La-Net

CHM424

COORDINATION CHEMISTRY

Course code: CHM 424
Course title: Coordination Chemistry
Course credit load: 2 Units
Series 1: Foundations Of Coordination Chemistry

Series 2: Nomenclature, Isomerism And Stereochemistry Of Complexes

Series 3: Theories Of Bonding And Structural Elucidation

Series 4: Spectral And Magnetic Properties Of Complexes

Series 5: Stability, Reactions And Technological Applications Of Complexes

Proposed Outline Series 1

1.1 Definition And Scope Of Coordination Compounds

- 1.1.1 Meaning of coordination compounds
- 1.1.2 Historical background and significance
- 1.1.3 Scope and applications in chemistry and industry

1.2 Recognition And Applications Of Coordination Compounds

- 1.2.1 Identifying coordination compounds in practice
- 1.2.2 Industrial and biological applications
- 1.2.3 Everyday relevance of coordination chemistry

1.3 Basic Concepts Of Coordination Chemistry

- 1.3.1 Coordination number and ligands
- 1.3.2 Types of ligands and donor atoms
- 1.3.3 General properties of coordination complexes

Introduction

Coordination chemistry is a central branch of inorganic chemistry that explores how metal atoms or ions bind with surrounding molecules or ions called ligands. These compounds are not only fascinating in their structures but also vital in many aspects of life, ranging from biological systems such as haemoglobin to industrial catalysts used in chemical manufacturing.

The aim of this Series is to introduce you to the foundations of coordination chemistry, helping you to define coordination compounds, recognise their applications, and explain the basic concepts that underpin their behaviour.

We shall commence this Series by examining the definition and scope of coordination compounds, including their historical background and significance. Next, we will explore how coordination compounds are recognised and applied in both industrial and biological contexts. Finally, we will conclude with basic concepts such as coordination number, ligands, and the general properties of complexes, thereby equipping you with the essential knowledge needed for deeper study in subsequent Series.

Series Learning Outcomes

Upon completing this Series, you should be able to:

- **SLO 1.1** define coordination compounds and explain their scope in chemistry,
- **SLO 1.2** describe the historical background and significance of coordination chemistry,
- **SLO 1.3** recognise coordination compounds and identify their applications in industry and biology,
- **SLO 1.4** explain the concept of coordination number and classify different types of ligands,
- **SLO 1.5** analyse the general properties of coordination complexes and their everyday relevance.

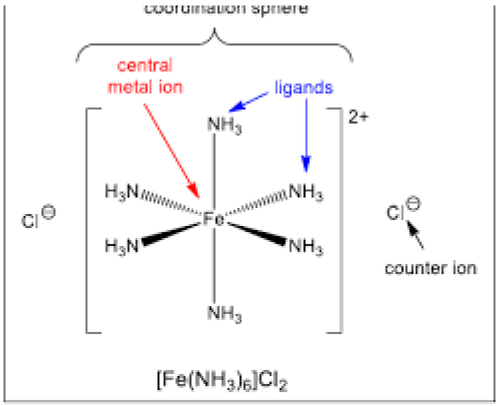
1.1 Definition And Scope Of Coordination Compounds

1.1.1 Meaning of coordination compounds

Coordination compounds are chemical substances in which a central metal atom or ion is bonded to surrounding molecules or ions, known as **ligands**, through coordinate covalent bonds. These compounds are distinct because the metal centre controls the geometry, bonding, and reactivity of the entire complex.

Coordination compounds are important because they explain the behaviour of many biological molecules, industrial catalysts, and coloured compounds.

Fill in the blank: Coordination compounds consist of a central metal atom or ion bonded to surrounding ______.



1.1.2 Historical background and significance

The study of coordination compounds began with **Alfred Werner**, who proposed the coordination theory in the late 19th century. Werner explained the structures of complex compounds and introduced the concept of coordination number, which refers to the number of ligand donor atoms attached to the central metal. His work earned him the Nobel Prize in Chemistry in 1913 and laid the foundation for modern coordination chemistry.

Fill in the blank: Alfred Werner introduced the concept of ______ number in coordination chemistry.

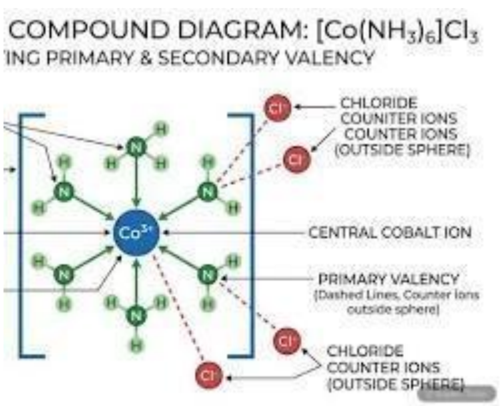


Plate 1.1: Alfred Werner and the coordination theory.

