
   **Answer:** c) $CN^-$

4. **The magnetic moment of $[Fe(CN)_6]^{4-}$ is zero because:**
   a) It has unpaired electrons
   b) It is a high-spin complex
   c) It is a low-spin complex
   d) It contains $Fe^{3+}$ ions
   **Answer:** c) It is a low-spin complex

5. **Which of the following statements about π-back bonding is true?**
   a) It involves electron donation from ligand to metal only
   b) It strengthens metal–ligand bonds by σ-overlap
   c) It involves metal-to-ligand electron donation into π* orbitals
   d) It weakens the metal–ligand bond
   **Answer:** c) It involves metal-to-ligand electron donation into π* orbitals

### 11.7.2 Short Answer Questions

1. What are coordination compounds? Give an example and explain its parts.
2. Explain the difference between Crystal Field Splitting in octahedral and tetrahedral complexes.
3. Define ligand field stabilization energy (LFSE) and its significance.

### 11.7.3 Long Answer Questions

1. Discuss in detail the postulates and applications of Werner's Coordination Theory.
2. Explain the splitting of d-orbitals in octahedral and tetrahedral fields using Crystal Field Theory.
3. Describe the bonding in metal carbonyl complexes using Molecular Orbital Theory.
4. Compare and contrast Crystal Field Theory and Molecular Orbital Theory of coordination compounds.

5. Explain the factors affecting the stability and geometry of coordination compounds with examples.

## 11.8 References and Suggested Readings

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## Unit 12: Energy Profile to reactions

**Structure**



### 12.1 Introduction

Every chemical reaction is accompanied by a change in energy. This change occurs because chemical bonds in the reactant molecules are broken and new bonds are formed in the product molecules. The process of bond breaking requires energy, whereas bond formation releases energy. The difference between the energy absorbed and the energy released determines whether the reaction is **exothermic** (releasing energy) or **endothermic** (absorbing energy).

The concept of **energy profile** provides a graphical representation of these energy changes as a reaction progresses from reactants to products. It helps us visualize how the energy of the system varies along the reaction pathway, also known as the **reaction coordinate**. The energy profile illustrates the formation of an activated complex or **transition state**, which is a high-energy intermediate that determines the **rate of the reaction**.

In physical chemistry, understanding the energy profile is essential because it connects **thermodynamics** (energy change) with **kinetics** (reaction rate). While thermodynamics tells us whether a reaction is possible, kinetics explains how fast it will occur. The energy profile thus bridges these two aspects, allowing chemists to predict and control reactions efficiently.

In this unit, we will discuss the nature of energy changes during reactions, the concept of **activation energy**, the formation of **transition states**, and how catalysts and other factors modify the energy profile. These concepts are crucial not only for theoretical

understanding but also for practical applications such as designing catalysts, optimizing reaction conditions, and studying reaction mechanisms.

## 12.2 Objectives

After studying this unit, learners will be able to:

- Understand the concept of energy changes during chemical reactions.
- Explain the terms **activation energy**, **transition state**, and **reaction coordinate**.
- Interpret and draw **energy profile diagrams** for exothermic and endothermic reactions.
- Describe how catalysts influence the energy profile of reaction.

## 12.3 Activation Energy and Transition State Theory

In any chemical reaction, the reactant molecules must collide with sufficient energy to form products. However, not every collision leads to a successful reaction. Only those collisions that possess a minimum required energy — known as the **activation energy (Ea)** — can overcome the energy barrier separating reactants from products.

**Activation energy** can be defined as the minimum amount of energy that reacting species must possess in order to transform into products. It represents the energy required to break existing bonds and to rearrange atoms so that new bonds can form. This concept was first introduced by Arrhenius, who expressed the rate of a reaction in terms of activation energy through the equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

where $k$ is the rate constant, $A$ is the frequency factor, $Ea$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature.
This relationship shows that the rate of a reaction increases with temperature, as more molecules acquire the energy necessary to overcome the activation barrier.

According to the **Transition State Theory (TST)**, when reactant molecules approach each other, they form a short-lived, unstable intermediate state known as the **activated complex** or **transition state**.

This species exists momentarily at the highest energy point on the reaction pathway. It is neither a reactant nor a product, but rather a configuration in which bonds are partially broken and partially formed. Once this state is achieved, the system can proceed to form products by releasing energy.

The reaction can thus be viewed as:

Reactants → Activated Complex → Products

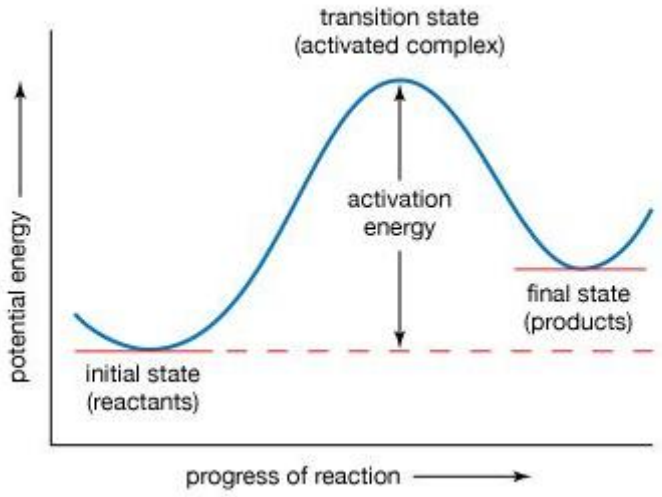


**Fig: Activation Energy and Transition State Theory**

The energy difference between the reactants and the activated complex corresponds to the **activation energy**. A lower activation energy means a faster reaction, as more molecules can successfully cross the energy barrier.

## 12.4 Potential Energy Surface and Reaction Coordinate

The **reaction coordinate** is an imaginary line that represents the progress of a reaction from reactants to products. Along this line, the potential energy of the system changes as bonds are broken and formed. The graphical representation of this variation of energy with reaction progress is called the **potential energy surface (PES)**.

In a simple one-step reaction, the potential energy increases as reactant molecules approach each other and reach the transition state. After that, the energy decreases as products form. In more complex reactions, the potential energy surface may have several peaks and valleys, each corresponding to intermediate states and transition states.

This concept helps chemists visualize not just the overall energy change, but also the stepwise mechanism of a reaction. A deep valley on the energy surface represents a **stable intermediate**, while a peak indicates a **transition state**. Computational chemistry often uses potential energy surfaces to study reaction mechanisms and predict the most favorable pathways.

## 12.5 Energy Profile Diagrams: Exothermic and Endothermic Reactions

An **energy profile diagram** is a graphical representation showing how the energy of a reaction system changes along the reaction coordinate. It illustrates the activation energy, transition state, and the overall energy change (ΔH) of the reaction.

1. **Exothermic Reactions:**
   In these reactions, energy is released to the surroundings as the products are formed. The products have lower energy than the reactants, and thus ΔH is negative. The energy profile shows a downward slope from reactants to products, with the activation energy peak in between. Combustion reactions and neutralization reactions are typical examples.

2. **Endothermic Reactions:**
   These reactions absorb energy from the surroundings. The products have higher energy than the reactants, so ΔH is positive. The energy profile shows an upward slope. Examples include photosynthesis and thermal decomposition reactions.

In both types, the peak represents the **transition state**, and the height of the peak above the reactants gives the **activation energy**. The larger the activation energy, the slower the reaction under normal conditions.

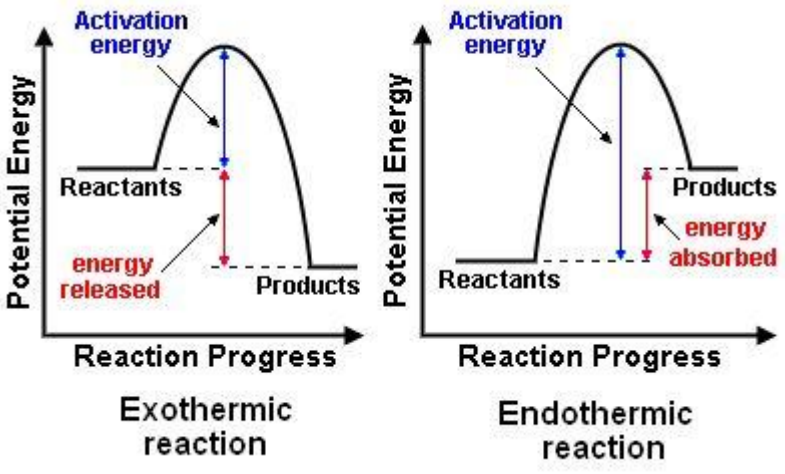

**Fig: Energy Profile Diagrams: Exothermic and Endothermic Reactions**

## 12.6 Reaction Mechanism and Rate-Determining Step

Most reactions occur through a series of elementary steps rather than a single-step process. The **reaction mechanism** describes the sequence of these steps and the species involved in each. Some steps are fast, while others are slow. The **rate-determining step (RDS)** is the slowest step in the mechanism and thus controls the overall rate of the reaction.

The energy profile of a multi-step reaction shows multiple peaks and valleys — each peak corresponds to a transition state, and each valley represents an intermediate. The highest peak usually represents the rate-determining step, as it has the largest activation energy barrier.

By analyzing the energy profile and identifying the RDS, chemists can modify reaction conditions or introduce catalysts to make the process faster and more efficient.

### Factors Affecting the Energy Profile

Several factors can influence the shape and height of the energy barrier in a reaction:

- **Catalysts:** Catalysts lower the activation energy by providing an alternative reaction pathway. They do not affect the overall energy change (ΔH) but make it easier for reactants to reach the transition state.
- **Temperature:** Increasing temperature provides more kinetic energy to molecules, allowing more of them to overcome the activation barrier.
- **Nature of Reactants:** Stronger bonds or more complex molecular structures require higher activation energy.
- **Solvent and Medium:** Polar or non-polar solvents can stabilize or destabilize intermediates and transition states, thereby affecting reaction rates.

Understanding these factors allows chemists to control reaction conditions effectively for industrial and laboratory processes.

### Check Your Progress

1. What is meant by activation energy?

_____
_____
_____
_____

2. What does the **peak** in an energy profile diagram represent?

_____
_____
_____
_____

## 12.7 Summary

- Chemical reactions involve energy changes associated with the breaking and formation of chemical bonds.
- The **energy profile** of a reaction represents the variation of potential energy along the **reaction coordinate**.
- The **activation energy (Ea)** is the minimum energy required to convert reactants into products.
- The **transition state** or **activated complex** represents the highest energy point along the reaction path.
- **Exothermic reactions** release energy ($\Delta H < 0$), while **endothermic reactions** absorb energy ($\Delta H > 0$).
- The **rate-determining step** is the slowest step in a multi-step reaction and governs the overall rate.
- **Catalysts** lower the activation energy without affecting the overall enthalpy change.
- Factors like temperature, nature of reactants, and solvent affect the energy profile.
- Understanding energy profiles is essential for controlling reaction rates, designing catalysts, and optimizing industrial and biological processes.

## 12.8 Exercises

### 12.8.1 Multiple Choice Questions (MCQs)

1. The peak of an energy profile diagram represents the:
   a) Reactants
   b) Products

c) Transition state
d) Activation energy
**Answer:** c) Transition state

2. The minimum energy required for molecules to react is called:
   a) Potential energy
   b) Activation energy
   c) Free energy
   d) Ionization energy
   **Answer:** b) Activation energy

3. In an exothermic reaction, the enthalpy change (ΔH) is:
   a) Positive
   b) Zero
   c) Negative
   d) Unpredictable
   **Answer:** c) Negative

4. The slowest step in a multi-step reaction is known as:
   a) Fast step
   b) Rate-determining step
   c) Transition step
   d) Intermediate step
   **Answer:** b) Rate-determining step

5. Catalysts increase the rate of a reaction by:
   a) Raising the activation energy
   b) Lowering the activation energy
   c) Changing the enthalpy of reaction
   d) Increasing the reactant concentration
   **Answer:** b) Lowering the activation energy

### 12.8.2 Short Answer Questions

1. What is meant by an energy profile of a chemical reaction?
2. Define activation energy and explain its importance in determining the rate of reaction.
3. Differentiate between exothermic and endothermic reactions with the help of energy diagrams.
4. What role does a catalyst play in modifying the energy profile of a reaction?
5. Explain the term “transition state” and its significance in reaction kinetics.

### 12.8.3 Long Answer Questions

1. Explain the concept of activation energy and describe how it affects the rate of chemical reactions. Illustrate your answer with a neat energy profile diagram.
2. Discuss the potential energy surface and explain the role of reaction coordinate in understanding reaction mechanisms.
3. Compare and contrast the energy profiles of exothermic and endothermic reactions. How does the value of ΔH affect the shape of the energy cur

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## Unit 13: Kinetics of Octahedral Substitutions

**Structure**



### 13.1 Introduction

In coordination chemistry, understanding the **kinetics of ligand substitution reactions** is essential for explaining how metal complexes react and transform. The rate at which one ligand in a metal complex is replaced by another depends on several factors such as the nature of the metal center, the leaving and entering ligands, and the surrounding environment.

In **octahedral complexes**, the metal ion is surrounded by six ligands arranged symmetrically around it. These complexes are commonly found in transition metal chemistry, where substitution reactions occur in solution through different mechanistic pathways. The study of **octahedral substitution kinetics** provides insight into the stability, reactivity, and bonding characteristics of coordination compounds.

A typical substitution reaction can be represented as:

$$[\mathrm{ML}_6]^{n+} + Y \rightarrow [\mathrm{ML}_5Y]^{n+} + L$$

where $L$ is the leaving ligand and $Y$ is the incoming ligand. The rate at which this substitution occurs depends on how easily the original ligand detaches and how readily the new ligand attaches.

Kinetic studies of these reactions not only help in understanding fundamental chemical principles but also have practical significance in fields like **bioinorganic chemistry**, **catalysis**, **industrial chemistry**, and **environmental science**. The mechanisms governing such substitutions (dissociative, associative, and interchange) reveal the dynamic behavior of coordination complexes and the energy changes involved in their transformations.

## 13.2 Objectives

After studying this unit, learners will be able to:

- Understand the concept of **ligand substitution** in octahedral complexes.
- Distinguish between **dissociative (D)**, **associative (A)**, and **interchange (I)** mechanisms.
- Explain the factors influencing the rate of substitution reactions in octahedral systems.
- Describe the **acid and base hydrolysis** mechanisms in octahedral complexes.
- Understand the role of the **trans effect** in substitution reactions.
- Compare the substitution behavior of octahedral and square planar complexes.
- Recognize the importance of kinetic studies in explaining the reactivity of transition metal complexes.

## 13.3 Ligand Substitution Reactions in Octahedral Complexes

A **ligand substitution reaction** occurs when one ligand in a coordination complex is replaced by another. These reactions are fundamental in coordination chemistry, as they determine how metal complexes behave in different chemical environments. In **octahedral complexes**, the central metal ion is coordinated to six ligands positioned at the corners of an octahedron. The general form of a substitution reaction is:

$$[\mathrm{ML}_6]^{n+} + Y \rightarrow [\mathrm{ML}_5Y]^{n+} + L$$

where:

- **M** = central metal ion
- **L** = original (leaving) ligand

- **Y** = incoming ligand

The reaction involves the **breaking** of a metal–ligand bond (M–L) and the **formation** of a new metal–ligand bond (M–Y). The rate of this process depends on how easily the leaving ligand detaches and how readily the incoming ligand attaches to the metal center.

Ligand substitution reactions in octahedral complexes can be broadly classified into two types:

1. **Dissociative (D) mechanism** — where a ligand first leaves the metal center, reducing the coordination number.
2. **Associative (A) mechanism** — where an incoming ligand attaches before one of the original ligands leaves.

In addition to these, some reactions proceed through a combination of both, known as **interchange (I)** mechanisms.

Kinetic measurements — such as rate constants, activation parameters, and solvent effects — help chemists determine which mechanism is operating in a given system. For example, complexes of **Cr(III)**, **Co(III)**, and **Pt(IV)** typically undergo slow ligand substitution (inert complexes), whereas complexes of **Ni(II)**, **Cu(II)**, and **Zn(II)** show fast substitution (labile complexes).

### 13.4 Mechanistic Pathways: Dissociative (D), Associative (A), and Interchange (I) Mechanisms

Ligand substitution in octahedral complexes can occur through different mechanistic routes. Understanding these mechanisms is essential to predict how quickly and under what conditions substitution will take place.

#### (a) Dissociative Mechanism (D)

In a **dissociative mechanism**, the reaction begins with the **loss of one ligand** from the coordination sphere, forming an **intermediate of lower coordination number**. The incoming ligand then attaches to the metal ion.

This can be represented as:

$$[ML_6]^{n+} \rightarrow [ML_5]^{n+} + L$$
$$[ML_5]^{n+} + Y \rightarrow [ML_5Y]^{n+}$$

Here, the rate-determining step (slow step) is the **dissociation** of the ligand.
The rate law is independent of the concentration of the incoming ligand

($Y$), and hence the reaction is said to be **first-order** with respect to the complex only.

**Rate law:**

$$\text{Rate} = k[\text{ML}_6]$$

**Characteristics:**

- Rate depends only on the complex.
- Favored by complexes with strong metal–ligand bonds and low-spin configurations.
- Entropy of activation (ΔS‡) is positive because dissociation increases disorder.

**Examples:**
Substitution reactions of inert complexes such as **$[Co(NH_3)_6]^{3+}$** and **$[Cr(H_2O)_6]^{3+}$** often follow the dissociative pathway.

**(b) Associative Mechanism (A)**

In an **associative mechanism**, the incoming ligand first associates with the complex before any ligand departs. This leads to the formation of a **seven-coordinate intermediate** (or transition state) which then loses one ligand to restore the octahedral geometry.

$$[\text{ML}_6]^{n+} + Y \rightarrow [\text{ML}_6Y]^{n+} \rightarrow [\text{ML}_5Y]^{n+} + L$$

Here, the rate-determining step is the **association** of the incoming ligand with the metal center.
The rate law depends on both the complex and the incoming ligand.

**Rate law:**

$$\text{Rate} = k[\text{ML}_6][Y]$$

**Characteristics:**

- Favored when the incoming ligand is small and nucleophilic.
- Entropy of activation (ΔS‡) is negative because association reduces randomness.
- Typical for complexes with metals that can expand their coordination number temporarily (e.g., 3d metals with vacant orbitals).

**Examples:**
Reactions of $[Co(NH_3)_5Cl]^{2+}$ with nucleophiles such as water or hydroxide sometimes follow the associative mechanism.

### (c) Interchange Mechanism (I)

In many reactions, the substitution does not occur purely by dissociation or association but through an **intermediate pathway** called the **interchange mechanism**. In this case, bond breaking and bond making occur **simultaneously** and to a comparable extent.

The interchange mechanism can be further classified into:

1. **Interchange Dissociative (I_d):**
   The process resembles the dissociative mechanism; bond breaking dominates over bond making.
   - Rate law: Rate ≈ $k$[complex]
   - Example: Substitution in some Co(III) and Cr(III) complexes.
2. **Interchange Associative (I_a):**
   The process resembles the associative mechanism; bond formation dominates over bond breaking.
   - Rate law: Rate ≈ $k$[complex][Y]
   - Example: Substitution in labile complexes of Ni(II), Zn(II), and Mn(II).

Thus, interchange mechanisms provide a continuum between the purely dissociative and purely associative extremes.

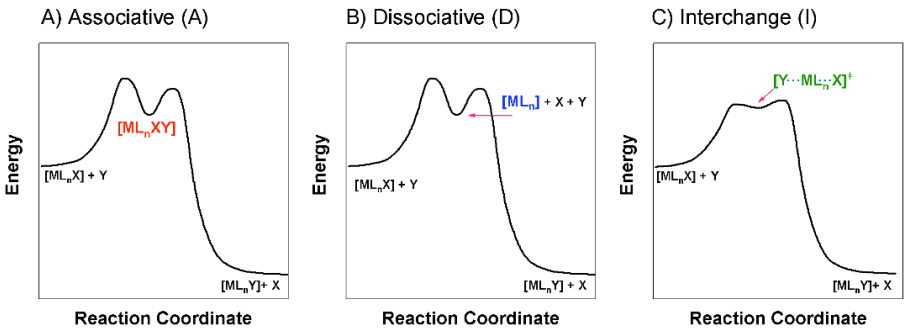



**Fig: Energy Profile Diagram for Associative Dissociative and Interchange Mechanism**

### Summary of Mechanistic Types

| Mechanism Type | Intermediate Formed | Rate Law Dependence | Typical Metal Centers | ΔS‡ Sign | Example |
|---|---|---|---|---|---|
| Dissociative (D) | $[ML_5]^{n+}$ | [Complex] only | Co(III), Cr(III) | + | $[Co(NH_3)_6]^{3+}$ |
| Associative (A) | $[ML_6Y]^{n+}$ | [Complex][Y] | Ni(II), Zn(II) | − | $[Ni(H_2O)_6]^{2+}$ |
| Interchange ($I_a$/I_d) | No stable intermediate | Mixed | Variable | ± | $[Co(NH_3)_5Cl]^{2+}$ |

### 13.5 Factors Affecting the Rate of Substitution

The rate of ligand substitution in octahedral complexes depends on several factors related to the metal center, the ligands involved, and the reaction environment. Understanding these factors helps in predicting and controlling the reactivity of metal complexes.