1.1.3 Scope and applications in chemistry and industry

Coordination compounds have wide-ranging applications:

- **Biological systems**: Haemoglobin, chlorophyll, and vitamin B12 are coordination compounds essential for life.
- **Industrial processes**: Complexes are used as catalysts in polymerisation, hydrogenation, and other chemical reactions.
- **Analytical chemistry**: Coordination compounds help in detecting and quantifying metal ions.
- **Medicine**: Complexes such as cisplatin are used in cancer treatment.

Fill in the blank: Haemoglobin, chlorophyll, and vitamin B12 are examples of coordination compounds found in ______ systems.

Coordination compounds play critical roles across various fields due to their unique structural and chemical properties.

Applications of Coordination Compounds

- **Biology:** Essential for life, these compounds form the active sites of many enzymes and proteins. Examples include hemoglobin (iron-porphyrin complex for oxygen transport), chlorophyll (magnesium-porphyrin for photosynthesis), and vitamin B12 (cobalt complex).
- **Medicine:** They are widely used in therapy and diagnostics. Cisplatin is a major chemotherapy agent for treating cancer, while gadolinium complexes are standard contrast agents for MRI scans.
- **Industry:** They act as catalysts for key industrial processes. The Ziegler-Natta catalyst (titanium-aluminum complexes) is fundamental to the production of polyethylene and polypropylene plastics.
- **Analytical Chemistry:** They are utilized for identification and quantification. Chelating agents like EDTA are used in titrations to determine water hardness by sequestering calcium and magnesium ions.

Box 1.1: Applications of coordination compounds.

Pilot questions 1.1

1. Which of the following best defines coordination compounds? a. Compounds with a central metal atom or ion bonded to ligands b. Compounds formed only by ionic bonds c. Compounds formed only by covalent bonds d. Compounds with no metal atoms
2. Fill in the blank: Coordination compounds consist of a central metal atom or ion bonded to surrounding ______.
3. Who introduced the coordination theory in the late 19th century? a. Alfred Werner b. Linus Pauling c. Marie Curie d. Robert Boyle
4. Fill in the blank: Alfred Werner introduced the concept of ______ number in coordination chemistry.
5. Which of the following is an application of coordination compounds? a. Haemoglobin in biological systems b. Catalysts in industrial processes c. Cisplatin in medicine d. All of the above

1.2 Recognition And Applications Of Coordination Compounds

1.2.1 Identifying coordination compounds in practice

To recognise a **coordination compound**, you need to look for a central metal atom or ion surrounded by ligands. These ligands donate electron pairs to the metal, forming coordinate covalent bonds. The compound is usually represented by a **coordination formula**, which shows the metal, ligands, and overall charge.

For example, $[Co(NH_3)_6]^{3+}$ is a coordination compound where cobalt is the central metal ion and six ammonia molecules act as ligands.

Fill in the blank: A coordination formula shows the metal, ligands, and overall ______ of the complex.

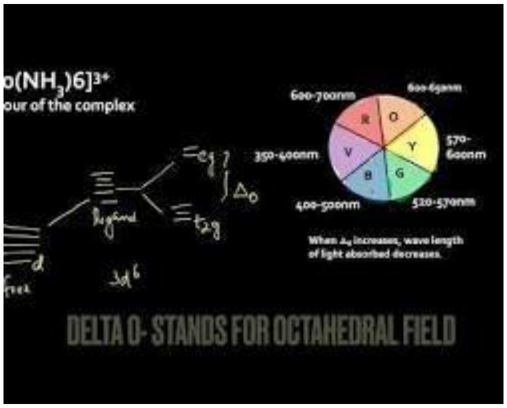


Figure 1.2: Example of a coordination compound.

1.2.2 Industrial and biological applications

Coordination compounds play vital roles in both industry and biology:

- **Industrial applications**: Complexes are used as catalysts in processes such as hydrogenation, polymerisation, and electroplating.
- **Biological applications**: Haemoglobin, which carries oxygen in blood, and chlorophyll, which enables photosynthesis, are coordination compounds.

These examples show how coordination chemistry bridges laboratory science with real-world processes.

Fill in the blank: Haemoglobin and chlorophyll are examples of coordination compounds found in ______ systems.

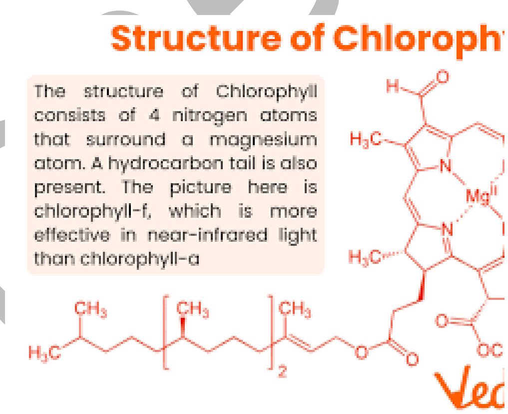


Plate 1.2: Biological coordination compounds.

1.2.3 Everyday relevance of coordination chemistry

Beyond industry and biology, coordination compounds are part of everyday life. They are responsible for the colours of many dyes and pigments, the effectiveness of medicines such as cisplatin in cancer treatment, and the removal of toxic metals from the environment through chelation therapy.

Fill in the blank: Cisplatin is a coordination compound widely used in the treatment of ______.

Field	Application	Example / Mechanism
Dyes & Pigments	Coloration	Phthalocyanine complexes are used to produce intense blue and green colors in paints, inks, and plastics.
Medicines	Therapeutic Agents	Cisplatin and carboplatin are platinum-based complexes used to inhibit DNA replication in cancer cells.
Environmental	Water Treatment	Chelating agents are used to soften water by sequestering heavy metal ions, and some complexes help remove pollutants from industrial effluent.

Box 1.2: Everyday relevance of coordination compounds.

Pilot questions 1.2

1. Which of the following best defines a coordination formula? a. A representation showing the metal, ligands, and overall charge b. A formula showing only ionic bonds c. A formula showing only covalent bonds d. A formula with no ligands
2. Fill in the blank: A coordination formula shows the metal, ligands, and overall ______ of the complex.
3. Which of the following is an industrial application of coordination compounds? a. Hydrogenation catalysts b. Polymerisation catalysts c. Electroplating d. All of the above
4. Fill in the blank: Haemoglobin and chlorophyll are examples of coordination compounds found in ______ systems.
5. Which of the following is an everyday relevance of coordination compounds? a. Colours of dyes and pigments b. Medicines such as cisplatin c. Environmental chelation therapy d. All of the above

Series Summary

In this Series, we explored the **foundations of coordination chemistry**, beginning with the definition and scope of coordination compounds. We examined their historical background, particularly the contributions of Alfred Werner, and highlighted their wide-ranging applications in biology, industry, medicine, and everyday life. We then studied how coordination compounds are recognised and represented through coordination formulas, before considering their industrial and biological importance. Finally, we introduced basic concepts such as coordination number, ligands, and the general properties of complexes, including colour, magnetism, reactivity, and stability. Altogether, this Series has provided learners with the essential groundwork for understanding coordination chemistry and prepared them for more advanced topics in subsequent Series.

Glossary of Terms

- **Coordination compound**: A chemical substance consisting of a central metal atom or ion bonded to surrounding ligands.
- **Ligand**: An ion or molecule that donates an electron pair to a central metal atom or ion.
- **Coordination formula**: A representation showing the metal, ligands, and overall charge of a complex.
- **Coordination number**: The number of ligand donor atoms directly bonded to the central metal atom or ion.
- **Monodentate ligand**: A ligand with a single donor atom.
- **Bidentate ligand**: A ligand with two donor atoms.
- **Polydentate ligand**: A ligand with multiple donor atoms.
- **Donor atom**: The atom within a ligand that donates an electron pair to the metal.
- **Complex geometry**: The spatial arrangement of ligands around the central metal ion, such as octahedral or tetrahedral.

Concept Check Questions 1

Objective questions

1. Coordination compounds consist of a central metal atom or ion bonded to surrounding ______. (Linked to SLO 1.1)
2. Alfred Werner introduced the concept of ______ number in coordination chemistry. (Linked to SLO 1.2)
3. A coordination formula shows the metal, ligands, and overall ______ of the complex. (Linked to SLO 1.3)
4. Ethylenediamine (en) is an example of a ______ ligand. (Linked to SLO 1.4)
5. The vivid colours of many coordination complexes are due to electronic transitions within the ______ orbitals of the metal. (Linked to SLO 1.5)

Short-answer questions

6. Define coordination compounds and explain their scope in chemistry. (Linked to SLO 1.1)

7. Describe Alfred Werner's contribution to coordination chemistry. (Linked to SLO 1.2)

8. Explain how coordination compounds are recognised in practice. (Linked to SLO 1.3)

9. Classify ligands into monodentate, bidentate, and polydentate with examples. (Linked to SLO 1.4)

Long-answer questions

10. Analyse the applications of coordination compounds in biology, industry, medicine, and everyday life. (Linked to SLO 1.3, 1.5)

11. Discuss the general properties of coordination complexes, including colour, magnetism, reactivity, and stability. (Linked to SLO 1.5)

12. Evaluate the importance of coordination number and ligand type in determining the geometry and properties of complexes. (Linked to SLO 1.4, 1.5)

Answers To Pilot Questions 1

Part 1.1: 1.a, 2.ligands, 3.a, 4.coordination, 5.d **Part 1.2**: 1.a, 2.charge, 3.d, 4.biological, 5.d **Part 1.3**: 1.a, 2.ligand, 3.a, 4.bidentate, 5.d