#### 1. Nature of the Metal Ion

The type of metal ion plays a crucial role in determining the speed of substitution.

- **Labile complexes** (react quickly): usually involve metal ions with low positive charge and large ionic size (e.g., $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$).
- **Inert complexes** (react slowly): usually involve metal ions with high positive charge and low-spin configurations (e.g., $Cr^{3+}$, $Co^{3+}$, $Pt^{4+}$).

In general, the higher the **oxidation state** and the stronger the metal–ligand bond, the slower the substitution rate.

#### 2. Nature of the Ligands

Both the **leaving ligand** and the **incoming ligand** influence the rate of substitution.

- **Leaving Ligand:** The weaker the bond between the metal and the leaving ligand, the easier its dissociation. For example, $H_2O$ and $Cl^-$ are more easily displaced than $CN^-$ or $NH_3$.

- **Incoming Ligand:** The stronger the nucleophile, the faster it can attack the metal center. Ligands such as $OH^-$, $CN^-$, and $NH_3$ are good nucleophiles and promote faster substitution.

Additionally, ligands that can **stabilize transition states** (by π-backbonding or hydrogen bonding) can also increase reaction rates.

### 3. Charge on the Complex Ion

Charge strongly influences substitution kinetics:

- Complexes with **higher positive charge** attract nucleophilic ligands more strongly, favoring associative or interchange associative mechanisms.
- Complexes with **lower charge** or neutral charge tend to favor dissociative mechanisms, as ligand loss is easier.

For example, $[Co(NH_3)_6]^{3+}$ is less reactive than $[Co(NH_3)_6]^{2+}$ because of its greater positive charge, which strengthens the metal–ligand bond.

### 4. Nature of the Solvent

The solvent can stabilize either the reactants, the intermediates, or the transition state.

- **Polar solvents** (like water) stabilize charged species and promote ionic dissociation.
- **Non-polar solvents** may favor associative mechanisms by stabilizing neutral or partially bonded transition states.

For example, substitution reactions in aqueous solutions often proceed faster than those in nonpolar organic solvents due to solvation effects.

### 5. Temperature

As in all chemical reactions, increasing temperature increases molecular motion and collision frequency, leading to faster substitution rates.
The relationship between rate and temperature is given by the **Arrhenius equation**:

$$k = Ae^{-\frac{E_a}{RT}}$$

where $E_a$ is the activation energy. Lower $E_a$ values correspond to faster reactions.

### 6. Steric Effects

Bulky ligands around the metal center can hinder the approach of incoming ligands and slow down associative reactions. In contrast, small ligands allow easier approach, facilitating substitution. For instance, $[Co(en)_3]^{3+}$ (with bulky ethylenediamine ligands) is more inert than $[Co(NH_3)_6]^{3+}$.

### 7. Electronic Effects

Ligand substitution rates are influenced by the electronic configuration of the metal center.

- **Low-spin $d^6$ and $d^3$ complexes** (e.g., $Co^{3+}$, $Cr^{3+}$) are often kinetically inert due to strong ligand field stabilization.
- **High-spin $d^5$ and $d^7$ complexes** (e.g., $Fe^{3+}$, $Co^{2+}$) are generally more labile.

The presence of unpaired electrons can also cause electronic repulsion, aiding ligand displacement.

### 8. Presence of Catalysts or Other Ions

Certain ions or molecules in the reaction medium can catalyze substitution by forming transient intermediates or by changing the charge of the complex.
For example, protonation in acid medium or hydroxide ions in base medium can alter the reactivity of aquo complexes, leading to acid or base hydrolysis mechanisms.

## 13.6 Kinetics of Acid and Base Hydrolysis of Octahedral Complexes

Ligand substitution reactions of octahedral complexes in aqueous solutions often involve **hydrolysis**, where a coordinated water molecule or hydroxide ion participates in the reaction. Depending on the pH, these reactions are categorized as **acid hydrolysis** or **base hydrolysis**.

### A. Acid Hydrolysis (Anation Reaction)

In acid hydrolysis, a ligand in an octahedral complex (commonly a halide or neutral molecule) is replaced by a water molecule. The rate of reaction increases with increasing acidity of the solution.

Example:

$$[Co(NH_3)_5Cl]^{2+} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + Cl^-$$

This process is called **anation** (since a neutral molecule replaces an anion).

**Mechanism:**

- Protonation of the leaving group ($Cl^-$) weakens the metal–ligand bond.
- The water molecule then enters to form the aquo complex.

**Kinetics:**
Rate law for acid hydrolysis often shows a first-order dependence on the complex:

$$\text{Rate} = k[\text{Complex}]$$

This suggests a **dissociative mechanism** where ligand loss is the rate-determining step.

**Example Complexes:**

- $[Co(NH_3)_5Cl]^{2+}$
- $[Cr(H_2O)_6]^{3+}$

These complexes are inert but can slowly undergo hydrolysis in acidic solutions.

**B. Base Hydrolysis (Anation or Hydroxo Substitution)**

In base hydrolysis, substitution occurs by the attack of hydroxide ions ($OH^-$) on the complex, usually replacing a coordinated water molecule or halide.

Example:

$$[Co(NH_3)_5Cl]^{2+} + OH^- \rightarrow [Co(NH_3)_5(OH)]^{2+} + Cl^-$$

This reaction is also known as **hydroxo substitution**.

**Mechanism:**
Two types of pathways are possible:

1. **Associative (A) mechanism:** $OH^-$ attacks the metal center forming a seven-coordinate intermediate, which then loses $Cl^-$.
2. **Interchange ($I_a$) mechanism:** The attack and departure occur almost simultaneously.

**Kinetics:** Base hydrolysis often shows second-order kinetics — first order in the complex and first order in hydroxide concentration:

$$\text{Rate} = k[\text{Complex}][OH^-]$$

**Factors affecting base hydrolysis:**

- Increasing $[OH^-]$ increases rate linearly.
- The reaction rate is influenced by temperature and the basicity of the medium.
- Complexes with electron-withdrawing ligands show faster base hydrolysis due to increased electrophilicity of the metal center.

**C. Comparison of Acid and Base Hydrolysis**

| **Feature** | **Acid Hydrolysis** | **Base Hydrolysis** |
|---|---|---|
| Medium | Acidic | Basic |
| Nucleophile | $H_2O$ | $OH^-$ |
| Mechanism | Mostly Dissociative | Mostly Associative or Interchange |
| Rate Law | Rate = k[Complex] | Rate = k[Complex][$OH^-$] |
| Example | $[Co(NH_3)_5Cl]^{2+}$ + $H_2O$ | $[Co(NH_3)_5Cl]^{2+} + OH^-$ |
| Favored Condition | Low pH | High pH |

Thus, acid and base hydrolysis studies provide valuable insight into how the reaction environment alters substitution pathways and rates in octahedral complexes.

## 13.7 Trans Effect and Its Kinetic Influence

The **trans effect** is an important concept in coordination chemistry that helps to explain and predict the rate and direction of substitution reactions, especially in **square planar** and sometimes **octahedral complexes**.
It refers to the influence that a ligand exerts on the rate of substitution of another ligand *trans* (opposite) to it in a coordination complex.

### Definition

The *trans effect* may be defined as:

*"The ability of a ligand already coordinated to a metal center to increase the rate of substitution of the ligand trans to itself."*

In simple terms, certain ligands make the ligand opposite to them more easily replaceable.

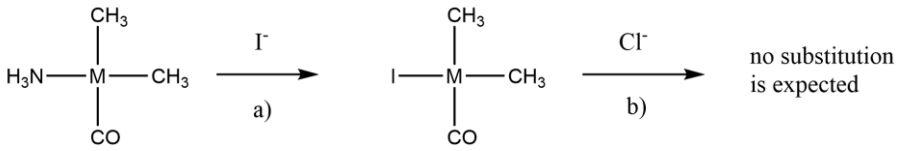
### Origin of Trans Effect

The trans effect arises mainly due to two factors:

1. **σ (sigma) Bonding Effect (Ground State Effect):** Strong σ-donor ligands weaken the bond of the ligand trans to them by donating electron density into the same metal orbital that overlaps with the trans ligand. This weakens the M–L (trans) bond and promotes substitution.
2. **π (pi) Bonding Effect (Transition State Effect):** Strong π-acceptor ligands (like CO, $CN^-$, or $C_2H_4$) stabilize the transition state by back-donation of electron density from the metal, facilitating the substitution of the trans ligand.

Thus, both σ-donation and π-acceptance can increase substitution rates, but through slightly different mechanisms.

**trans-effect:** $CO > CH_3^- > I^- > Cl^- > NH_3$




### Trans Effect Series

The magnitude of the trans effect depends on the nature of the ligand. Below is a general **trans effect series** (from weak to strong):

$$H_2O < NH_3 < OH^- < Cl^- < Br^- < I^- < SCN^- < NO_2^- < PPh_3 < CN^- < CO$$

Ligands on the right-hand side of the series exert a **stronger trans effect**, meaning they increase substitution rates more effectively.

**Illustrative Example**

Consider the synthesis of **$[Pt(NH_3)_2Cl_2]$** complexes.

When substitution occurs on $[PtCl_4]^{2-}$ by $NH_3$, two possible products are formed:

1. **cis-$[Pt(NH_3)_2Cl_2]$**
2. **trans-$[Pt(NH_3)_2Cl_2]$**

The trans effect determines which isomer predominates. If the entering $NH_3$ ligand replaces a chloride trans to a strong trans-effect ligand (like $Cl^-$ or $I^-$), it directs further substitution to occur opposite to it. This is why **trans-$[Pt(NH_3)_2Cl_2]$** can be selectively formed using ligands with high trans effects.

**Trans Influence vs. Trans Effect**

| Aspect | Trans Effect | Trans Influence |
|---|---|---|
| Nature | Kinetic effect | Thermodynamic effect |
| Stage | Operates in transition state | Operates in ground state |
| Measurement | Observed in substitution rate | Observed in bond length or strength |
| Example | $[Pt(NH_3)_2Cl_2]$ formation | Longer M–L bond opposite to CO |

**Kinetic Importance of Trans Effect**

- Determines **rate of substitution** of the trans ligand.
- Helps in **predicting product geometry** (cis or trans).

- Plays a crucial role in **inorganic synthesis**, such as the stepwise preparation of **cisplatin**, the well-known anticancer drug $[Pt(NH_3)_2Cl_2]$.
- Aids in understanding **transition state stabilization** during substitution.

Even though the trans effect is more pronounced in **square planar complexes**, similar though weaker influences are sometimes observed in **octahedral complexes**, especially in low-spin $d^6$ systems like $[Co(NH_3)_5L]^{3+}$.

## 13.8 Comparison of Octahedral and Square Planar Substituion Mechanisms

Ligand substitution reactions in **octahedral** and **square planar** complexes differ significantly because of differences in geometry, coordination number, and electronic configuration of the central metal ion. Understanding these differences helps in predicting how substitution reactions proceed in various types of complexes.

### 1. Geometry and Coordination Number

| Feature | Octahedral Complex | Square Planar Complex |
|---|---|---|
| Coordination number | 6 | 4 |
| Shape | Symmetrical, 3D | Flat, 2D |
| Typical metals | 1st-row transition metals ($Co^{3+}$, $Cr^{3+}$, $Fe^{2+}$) | 2nd and 3rd-row transition metals ($Pt^{2+}$, $Pd^{2+}$, $Ni^{2+}$) |

The higher coordination number (6) in octahedral complexes allows more space for ligand approach and often stabilizes intermediate species like 7-coordinate complexes.

### 2. Mechanistic Pathways

| Mechanism Type | Octahedral Complexes | Square Planar Complexes |
|---|---|---|
| Associative (A) | Rare (7-coordinate transition state) | Common (5-coordinate intermediate) |
| Dissociative (D) | Common (loss of ligand forms 5-coordinate intermediate) | Less common |
| Interchange (I) | Frequently observed | Common as a combination of A and D |

- Octahedral substitution often involves **dissociative** or **interchange dissociative (I_D)** mechanisms.
- Square planar complexes, especially those of **$d^8$ metals ($Pt^{2+}$, $Pd^{2+}$, $Ni^{2+}$)**, favor **associative** or **interchange associative (I_A)** mechanisms.

### 3. Influence of Electronic Configuration

| Complex Type | Electronic Configuration | Kinetic Behavior |
|---|---|---|
| Octahedral ($Co^{3+}$, $Cr^{3+}$) | Low-spin $d^6$ or $d^3$ | Inert |
| Octahedral ($Fe^{2+}$, $Co^{2+}$) | High-spin $d^6$ or $d^7$ | Labile |
| Square Planar ($Pt^{2+}$, $Pd^{2+}$) | $d^8$ | Inert but predictable mechanism |

Octahedral complexes of 3d metals often show variable reactivity depending on spin state, while square planar complexes of 4d and 5d metals are typically **slow but well-defined** in their mechanism.

### 4. Role of Trans Effect

The **trans effect** is more dominant in square planar systems (especially Pt(II) complexes) than in octahedral systems.
In octahedral complexes, the geometric constraint and high coordination number distribute electronic effects evenly, reducing directional substitution preferences.

### 5. Reaction Intermediates and Transition States

| Aspect | Octahedral | Square Planar |
|---|---|---|
| Intermediate | 5- or 7-coordinate | 5-coordinate |
| Stability | Often short-lived | More stable, sometimes isolable |
| Example | $[Co(NH_3)_5H_2O]^{3+}$ intermediate | $[Pt(NH_3)_2Cl(H_2O)]^{+}$ intermediate |

### 6. Reaction Rate and Conditions

Octahedral substitutions are generally **slower** for low-spin 3+ complexes but **faster** for divalent ions. Square planar substitutions are typically **sluggish**, requiring elevated temperatures or specific trans-effect ligands to proceed.

### Summary Table

| Parameter | Octahedral Complexes | Square Planar Complexes |
|---|---|---|
| Coordination Number | 6 | 4 |
| Common Metals | $Co^{3+}$, $Cr^{3+}$, $Fe^{2+}$ | $Pt^{2+}$, $Pd^{2+}$, $Ni^{2+}$ |
| Typical Mechanism | D or I_D | A or I_A |
| Geometry Change | Often temporary | Partial flattening or expansion |
| Trans Effect | Weak | Strong |
| Intermediate Type | 5- or 7-coordinate | 5-coordinate |
| Kinetic Behavior | Varies (labile/inert) | Predictably inert but directed by trans effect |

Thus, while both octahedral and square planar complexes undergo ligand substitution reactions, their mechanisms, rates, and influencing factors differ significantly due to geometry and electronic factors.

Understanding these distinctions is essential for interpreting and designing coordination compounds in inorganic and bioinorganic systems.

## 13.9 Applications of Kinetic Studies in Coordination Chemistry

Kinetic studies of ligand substitution reactions are not only important for theoretical understanding but also have significant **practical applications** in chemistry, biology, catalysis, and industrial processes. They help chemists to **control, predict, and utilize** metal complex reactivity in real systems.

### 1. Determination of Reaction Mechanism

Kinetic data such as rate laws, activation energies, and order of reaction help in identifying the **mechanistic pathway** (dissociative, associative, or interchange).
For example, studying the rate of substitution in $[Co(NH_3)_5Cl]^{2+}$ helps distinguish whether ligand loss or ligand attack is the rate-determining step.

### 2. Understanding Metal–Ligand Bond Strength

Kinetic parameters like rate constants and activation energies indicate the **strength and stability** of metal–ligand bonds.
Slow substitution rates imply strong metal–ligand bonding and high thermodynamic stability, as in $[Cr(H_2O)_6]^{3+}$.
Fast substitution rates suggest weaker bonding and higher lability, as in $[Ni(H_2O)_6]^{2+}$.

### 3. Synthesis of Coordination Compounds

Kinetic principles guide the **stepwise preparation** of complex molecules.
By understanding the trans effect and substitution rates, chemists can selectively synthesize specific **isomers** (cis or trans).
A notable example is the controlled synthesis of **cis-$[Pt(NH_3)_2Cl_2]$ (cisplatin)** — an important anticancer drug.

### 4. Catalysis

Many catalytic reactions involve **metal complexes** as intermediates. Kinetic studies reveal how ligands are substituted during catalytic cycles, providing insight into **reaction rates, turnover numbers, and efficiency**.
For example, substitution kinetics of metal–carbonyl complexes help design better **homogeneous catalysts** in industrial chemistry.

### 5. Bioinorganic Chemistry

In biological systems, many enzymes contain **metal centers** (like Fe, Cu, Zn, and Co).
Ligand substitution kinetics explain how these metal ions interact with substrates and cofactors.
For instance, oxygen binding and release in hemoglobin involve substitution reactions at the $Fe^{2+}$ center.

### 6. Environmental and Analytical Applications

Kinetic studies assist in understanding how **metal ions are transported or detoxified** in the environment.
In analytical chemistry, substitution rates are exploited in **complexometric titrations** and **indicator reactions** to detect or quantify metal ions.

### 7. Industrial and Medicinal Applications

- Design of **anticancer drugs** like cisplatin depends on substitution kinetics of Pt(II) complexes.
- Kinetic control is used in **electroplating**, **water treatment**, and **material synthesis** involving metal complexes.

Thus, the study of kinetics provides both **theoretical insight** and **practical control** over coordination chemistry reactions.

### Check Your Progress

1. What do you mean by ligand substitution reaction?

_____
_____
_____
_____

2. What is meant by the trans effect?

## 13.10 Summary

- Ligand substitution reactions involve the replacement of one ligand in a coordination complex by another.
- In **octahedral complexes**, substitution may follow **dissociative (D)**, **associative (A)**, or **interchange (I)** mechanisms.
- The rate of substitution depends on the **metal ion**, **ligands**, **solvent**, **temperature**, and **electronic configuration**.
- **Acid and base hydrolysis** are common pathways for substitution in aqueous media.
- The **trans effect** influences the substitution rate of ligands located trans to certain strong σ-donor or π-acceptor ligands.
- Octahedral and square planar complexes differ in their substitution behavior due to differences in coordination number and geometry.
- Kinetic studies help in **understanding mechanisms**, **predicting stability**, and **designing metal-based drugs and catalysts**.

In summary, the kinetics of octahedral substitutions provide a foundation for interpreting and applying the chemistry of metal complexes in both natural and synthetic systems.

## 13.11 Exercises

### 13.11.1 Multiple Choice Questions

1. The rate of substitution in $[Cr(H_2O)_6]^{3+}$ is slow because it is:
   a) Labile complex
   b) Inert complex
   c) Unstable complex
   d) Neutral complex
   → **Answer:** b) Inert complex
2. The trans effect is primarily a:
   a) Thermodynamic effect
   b) Kinetic effect

c) Magnetic effect
d) Solvation effect
→ **Answer:** b) Kinetic effect

3. In base hydrolysis, the attacking nucleophile is:
   a) $H_2O$
   b) $H^+$
   c) $OH^-$
   d) $Cl^-$
   → **Answer:** c) $OH^-$

4. Which of the following ligands has the strongest trans effect?
   a) $H_2O$
   b) $Cl^-$
   c) $CN^-$
   d) $NH_3$
   → **Answer:** c) $CN^-$

5. The mechanism involving both ligand loss and attack in one step is called:
   a) Associative
   b) Dissociative
   c) Interchange
   d) Ionization
   → **Answer:** c) Interchange

**Short Answer Questions**

1. Define the trans effect and give one example.
2. What is the difference between labile and inert complexes?
3. Explain how solvent affects the rate of substitution in octahedral complexes.
4. State two factors that influence ligand substitution rates.
5. What is the main difference between acid and base hydrolysis mechanisms?