References And Attributions 1

- Figures 1.1–1.3: Suggested AI prompts for diagrams showing coordination compound structures, octahedral complexes, and coordination formulas.
- Plates 1.1–1.3: Suggested AI prompts for images of Alfred Werner, haemoglobin and chlorophyll, and ligand types.
- Boxes 1.1–1.3: Suggested AI prompts for tables summarising applications, everyday relevance, and properties of coordination compounds.
- Open Educational Resources (OER) suggested search strings:
  - "OER diagram coordination compound chemistry"
  - "OER image Alfred Werner coordination theory"
  - "OER image haemoglobin chlorophyll coordination chemistry"
  - "OER image types of ligands chemistry"
  - "OER table coordination compound applications chemistry"
  - "OER table coordination compounds everyday uses chemistry"
  - "OER table properties of coordination complexes chemistry"

- Attribution style: APA (institutional standard assumed). Example: OpenStax. (2016). *Chemistry*. OpenStax CNX. Retrieved from https://openstax.org/books/chemistry

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Proposed Outline Series 2

2.1 Nomenclature Of Coordination Compounds

- 2.1.1 Rules of IUPAC nomenclature
- 2.1.2 Naming ligands and metals
- 2.1.3 Examples of coordination compound names

2.2 Isomerism In Coordination Compounds

- 2.2.1 Structural isomerism (linkage, ionisation, hydration)
- 2.2.2 Stereoisomerism (geometrical and optical)
- 2.2.3 Examples and significance of isomerism

2.3 Stereochemistry Of Complex Molecules

- 2.3.1 Coordination number and geometry
- 2.3.2 Common geometrical arrangements (octahedral, tetrahedral, square planar)
- 2.3.3 Stereochemical implications in reactivity and properties

Introduction

In the last Series, we explored the foundations of coordination chemistry, focusing on definitions, scope, applications, and basic concepts such as coordination number and ligands.

Building on that knowledge, we now turn to the language and structural features that allow chemists to describe and classify coordination compounds with precision.

The aim of this Series is to equip you with the ability to name coordination compounds correctly, identify different types of isomerism, and explain the stereochemistry of complex molecules.

We shall commence this Series by examining the nomenclature of coordination compounds, including the rules of IUPAC naming and examples of ligands and metals. Next, we will explore isomerism, considering both structural and stereoisomerism with practical examples. Finally, we will conclude with stereochemistry, focusing on coordination numbers, geometrical arrangements, and the implications of stereochemistry for the properties and reactivity of complexes.

Series Learning Outcomes

Upon completing this Series, you should be able to:

- **SLO 2.1** define and apply the rules of IUPAC nomenclature for coordination compounds,
- **SLO 2.2** identify and name ligands and central metal atoms in coordination formulas,
- **SLO 2.3** demonstrate how to write correct names for given coordination compounds,
- **SLO 2.4** explain structural isomerism in coordination compounds,
- **SLO 2.5** describe stereoisomerism, including geometrical and optical forms,
- **SLO 2.6** analyse examples of isomerism and evaluate their significance,
- **SLO 2.7** explain the relationship between coordination number and molecular geometry,
- **SLO 2.8** describe common geometrical arrangements such as octahedral, tetrahedral, and square planar,
- **SLO 2.9** evaluate the stereochemical implications of complex molecules in terms of reactivity and properties.

2.1 Nomenclature Of Coordination Compounds

2.1.1 Rules of IUPAC nomenclature

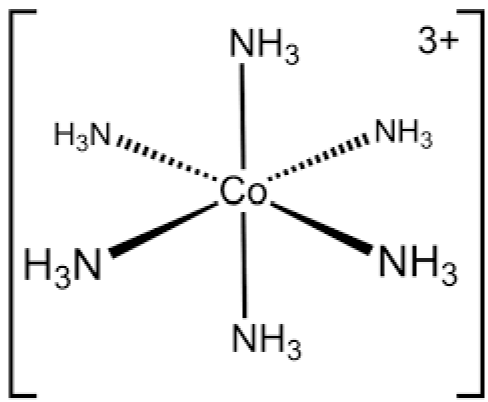
Nomenclature refers to the system of naming chemical compounds according to established rules. For coordination compounds, the International Union of Pure and Applied Chemistry (IUPAC) provides guidelines to ensure clarity and uniformity.

The basic rules include:

- Naming ligands first, followed by the central metal atom or ion.
- Indicating the number of ligands using prefixes such as mono-, di-, tri-, etc.
- Using oxidation state of the metal in Roman numerals within parentheses.
- For anionic complexes, the metal name ends with the suffix "-ate".

For example, $[Co(NH_3)_6]Cl_3$ is named **hexaamminecobalt(III) chloride**.

Fill in the blank: In coordination compound nomenclature, the oxidation state of the metal is indicated using ______ numerals.



2.1.2 Naming ligands and metals

Ligands are named according to specific rules:

- Neutral ligands are usually named as the molecule (e.g., NH_3 as ammine, H_2O as aqua).
- Anionic ligands end with "-o" (e.g., Cl^- as chloro, CN^- as cyano).
- Complex ligands may have special names (e.g., ethylenediamine as en).