**Long Answer Questions**

1. Describe in detail the different mechanistic pathways (D, A, and I) for ligand substitution in octahedral complexes with suitable examples.
2. Explain the trans effect and its importance in determining the product geometry of substitution reactions.
3. Compare the substitution mechanisms in octahedral and square planar complexes.

4. Discuss the kinetic factors affecting ligand substitution in transition metal complexes.
5. Write a detailed note on the role of kinetic studies in coordination chemistry and its applications in industry and medicine.

## 13.12 References and suggested readings

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# Unit 14: Anation Reactions

**Structure**



## 14.1 Introduction

Anation reactions are an important class of substitution reactions in coordination chemistry. The term *anation* refers to the process in which a neutral ligand in a coordination complex is replaced by an anionic ligand. In other words, it is the **reverse of aquation**, where a water molecule replaces an anion. These reactions are very common in the chemistry of transition metal complexes, particularly those involving cobalt(III), chromium(III), and platinum(II) ions.

For example, the substitution of a coordinated water molecule in a hexaaquacobalt(III) complex by a chloride ion is an anation reaction:

$$[Co(H_2O)_6]^{3+} + Cl^- \rightarrow [Co(H_2O)_5Cl]^{2+} + H_2O$$

Anation reactions help in understanding the **kinetic behavior** of metal complexes and the influence of ligands on reaction rates. They are also important in **industrial catalysis** and **coordination compound synthesis**, where the choice of ligand controls reactivity and product stability.

## 14.2 Objectives

After studying this unit, you should be able to:

1. Explain what anation reactions are and how they differ from aquation reactions.
2. Describe the mechanisms involved in anation reactions (dissociative, associative, and interchange).
3. Discuss the factors affecting the rate of anation reactions.
4. Identify examples of anation in transition metal complexes.
5. Understand the practical and industrial applications of anation processes.

## 14.3 Definition and General Features of Anation

### Definition

The term **anation** comes from the word *anion*.
It refers to a **ligand substitution reaction** in which a **neutral ligand** (such as $H_2O$ or $NH_3$) in a coordination complex is replaced by an **anionic ligand** (such as $Cl^-$, $Br^-$, or $CN^-$).

$$[M–L]^{n+} + X^- \rightarrow [M–X]^{(n-1)+} + L$$

For example:

$$[Co(H_2O)_6]^{3+} + Cl^- \rightarrow [Co(H_2O)_5Cl]^{2+} + H_2O$$

Here, the chloride ion replaces one coordinated water molecule. Thus, **anation is the reverse of aquation**.

### General Features

1. **Reverse of Aquation:**
    - In aquation, an anion is replaced by water.
    - In anation, water (or a neutral ligand) is replaced by an anion.
      Example:

$$[Cr(H_2O)_6]^{3+} + Cl^- \rightarrow [Cr(H_2O)_5Cl]^{2+} + H_2O$$

2. **Involves Nucleophilic Attack:**
   The incoming anionic ligand acts as a **nucleophile**, attacking the metal center or an intermediate complex.
3. **Common in Substitutionally Inert Complexes:**
   Anation is usually observed in complexes of **low-spin $d^6$ ions** like Co(III), Cr(III), and Pt(II), which are kinetically inert.
4. **Influence of Solvent:**
   These reactions are usually carried out in **aqueous or polar solvents**, where the anions are solvated and can easily attack the complex.
5. **Mechanistic Pathways:**
   Anation reactions can follow:
   - **Dissociative (D)** pathway — neutral ligand leaves first.
   - **Associative (A)** pathway — anion attaches first.
   - **Interchange (I)** pathway — both processes occur simultaneously.
6. **Dependence on Ionic Strength and Dielectric Constant:**
   Reaction rates increase in solvents of **lower dielectric constant**, because anionic attack on positively charged complexes is more favorable.
7. **Temperature Sensitivity:**
   Like other substitution reactions, rate increases with temperature due to lowering of activation energy.

**Example Table: Common Anation Reactions**

| Metal Complex | Incoming Anion | Product Formed |
|---|---|---|
| $[Co(H_2O)_6]^{3+}$ | $Cl^-$ | $[Co(H_2O)_5Cl]^{2+}$ |
| $[Cr(H_2O)_6]^{3+}$ | $SCN^-$ | $[Cr(H_2O)_5(SCN)]^{2+}$ |
| $[Pt(H_2O)_4]^{2+}$ | $Br^-$ | $[Pt(H_2O)_3Br]^+$ |
| $[Ni(H_2O)_6]^{2+}$ | $CN^-$ | $[Ni(H_2O)_5(CN)]^-$ |

## 14.4 Mechanism of Anation Reactions

Anation reactions, like other ligand substitution processes, can proceed through different mechanistic pathways. The main types are **Dissociative (D)**, **Associative (A)**, and **Interchange (I)** mechanisms. The route followed by a particular reaction depends on the nature of the metal ion, the leaving ligand, and the entering anion.

### (a) Dissociative Mechanism (D Mechanism)

**Stepwise Process:**

1. The coordinated neutral ligand (usually $H_2O$ or $NH_3$) **first leaves** the coordination sphere of the metal ion, forming a **five-coordinate intermediate**.
2. The anionic ligand then **attacks the vacant site**, forming the new complex.

$$[ML_6]^{n+} \xrightarrow{\text{slow}} [ML_5]^{n+} + L$$
$$[ML_5]^{n+} + X^- \xrightarrow{\text{fast}} [ML_5X]^{(n-1)+}$$

**Example:**

$$[Co(H_2O)_6]^{3+} + Cl^- \rightarrow [Co(H_2O)_5Cl]^{2+} + H_2O$$

Here, a water molecule leaves first, followed by coordination of the chloride ion.

**Energy Profile:**

The energy diagram shows a **high activation energy**, corresponding to the loss of the ligand.

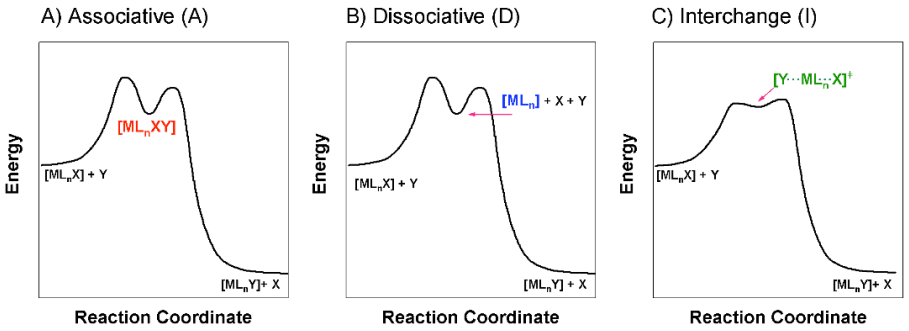

**Fig:***Energy profile for a associative dissociative and interchange anation mechanism*

**(b) Associative Mechanism (A Mechanism)**

**Stepwise Process:**

1. The anionic ligand **first associates** with the metal complex to form a **seven-coordinate intermediate**.
2. One neutral ligand is then **released** from the coordination sphere.

$$[ML_6]^{n+} + X^- \xrightarrow{\text{slow}} [ML_6X]^{(n-1)+}$$
$$[ML_6X]^{(n-1)+} \xrightarrow{\text{fast}} [ML_5X]^{(n-1)+} + L$$

**Example:**

This mechanism is rare in octahedral Co(III) complexes but may occur in soft metal centers such as Pt(II) or Pd(II) complexes in low dielectric solvents.

**Energy Profile:**

A smaller activation energy compared to the dissociative pathway.

**(c) Interchange Mechanism (I Mechanism)**

In many cases, bond breaking and bond forming occur **simultaneously**. The reaction shows features of both D and A mechanisms.

**Types:**

- **Interchange Dissociative (I_D):** bond breaking dominates.
- **Interchange Associative (I_A):** bond formation dominates.

$$[ML_6]^{n+} + X^- \rightarrow [ML_5X]^{(n-1)+} + L$$

There is **no distinct intermediate**, but rather a **transition state** where both ligands interact with the metal.

**Example:**

$$[Cr(H_2O)_6]^{3+} + SCN^- \rightarrow [Cr(H_2O)_5(SCN)]^{2+} + H_2O$$

This proceeds through an **I_D mechanism**.

**Energy Profile:**

Single smooth curve without intermediate peaks.

**Factors Deciding Mechanism:**

| Condition | Favored Mechanism |
|---|---|
| Strongly bound neutral ligands (slow to leave) | Dissociative |
| Large, soft incoming anions | Associative |
| Polar solvents with high dielectric constant | Dissociative |
| Low-spin $d^6$ ions (e.g., $Co^{3+}$, $Cr^{3+}$) | Dissociative |
| Transition states with mixed bonding | Interchange |

## 14.5 Factors Affecting Rate of Anation Reactions

The **rate of anation reactions** depends on several factors related to the **metal ion**, **ligands**, and **reaction conditions**. Understanding these factors helps to explain why some complexes undergo anation rapidly while others react very slowly.

### 1. Nature of the Metal Ion

- The **charge and size** of the metal ion have a direct effect on the rate of substitution.
- **Highly charged and small-sized ions** (like $Co^{3+}$, $Cr^{3+}$) form **strong metal–ligand bonds** and are therefore **kinetically inert**.
- Lower oxidation states or larger metal ions (like $Ni^{2+}$, $Cu^{2+}$) tend to be **more labile**, reacting faster.

**Metal Complex Relative Reactivity**

| | |
|---|---|
| $[Co(H_2O)_6]^{3+}$ | Very slow |
| $[Cr(H_2O)_6]^{3+}$ | Slow |

| Metal Complex | Relative Reactivity |
|---|---|
| $[Ni(H_2O)_6]^{2+}$ | Moderate |
| $[Cu(H_2O)_6]^{2+}$ | Fast |

**2. Nature of the Leaving Ligand**

- A ligand that is **weakly bound** to the metal center will leave easily, increasing the rate.
- For example, $H_2O$ is a weakly bound ligand and is easily replaced by anions like $Cl^-$ or $SCN^-$.
- Strong donor ligands (like $NH_3$ or $CN^-$) are less easily replaced, slowing the reaction.

**3. Nature of the Incoming Anionic Ligand**

- The **basicity** and **nucleophilicity** of the entering anion influence the rate.
- Stronger nucleophiles attack the metal center more readily.

| Anionic Ligand | Nucleophilicity (increasing order) |
|---|---|
| $NO_3^-$ < $Cl^-$ < $Br^-$ < $I^-$ < $SCN^-$ < $CN^-$ | |

Thus, $CN^-$ and $SCN^-$ promote faster anation reactions.

**4. Solvent Effect**

- The **dielectric constant** and **solvation power** of the solvent affect reaction rate.
- **Aqueous solvents** stabilize ions, slowing down nucleophilic attack.
- **Less polar solvents** (like alcohol-water mixtures) increase the rate by reducing solvation of the anion.

Example:
Rate of $Cl^-$ substitution increases when water is replaced partly by ethanol.

**5. Temperature**

- Like most chemical reactions, the rate of anation increases with temperature.
- The relationship follows the **Arrhenius equation**:

$$k = Ae^{-E_a/RT}$$

where $E_a$ is the activation energy.

**6. Ionic Strength of Medium**

- The rate of anation between two oppositely charged species increases with **ionic strength** of the solution.
- For example, in a positively charged complex reacting with an anion, increasing the concentration of inert salts (like $NaNO_3$) enhances the reaction rate by reducing electrostatic repulsion.

**7. Presence of Catalysts**

- Certain species (like acids or bases) can catalyze anation reactions.
- Example: Base-catalyzed anation occurs when $OH^-$ facilitates ligand exchange by forming a transient hydroxo intermediate.

**Summary Table: Factors and Their Effects**

| Factor | Effect on Rate | Example/Remark |
|---|---|---|
| High oxidation state | Slows down | $Co^{3+}$ slower than $Co^{2+}$ |
| Weak leaving group | Speeds up | $H_2O$ leaves easily |
| Strong nucleophile | Speeds up | $SCN^-$, $CN^-$ very fast |
| Low dielectric solvent | Speeds up | Ethanol-water > pure water |
| High temperature | Speeds up | Rate doubles for 10°C rise |
| High ionic strength | Speeds up | Reduces electrostatic barrier |

**14.6 Examples of Anation Reactions**

Anation reactions are widely observed in transition metal chemistry, especially in complexes of **cobalt(III)**, **chromium(III)**, and **platinum(II)**.
These examples help illustrate the **mechanism**, **reactivity**, and **product formation** patterns typical of such reactions.

**Example 1: Chloride Anation of Hexaaquacobalt(III)**

$$[Co(H_2O)_6]^{3+} + Cl^- \rightarrow [Co(H_2O)_5Cl]^{2+} + H_2O$$

- This is the **most common example** of an anation reaction.
- It proceeds via a **dissociative (D)** or **interchange dissociative (I_D)** mechanism.
- The rate of reaction depends on temperature and chloride ion concentration.
- The product is a **pentaamminechlorocobalt(III)** type complex.

**Example 2: Bromide Anation in Chromium(III) Complexes**

$$[Cr(H_2O)_6]^{3+} + Br^- \rightarrow [Cr(H_2O)_5Br]^{2+} + H_2O$$

- Similar to cobalt(III), **chromium(III)** complexes are substitutionally inert.
- The reaction is slow and follows a **dissociative mechanism**.
- The rate increases in mixed solvents like ethanol–water because solvation of $Br^-$ decreases.

**Example 3: Cyanide Anation in Nickel(II) Complex**

$$[Ni(H_2O)_6]^{2+} + CN^- \rightarrow [Ni(H_2O)_5(CN)]^{+} + H_2O$$

- The incoming $CN^-$ is a **strong field ligand**, which readily replaces a water molecule.
- This reaction leads to increased ligand field stabilization and often continues to form fully substituted species like $[Ni(CN)_4]^{2-}$.
- Mechanism tends to be **associative (A)** because $CN^-$ is strongly nucleophilic.

**Key Observations from Examples**

| Metal Center | Anion ($X^-$) | Mechanism Type | Relative Rate | Product |
|---|---|---|---|---|
| $Co^{3+}$ | $Cl^-$ | I_D / D | Slow | $[Co(H_2O)_5Cl]^{2+}$ |
| $Cr^{3+}$ | $SCN^-$ | I_D | Moderate | $[Cr(H_2O)_5(SCN)]^{2+}$ |
| $Ni^{2+}$ | $CN^-$ | A | Fast | $[Ni(H_2O)_5(CN)]^{+}$ |

## 14.7 Applications of Anation Reactions

Anation reactions are not only important from a theoretical point of view but also have **practical significance** in **coordination chemistry**, **industrial catalysis**, and **bioinorganic systems**. Understanding anation helps chemists control ligand exchange processes, design stable complexes, and synthesize specific coordination compounds.

### 1. Synthesis of Coordination Compounds

Anation reactions are widely used for the **preparation of complex ions** containing anionic ligands.

**Example:**

$$[Co(H_2O)_6]^{3+} + Cl^- \rightarrow [Co(H_2O)_5Cl]^{2+} + H_2O$$

The above reaction is used to prepare **chloropentaamminecobalt(III)** or related derivatives by replacing a water molecule with a chloride ion. This step is essential in multi-stage syntheses of coordination compounds in inorganic laboratories.

### 2. Understanding Reaction Mechanisms in Coordination Chemistry

- The study of anation reactions provides insight into **how ligands are substituted** in metal complexes.

- By studying rate constants and activation parameters, chemists can determine whether a complex follows a **dissociative**, **associative**, or **interchange** pathway.
- This knowledge is crucial in predicting the behavior of complexes in different environments.

### 3. Control of Ligand Environment in Metal Complexes

- Through controlled anation, chemists can selectively **introduce desired anionic ligands** (like $Cl^-$, $CN^-$, or $SCN^-$) into a complex.
- This control is useful in tailoring **electronic, magnetic, and optical properties** of coordination compounds.
- Example: Substitution of water with $CN^-$ increases ligand field strength and changes color or spin state.

### 4. Industrial and Catalytic Applications

- In catalytic systems, anation reactions help in **ligand exchange** at metal centers, which is a key step in many catalytic cycles.
- For example, in **homogeneous catalysis** using Co(III) or Pt(II) complexes, anion substitution controls reactivity.
- **Anation of aquo complexes** can activate the catalyst or regenerate the active species.

### 5. Medicinal Chemistry Applications

- The well-known anticancer drug **cisplatin**, *cis-*$[Pt(NH_3)_2Cl_2]$, is synthesized through a sequence of **anation and aquation** reactions.
- The control of chloride substitution during synthesis ensures the **cis configuration**, which is essential for biological activity.
- Understanding anation is also important for studying how metal-based drugs interact with biomolecules in the body.

### 6. Analytical Chemistry

- Anation reactions are used in **qualitative and quantitative analysis** to prepare stable coordination compounds for detection.
- Example: Formation of colored complexes like $[Co(SCN)_4]^{2-}$ is used in colorimetric analysis of cobalt ions.

**7. Environmental and Biological Relevance**

- In natural systems, anation-like processes occur when **anionic species** (like $Cl^-$, $OH^-$, or $SO_4^{2-}$) replace water molecules in metal centers of enzymes or minerals.
- Understanding these reactions helps explain **metal ion transport**, **enzyme reactivity**, and **biochemical metal exchange**.

**Check Your Progress**

1. What is replaced in an anation reaction?

_____
_____
_____
_____

2. Name a common metal center used in anation reactions.

_____
_____
_____
_____

**14.8 Summary**

- **Anation reactions** are ligand substitution reactions in which a **neutral ligand** (like $H_2O$ or $NH_3$) is replaced by an **anionic ligand** (like $Cl^-$, $Br^-$, $CN^-$, $SCN^-$).
- These reactions are the **reverse of aquation**.

$$[M(H_2O)_6]^{n+} + X^- \rightarrow [M(H_2O)_5X]^{(n-1)+} + H_2O$$

- **Mechanistic pathways**:
    1. **Dissociative (D):** Neutral ligand leaves first forming an intermediate.

2. **Associative (A):** Anion attaches first forming a transient seven-coordinate intermediate.
3. **Interchange (I):** Simultaneous ligand departure and anion attack; may be **I_D** or **I_A**.

- **Factors affecting rate**:
  - Metal ion (charge and size)
  - Leaving ligand strength
  - Nature and nucleophilicity of the anionic ligand
  - Solvent polarity and dielectric constant
  - Temperature and ionic strength
  - Catalysts (acid/base)
- **Examples**:
  - $[Co(H_2O)_6]^{3+} + Cl^- \rightarrow [Co(H_2O)_5Cl]^{2+}$
  - $[Cr(H_2O)_6]^{3+} + SCN^- \rightarrow [Cr(H_2O)_5(SCN)]^{2+}$
  - $[Ni(H_2O)_6]^{2+} + CN^- \rightarrow [Ni(H_2O)_5(CN)]^{+}$
  - $[Pt(H_2O)_4]^{2+} + Br^- \rightarrow [Pt(H_2O)_3Br]^{+}$
- **Applications**:
  - Synthesis of coordination compounds
  - Mechanistic studies in coordination chemistry
  - Catalysis and industrial processes
  - Medicinal chemistry (e.g., cisplatin synthesis)
  - Analytical chemistry (colorimetric detection)
  - Biological and environmental metal exchange
- **Key Concept:**
  Anation reactions demonstrate how **ligand type, metal characteristics, and reaction conditions** influence the **kinetics, mechanism, and outcome** of substitution in metal complexes.

## 14.9 Exercises

### Multiple Choice Questions

1. Anation reaction refers to the replacement of a:
   a) Neutral ligand by another neutral ligand
   b) Anionic ligand by a neutral ligand

c) Neutral ligand by an anionic ligand
d) Metal center by an anionic ligand
→ **Answer:** c) Neutral ligand by an anionic ligand

2. Which of the following complexes undergoes anation most slowly?
a) $[Co(H_2O)_6]^{3+}$
b) $[Ni(H_2O)_6]^{2+}$
c) $[Cu(H_2O)_6]^{2+}$
d) $[Pt(H_2O)_4]^{2+}$
→ **Answer:** a) $[Co(H_2O)_6]^{3+}$

3. The anation reaction of $[Cr(H_2O)_6]^{3+}$ with $SCN^-$ proceeds via:
a) Dissociative (D) mechanism
b) Associative (A) mechanism
c) Interchange dissociative (I_D) mechanism
d) None of the above
→ **Answer:** c) Interchange dissociative (I_D) mechanism

4. Which of the following anions has the strongest nucleophilic effect in anation reactions?
a) $Cl^-$
b) $Br^-$
c) $SCN^-$
d) $CN^-$
→ **Answer:** d) $CN^-$

5. Anation reactions are important in the synthesis of which anticancer drug?
a) Cisplatin
b) Penicillin
c) Aspirin
d) Ferrocene
→ **Answer:** a) Cisplatin

**Short Answer Questions**

1. Define anation reaction and give one example.
2. What is the difference between aquation and anation?
3. Name two factors affecting the rate of anation reactions.