Metals are named according to their element, with oxidation state indicated. For anionic complexes, the metal name is modified (e.g., ferrate for Fe, cuprate for Cu).

Fill in the blank: In anionic complexes, the name of the metal ends with the suffix ______.

	bromo or bromido*
	iodo or iodido*
	cyanido or cyanido-C* (C-bonded)
	isocyanido or cyanido-N* (N-bonded)
o	thiocyanato-S(S-bonded)
ano	thiocyanato-N(N-bonded)
(cyanate)	cyanato-O (O-bonded)
to (isocyanate)	cyanato-N (N-bonded)
	hydroxo or hydroxido*
	nitrito–N (N–bonded)
	nitrito–O (O–bonded)
	nitrato

Plate 2.1: Naming ligands and metals in coordination compounds.

2.1.3 Examples of coordination compound names

Applying the rules, here are some examples:

- $[Pt(NH_3)_2Cl_2]$ is **diammine dichloroplatinum(II)**.
- $[Fe(CN)_6]^{3-}$ is **hexacyanoferrate(III)**.
- $[Cu(H_2O)_4]^{2+}$ is **tetraaquacopper(II)**.

These examples show how systematic naming ensures that chemists can easily identify the composition and structure of complexes.

Fill in the blank: $[Fe(CN)_6]^{3-}$ is named hexacyano______ (III).

Formula	Systematic Name
$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$[Cu(H_2O)_4]SO_4$	Tetraaquacopper(II) sulfate
$Na[Al(OH)_4]$	Sodium tetrahydroxoaluminate(III)

Box 2.1: Examples of coordination compound names.

Pilot questions 2.1

1. Which of the following is the correct order in naming coordination compounds? a. Metal first, then ligands b. Ligands first, then metal c. Charge first, then ligands d. Oxidation state first, then ligands
2. Fill in the blank: In coordination compound nomenclature, the oxidation state of the metal is indicated using _______ numerals.
3. Which of the following is the correct name for $[Co(NH_3)_6]Cl_3$? a. Hexaamminecobalt(III) chloride b. Cobalt hexaammine chloride c. Tricobalt hexachloride d. Hexaamminecobalt chloride

4. Fill in the blank: In anionic complexes, the name of the metal ends with the suffix ______.
5. Which of the following is the correct name for $[Pt(NH_3)_2Cl_2]$? a. Dichlorodiammineplatinum(II) b. Diammine dichloroplatinum(II) c. Platinum dichloride ammine complex d. Tetrachloroplatinum(II)

2.2 Isomerism In Coordination Compounds

2.2.1 Structural isomerism

Structural isomerism occurs when coordination compounds have the same chemical formula but differ in the way atoms or groups are connected. Types include:

- **Linkage isomerism**: Occurs when a ligand can coordinate through different donor atoms, e.g., NO_2^- bonding through nitrogen (nitro) or oxygen (nitrito).
- **Ionisation isomerism**: Arises when ligands inside and outside the coordination sphere exchange places, e.g., $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$.
- **Hydration isomerism**: Involves water molecules either inside or outside the coordination sphere, e.g., $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ and $[Cr(H_2O)_6]Cl_3$.

Fill in the blank: Linkage isomerism occurs when a ligand can coordinate through different ______ atoms.

Feature	Nitro Isomer	Nitrito Isomer
Donor Atom	Nitrogen ($\ce{N}$)	Oxygen ($\ce{O}$)
Bonding	$\ce{Metal-N}$	$\ce{Metal-O-N=O}$
Properties	Generally more stable	Typically less stable; can convert to nitro

2.2.2 Stereoisomerism

Stereoisomerism occurs when compounds have the same connectivity but differ in spatial arrangement. Types include:

- **Geometrical isomerism**: Found in square planar and octahedral complexes, e.g., cis-$[Pt(NH_3)_2Cl_2]$ and trans-$[Pt(NH_3)_2Cl_2]$.
- **Optical isomerism**: Occurs when complexes are non-superimposable mirror images, known as enantiomers. These are important in biological systems and pharmaceuticals.

Fill in the blank: Cis-$[Pt(NH_3)_2Cl_2]$ and trans-$[Pt(NH_3)_2Cl_2]$ are examples of ______ isomerism.

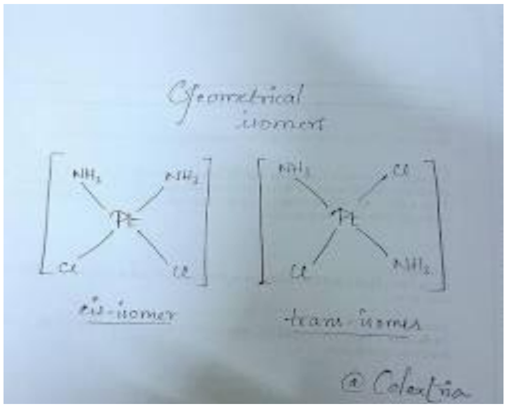


Plate 2.2: Geometrical isomerism in square planar complexes.

2.2.3 Examples and significance of isomerism

Isomerism is significant because different isomers can have distinct physical, chemical, and biological properties. For example:

- Cisplatin (cis-$[Pt(NH_3)_2Cl_2]$) is an effective anti-cancer drug, while its trans-isomer is inactive.
- Optical isomers of coordination compounds may interact differently with biological molecules, leading to varied effects.

Fill in the blank: Cisplatin is an effective anti-cancer drug, while its ______ isomer is inactive.

Isomer Type	Example	Significance
Structural (Linkage)	$[Co(NH_3)_5(NO_2)]Cl_2$ vs $[Co(NH_3)_5(ONO)]Cl_2$	Demonstrates how the same ligand can bind through different atoms (N vs O), altering chemical stability.
Structural (Ionization)	$[Co(NH_3)_5Br]SO_4$ vs $[Co(NH_3)_5SO_4]Br$	Leads to different ions in solution, resulting in different precipitation reactions.
Stereo (Geometric)	*cis*- vs *trans*-$[Pt(NH_3)_2Cl_2]$	*cis*-isomer (Cisplatin) acts as a potent anticancer agent; *trans*-isomer is clinically inactive.
Stereo (Optical)	$[Co(en)_3]^{3+}$ enantiomers	Mirror-image forms interact differently with chiral environments, crucial in stereospecific catalysis.

Box 2.2: Significance of isomerism in coordination compounds.

Pilot questions 2.2

1. Which of the following best defines structural isomerism? a. Compounds with the same formula but different connectivity b. Compounds with the same connectivity but different spatial arrangement c. Compounds with different oxidation states d. Compounds with different charges
2. Fill in the blank: Linkage isomerism occurs when a ligand can coordinate through different ______ atoms.
3. Which of the following is an example of geometrical isomerism? a. Cis-$[Pt(NH_3)_2Cl_2]$ and trans-$[Pt(NH_3)_2Cl_2]$ b. $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ c. $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$ and $[Cr(H_2O)_6]Cl_3$ d. All of the above
4. Fill in the blank: Cis-$[Pt(NH_3)_2Cl_2]$ and trans-$[Pt(NH_3)_2Cl_2]$ are examples of ______ isomerism.
5. Which of the following statements is true about cisplatin? a. Cisplatin is inactive as a drug b. Transplatin is effective as a drug c. Cisplatin is effective as an anti-cancer drug d. Both cisplatin and transplatin are equally effective

2.3 Stereochemistry Of Complex Molecules

2.3.1 Coordination number and geometry

Coordination number is the number of ligand donor atoms directly bonded to the central metal ion. It plays a crucial role in determining the **geometry** of the complex. For example:

- Coordination number 4 may lead to tetrahedral or square planar geometry.
- Coordination number 6 typically results in octahedral geometry.

The geometry influences the physical and chemical properties of the complex, including colour, magnetism, and reactivity.

Fill in the blank: A coordination number of 6 usually results in ______ geometry.

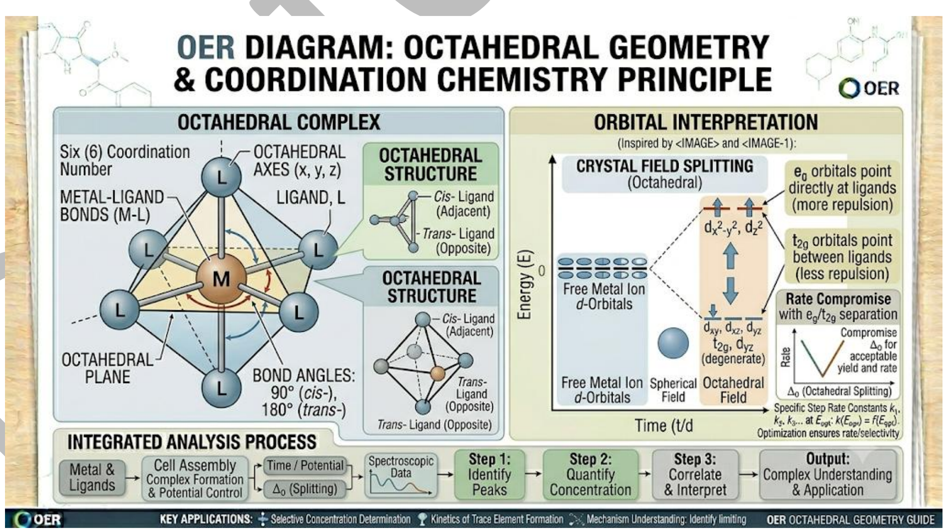


Figure 2.3: Octahedral geometry in coordination complexes.