**Long Answer Questions**

1. Describe the dissociative, associative, and interchange mechanisms of anation reactions with suitable examples.
2. Explain the factors affecting the rate of anation reactions and how each factor influences the rate.

3. Discuss at least four practical applications of anation reactions in chemistry, industry, or medicine.

## 14.10 References and suggested readings

1. Basolo, F., & Pearson, R. G. (1967). *Mechanisms of Inorganic Reactions* (2nd ed.). Wiley-Interscience.

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BLOCK 4

# REACTION MECHANISM OF TRANSITION METAL COMPLEX-PART II

## Unit 15: Substitution Reactions in Square Planar Complexes

**Structure**



### 15.1 Introduction

Square planar complexes are predominantly observed in **$d^8$ metal ions** like **Pt(II), Pd(II), Ni(II)**.

- These complexes are **kinetically labile** in some cases and **inert** in others, but they **undergo substitution reactions** much differently than octahedral complexes.
- The **geometry** (planar arrangement of ligands around the metal) allows for **associative mechanisms** and introduces the concept of the **trans effect**, which influences the **rate and position of substitution**.

For example, the substitution of a chloride in $[PtCl_4]^{2-}$by ammonia demonstrates a **trans effect** controlled reaction:

$$[PtCl_4]^{2-} + 2NH_3 \rightarrow [PtCl_2(NH_3)_2] + 2Cl^-$$

Understanding substitution in square planar complexes is crucial for **medicinal chemistry**, such as in the design of **cisplatin**.

## 15.2 Objectives

After studying this unit, you should be able to:

1. Describe the **general features** of square planar complexes.
2. Explain the **mechanism** of substitution reactions in square planar complexes.
3. Identify and explain the **factors affecting substitution rate**.
4. Discuss **examples** of substitution reactions in Pt(II) and Pd(II) complexes.
5. Understand the concept of the **trans effect** and its influence on reaction pathways.
6. Recognize the **practical applications** of substitution reactions in chemistry and medicine.

## 15.3 General Features of Square Planar Complexes

Square planar complexes are commonly formed by **$d^8$ metal ions**, such as **Pt(II), Pd(II), Ni(II)**. They have unique structural and chemical properties that distinguish them from octahedral complexes.

### 1. Geometry and Bonding

- The metal center is at the **center of a square plane**, with **four ligands at the corners**.
- Bond angles are approximately **90°**, giving a planar arrangement.
- Example: $[PtCl_4]^{2-}$, $[Pt(NH_3)_2Cl_2]$.

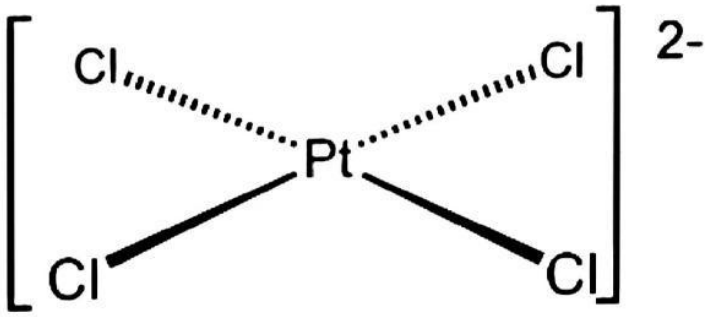


**Fig:** *Square planar geometry of* $[PtCl_4]^{2-}$

**2. Electronic Configuration**

- Square planar complexes are typically **low-spin $d^8$ complexes**.
- The **splitting of d-orbitals** in square planar geometry stabilizes the planar structure.
- $d^8$ configuration favors **planar arrangement over tetrahedral or octahedral** due to ligand field stabilization.

**3. Kinetic Properties**

- Most square planar complexes of Pt(II) and Pd(II) are **kinetically labile**, meaning **they undergo substitution reactions readily**.
- In contrast, Ni(II) complexes are usually **less reactive**.

**4. Stereochemistry**

- **Cis and trans isomers** are possible when the ligands are different.
- Example: $[Pt(NH_3)_2Cl_2]$exists as **cis** (active in cisplatin) and **trans** isomers.

**5. General Features of Substitution**

- Substitution occurs mainly via an **associative mechanism** (incoming ligand attacks the metal center forming a five-coordinate intermediate).
- The **trans effect** influences which ligand is replaced first, controlling the substitution pathway.

**15.4 Mechanism of Substitution Reactions**

Substitution reactions in **square planar complexes** mainly involve **$d^8$ metal ions** like Pt(II) and Pd(II). These reactions proceed **very differently** from octahedral complexes because of the **planar geometry** and electronic configuration.

**Associative Mechanism (A Mechanism)**

This is the **most common mechanism** for square planar substitution.

**Stepwise Process**

1. **Attack by Incoming Ligand (L′):**
    - The incoming ligand approaches the metal center **opposite to the leaving ligand or along the plane**.
    - A **five-coordinate intermediate** is formed (often called a **trigonal bipyramidal or square pyramidal intermediate**).

$[PtCl_4]^{2-} + NH_3 \rightarrow [PtCl_4(NH_3)]^{2-}$ (five-coordinate intermediate)

2. **Departure of Leaving Ligand (L):**
    - One of the original ligands leaves, restoring the **square planar geometry**.

$$[PtCl_4(NH_3)]^{2-} \rightarrow [PtCl_3(NH_3)]^{-} + Cl^{-}$$

**Overall Reaction:**

$$[PtCl_4]^{2-} + NH_3 \rightarrow [PtCl_3(NH_3)]^{-} + Cl^{-}$$

**Key Features of the Associative Mechanism**

| Feature | Description |
|---|---|
| Intermediate | Five-coordinate (square pyramidal or trigonal bipyramidal) |

| Feature | Description |
|---|---|
| Rate Law | Rate depends on both the **metal complex** and **incoming ligand**: Rate $= k[\mathrm{ML_4}][\mathrm{L'}]$ |
| Geometry | Square planar → five-coordinate intermediate → square planar |
| Stereochemistry | The **trans effect** determines which ligand is replaced |

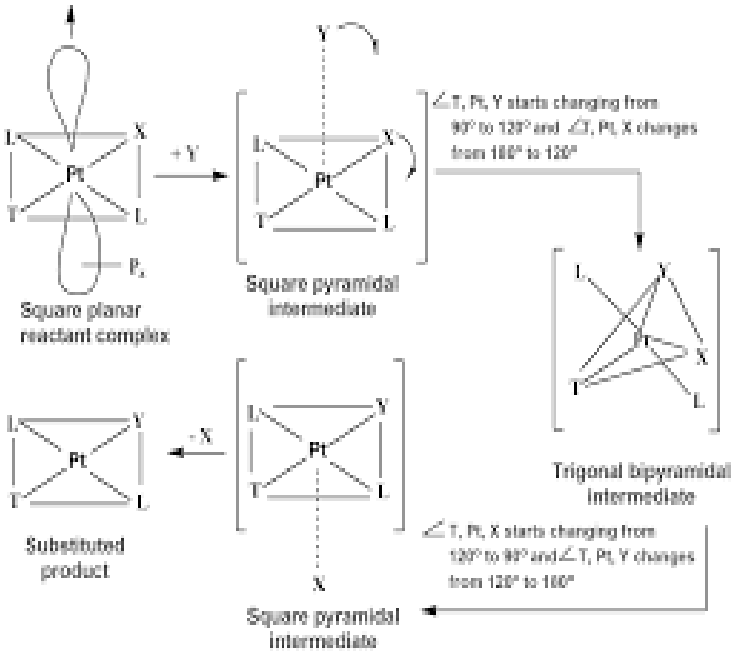


**Fig:** *Energy diagram of associative substitution in square planar complexes*

- Shows **reactants → five-coordinate intermediate → products**
- The energy barrier corresponds to formation of the intermediate.

**Special Note: Trans Effect**

- Certain ligands in square planar complexes **facilitate substitution of ligands trans to themselves**.
- Strong trans-effect ligands (e.g., $CN^-$, CO, $PR_3$) accelerate the reaction.
- Weak trans-effect ligands (e.g., $NH_3$, $H_2O$) slow the substitution.

Example:

$$[PtCl_2(CN)_2]^{2-} + NH_3 \rightarrow [PtCl(CN)_2(NH_3)]^- + Cl^-$$ (Cl opposite CN replaced)

## 15.5 Factors Affecting Rate of Substitution

The **rate of substitution** in square planar complexes depends on **metal properties, ligands, and reaction conditions**. Understanding these factors is crucial for predicting and controlling reaction outcomes.

### 1. Nature of the Metal Ion

- Square planar substitution is common for **$d^8$ metal ions** (Pt(II), Pd(II), Ni(II)).
- **Factors influencing rate:**
    - **Charge on the metal:** Higher charge → slower reaction (stronger metal–ligand bonds).
    - **Size of the metal:** Smaller ions stabilize the intermediate, accelerating reaction.
- **Example:** Pt(II) complexes react faster than Ni(II) complexes due to more favorable orbital overlap.

### 2. Nature of the Leaving Ligand

- Ligands that **leave easily** increase the reaction rate.
- Weak field ligands ($Cl^-$, $Br^-$, $H_2O$) are replaced more readily.
- Stronger ligands ($NH_3$, $CN^-$) are less likely to leave quickly.

### 3. Nature of the Incoming Ligand

- The **nucleophilicity** of the incoming ligand affects the rate:
    - Strong nucleophiles ($NH_3$, $CN^-$, $SCN^-$) → faster substitution.
    - Weak nucleophiles ($H_2O$, $NO_3^-$) → slower substitution.

**4. Trans Effect**

- The **trans effect** is the most important factor in square planar substitution.
- Certain ligands **weaken the bond trans to themselves**, making it easier to replace.
- **Order of trans-effect ligands** (strong → weak):

$$CN^- > CO > PR_3 > NO_2^- > I^- > Br^- > Cl^- > NH_3 > H_2O$$

- **Example:** In $[PtCl_2(CN)_2]$, Cl trans to $CN^-$ is replaced faster than Cl trans to $NH_3$.

**5. Solvent Effect**

- Polar solvents stabilize the metal complex and the leaving ligand.
- Protic solvents (like $H_2O$ or alcohol) often increase substitution rates by stabilizing charged intermediates.

**6. Temperature**

- Increasing temperature generally **increases the rate** of substitution reactions.
- Follows the Arrhenius relationship:

$$k = Ae^{-E_a/RT}$$

where $E_a$ is the activation energy.

**15.6 Examples of Substitution Reactions**

Substitution reactions in square planar complexes are common for **Pt(II), Pd(II), and Ni(II)** complexes. They illustrate the **associative mechanism** and the influence of the **trans effect**.

**Example 1: Substitution of Chloride in $[PtCl_4]^{2-}$ by Ammonia**

$$[PtCl_4]^{2-} + NH_3 \rightarrow [PtCl_3(NH_3)]^- + Cl^-$$

- **Mechanism:** Associative (A)

- **Trans effect:** Weak ligand $Cl^-$ is replaced; the intermediate is five-coordinate.
- Further substitution with $NH_3$ can give $[PtCl_2(NH_3)_2]$as cis or trans isomers.

**Example 2: Cisplatin Formation**

$$[PtCl_4]^{2-} + 2NH_3 \rightarrow cis - [Pt(NH_3)_2Cl_2]$$

- **Mechanism:** Associative
- **Stereochemistry:** Only **cis isomer** forms under controlled conditions.
- **Importance:** Cisplatin is a widely used anticancer drug.

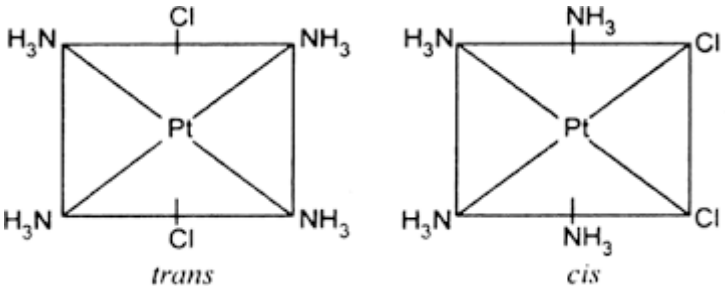


**Fig:** *Cis and trans isomers of $[Pt(NH_3)_2Cl_2]$*

**Example 3: Substitution in $[PtCl_2(CN)_2]^{2-}$**

$$[PtCl_2(CN)_2]^{2-} + NH_3 \rightarrow [PtCl(CN)_2(NH_3)]^- + Cl^-$$

- **Trans effect in action:**
  - $CN^-$ is a strong trans-effect ligand.
  - The Cl ligand **trans to $CN^-$** is replaced first.

**Example 4: Thiourea Substitution in Pt(II) Complexes**

$$[PtCl_4]^{2-} + 2SC(NH_2)_2 \rightarrow [Pt(SC(NH_2)_2)_2Cl_2]$$

- **Mechanism:** Associative
- **Stereochemistry:** Cis and trans isomers possible.
- **Application:** Formation of soft ligand complexes, important in coordination chemistry studies.

**Example 5: Palladium(II) Substitution**

$$[PdCl_4]^{2-} + 2NH_3 \rightarrow [PdCl_2(NH_3)_2]$$

- Palladium(II) shows **similar substitution behavior** to Pt(II).
- The reaction is faster due to **weaker Pd–Cl bonds**.

## 15.7 Trans Effect in Square Planar Complexes

The **trans effect** is a unique and important concept in **square planar substitution reactions**. It explains why certain ligands preferentially influence the substitution of the ligand **trans to themselves**.

### 1. Definition

**Trans effect:**

The **ability of a ligand in a square planar complex to labilize the ligand opposite (trans) to itself**, making it easier to substitute.

- Strong trans-effect ligands **accelerate substitution** of the trans ligand.
- Weak trans-effect ligands have **little or no influence**.

### 2. Factors Determining Trans Effect

The trans effect depends on **electronic properties** of the ligand:

1. **σ-Donor Ability:**
    - Strong σ-donor ligands weaken the bond trans to them.
    - Example: $PR_3$, $NH_3$ (moderate effect)
2. **π-Acceptor Ability:**
    - Strong π-acceptor ligands stabilize the metal and increase trans lability.
    - Example: CO, $CN^-$ (strong effect)
3. **Polarizability:**
    - Larger, more polarizable ligands ($I^-$, $SCN^-$) increase trans lability.

**3. Common Trans-Effect Series**

**Order of ligands (strong → weak trans effect):**

$$CN^- > CO > PR_3 > NO_2^- > I^- > Br^- > Cl^- > NH_3 > H_2O$$

- **Example:** In $[PtCl_2(CN)_2]^{2-}$, Cl trans to $CN^-$ is replaced faster than Cl trans to Cl.

**4. Mechanistic Significance**

- In **associative substitution**, the trans effect determines **which ligand leaves first**.
- Helps in **stereospecific synthesis**, e.g., formation of **cisplatin** vs **trans-$[Pt(NH_3)_2Cl_2]$**.

**5. Practical Examples**

1. **Cisplatin Synthesis**
   $$[PtCl_4]^{2-} + 2NH_3 \rightarrow cis - [Pt(NH_3)_2Cl_2]$$
   - Controlled substitution using $Cl^-$ trans to $NH_3$ yields **cis isomer**.
2. **$[PtCl_2(CN)_2]^{2-} + NH_3 \rightarrow [PtCl(CN)_2(NH_3)]^-$**
   - $CN^-$ is a strong trans-effect ligand → Cl trans to $CN^-$ is replaced first.
3. **Thiourea Substitution**
   - $SC(NH_2)_2$ has a strong trans effect → facilitates substitution of trans $Cl^-$.

## 15.8 Applications of Substitution Reactions in Square Planar Complexes

Substitution reactions in square planar complexes are important not only **theoretically** but also **practically** in **medicine, industry, and analytical chemistry**.

**1. Medicinal Chemistry**

- **Cisplatin ($[Pt(NH_3)_2Cl_2]$)** is a widely used **anticancer drug**.

- Its synthesis relies on **controlled substitution reactions** and the **trans effect**.
- The **cis isomer** is active against cancer, while the **trans isomer** is largely inactive.

- **Other platinum drugs** also use substitution to modify ligands for **better activity or lower toxicity**.

**2. Industrial Chemistry**

- Substitution reactions of square planar Pd(II) and Pt(II) complexes are used in **homogeneous catalysis**, such as:
  - **Hydrogenation**
  - **Carbon–carbon coupling reactions** (Heck, Suzuki reactions)
- Controlling substitution allows chemists to design **catalysts with specific reactivity**.

**3. Analytical Chemistry**

- Square planar substitution reactions are used to prepare **stable, colored complexes** for analysis:
  - Example: Formation of **$[Pt(NH_3)_2Cl_2]$** derivatives for **quantitative determination of Pt(II)**.
- Ligand substitution reactions help in **selective detection** of certain metal ions.

**4. Coordination Chemistry Studies**

- Substitution reactions in square planar complexes serve as **model systems** to study:
  - Mechanistic pathways (**associative mechanism**)
  - Influence of the **trans effect**
  - Ligand field stabilization and stereochemistry

**5. Synthesis of New Complexes**

- Square planar substitution allows **selective replacement of ligands**, enabling synthesis of:

- Mixed-ligand complexes
- Cis or trans stereoisomers
- Ligand-modified catalysts

**Check Your Progress**

1. What is the main mechanism of substitution in square planar complexes?

_____
_____
_____
_____
_____

2. Give one example of a square planar complex where the trans effect influences substitution.

_____
_____
_____
_____
_____

## 15.9 Summary

- **Square planar complexes** are predominantly formed by **$d^8$ metal ions** such as **Pt(II), Pd(II), and Ni(II)**.
- They have a **planar geometry** with four ligands at ~90° angles.
- **Substitution reactions** in these complexes primarily follow the **associative mechanism**, involving a **five-coordinate intermediate**.
- **Rate of substitution** is influenced by:
    1. **Nature of the metal ion** – charge and size
    2. **Leaving ligand** – weaker ligands leave faster
    3. **Incoming ligand** – stronger nucleophiles increase rate
    4. **Trans effect** – ligands with strong trans effect accelerate substitution of the ligand opposite them
    5. **Solvent** – polar/protic solvents stabilize intermediates
    6. **Temperature** – higher temperature increases the rate

- **Trans effect** is critical for **controlling substitution stereochemistry**, especially in the synthesis of **cisplatin** and related complexes.
- **Applications** of substitution reactions include:
    - **Medicinal chemistry** – synthesis of cisplatin and other drugs
    - **Industrial catalysis** – modification of Pd(II)/Pt(II) catalysts
    - **Analytical chemistry** – preparation of colored complexes for detection
    - **Coordination chemistry studies** – understanding mechanism and stereochemistry
    - **Synthesis of new complexes** – selective formation of mixed-ligand complexes
- **Key Concept:**
  Substitution in square planar complexes is **associative, trans-effect controlled**, and highly **relevant in chemistry and medicine**.

## 15.10 Exercises

### 15.10.1 Multiple Choice Questions

1. Square planar complexes are most commonly formed by which metal ions?
   a) $d^6$
   b) $d^8$
   c) $d^{10}$
   d) $d^5$
   → **Answer:** b) $d^8$
2. The main mechanism of substitution in square planar complexes is:
   a) Dissociative
   b) Associative
   c) Interchange
   d) Radical
   → **Answer:** b) Associative
3. In $[PtCl_2(CN)_2]^{2-}$, which ligand is replaced first due to the trans effect?

a) Cl trans to Cl
b) Cl trans to $CN^-$
c) $CN^-$ trans to Cl
d) $NH_3$ trans to Cl
→ **Answer:** b) Cl trans to $CN^-$

4. Which of the following ligands has the strongest trans effect?
   a) $NH_3$
   b) $Cl^-$
   c) $CN^-$
   d) $H_2O$
   → **Answer:** c) $CN^-$

5. Cisplatin is active against cancer because:
   a) It is a trans isomer
   b) It is a cis isomer
   c) It has no substitution reactions
   d) It forms a tetrahedral complex
   → **Answer:** b) It is a cis isomer

**Short Answer Questions**

1. Define substitution reactions in square planar complexes with one example.
2. What is the trans effect? Give one example.
3. Name two factors that affect the rate of substitution in Pt(II)

**Long Answer Questions**

1. Explain the associative mechanism of substitution in square planar complexes with a diagram.
2. Discuss the factors affecting the rate of substitution reactions in Pt(II) complexes.
3. Describe the trans effect and its importance in the synthesis of cisplatin.