2.3.2 Common geometrical arrangements

Coordination complexes exhibit several common geometrical arrangements:

- **Octahedral**: Six ligands arranged symmetrically around the central metal ion.
- **Tetrahedral**: Four ligands arranged around the central metal ion in a three-dimensional shape.
- **Square planar**: Four ligands arranged in a plane around the central metal ion, common for d^8 metal ions such as Pt(II).

These arrangements are determined by the electronic configuration of the metal and the nature of the ligands.

Fill in the blank: Square planar geometry is common for metal ions with a ______ electronic configuration.

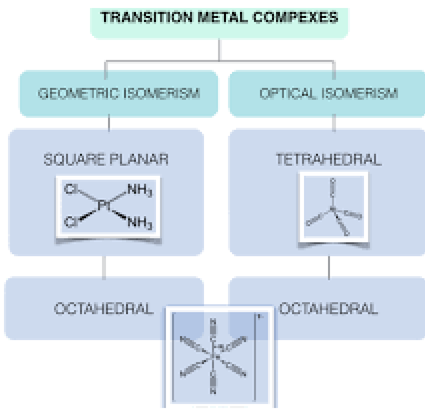


Plate 2.3: Common geometrical arrangements in coordination complexes.

2.3.3 Stereochemical implications in reactivity and properties

The stereochemistry of complexes has significant implications:

- **Reactivity**: Geometrical arrangement affects how ligands are substituted in reactions.
- **Optical activity**: Certain geometries lead to optical isomers that interact differently with biological systems.
- **Magnetic properties**: Geometry influences electron distribution and magnetic behaviour.
- **Biological activity**: The stereochemistry of complexes such as cisplatin determines their effectiveness in medicine.

Fill in the blank: The stereochemistry of cisplatin determines its effectiveness as an ______ drug.

Property	Influence of Stereochemistry	Example/Context
Reactivity	Geometry determines the availability of coordination sites for incoming substrates.	*cis*-Isomers often react differently than *trans*-isomers due to steric hindrance and electronic effects.
Optical Activity	Chiral geometries (lack of internal symmetry) allow interaction with plane-polarized light.	Enantiomers (e.g., $[Co(en)_3]^{3+}$) rotate light in opposite directions; crucial for asymmetric catalysis.
Magnetic Properties	Ligand spatial arrangement affects d-orbital splitting (Δ), dictating electron spin state.	High-spin vs. low-spin states are influenced by the strength and geometry of the ligand field.
Biological Activity	Molecular shape determines "lock-and-key" fit into biological receptors or DNA.	*cis*-Platin binds effectively to DNA to inhibit replication; its *trans* counterpart is less effective.

Box 2.3: Stereochemical implications of coordination complexes.

Pilot questions 2.3

1. Which of the following best defines coordination number? a. Number of ligand donor atoms directly bonded to the central metal ion b. Number of protons in the nucleus c. Number of electrons in the outer shell d. Number of bonds in a molecule
2. Fill in the blank: A coordination number of 6 usually results in ______ geometry.
3. Which of the following geometrical arrangements is common for d^8 metal ions such as Pt(II)? a. Octahedral b. Tetrahedral c. Square planar d. Linear
4. Fill in the blank: Square planar geometry is common for metal ions with a ______ electronic configuration.
5. Which of the following is an implication of stereochemistry in coordination complexes? a. Reactivity in substitution reactions b. Optical activity c. Magnetic properties d. All of the above

Series Summary

In this Series, we examined the **nomenclature, isomerism, and stereochemistry of coordination complexes**. We began with the rules of IUPAC nomenclature, learning how to name ligands, metals, and entire complexes systematically. We then explored isomerism, distinguishing between structural types such as linkage, ionisation, and hydration, and stereoisomerism including geometrical and optical forms. Finally, we studied stereochemistry, focusing on coordination numbers, common geometrical arrangements, and the implications of stereochemistry for reactivity, magnetism, and biological activity. Altogether, this Series has provided learners with the essential language and structural understanding needed to describe and classify coordination compounds accurately.

Glossary of Terms

- **Nomenclature**: The systematic naming of chemical compounds according to established rules.
- **Ligand**: An ion or molecule that donates an electron pair to a central metal atom or ion.
- **Oxidation state**: The charge on the central metal ion, indicated in Roman numerals.
- **Structural isomerism**: Isomerism arising from differences in connectivity of atoms or groups.
- **Linkage isomerism**: Isomerism where a ligand coordinates through different donor atoms.
- **Ionisation isomerism**: Isomerism involving exchange of ligands inside and outside the coordination sphere.
- **Hydration isomerism**: Isomerism involving water molecules inside or outside the coordination sphere.
- **Stereoisomerism**: Isomerism arising from differences in spatial arrangement of ligands.
- **Geometrical isomerism**: Isomerism involving cis and trans arrangements of ligands.
- **Optical isomerism**: Isomerism involving non-superimposable mirror images (enantiomers).
- **Coordination number**: The number of ligand donor atoms directly bonded to the central metal ion.
- **Geometry**: The spatial arrangement of ligands around the central metal ion, e.g., octahedral, tetrahedral, square planar.