**References and suggested readings**

**1**. Purcell, K. F., & Kotz, J. C. (1980). *Inorganic Chemistry*. Saunders College Publishing.Saunders College Publishing, 6277 Sea Harbor Drive, Orlando, FL 32887, USA.

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# Unit 16: Redox Reactions in Metal Complexes

**Structure**



## 16.1 Introduction

Redox reactions play a **vital role in coordination chemistry**, where the **oxidation state of the metal changes** during the reaction.

- These reactions are important for understanding **electron transfer processes**, **catalysis**, **biochemical processes**, and **electrochemical applications**.
- Metal complexes can act as **oxidizing agents** or **reducing agents** depending on the **metal, ligands, and reaction conditions**.

**Example:**

$$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$$

- Here, Fe(III) is **reduced** to Fe(II), showing a simple redox reaction in a metal complex.

## 16.2 Objectives

After studying this unit, you should be able to:

1. Define **redox reactions in metal complexes**.
2. Identify the **types of redox reactions**.
3. Explain the **factors affecting redox behavior** of metal complexes.
4. Give **examples** of redox reactions with different metals.
5. Understand the **applications** of redox reactions in coordination chemistry, catalysis, and electrochemistry.

## 16.3 Definition of Redox Reactions in Metal Complexes

A **redox reaction in a metal complex** is defined as:

A chemical reaction in which the **oxidation state of the central metal ion changes** due to **electron transfer**, either by gaining or losing electrons.

- **Oxidation:** Metal loses electrons → increase in oxidation state
- **Reduction:** Metal gains electrons → decrease in oxidation state

**Example 1:**

$$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$$

- Fe(III) → Fe(II) (reduction)

**Example 2:**

$$[Co(NH_3)_6]^{2+} \rightarrow [Co(NH_3)_6]^{3+} + e^-$$

- Co(II) → Co(III) (oxidation)

## 16.4 Types of Redox Reactions in Metal Complexes

Redox reactions in metal complexes can be classified into the following types:

### 1. Electron Transfer Reactions

- Direct transfer of electrons from one metal complex to another.
- **Outer-sphere mechanism:** Electron transfer without breaking metal–ligand bonds
- **Inner-sphere mechanism:** Electron transfer via a **bridging ligand**

**Example:**

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + [Cr(H_2O)_5Cl]^{2+}$$

- $Cl^-$ acts as a bridging ligand → **inner-sphere mechanism**

**2. Oxidation Reactions**

- Metal in a complex **loses electrons** (oxidation).
- Often facilitated by **strong oxidizing agents**.

**Example:**

$$[Fe(H_2O)_6]^{2+} \rightarrow [Fe(H_2O)_6]^{3+} + e^-$$

- Fe(II) → Fe(III)

**3. Reduction Reactions**

- Metal in a complex **gains electrons** (reduction).
- Often occurs in **electrochemical cells** or **photochemical processes**.

**Example:**

$$[Cr(H_2O)_6]^{3+} + e^- \rightarrow [Cr(H_2O)_6]^{2+}$$

- Cr(III) → Cr(II)

**4. Disproportionation Reactions**

- A single metal species is **simultaneously oxidized and reduced**.
- Occurs in **intermediate oxidation states**.

**Example:**

$$3Cu^+ \rightarrow 2Cu^{2+} + Cu$$

- Cu(I) is both oxidized to Cu(II) and reduced to Cu(0)

**5. Comproportionation Reactions**

- Two metal species of **different oxidation states** react to form a **single intermediate oxidation state**.

**Example:**

$$Cu^{+} + Cu^{3+} \rightarrow 2Cu^{2+}$$

### 16.5 Factors Affecting Redox Reactions in Metal Complexes

Redox reactions in metal complexes are influenced by several **structural, electronic, and environmental factors**. Understanding these factors helps predict the **ease of oxidation or reduction** of a metal complex.

**1. Nature of the Metal Ion**

- **Oxidation state:** Higher oxidation states are generally easier to reduce, while lower oxidation states are easier to oxidize.
- **Atomic number/size:** Smaller metal ions with high charge density are more easily stabilized in higher oxidation states.

**Example:**

$$[Fe(H_2O)_6]^{3+} + e^{-} \rightarrow [Fe(H_2O)_6]^{2+}$$

- Fe(III) → Fe(II) is favored due to relative stability of Fe(II) in aqueous solution.

**2. Ligand Effects (Ligand Field Stabilization)**

- **Strong field ligands** ($CN^-$, CO) stabilize **higher oxidation states** → easier oxidation.
- **Weak field ligands** ($H_2O$, $F^-$) favor lower oxidation states → easier reduction.
- **Chelating ligands** can stabilize specific oxidation states via **chelate effect**.

**Example:**

$$[Fe(CN)_6]^{3-} + e^{-} \rightarrow [Fe(CN)_6]^{4-}$$

- $CN^-$ stabilizes Fe(III), making reduction to Fe(II) easier under controlled conditions.

**3. Solvent Effects**

- Polar solvents stabilize charged species → affect redox potential.

- Protic solvents stabilize **reduced metal ions** via hydrogen bonding.
- Aprotic solvents often **increase reaction rates** for electron transfer.

**4. Temperature**

- Increase in temperature generally **increases reaction rate**.
- Thermodynamic feasibility may change depending on ΔG of reaction.

**5. Electrochemical Factors**

- **Electrode potential** of metal ions in solution influences whether oxidation or reduction occurs spontaneously.
- Nernst equation can be used to calculate redox potential:

$$E = E^0 - \frac{0.059}{n} \log \frac{[Red]}{[Ox]}$$

**6. Steric and Geometric Factors**

- Bulky ligands can **hinder approach of reactants** → slow redox reactions.
- Geometry of complex affects **overlap of orbitals** and electron transfer efficiency.

**16.6 Examples of Redox Reactions in Metal Complexes**

Redox reactions in metal complexes occur widely in **aqueous, non-aqueous, and biological systems**. Here are some typical examples:

**1. Reduction of Hexacyanoferrate(III)**

$$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$$

- Fe(III) → Fe(II)
- Ligand $CN^-$ **stabilizes the metal ion**, making reduction easier.
- Example of **ligand effect and electron transfer**.

**2. Oxidation of Hexaaquacobalt(II)**

$$[Co(H_2O)_6]^{2+} \rightarrow [Co(H_2O)_6]^{3+} + e^-$$

- Co(II) → Co(III)
- Slow in aqueous solution due to **high charge density** of Co(III).
- Reaction can be accelerated using **strong field ligands** (e.g., $NH_3$ replacing $H_2O$).

**3. Inner-Sphere Electron Transfer**

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + [Cr(H_2O)_5Cl]^{2+}$$

- $Cl^-$ acts as a **bridging ligand**, facilitating electron transfer.
- Example of **inner-sphere mechanism**.

**4. Outer-Sphere Electron Transfer**

$$[Fe(CN)_6]^{3-} + [Ru(NH_3)_6]^{2+} \rightarrow [Fe(CN)_6]^{4-} + [Ru(NH_3)_6]^{3+}$$

- Electron transfers **without breaking metal–ligand bonds**.
- Example of **outer-sphere mechanism**.

**5. Disproportionation Reaction**

$$2[Cu(H_2O)_4]^{+} \rightarrow [Cu(H_2O)_4]^{2+} + Cu$$

- Cu(I) is **simultaneously oxidized** to Cu(II) and **reduced** to Cu(0).

**6. Comproportionation Reaction**

$$Cu^{+} + Cu^{3+} \rightarrow 2Cu^{2+}$$

- Metal ions in **different oxidation states** form a **single intermediate oxidation state**.

## 16.7 Applications of Redox Reactions in Metal Complexes

Redox reactions in metal complexes have **wide applications** in **industry, medicine, analytical chemistry, and biological systems**.

**1. Industrial Applications**

- **Catalysis:**
  - Metal complexes participate in **redox cycles** during catalytic reactions.
  - Example: **$[V_2O_5]$ in the contact process** for sulfuric acid production.
  - Example: **$[Co(acac)_2]$** in oxidation of organic substrates.
- **Electroplating and Metal Refining:**
  - Redox reactions control **metal deposition and extraction**.
  - Example: **$Ni^{2+} \rightarrow Ni^0$** in electroplating of nickel.

**2. Analytical Chemistry**

- Redox reactions are used in **quantitative and qualitative analysis** of metal ions.
- Example: **$[Fe(CN)_6]^{3-}$ / $[Fe(CN)_6]^{4-}$** redox pair used in **potentiometric titrations**.
- **Indicator reactions** in complexometric analysis often involve redox processes.

**3. Biological Systems**

- Many **metalloenzymes** rely on redox reactions of metal centers:
  - **Cytochromes:** Fe in heme cycles between $Fe^{3+}$ and $Fe^{2+}$ to transfer electrons in respiration.
  - **Blue copper proteins:** Cu cycles between $Cu^{2+}$ and $Cu^{+}$ in electron transport.

**4. Synthesis of New Complexes**

- Redox reactions help in **preparing complexes in specific oxidation states**.
- Example: Oxidation of **$[Co(NH_3)_6]^{2+} \rightarrow [Co(NH_3)_6]^{3+}$** for chemical studies.

**5. Photochemical Applications**

- Redox-active metal complexes are used in **light-driven electron transfer**:
    - Example: **$[Ru(bpy)_3]^{2+}$** in photochemical solar cells.
    - Electron transfer from excited state → drives chemical reactions.

**Check Your Progress**

1. Give an example of an inner-sphere electron transfer reaction.

_____
_____
_____
_____
_____

2. What is the difference between disproportionation and comproportionation reactions?

_____
_____
_____
_____
_____

## 16.8 Summary

- **Redox reactions in metal complexes** involve a **change in the oxidation state of the central metal ion** via **electron transfer**.
- **Oxidation:** Metal loses electrons → increase in oxidation state.
- **Reduction:** Metal gains electrons → decrease in oxidation state.
- **Types of redox reactions in metal complexes:**
    1. **Electron transfer reactions** – outer-sphere and inner-sphere mechanisms
    2. **Oxidation reactions** – metal loses electrons
    3. **Reduction reactions** – metal gains electrons

4. **Disproportionation reactions** – same metal undergoes simultaneous oxidation and reduction
5. **Comproportionation reactions** – metals of different oxidation states form a single intermediate oxidation state

- **Factors affecting redox reactions:**
  - Nature of metal ion (charge, size, oxidation state)
  - Ligands (field strength, chelation, electronic effects)
  - Solvent (stabilization of ions)
  - Temperature (kinetic effect)
  - Electrochemical potential (spontaneity)
  - Steric and geometric factors
- **Examples:**
  - Reduction: $[Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{4-}$
  - Oxidation: $[Co(H_2O)_6]^{2+} \rightarrow [Co(H_2O)_6]^{3+}$
  - Inner-sphere ET: $[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+}$
  - Outer-sphere ET: $[Fe(CN)_6]^{3-} + [Ru(NH_3)_6]^{2+}$
  - Disproportionation: $2Cu^{+} \rightarrow Cu^{2+} + Cu$
- **Applications:**
  - Industrial catalysis and electroplating
  - Analytical chemistry (potentiometric titrations)
  - Biological electron transfer (cytochromes, blue copper proteins)
  - Photochemistry and solar energy conversion
  - Synthesis of metal complexes in specific oxidation states

**Key Concept:**

Redox reactions in metal complexes are **central to electron transfer processes**, influenced by ligands, metal properties, and environment, and have **wide applications in chemistry, biology, and industry**.

## 16.9 Exercises

### 16.9.1 Multiple Choice Questions

1. Which of the following is an example of a redox reaction in a metal complex?
   a) $[Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{4-}$
   b) $[Co(NH_3)_6]^{3+} + H_2O \rightarrow [Co(NH_3)_6(H_2O)]^{3+}$
   c) $[Ni(CO)_4] \rightarrow [Ni(CO)_4]$
   d) $[PtCl_4]^{2-} + NH_3 \rightarrow [PtCl_3(NH_3)]^-$
   → **Answer:** a) $[Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{4-}$

2. Which mechanism involves a **bridging ligand** during electron transfer?
   a) Outer-sphere
   b) Inner-sphere
   c) Associative
   d) Dissociative
   → **Answer:** b) Inner-sphere

3. In a disproportionation reaction, the metal:
   a) Only gets oxidized
   b) Only gets reduced
   c) Gets both oxidized and reduced
   d) Does not change oxidation state
   → **Answer:** c) Gets both oxidized and reduced

4. The reduction of $[Cr(H_2O)_6]^{3+}$to $[Cr(H_2O)_6]^{2+}$is:
   a) Oxidation
   b) Reduction
   c) Disproportionation
   d) Comproportionation
   → **Answer:** b) Reduction

5. Which of the following is a biological application of metal complex redox reactions?
   a) Nickel electroplating
   b) Cytochrome electron transport
   c) Synthesis of cisplatin
   d) Photochemical solar cells
   → **Answer:** b) Cytochrome electron transport

### 16.9.2 Short Answer Questions

1. Define redox reactions in metal complexes with one example.
2. Differentiate between inner-sphere and outer-sphere electron transfer.

3. What is a disproportionation reaction? Give an example.

### 16.9.3 Long Answer Questions

1. Explain the types of redox reactions in metal complexes with suitable examples.
2. Discuss the factors affecting redox reactions in metal complexes with examples.
3. Describe the mechanism of inner-sphere electron transfer with a diagram.

## 16.10 References and suggested readings

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# Unit 17: Outer-Sphere & Inner-Sphere Reactions

**Structure**



## 17.1 Introduction

Electron transfer reactions are fundamental in coordination chemistry.

- In metal complexes, electron transfer can occur **without breaking metal-ligand bonds** or **through a bridging ligand**.
- Understanding these reactions is important for **redox chemistry, catalysis, and biological electron transfer**.
- These reactions are classified into **Outer-Sphere** and **Inner-Sphere** mechanisms.

## 17.2 Objectives

After studying this unit, you should be able to:

1. Define **outer-sphere** and **inner-sphere electron transfer reactions**.
2. Explain the **mechanisms** of both reaction types.
3. Understand the **factors affecting electron transfer**.
4. Give **examples** of each type.
5. Identify **applications** in chemistry, industry, and biology.

## 17.3 Definition of Outer-Sphere and Inner-Sphere Reactions

### 1. Outer-Sphere Reactions:

Electron transfer occurs **without any direct bonding** between the two metal complexes.

- The **metal-ligand bonds remain intact**.
- Electron moves through **space or solvent-mediated pathways**.

**Example:**

$$[Fe(H_2O)_6]^{2+} + [Ru(NH_3)_6]^{3+} \rightarrow [Fe(H_2O)_6]^{3+} + [Ru(NH_3)_6]^{2+}$$

- No bridging ligand; only electron transfer occurs.

### 2. Inner-Sphere Reactions:

Electron transfer occurs via a **ligand that bridges the two metal centers**.

- Requires a **shared ligand** connecting donor and acceptor complexes.
- Often faster than outer-sphere reactions due to **direct orbital overlap**.

**Example:**

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + [Cr(H_2O)_5Cl]^{2+}$$

- $Cl^-$ acts as a **bridging ligand**, allowing electron transfer.

## 17.4 Mechanism of Outer-Sphere Reactions

- **Step 1: Formation of Encounter Complex**
  - Two metal complexes approach each other without forming new bonds.
- **Step 2: Electron Transfer**
  - Electron moves from donor to acceptor via **space or solvent mediation**.
- **Step 3: Separation**

- Oxidized and reduced complexes separate, maintaining original metal-ligand bonds.

**Key Points:**

- No ligand exchange occurs.
- Reaction rate depends on **metal-ligand bond strength**, **reorganization energy**, and **solvent effects**.

**Example:**

$$[Fe(CN)_6]^{4-} + [Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{3-} + [Fe(CN)_6]^{4-}$$

- Electron moves without ligand exchange.

### 17.5 Mechanism of Inner-Sphere Reactions

- **Step 1: Formation of Bridged Complex**
  - A ligand (often halide or $OH^-$) bridges donor and acceptor metal centers.
- **Step 2: Electron Transfer**
  - Electron moves through the bridging ligand.
- **Step 3: Ligand Exchange (if applicable)**
  - One metal may acquire a new ligand from the bridge.

**Key Points:**

- Requires at least one **labile ligand** that can bridge metals.
- Faster than outer-sphere if bridge formation is favorable.

**Example:**

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + [Cr(H_2O)_5Cl]^{2+}$$

- $Cl^-$ acts as bridging ligand → electron transfer occurs through it.

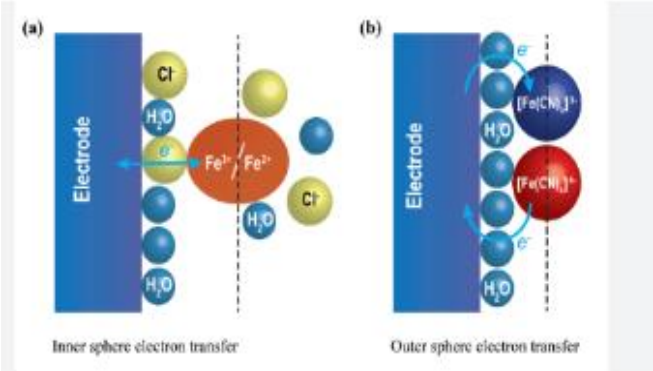


**Fig: Comparison schematic: Outer-sphere vs Inner-sphere mechanisms**

### 17.6 Factors Affecting Electron Transfer Reactions

The rate and feasibility of electron transfer reactions in metal complexes depend on several **key factors**:

#### 1. Nature of the Metal Ion

- **Oxidation state:** Higher oxidation states are generally more easily reduced, while lower oxidation states are more easily oxidized.
- **Electronic configuration:** d-electron count influences redox potential.
- **Example:** $Fe^{3+}$ is more easily reduced than $Fe^{2+}$ is oxidized.

#### 2. Ligand Effects

- **Field strength:** Strong field ligands stabilize certain oxidation states → affect redox potential.
- **Lability:** Labile ligands facilitate **inner-sphere reactions** by forming bridges.
- **Chelation:** Chelating ligands stabilize specific oxidation states → influence electron transfer.
- **Example:** $CN^-$ stabilizes Fe(III), making $Fe^{3+} \rightarrow Fe^{2+}$ reduction favorable.

**3. Type of Mechanism**

- **Outer-sphere:** Rate depends on **reorganization energy** and **solvent effects**.
- **Inner-sphere:** Rate depends on **ease of bridge formation** (labile ligand availability).

**4. Solvent and Medium**

- Polar solvents stabilize **charged species** → faster electron transfer.
- Protic solvents can form **hydrogen bonds**, influencing reaction rate.
- Viscosity affects the approach of complexes → affects outer-sphere rates.

**5. Temperature**

- Higher temperature increases **kinetic energy** → higher reaction rate.
- Thermodynamically unfavorable reactions may proceed at higher temperatures.

**6. Steric and Geometric Factors**

- Bulky ligands hinder **approach of metal centers**, slowing inner-sphere reactions.
- Geometry affects orbital overlap → electron transfer efficiency.

## 17.7 Examples of Outer-Sphere and Inner-Sphere Reactions

Electron transfer reactions in metal complexes can be illustrated with **real examples**.

**1. Outer-Sphere Electron Transfer**

- **Definition:** Electron transfer occurs **without breaking metal-ligand bonds**; complexes remain intact.

**Example 1:**

$$[Fe(H_2O)_6]^{2+} + [Ru(NH_3)_6]^{3+} \rightarrow [Fe(H_2O)_6]^{3+} + [Ru(NH_3)_6]^{2+}$$

- Electron is transferred through **solvent mediation**, no bridging ligand involved.

**Example 2:**

$$[Fe(CN)_6]^{4-} + [Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{3-} + [Fe(CN)_6]^{4-}$$

- Simple electron exchange between hexacyanoferrate complexes.

**2. Inner-Sphere Electron Transfer**

- **Definition:** Electron transfer occurs via a **ligand that bridges** the donor and acceptor metal centers.

**Example 1:**

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + [Cr(H_2O)_5Cl]^{2+}$$

- **$Cl^-$** acts as a bridging ligand, enabling electron transfer.

**Example 2:**

$$[Co(NH_3)_5Br]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + [Cr(H_2O)_5Br]^{2+}$$

- **$Br^-$** acts as a bridging ligand; reaction follows inner-sphere mechanism.

**3. Comparison Table: Outer-Sphere vs Inner-Sphere**

| Feature | Outer-Sphere | Inner-Sphere |
|---|---|---|
| Ligand involvement | No bridging ligand | Requires bridging ligand |
| Metal-ligand bonds | Intact | May exchange ligands |
| Rate | Slower (depends on reorganization) | Faster if bridge forms easily |

| Feature | Outer-Sphere | Inner-Sphere |
|---|---|---|
| Example | $[Fe(H_2O)_6]^{2+}$ + $[Ru(NH_3)_6]^{3+}$ | $[Co(NH_3)_5Cl]^{2+}$ + $[Cr(H_2O)_6]^{2+}$ |
| Mechanistic step | Electron jumps through space | Electron passes via bridge |

## 17.8 Applications of Outer-Sphere and Inner-Sphere Reactions

Electron transfer reactions in metal complexes have **important applications** in chemistry, industry, and biology.

### 1. Biological Applications

- **Metalloenzymes and Electron Transport:**
    - **Cytochromes:** Fe in heme cycles between $Fe^{3+}$ and $Fe^{2+}$ via **outer-sphere electron transfer**.
    - **Blue copper proteins:** Cu cycles between $Cu^{2+}$ and $Cu^{+}$ in electron transport chains.
    - **Significance:** Supports respiration, photosynthesis, and other metabolic processes.

### 2. Industrial Applications

- **Catalysis:**
    - Metal complexes undergo electron transfer to catalyze oxidation/reduction reactions.
    - Example: **$V_2O_5$ in contact process**; electron transfer helps in oxidation of $SO_2 \rightarrow SO_3$.
- **Electroplating and Metal Refining:**
    - Electron transfer controls **metal deposition**.
    - Example: $Ni^{2+} \rightarrow Ni^{0}$ in electroplating.

### 3. Analytical Applications

- **Redox titrations and potentiometry:**

- Outer-sphere electron transfer reactions are used to determine **metal ion concentration**.
- Example: $Fe^{2+}/Fe^{3+}$ redox pair in titrations.

**4. Photochemical Applications**

- Electron transfer in **light-excited metal complexes** is crucial in **solar energy conversion**.
- Example: **$[Ru(bpy)_3]^{2+}$** transfers electrons to acceptors in photochemical reactions.

**Check Your Progress**

1. Give one example each of an **outer-sphere** and an **inner-sphere** electron transfer reaction.

_____
_____
_____
_____

2. What is the main **difference between outer-sphere and inner-sphere reactions**?

_____
_____
_____
_____

## 17.9 Summary

- **Outer-sphere reactions:** Electron transfer occurs **without breaking metal-ligand bonds**. Electron moves through **space or solvent-mediated pathways**.
- **Inner-sphere reactions:** Electron transfer occurs **via a bridging ligand**, which connects donor and acceptor metals. Ligand exchange may occur.

**Key Mechanistic Points:**

- **Outer-sphere:** Formation of encounter complex → electron transfer → separation
- **Inner-sphere:** Formation of bridged complex → electron transfer → ligand exchange (if applicable)

**Factors affecting electron transfer reactions:**

1. Nature of the metal ion (oxidation state, d-electron configuration)
2. Ligand effects (field strength, lability, chelation)
3. Type of mechanism (outer vs inner sphere)
4. Solvent and medium (polarity, hydrogen bonding)
5. Temperature
6. Steric and geometric effects

**Applications:**

- **Biological:** Cytochromes, blue copper proteins (electron transport)
- **Industrial:** Catalysis ($V_2O_5$, Co complexes), electroplating ($Ni^{2+} \rightarrow Ni^0$)
- **Analytical:** Redox titrations, potentiometry
- **Photochemical:** Light-driven electron transfer ($[Ru(bpy)_3]^{2+}$)

**Comparison Table: Outer-Sphere vs Inner-Sphere**

| Feature | Outer-Sphere | Inner-Sphere |
|---|---|---|
| Ligand involvement | None | Bridging ligand required |
| Metal-ligand bonds | Intact | May exchange |
| Rate | Slower | Faster if bridge forms easily |
| Example | $[Fe(H_2O)_6]^{2+}$ + $[Ru(NH_3)_6]^{3+}$ | $[Co(NH_3)_5Cl]^{2+}$ + $[Cr(H_2O)_6]^{2+}$ |

## 17.10 Exercises

### 17.10.1 Multiple Choice Questions

1. Outer-sphere electron transfer occurs:
   a) With a bridging ligand
   b) Without breaking metal-ligand bonds
   c) Only in photochemical reactions
   d) Only in biological systems
   → **Answer:** b

2. Inner-sphere electron transfer requires:
   a) Solvent mediation
   b) Ligand bridging donor and acceptor
   c) No ligand involvement
   d) High temperature only
   → **Answer:** b

3. Which of the following is an example of an outer-sphere reaction?
   a) $[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+}$
   b) $[Fe(H_2O)_6]^{2+} + [Ru(NH_3)_6]^{3+}$
   c) $Ni^{2+} \rightarrow Ni^0$ in plating
   d) $Cu^+$ disproportionation
   → **Answer:** b

4. A reaction where a ligand bridges two metal centers for electron transfer is called:
   a) Outer-sphere
   b) Inner-sphere
   c) Disproportionation
   d) Comproportionation
   → **Answer:** b

5. Which factor does NOT affect electron transfer rate?
   a) Metal oxidation state
   b) Solvent polarity
   c) Temperature
   d) Color of the complex
   → **Answer:** d

### 17.10.2Short Answer Questions

1. Define outer-sphere and inner-sphere electron transfer reactions with examples.
2. List three factors affecting electron transfer reactions in metal complexes.
3. Give one biological and one industrial application of inner-sphere reactions.

### 17.10.3 Long Answer Questions

1. Discuss the mechanism of outer-sphere and inner-sphere electron transfer reactions with examples.
2. Explain the factors affecting electron transfer reactions in metal complexes.

3. Describe biological applications of outer- and inner-sphere reactions with diagrams.

## 17.11 References and suggested readings

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**BLOCK 5**

**METAL AND COMPLEXES**

## Unit 18: Introduction to Metal Complexes

**Structure**



### 18.1 Introduction

- Metal complexes are **central to inorganic chemistry**, forming when **metal ions bind with molecules or ions called ligands**.
- These complexes have unique **chemical, physical, and biological properties** compared to the individual metal ions.
- Metal complexes play a role in **catalysis, biological systems, materials, and analytical chemistry**.
- Understanding the basics of metal complexes is essential before studying **their reactions, bonding, and kinetics**.

## 18.2 Objectives

After studying this unit, you should be able to:

1. Define **metal complexes** and understand their significance.
2. Describe the **nomenclature** and **classification** of metal complexes.
3. Explain **coordination number, geometry**, and types of ligands.
4. Understand the **basic bonding concepts** in metal complexes.
5. Identify some **applications** of metal complexes in industry and biology.

## 18.3 Definition of Metal Complexes

- **Metal Complex:**

A metal complex is a chemical species consisting of a **central metal ion** bonded to **molecules or ions called ligands** through coordinate (dative covalent) bonds.

**Key Points:**

- Central metal is usually a **transition metal**.
- Ligands donate **lone pair electrons** to the metal.
- Complexes can be **cationic, anionic, or neutral**.

**Examples:**

1. $[Fe(CN)_6]^{3-}$– anionic complex
2. $[Co(NH_3)_6]^{3+}$– cationic complex
3. $[Cu(NH_3)_4]SO_4$– neutral complex

## 18.4 Nomenclature of Metal Complexes

**General Rules (IUPAC):**

1. **Order of Naming:**
    - Name **ligands first**, then **metal ion**.
    - Ligands are named in **alphabetical order**, ignoring multiplicative prefixes (di-, tri-, etc.).
2. **Ligand Naming:**
    - Anionic ligands: $Cl^-$ → chloro, $OH^-$ → hydroxo, $CN^-$ → cyano

- Neutral ligands: $NH_3$ → ammine, $H_2O$ → aqua, CO → carbonyl

3. **Metal Naming:**
   - For **cationic complexes**, name the metal as usual.
   - For **anionic complexes**, metal ends with **-ate** (e.g., ferrate, cuprate).
4. **Oxidation State:**
   - Indicated in **Roman numerals** in parentheses after the metal.

**Examples:**

- $[Co(NH_3)_6]Cl_3$→ **hexaamminecobalt(III) chloride**
- $[Fe(CN)_6]^{3-}$→ **hexacyanoferrate(III)**
- $[Cu(H_2O)_4]SO_4$→ **tetraaquacopper(II) sulfate**

## 18.5 Classification of Metal Complexes

Metal complexes can be classified based on **various criteria**:

**1. Based on Charge**

- **Cationic complexes:** $[Co(NH_3)_6]^{3+}$
- **Anionic complexes:** $[Fe(CN)_6]^{3-}$
- **Neutral complexes:** $[Cu(NH_3)_4]SO_4$

**2. Based on Nature of Ligands**

- **Homoleptic:** Contain **one type of ligand** only (e.g., $[Fe(CN)_6]^{4-}$)
- **Heteroleptic:** Contain **more than one type of ligand** (e.g., $[Co(NH_3)_4Cl_2]^{+}$)

**3. Based on Coordination Number**

- **Tetrahedral (CN = 4):** $[Ni(CO)_4]$
- **Square planar (CN = 4):** $[Pt(NH_3)_2Cl_2]$
- **Octahedral (CN = 6):** $[Co(NH_3)_6]^{3+}$

**4. Based on Metal Type**

- **Transition metal complexes** – Most common, d-block metals

- **Main group metal complexes** – s- and p-block metals (e.g., $AlCl_4^-$, $BeCl_2 \cdot 2NH_3$)

**5. Based on Ligand Denticity**

- **Monodentate ligands:** Bind through **one donor atom** ($NH_3$, $H_2O$)
- **Polydentate ligands:** Bind through **multiple donor atoms** (en = ethylenediamine, EDTA)
- **Chelates:** Complexes with **bidentate or polydentate ligands forming rings**

## 18.6 Coordination Number and Geometry

**Coordination Number (CN):**

The number of ligand donor atoms directly bonded to the central metal ion is called the **coordination number**.

**Common Coordination Numbers and Geometries:**

| Coordination Number | Geometry | Example |
|---|---|---|
| 2 | Linear | $[Ag(NH_3)_2]^+$ |
| 4 | Tetrahedral | $[Ni(CO)_4]$ |
| 4 | Square planar | $[Pt(NH_3)_2Cl_2]$ |
| 6 | Octahedral | $[Co(NH_3)_6]^{3+}$ |
| 8 | Square antiprismatic | $[Mo(CN)_8]^{4-}$ |
| 12 | Cubic | $[Re_6(CO)_{12}]$ |

**Key Points:**

- Smaller metals with fewer ligands → **lower CN**
- Larger metals can accommodate **more ligands** → higher CN
- Ligand size and denticity also affect CN

**Geometry Determination:**

- **Steric effects**: Bulky ligands → tetrahedral rather than octahedral

- **Electronic effects**: d-electron configuration may favor square planar ($d^8$ metals like $Pt^{2+}$, $Pd^{2+}$)

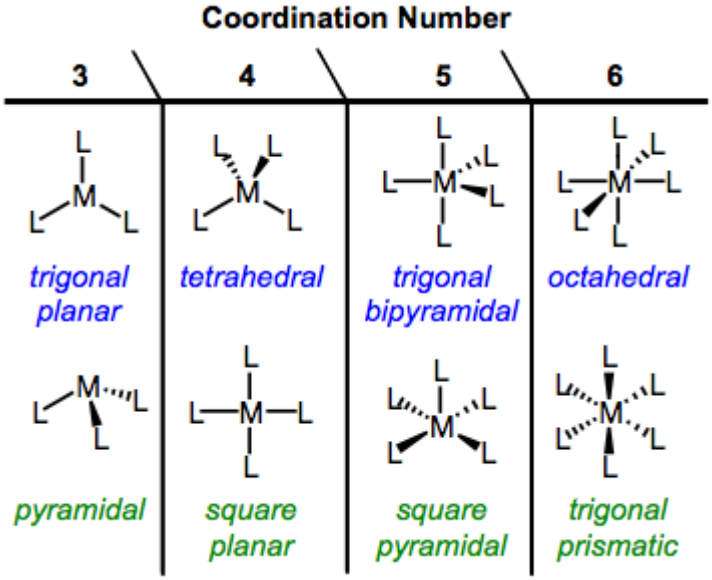


**Fig: Different coordination geometries (linear, tetrahedral, square planar, octahedral)**

**18.7 Ligands and Their Types**

**Ligands:** Molecules or ions that donate **one or more pairs of electrons** to the metal.

**Classification of Ligands:**

**1. Based on Charge**

- **Anionic ligands:** $Cl^-$, $CN^-$, $OH^-$
- **Neutral ligands:** $H_2O$, $NH_3$, CO

**2. Based on Denticity (Number of Donor Sites)**

- **Monodentate:** Single donor atom ($NH_3$, $H_2O$)
- **Bidentate:** Two donor atoms (en = ethylenediamine)
- **Polydentate:** Multiple donor atoms ($EDTA^{4-}$, porphyrin)

**3. Based on Nature of Donor Atom**

- **Hard ligands:** Donor atom is O, N, F (prefer hard metals)
- **Soft ligands:** Donor atom is S, P, I (prefer soft metals)
- **Borderline ligands:** $Cl^-$, $Br^-$

**4. Special Ligand Types**

- **Chelating ligands:** Form ring with metal center (en, $EDTA^{4-}$)
- **Ambidentate ligands:** Can bind through **two different atoms** ($NO_2^- \rightarrow$ N or O)
- **Bridging ligands:** Connect **two metal centers** ($OH^-$, $Cl^-$, $CN^-$)

**Examples:**

- Monodentate: $NH_3$ in $[Co(NH_3)_6]^{3+}$
- Bidentate: en in $[Co(en)_3]^{3+}$
- Polydentate: $EDTA^{4-}$ in $[Fe(EDTA)]^-$
- Bridging: μ-Cl in $[Co_2(\mu - Cl)_2Cl_4]^{2-}$

## 18.8 Bonding in Metal Complexes (Brief Overview)

**Metal-Ligand Bonding:**

- Ligands donate **lone pair electrons** to the vacant orbitals of the metal ion, forming **coordinate (dative covalent) bonds**.
- Bonding can be **ionic, covalent, or a mix**, depending on the metal and ligand.

**Types of Bonding:**

**1. Ionic Bonding**

- Predominant when the metal is highly **electropositive** and ligands are anionic.
- Example: $[Na(H_2O)_6]^+$

**2. Covalent (Coordinate) Bonding**

- Ligand donates **electron pair** to metal's vacant orbital.
- Example: $[Co(NH_3)_6]^{3+}$

**3. Crystal Field Theory (CFT) Overview**

- Treats ligands as **point charges** or dipoles.
- Explains **splitting of d-orbitals** in different geometries (octahedral, tetrahedral, square planar).
- Predicts **magnetic properties, color, and stability**.

**4. Molecular Orbital (MO) Theory Overview**

- Treats metal-ligand bonding as **overlap of metal d-orbitals with ligand orbitals**.
- Explains **bonding, antibonding orbitals, and delocalization**.

**Key Concept:**

Bonding in metal complexes determines **stability, geometry, magnetic properties, and reactivity**.

### 18.9 Applications of Metal Complexes

Metal complexes have **diverse applications** in chemistry, industry, and biology.

**1. Biological Applications**

- **Hemoglobin and Myoglobin:** $Fe^{2+}$ in heme binds $O_2$ reversibly.
- **Chlorophyll:** $Mg^{2+}$ complex captures light in photosynthesis.
- **Enzyme cofactors:** $Zn^{2+}$, $Mo^{6+}$ in metalloproteins facilitate catalysis.

**2. Industrial Applications**

- **Catalysis:**
  - $Fe(CO)_5$, Co complexes catalyze hydroformylation and hydrogenation.
- **Electroplating and metal recovery:**
  - $Ni^{2+}$ and $Cu^{2+}$ complexes for plating and refining metals.

**3. Analytical Applications**

- **Colorimetric indicators:** Fe(III)-thiocyanate complex produces red color for analysis.
- **Titrations:** EDTA-metal complexes for metal ion determination.

**4. Photochemistry and Materials**

- **Solar energy conversion:** $[Ru(bpy)_3]^{2+}$ absorbs light and transfers electrons.
- **Dyes and pigments:** Transition metal complexes provide vibrant colors (e.g., Cr, Co complexes).

## 18.12 Check Your Progress

1. Give one example of a **cationic** and one **anionic** metal complex.

_____
_____
_____
_____

2. Differentiate **monodentate** and **bidentate ligands** with examples.

_____
_____
_____
_____
_____

## 18.10 Summary

- **Metal complexes** are formed when a **central metal ion binds with ligands** through coordinate (dative covalent) bonds.
- **Nomenclature:** Ligands are named first (alphabetically), then metal, with oxidation state in Roman numerals.
- **Classification:**
    - Based on **charge**: cationic, anionic, neutral
    - Based on **ligand type**: homoleptic, heteroleptic
    - Based on **geometry/coordination number**: tetrahedral, square planar, octahedral
    - Based on **ligand denticity**: monodentate, bidentate, polydentate
- **Coordination number (CN):** Number of donor atoms attached to the metal. Determines **geometry**.
- **Ligands:** Classified by charge, denticity, donor atom type, and special features (chelating, ambidentate, bridging).
- **Bonding:**
    - Ionic, covalent (coordinate), explained briefly via **Crystal Field Theory (CFT)** and **Molecular Orbital Theory (MO)**.
- **Applications:**
    - **Biological:** Hemoglobin, chlorophyll, metalloproteins

- **Industrial:** Catalysis, electroplating
- **Analytical:** EDTA titrations, colorimetric assays
- **Photochemistry/Materials:** Dyes, solar energy conversion

**Key Concept:**

Understanding metal complexes lays the foundation for studying **their reactions, kinetics, bonding, and applications**.

## 18.11 Exercises

### 18.11.1Multiple Choice Questions

1. A complex with formula $[Co(NH_3)_6]Cl_3$is:
   a) Cationic
   b) Anionic
   c) Neutral
   d) None of these
   → **Answer:** a

2. In $[Fe(CN)_6]^{3-}$, $CN^-$ is a:
   a) Neutral ligand
   b) Anionic ligand
   c) Bridging ligand
   d) Ambidentate ligand
   → **Answer:** b

3. A ligand that can bind through two different donor atoms is called:
   a) Monodentate
   b) Bidentate
   c) Ambidentate
   d) Polydentate
   → **Answer:** c

4. The coordination number of Ni in $[Ni(CO)_4]$is:
   a) 2
   b) 4
   c) 6
   d) 8
   → **Answer:** b

5. Hemoglobin is a metal complex of:
   a) $Cu^{2+}$
   b) $Mg^{2+}$
   c) $Fe^{2+}$
   d) $Zn^{2+}$
   → **Answer:** c

### 18.11.2 Short Answer Questions

1. Define a metal complex and give one example.
2. What is the difference between homoleptic and heteroleptic complexes?
3. Name three types of ligands based on denticity.
4. Give one biological and one industrial application of metal complexes.
5. What is the coordination number and why is it important?

### 18.11.3 Long Answer Questions

1. Explain the nomenclature and classification of metal complexes with examples.
2. Discuss coordination number, geometry, and factors affecting it in metal complexes.
3. Describe different types of ligands with examples and special features.

### 18.12 References and suggested readings

1. Raj, G. (2019). *Advanced Inorganic Chemistry* (Vol. 1). Krishna Prakashan Media Pvt. Ltd., Meerut, India.
2. Huheey, J. E., Keiter, E. A., & Keiter, R. L. (2006). *Inorganic Chemistry: Principles of Structure and Reactivity* (5th ed.). Pearson Education, 221 River Street, Hoboken, NJ 07030, USA.
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# Unit 19: Metal Carbonyl Complexes

**Structure**



## 19.1 Introduction

- **Metal carbonyl complexes** are coordination compounds where a **metal atom is bonded to carbon monoxide (CO) ligands**.
- CO acts as a **neutral ligand** donating a lone pair from carbon to the metal.
- These complexes are important in **organometallic chemistry**, **catalysis**, and **industrial processes**.
- Famous examples include **$Fe(CO)_5$ (iron pentacarbonyl)** and **$Ni(CO)_4$ (nickel tetracarbonyl)**.

## 19.2 Objectives

After studying this unit, you should be able to:

1. Define **metal carbonyl complexes** and understand their significance.

2. Classify metal carbonyls based on **structure and bonding**.
3. Explain the **bonding in metal carbonyls** using **σ-donation and π-backbonding**.
4. Describe methods of **preparation** and discuss their **properties**.
5. Identify important **applications** in catalysis, industry, and research.

## 19.3 Definition of Metal Carbonyl Complexes

- **Metal Carbonyl Complex:**

A metal carbonyl complex is a coordination compound in which a **metal atom or ion is bonded to one or more carbon monoxide (CO) ligands**.

**Key Points:**

- CO is a **neutral ligand**.
- Forms **coordinate (dative covalent) bonds** with the metal.
- Often **transition metals** of groups 6–10 form stable carbonyl complexes.

**Examples:**

1. $[Fe(CO)_5]$– iron pentacarbonyl
2. $[Ni(CO)_4]$– nickel tetracarbonyl
3. $[Cr(CO)_6]$– chromium hexacarbonyl

## 19.4 Classification of Metal Carbonyl Complexes

Metal carbonyls can be classified based on **structure and nuclearity**:

**1. Mononuclear Carbonyls**

- Contain a **single metal center**.
- Example: $[Ni(CO)_4]$, $[Fe(CO)_5]$, $[Cr(CO)_6]$

**2. Polynuclear (Cluster) Carbonyls**

- Contain **two or more metal atoms**.
- Metal atoms may be **bonded to each other**.
- Example: $[Fe_2(CO)_9]$, $[Co_4(CO)_{12}]$

**3. Neutral, Cationic, and Anionic Carbonyls**

- **Neutral:** $Ni(CO)_4$, $Fe(CO)_5$

- **Cationic:** $[Fe(CO)_6]^{2+}$
- **Anionic:** $[Fe(CO)_4]^{2-}$

**4. Based on Coordination Number**

- CN = 4 → Tetrahedral: $Ni(CO)_4$
- CN = 5 → Trigonal bipyramidal: $Fe(CO)_5$
- CN = 6 → Octahedral: $Cr(CO)_6$

## 19.5 Bonding in Metal Carbonyl Complexes

**Bonding in metal carbonyls** is explained by **Synergic σ-Donation and π-Backbonding**:

**1. σ-Donation**

- CO donates a **lone pair of electrons from carbon** to an empty orbital of the metal.
- Forms a **σ bond** between C and metal.

**2. π-Backbonding**

- Metal **donates electrons from filled d-orbitals** into the *π antibonding orbitals of CO**.
- Strengthens metal-carbon bond and weakens C–O bond slightly.
- Responsible for **stability and characteristic IR absorption of CO**.

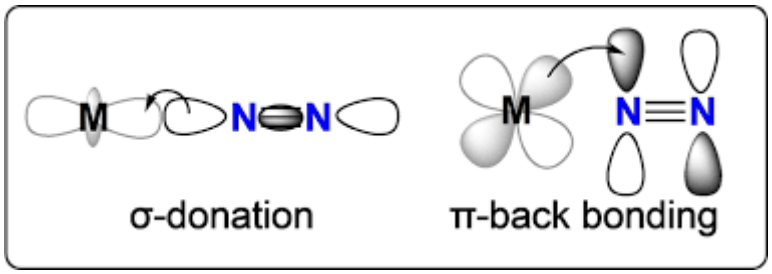


**Fig: σ-Donation and π-Backbonding schematic**

**Representation:**

$$M \leftrightarrow CO$$

- Metal → CO (π-backbonding)
- CO → Metal (σ-donation)

**Key Features:**

- Explains **low-spin octahedral complexes** of $d^6$ metals.
- IR spectroscopy: **CO stretching frequency decreases** with increasing π-backbonding.

**Example:**

- In $Cr(CO)_6$, CO ligands form **σ-bonds with Cr** and receive electron density via **π-backbonding** from Cr d-orbitals.

## 19.6 Preparation Methods of Metal Carbonyl Complexes

Metal carbonyls can be prepared using several methods, depending on the metal and conditions.

**1. Direct Method**

- **Reaction of metal or metal oxide with CO under high pressure and temperature.**
- Example:

$$Ni + 4CO \xrightarrow{100-200°C,50atm} Ni(CO)_4$$
$$Fe + 5CO \xrightarrow{200°C,50atm} Fe(CO)_5$$

- Typically used for **volatile, low-valent carbonyls**.

**2. Indirect Method (Reduction of Metal Halides)**

- **Metal halide reacts with CO in the presence of reducing agents** (e.g., $H_2$, Na, Zn).
- Example:

$$CrCl_3 + 6CO + 3Zn \rightarrow Cr(CO)_6 + 3ZnCl_2$$

**3. Carbonylation of Metal Salts**

- Metal salts in solution react with **CO in the presence of base or reducing agent**.
- Example:

$$FeCl_3 + 3CO + Al \rightarrow Fe(CO)_5 + AlCl_3$$

**4. Disproportionation and Cluster Formation**

- Some metal carbonyls are formed by **thermal decomposition of mononuclear carbonyls**, forming **polynuclear clusters**.
- Example:

$$2Fe(CO)_5 \xrightarrow{\Delta} Fe_2(CO)_9 + CO$$

## 19.7 Properties of Metal Carbonyl Complexes

Metal carbonyls exhibit **unique chemical and physical properties**:

**1. Physical Properties**

- **Volatility:** Many mononuclear carbonyls ($Ni(CO)_4$, $Fe(CO)_5$) are volatile liquids.
- **Color:** Most are **colorless** or pale yellow.
- **Solubility:** Soluble in organic solvents (ether, benzene), generally insoluble in water.

**2. Chemical Properties**

- **Thermal decomposition:**
  - Metal carbonyls decompose on heating, forming **metal and CO** or **clusters**.

- **Reaction with ligands (substitution):**
  - CO ligands can be replaced by **other ligands** ($NH_3$, $PPh_3$).

- **Oxidation:** Can be oxidized to **metal salts** in presence of oxidizing agents.

**3. Spectroscopic Properties**

- **Infrared (IR) spectroscopy:**
  - Strong **CO stretching bands** (≈ 1850–2100 $cm^{-1}$).

- Shifts in frequency indicate **extent of π-backbonding**.

- **Magnetic properties:**
  - Most mononuclear carbonyls are **diamagnetic** due to **low-spin $d^6$ configuration** (e.g., $Cr(CO)_6$, $Fe(CO)_5$).

## 19.8 Applications of Metal Carbonyl Complexes

Metal carbonyls have **wide applications** in chemistry, industry, and catalysis.

### 1. Catalysis

- **Hydroformylation:** Co or Rh carbonyls catalyze the addition of CO + $H_2$ to alkenes to form aldehydes.

$$\ce{RCH=CH2 + CO + H2 -> [Co(CO)8] RCH2CH2CHO}$$

- **Hydrogenation and carbonylation reactions:** $Ni(CO)_4$ and $Fe(CO)_5$ are precursors for catalysts.

### 2. Source of Pure Metals

- Metal carbonyls decompose to **pure metal** upon heating.

$$\ce{Ni(CO)4 -> [\Delta] Ni(s) + 4CO(g)}$$
$$\ce{Fe(CO)5 -> [\Delta] Fe(s) + 5CO(g)}$$

### 3. Organic Synthesis

- Substituted carbonyl complexes are used in **organometallic reactions** to introduce functional groups.

$$\ce{Fe(CO)5 + 2PPh3 -> Fe(CO)3(PPh3)2 + 2CO}$$

### 4. Industrial and Analytical Applications

- Used as **precursors** for deposition of thin films of metals (Ni, Fe).
- Serve as **ligand sources** for synthesis of other organometallic complexes.

**Check Your Progress**

1. Give one example each of a **mononuclear** and a **polynuclear metal carbonyl complex**.

_____
_____
_____
_____

2. What is the main difference between **σ-donation** and **π-backbonding** in metal carbonyls?

_____
_____
_____
_____
_____

## 19.9 Summary

- **Metal carbonyl complexes** are formed when **transition metals bond with CO ligands**.
- **Classification:** Mononuclear vs. polynuclear; neutral, cationic, anionic; based on CN.
- **Bonding:**
    - **σ-donation:** CO → metal
    - **π-backbonding:** Metal → CO
- **Preparation methods:**

1. Direct reaction with CO
2. Reduction of metal halides
3. Carbonylation of metal salts
4. Thermal decomposition (cluster formation)

- **Properties:** Volatile, low-spin, diamagnetic, soluble in organic solvents, thermally reactive.
- **Applications:** Catalysis, metal purification, organic synthesis, industrial deposition.

**Key Concept:**

CO acts as a strong field ligand forming **stable, low-spin complexes** with transition metals, essential in organometallic chemistry and industrial applications.

## 19.10 Exercises

### 19.10.1 Multiple Choice Questions

1. $Ni(CO)_4$ is:
   a) Tetrahedral
   b) Square planar
   c) Octahedral
   d) Linear
   → **Answer:** a

2. $Fe(CO)_5$ has:
   a) Tetrahedral geometry
   b) Trigonal bipyramidal geometry
   c) Octahedral geometry
   d) Square planar geometry
   → **Answer:** b

3. Which ligand shows π-backbonding?
   a) $NH_3$
   b) $H_2O$
   c) CO
   d) $Cl^-$
   → **Answer:** c

4. The decomposition of $Ni(CO)_4$ yields:
   a) $Ni^{2+} + CO_2$
   b) Ni (s) + CO
   c) $Ni(CO)_2$
   d) NiO + CO
   → **Answer:** b

5. Metal carbonyls are generally:
   a) Paramagnetic
   b) Diamagnetic
   c) Highly ionic
   d) Insoluble in organic solvents
   → **Answer:** b

### 19.10.2 Short Answer Questions

1. Define a metal carbonyl complex and give two examples.
2. What is the role of σ-donation and π-backbonding in bonding?
3. Name two methods for preparing metal carbonyls.

### 19.10.3 Long Answer Questions

1. Explain the bonding in metal carbonyl complexes using σ-donation and π-backbonding.
2. Describe the preparation methods of mononuclear and polynuclear metal carbonyls with equations.
3. Discuss physical and chemical properties of metal carbonyl complexes.

## 19.11 References and suggested readings

1. Raj, G. (2019). *Advanced Inorganic Chemistry* (Vol. 1). Krishna Prakashan Media Pvt. Ltd., 7/A Industrial Area, Saharanpur, Uttar Pradesh, India.
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# Unit 20: Transition Metal-Nitrosyl Complexes

**Structure**



## 20.1 Introduction

- **Transition metal-nitrosyl complexes** are coordination compounds in which a **nitric oxide (NO) molecule binds to a metal center**.
- NO acts as a **ligand**, which can bind through **nitrogen (linear)** or **oxygen (bent)**, depending on the electron configuration of the metal.
- These complexes are significant in **bioinorganic chemistry, catalysis, and organometallic reactions**.
- Examples include **$[Co(NO)(NH_3)_5]^{2+}$** and **$[Fe(CO)_2(NO)_2]$**.

## 20.2 Objectives

After studying this unit, you should be able to:

1 Define **transition metal-nitrosyl complexes** and understand their importance.
2. Classify nitrosyl complexes based on **bonding and geometry**.
3. Explain **bonding in metal-nitrosyl complexes** (linear vs bent NO).

4. Describe **methods of preparation** and **chemical properties**.
5. Recognize **applications** in catalysis, biology, and organometallic chemistry.

## 20.3 Definition of Metal-Nitrosyl Complexes

**Metal-nitrosyl complex:**

A transition metal complex in which **nitric oxide (NO) coordinates to the metal center** via the nitrogen atom or oxygen atom through a **σ bond**, often accompanied by π-backbonding.

**Characteristics:**

- NO is a **neutral, ambidentate ligand**, capable of binding **via nitrogen (most common) or oxygen**.
- The **M–NO bond can be linear or bent**, depending on the electron count of the metal.
- NO can act as a **one-electron donor (radical)** or **three-electron donor ($NO^+$ form)**.

**Examples:**

1. **$[Co(NO)(NH_3)_5]^{2+}$** – Linear NO
2. **$[Fe(CO)_2(NO)_2]$** – Bent NO

## 20.4 Classification of Nitrosyl Complexes

Metal-nitrosyl complexes are classified based on **geometry and bonding mode of NO**:

**1. Based on M–N–O Angle**

| Type | Geometry | Description | Example |
|---|---|---|---|
| Linear | M–N–O ≈ 180° | NO acts as **$NO^+$**, strong π-acceptor | $[Co(NO)(NH_3)_5]^{2+}$ |
| Bent | M–N–O < 140° | NO acts as **$NO^-$**, radical character | $[Fe(CO)_2(NO)_2]$ |

**2. Based on Electron Count**

- **Neutral NO complexes:** Metal + NO ligand (total electrons $18e^-$, stable).
- **Cationic NO complexes:** $[M(NO)L_n]^{2+}$, e.g., $[Co(NO)(NH_3)_5]^{2+}$

- **Anionic NO complexes:** $[M(NO)L_n]^-$

**3. Based on Bonding Mode**

- **End-on coordination ($\eta^1$-N):** NO binds via nitrogen (most common).
- **Side-on coordination ($\eta^2$-NO):** Rare; both N and O interact with metal.

**4. Based on Ligand Environment**

- **Mononuclear:** Single metal center, e.g., $[Co(NO)(NH_3)_5]^{2+}$
- **Polynuclear:** Cluster complexes with bridging NO ligands, e.g., $[Fe_2(NO)_2(CO)_6]$

## 20.5 Bonding in Metal-Nitrosyl Complexes

Bonding in M–NO complexes is described by **σ-donation and π-backbonding**, similar to CO ligands.

**1. σ-Donation**

- Lone pair on **nitrogen** of NO is donated to an empty **metal orbital** forming a σ bond.

**2. π-Backbonding**

- Filled metal d-orbitals donate electron density to the *π antibonding orbital of NO**.
- Stabilizes the metal-ligand bond and influences **M–N–O geometry**.

**Linear NO:**

- Strong π-backbonding
- NO behaves like **$NO^+$**, metal achieves **18-electron configuration**

**Bent NO:**

- Weaker π-backbonding
- NO behaves like **$NO^-$**, radical character retained

**3. Enemark-Feltham Notation**

- Used to describe **metal-NO electron configuration**: $\{M–NO\}^n$
- n = total **d-electrons on metal + 1 electron from NO**
- Example:

$\ce[Fe(CO)2(NO)2]: Fe–NO^8$

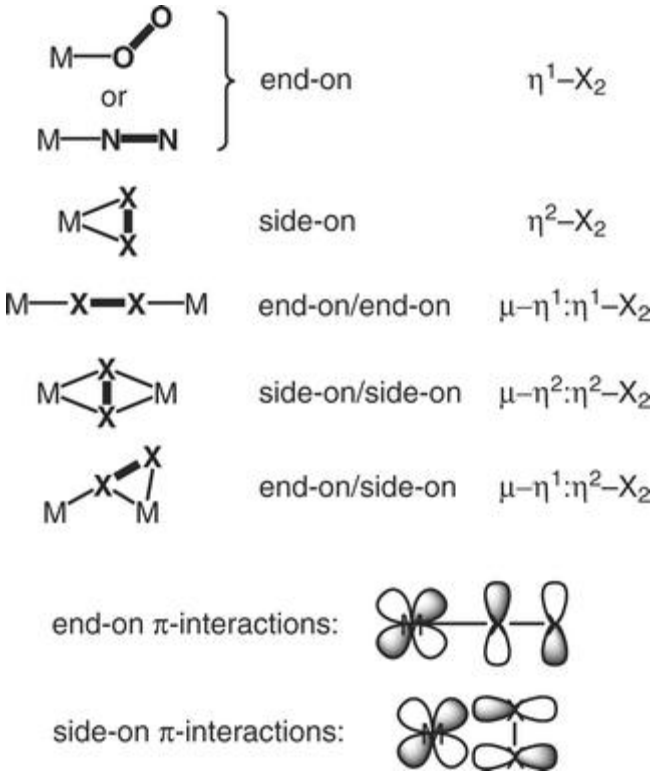


**Fig: Bonding in Metal-Nitrosyl Complexes**

### 20.6 Methods of Preparation of Metal-Nitrosyl Complexes

#### 1. Direct Reaction with NO

- Transition metals react directly with nitric oxide under **controlled temperature and pressure**.
- Example:

$$\ce[Co(NH3)5(H2O)]^{2+} + NO- > [roomtemp][Co(NH3)5(NO)]^{2+} + H2O$$

#### 2. Reduction of Metal-Nitrite Complex

- Metal nitrite complexes ($\ceM–ONO$) can be reduced by **reducing agents** to form M–NO complexes.
- Example:

$$\ce[Co(NH3)5(ONO)]^{2+} + Zn + HCl- > [Co(NH3)5(NO)]^{2+} + ZnCl2 + H2O$$

**3. Nitrosylation of Metal Carbonyls**

- Metal carbonyls react with **nitric oxide** to form mixed carbonyl-nitrosyl complexes.
- Example:

$$\ceFe(CO)5 + 2NO -> Fe(CO)3(NO)2 + 2CO$$

**4. Photochemical Methods**

- Some nitrosyl complexes are formed under **UV or visible light irradiation**.
- Example: Photolysis of Fe(CO)5 in presence of NO:

$$\ceFe(CO)5 + NO -> [h\nu]Fe(CO)4(NO) + CO$$

s

**20.7 Properties of Metal-Nitrosyl Complexes**

**1. Physical Properties**

- **Color:** Most complexes are colored due to **d–d transitions**.
- **Solubility:** Soluble in **polar organic solvents** (e.g., acetone, ethanol), less in water.
- **Magnetism:** Linear M–NO complexes are usually **diamagnetic** (low-spin), bent ones can be **paramagnetic** (unpaired electron).

**2. Chemical Properties**

**a. Ligand Substitution**

- NO ligand can be substituted by other ligands:

$$\ce[Co(NH3)5(NO)]^{2+} + PPh3 -> [Co(NH3)5(PPh3)]^{2+} + NO$$

**b. Oxidation and Reduction**

- Metal-nitrosyl complexes can be **oxidized** or **reduced**, altering NO bonding mode:

$$\ce[Fe(CO)2(NO)2] + [Fe(CN)6]^{3-} -> oxidizedproducts$$

**c. Protonation**

- Nitrosyl ligands can be **protonated** under acidic conditions:

  \ce$[Co(NH3)5(NO)]^{2+} + H^{+} -> [Co(NH3)5(NO^{+})]^{3+}$

**3. Spectroscopic Properties**

- **Infrared (IR) spectroscopy:**
  - ν(NO) stretching frequency depends on **linear (~1800–1900 $cm^{-1}$) or bent (~1600–1700 $cm^{-1}$)** geometry.
- **UV-Vis spectroscopy:** Shows **d–d and charge transfer bands**.
- **NMR spectroscopy:** Useful for **diamagnetic complexes** (linear NO).

## 20.8 Applications of Metal-Nitrosyl Complexes

1. **Biological Models**
   - Mimic **heme-NO interactions** in hemoproteins and enzymes.
   - Used in **studying NO signaling and transport**.
2. **Catalysis**
   - Serve as **catalysts or precursors** in hydroformylation and carbonylation reactions.
3. **Synthetic Chemistry**
   - Useful in **synthesis of mixed-ligand complexes**.
   - Serve as **NO donors** in controlled reactions.
4. **Medical Applications**
   - Some M–NO complexes act as **NO donors** in **vasodilation and therapeutic studies**.

**Check Your Progress**

1. Give one example each of a **linear** and a **bent nitrosyl complex**.

_____
_____
_____
_____

2. What is the main difference between **σ-donation** and **π-backbonding** in M–NO complexes?

_____
_____
_____
_____

## 20.9 Summary

- **Metal-nitrosyl complexes** are transition metal complexes with coordinated NO ligands.
- **Classification:** Linear vs bent NO; mononuclear vs polynuclear; neutral, cationic, or anionic.
- **Bonding:**
  - **σ-donation** from NO → metal
  - **π-backbonding** from metal → NO
  - Enemark-Feltham notation $\{M–NO\}^n$ describes electron count.
- **Preparation:** Direct reaction with NO, reduction of nitrites, reaction with metal carbonyls, photochemical methods.
- **Properties:** Colored, soluble in organic solvents, diamagnetic (linear NO), paramagnetic (bent NO).
- **Applications:** Biological models, catalysis, synthetic organometallic chemistry, NO donors in medicine.

## 20.10 Exercises

### 20.10.1 Multiple Choice Questions

1. In linear M–NO complexes, NO behaves as:
   a) $NO^-$
   b) $NO^+$
   c) Radical
   d) Neutral only
   → **Answer:** b

2. The ν(NO) stretching frequency of bent NO complexes is approximately:
   a) 1800–1900 $cm^{-1}$
   b) 1600–1700 $cm^{-1}$
   c) 2000–2100 $cm^{-1}$

d) 1400–1500 $cm^{-1}$
→ **Answer:** b

3. $[Co(NO)(NH_3)_5]^{2+}$ is:
   a) Linear
   b) Bent
   c) Tetrahedral
   d) Octahedral
   → **Answer:** a

4. Metal nitrosyl complexes are often prepared by:
   a) Reaction of metal with CO
   b) Reduction of metal nitrite
   c) Oxidation of metal carbonyl
   d) Reaction with water
   → **Answer:** b

5. The Enemark-Feltham notation for $[Fe(CO)_2(NO)_2]$ is:
   a) $\{Fe–NO\}^6$
   b) $\{Fe–NO\}^8$
   c) $\{Fe–NO\}^{10}$
   d) $\{Fe–NO\}^7$
   → **Answer:** b

### 20.10.2Short Answer Questions

1. Define a metal-nitrosyl complex and give two examples.
2. Differentiate between linear and bent NO bonding.
3. Name two methods for preparing M–NO complexes.

### 20.10.3 Long Answer Questions

1. Explain the bonding in metal-nitrosyl complexes using σ-donation and π-backbonding.
2. Describe the methods of preparation of metal-nitrosyl complexes with equations.
3. Discuss the physical, chemical, and spectroscopic properties of M–NO complexes.

## 20.11 References and suggested readings

1. Huheey, J. E., Keiter, E. A., & Keiter, R. L. (1993). *Inorganic chemistry: Principles of structure and reactivity* (4th ed.). Pearson Education, New Delhi, India.

2. Lee, J. D. (1996). *Concise inorganic chemistry* (5th ed.). Wiley India, New Delhi, India.
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# Unit 21: Dinitrogen & Dioxygen Complexes

**Structure**



## 21.1 Introduction

Transition metal complexes with **dinitrogen ($N_2$) and dioxygen ($O_2$) ligands** play a crucial role in **coordination chemistry, catalysis, and bioinorganic systems**.

- **Dinitrogen complexes (M–$N_2$):** These are metal complexes where **$N_2$ molecules are coordinated to transition metals**, often mimicking the activity of **nitrogenase enzymes**, which convert atmospheric $N_2$ into ammonia.
- **Dioxygen complexes (M–$O_2$):** Metal complexes where $O_2$ binds to the metal, often mimicking **hemoglobin, myoglobin, and hemocyanin**, which are involved in **oxygen transport and storage in biological systems**.

**Significance:**

1. **Biological:** Understanding $O_2$ and $N_2$ binding in metalloproteins helps in **enzyme and transport system studies**.

2. **Industrial:** Models for **nitrogen fixation** and **oxidation catalysts**.
3. **Chemical:** Activation of chemically inert molecules (N≡N, O=O) via **metal-ligand interactions**.

**Examples:**

- **Dinitrogen complex:** $[Mo(N_2)_2(PPh_3)_4]$
- **Dioxygen complex:** $[Co(O_2)(en)_2]^{3+}$, $[Fe(O_2)(EDTA)]^-$

## 21.2 Objectives

After completing this unit, you should be able to:

- Describe **dinitrogen and dioxygen metal complexes**.
- Explain **bonding modes** of $N_2$ and $O_2$ in metal complexes.
- Understand **methods of preparation** of these complexes.
- Discuss **physical, chemical, and spectroscopic properties**.
- Recognize **applications in biology, catalysis, and industry**.

## 21.3 Dinitrogen Complexes (M–$N_2$)

**Definition:**

Dinitrogen complexes are **transition metal complexes in which $N_2$ molecules are coordinated to the metal center**, either terminally (end-on) or bridging between metals.

**Bonding Modes:**

1. **Terminal (End-on) $N_2$:**
    - $N_2$ binds through **one nitrogen atom** to a single metal.
    - Example: $[Mo(N_2)_2(PPh_3)_4]$
2. **Bridging (Side-on) $N_2$:**
    - $N_2$ bridges **two or more metal centers**, binding via **both nitrogens ($\eta^2$)**.
    - Example: $[Fe_2(\mu - N_2)(CO)_8]$

**Significance:**

- Activation of N≡N bond for **chemical reduction to ammonia**.
- Models the **enzymatic nitrogenase process**.

**Equation Example – Formation of Terminal $N_2$ Complex:**

$$\ce{Mo(PPh3)4 + N2 -> [room temp][Mo(N2)(PPh3)4]}$$

## 21.4 Dioxygen Complexes (M–$O_2$)

**Definition:**

Dioxygen complexes are metal complexes where $O_2$ is coordinated to the metal, either **end-on (superoxo)** or **side-on (peroxo)**.

**Bonding Modes:**

1. **End-on ($\eta^1$-$O_2$, superoxo):** Metal binds to **one oxygen atom**.
   - Example: $[Co(O_2)(en)_2]^{3+}$
2. **Side-on ($\eta^2$-$O_2$, peroxo):** Metal binds to **both oxygen atoms**, forming a ring structure.
   - Example: $[Fe(O_2)(EDTA)]^-$

**Significance:**

- Mimics **oxygen binding in hemoglobin and myoglobin**.
- $O_2$ complexes act as **oxidants in chemical reactions**.

## 21.5 Bonding in Dinitrogen Complexes

**1. σ-Donation:**

- Lone pair on N atom **donates electron density** to empty metal orbital.

**2. π-Backbonding:**

- Metal **donates electron density** from filled d-orbitals into $N_2$ $\pi$ *antibonding orbital**, weakening the N≡N bond.

**Example – Mo Dinitrogen Complex:** $[Mo(N_2)_2(PPh_3)_4]$

- N–N bond length increases from **1.10 Å (free $N_2$)** to **1.12–1.15 Å** in the complex.

**Effect:**

- Activation of $N_2$ for **further chemical reactions**, e.g., reduction to ammonia.

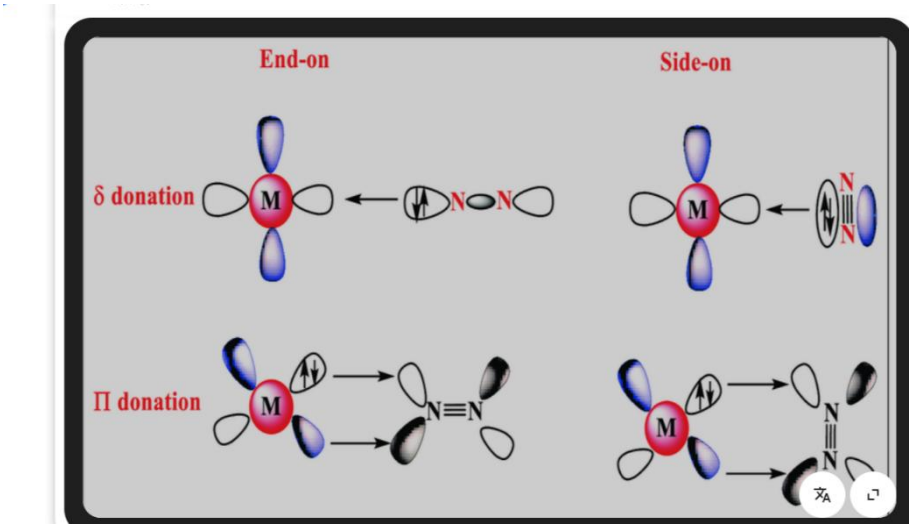


**Fig: Bonding in Dinitrogen Complexes**

## 21.6 Bonding in Dioxygen Complexes

**1. End-on (Superoxo) M–$O_2$:**

- $O_2$ behaves as **$O_2^-$ (one-electron donor)**.
- Metal is usually **low-spin**.

**2. Side-on (Peroxo) M–$O_2$:**

- $O_2$ behaves as **$O_2^{2-}$ (two-electron donor)**.
- Strong **π-backbonding stabilizes the complex**.

**Example – Fe Complex:**

- Hemoglobin: $Fe^{2+}$ binds $O_2$ end-on; reversible $O_2$ binding.
- Peroxo complex: $Fe(O_2)(EDTA)^-$, used in oxidation reactions.

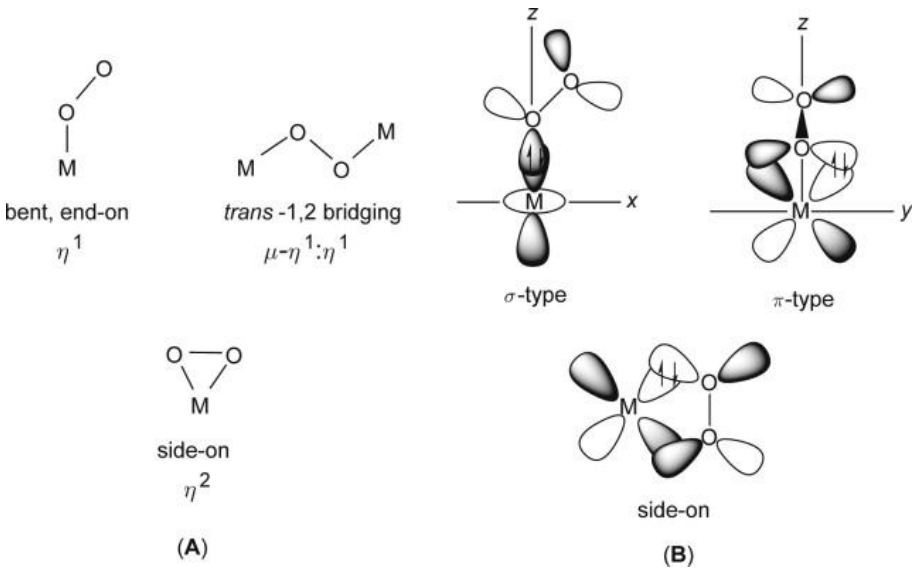


**Fig: Bonding in Dioxygen Complexes**

## 21.7 Methods of Preparation

### 1. Direct Reaction

$$\ce{Mo(PPh3)4 + N2 -> [ambient][Mo(N2)(PPh3)4]}$$

### 2. Reduction of Metal Halides or Carbonyls

- Example:

$$\ce{Fe(CO)5 + O2 -> Fe(CO)4(O2) + CO}$$

### 3. Ligand Substitution

- Oxygen or nitrogen replaces weaker ligand:

$$\ce{[Co(Cl)(en)2]^{2+} + O2 -> [Co(O2)(en)2]^{3+} + Cl^-}$$

## 21.8 Properties

### 1. Physical Properties

- Colored complexes; solubility in **organic solvents**; magnetism depends on spin state.

### 2. Chemical Properties

- $N_2$ complexes: **reduce to $NH_3$**, undergo **ligand substitution**.

- $O_2$ complexes: **release $O_2$**, act as **oxidants**, or form **peroxo species**.

**3. Spectroscopic Properties**

- **IR spectroscopy:**
  - N≡N stretching frequency decreases upon coordination.
  - O–O stretching: superoxo (~1100–1200 $cm^{-1}$), peroxo (~800–900 $cm^{-1}$).
- **UV-Vis:** d–d and charge transfer bands.

**21.9 Applications**

1. **Biological Models:**
   - Hemoglobin, myoglobin ($O_2$), nitrogenase ($N_2$).
2. **Catalysis:**
   - $N_2$ complexes: models for **ammonia synthesis**.
   - $O_2$ complexes: oxidation reactions.
3. **Synthetic Chemistry:**
   - Activation of **inert $N_2$ and $O_2$ molecules** for organometallic reactions.
4. **Industrial Relevance:**
   - Nitrogen fixation; oxidation catalysts.

**Check Your Progress**

1. Give one example each of a **dinitrogen** and a **dioxygen** complex.

_____
_____
_____

2. What is the main difference between **end-on and side-on $O_2$ binding**?

_____
_____
_____

## 21.10 Summary

- Transition metal **dinitrogen and dioxygen complexes** are crucial in **bioinorganic and industrial chemistry**.
- **Dinitrogen complexes:** Linear (end-on) or bridging (side-on), activate N≡N bond.
- **Dioxygen complexes:** End-on (superoxo) or side-on (peroxo), mimic oxygen transport.
- **Bonding:** σ-donation from ligand → metal, π-backbonding from metal → ligand.
- **Preparation:** Direct reaction, reduction, or ligand substitution.
- **Applications:** Biological models, catalysis, nitrogen fixation, synthetic chemistry.

## 21.11 Exercises

### 21.11.1 Multiple Choice Questions

1. In M–$N_2$ complexes, $N_2$ binds:
   a) Terminal
   b) Bridging
   c) Both a & b
   d) Neither
   **Answer:** c

2. O–O stretching frequency for peroxo complexes:
   a) 800–900 $cm^{-1}$
   b) 1100–1200 $cm^{-1}$
   c) 1400–1500 $cm^{-1}$
   d) 600–700 $cm^{-1}$
   **Answer:** a

3. $[Mo(N_2)_2(PPh_3)_4]$ is:
   a) Dioxygen complex
   b) Dinitrogen complex
   c) Nitrosyl complex
   d) Carbonyl complex
   **Answer:** b

4. Metal–$O_2$ complexes in hemoglobin bind $O_2$:
   a) End-on
   b) Side-on
   c) Both
   d) Neither
   **Answer:** a

5. $N_2$ complexes are important in:
   a) Oxygen transport
   b) Nitrogen fixation
   c) Hydroformylation
   d) Hydrogenation
   **Answer:** b

### 21.11.2 Short Answer Questions

1. Define a dinitrogen complex and give an example.
2. Define a dioxygen complex and give an example.
3. Differentiate end-on and side-on binding of $O_2$.
4. State the IR frequency range for coordinated $O_2$.
5. Mention one biological and one industrial application.

### 21.11.3 Long Answer Questions

1. Explain bonding in M–$N_2$ and M–$O_2$ complexes.
2. Discuss preparation methods with chemical equations.
3. Describe physical, chemical, and spectroscopic properties.

## 21.12 References and suggested readings

1. Housecroft, C. E., & Sharpe, A. G. (2012). *Inorganic chemistry* (4th ed.). Pearson Education, Harlow, United Kingdom.
2. Basolo, F., & Pearson, R. G. (1967). *Mechanisms of inorganic reactions* (2nd ed.). Wiley, New York, United States.
3. Rao, C. N. R. (2002). *Chemistry of nanomaterials: Synthesis, properties and applications* (Vol. 1). Wiley-VCH, Weinheim, Germany.

# Glossary

## A

**Activation Energy** – The minimum energy required for a chemical reaction to occur.

**Anation Reaction** – A substitution reaction in which a neutral ligand (like $H_2O$) is replaced by an anionic ligand (such as $Cl^-$ or $NO_3^-$).

**Antiferromagnetism** – A type of magnetic behavior in which adjacent magnetic moments align antiparallel, resulting in zero net magnetization.

**Aqua Complex** – A coordination compound in which water molecules act as ligands to the central metal ion.

## B

**Bonding Molecular Orbital** – A molecular orbital formed by the constructive overlap of atomic orbitals, leading to increased electron density between nuclei.

**Blocking Temperature ($T^B$)** – The temperature below which a single-molecule magnet retains its magnetization.

## C

**Chelate Effect** – The enhanced stability of complexes containing chelating (multidentate) ligands compared to similar complexes with monodentate ligands.

**Charge Transfer Transition** – An electronic transition where an electron moves between a metal and a ligand, leading to intense color.

**Complex Ion** – A charged species consisting of a central metal ion bonded to surrounding ligands.

**Crystal Field Theory (CFT)** – A model describing how the arrangement of ligands around a metal ion affects the energies of the d-orbitals.

**Curie's Law** – A principle stating that the magnetic susceptibility of a paramagnetic substance is inversely proportional to its absolute temperature.

**D**

**d–d Transition** – An electronic transition between different d-orbitals of a transition metal ion under the influence of a ligand field.

**Diamagnetism** – Weak magnetism exhibited by substances with all electrons paired, repelled slightly by magnetic fields.

**Denticity** – The number of donor atoms in a ligand that coordinate directly to the metal ion.

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**E**

**Electronic Spectrum** – The spectrum arising from electronic transitions within a molecule or complex, usually observed in the UV–visible region.

**Exchange Interaction** – Magnetic interaction between unpaired electrons of adjacent metal centers, leading to ferromagnetic or antiferromagnetic coupling.

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**F**

**Ferromagnetism** – Magnetic behavior in which spins align parallel, producing spontaneous magnetization even without an external magnetic field.

**Field Strength (Ligand Field Strength)** – The measure of how strongly a ligand splits the d-orbitals of a central metal ion.

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**G**

**Ground State** – The lowest energy electronic state of an atom or molecule.

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**H**

**High-Spin Complex** – A complex in which ligands cause small splitting of d-orbitals, resulting in maximum unpaired electrons.

**Hybridization** – The combination of atomic orbitals to form new hybrid orbitals used in bonding within a complex.

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**I**

**Inner-Sphere Mechanism** – A redox reaction mechanism involving a bridging ligand through which electron transfer occurs directly between metal centers.

**Isomerism** – The phenomenon where compounds have the same molecular formula but different arrangements of atoms or ligands.

---

**J**

**Jahn–Teller Effect** – The geometric distortion of a non-linear molecule in a degenerate electronic state, which removes the degeneracy and lowers energy.

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**K**

**Kinetic Stability** – The resistance of a complex to ligand substitution, independent of thermodynamic stability.

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**L**

**Ligand** – An ion or molecule that donates one or more pairs of electrons to a metal center to form a coordinate bond.

**Ligand Field Stabilization Energy (LFSE)** – The energy stabilization gained by a metal ion due to the splitting of d-orbitals in the presence of a ligand field.

**Low-Spin Complex** – A complex in which strong-field ligands cause large splitting of d-orbitals, resulting in fewer unpaired electrons.

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**M**

**Magnetic Anisotropy** – The directional dependence of magnetic properties in a material or molecule.

**Magnetic Moment (μ)** – A quantitative measure of the magnetic strength of a complex, typically expressed in Bohr magnetons (B.M.).

**Metal Carbonyl** – A complex containing carbon monoxide (CO) ligands coordinated to a metal center.

**Metal π-Complex** – A coordination compound where ligands such as CO, NO, $N_2$, or $O_2$ form π-type bonds with the metal center.

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**N**

**Nitrosyl Complex** – A metal complex containing nitric oxide (NO) as a ligand, often showing varied bonding modes (linear or bent).

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**O**

**Octahedral Complex** – A coordination compound in which six ligands are symmetrically arranged around a central metal ion.

**Orgel Diagram** – A qualitative energy-level diagram used to explain the electronic transitions of high-spin transition metal ions.

**Outer-Sphere Mechanism** – A redox reaction mechanism where electron transfer occurs without a bridging ligand, through space or solvent.

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**P**

**Paramagnetism** – Magnetic behavior due to the presence of one or more unpaired electrons, attracted to magnetic fields.

**Polynuclear Complex** – A complex containing two or more metal centers bridged by ligands.

**π-Acceptor Ligand** – A ligand capable of accepting electron density from the metal's d-orbitals into its empty π* orbitals (e.g., CO, $CN^-$).

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**R**

**Redox Reaction** – A chemical reaction involving the transfer of electrons between two species, leading to oxidation and reduction.

---

**S**

**Spectrochemical Series** – An empirical list of ligands arranged in order of increasing field strength.

**Spin Crossover** – The reversible interconversion between high-spin and low-spin states of a metal complex due to external stimuli like temperature or light.

**Spin-Orbit Coupling** – The interaction between an electron's spin and its orbital angular momentum, significant in heavy-metal complexes.

**Square Planar Complex** – A coordination compound where four ligands are arranged in a single plane around the metal center.

**Stability Constant (Kf)** – The equilibrium constant for the formation of a coordination complex, indicating its thermodynamic stability.

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**T**

**Tanabe–Sugano Diagram** – A diagram representing the relationship between electronic energy levels and ligand field strength for various electronic configurations.

**Transition Metal** – An element with partially filled d-orbitals capable of forming coordination compounds with variable oxidation states.

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**V**

**Valence Bond Theory (VBT)** – A theory explaining the bonding in coordination compounds in terms of hybridization and overlap of metal and ligand orbitals.

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**Z**

**Zero-Field Splitting** – The separation of electronic spin energy levels in the absence of an external magnetic field, due to internal magnetic interactions.

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