Concept Check Questions 2

Objective questions

1. In coordination compound nomenclature, the oxidation state of the metal is indicated using ______ numerals. (Linked to SLO 2.1)
2. In anionic complexes, the name of the metal ends with the suffix ______. (Linked to SLO 2.2)
3. Cis-[$Pt(NH_3)_2Cl_2$] and trans-[$Pt(NH_3)_2Cl_2$] are examples of ______ isomerism. (Linked to SLO 2.5)
4. A coordination number of 6 usually results in ______ geometry. (Linked to SLO 2.7)
5. Square planar geometry is common for metal ions with a ______ electronic configuration. (Linked to SLO 2.8)

Short-answer questions

6. Define nomenclature and explain its importance in coordination chemistry. (Linked to SLO 2.1)
7. Describe the rules for naming ligands and metals in coordination compounds. (Linked to SLO 2.2)
8. Explain structural isomerism with examples. (Linked to SLO 2.4)
9. Describe stereoisomerism and give an example of geometrical isomerism. (Linked to SLO 2.5)

Long-answer questions

10. Analyse the significance of isomerism in coordination compounds, with reference to cisplatin and its trans-isomer. (Linked to SLO 2.6)
11. Discuss the relationship between coordination number and geometry, giving examples of octahedral, tetrahedral, and square planar complexes. (Linked to SLO 2.7, 2.8)
12. Evaluate the stereochemical implications of coordination complexes in terms of reactivity, optical activity, magnetic properties, and biological activity. (Linked to SLO 2.9)

Answers To Pilot Questions 2

Part 2.1: 1.b, 2.Roman, 3.a, 4.-ate, 5.b **Part 2.2**: 1.a, 2.donor, 3.a, 4.geometrical, 5.c **Part 2.3**: 1.a, 2.octahedral, 3.c, 4.d^8, 5.d

References And Attributions 2

- Figures 2.1–2.3: Suggested AI prompts for diagrams showing nomenclature examples, linkage isomerism, and octahedral geometry.
- Plates 2.1–2.3: Suggested AI prompts for images of ligand naming, cis/trans geometrical isomers, and common geometrical arrangements.
- Boxes 2.1–2.3: Suggested AI prompts for tables summarising examples of compound names, significance of isomerism, and stereochemical implications.
- Open Educational Resources (OER) suggested search strings:
    - "OER diagram IUPAC nomenclature coordination compounds chemistry"
    - "OER image ligand and metal naming chemistry"
    - "OER diagram linkage isomerism coordination chemistry"
    - "OER image geometrical isomerism coordination chemistry"
    - "OER image geometrical arrangements coordination chemistry"
    - "OER table examples coordination compound names chemistry"
    - "OER table isomerism coordination compounds chemistry"
    - "OER table stereochemical implications coordination chemistry"
- Attribution style: APA (institutional standard assumed). Example: OpenStax. (2016). *Chemistry*. OpenStax CNX. Retrieved from https://openstax.org/books/chemistry

Course credit load: 2 Units
Series 1: Foundations Of Coordination Chemistry

Series 2: Nomenclature, Isomerism And Stereochemistry Of Complexes

Series 3: Theories Of Bonding And Structural Elucidation

Series 4: Spectral And Magnetic Properties Of Complexes

Series 5: Stability, Reactions And Technological Applications Of Complexes

Proposed Outline Series 3

3.1 Werner's Theory Of Coordination Compounds

- 3.1.1 Historical background and principles
- 3.1.2 Strengths and limitations

3.2 Valence Bond Theory (VBT)

- 3.2.1 Basic principles of VBT
- 3.2.2 Applications to coordination complexes
- 3.2.3 Limitations of VBT

3.3 Crystal Field And Ligand Field Theories

- 3.3.1 Crystal field splitting in octahedral and tetrahedral complexes
- 3.3.2 Ligand field theory as an extension of CFT
- 3.3.3 Advantages and limitations

3.4 Physicochemical Methods Of Structural Elucidation

- 3.4.1 Spectroscopic methods (UV-Vis, IR, NMR)
- 3.4.2 Magnetic measurements
- 3.4.3 X-ray crystallography

Introduction

In the last Series, we studied how coordination compounds are named, classified, and described through isomerism and stereochemistry. To deepen our understanding, we now turn to the theories that explain how these compounds form, bond, and acquire their unique properties.

The aim of this Series is to introduce you to the major bonding theories in coordination chemistry and to show how physicochemical methods are used to elucidate the structures of complexes.

We shall commence this Series by examining Werner's theory, which laid the foundation for coordination chemistry. Next, we will explore valence bond theory and its applications to complexes. Following that, we will consider crystal field and ligand field theories, which explain electronic structures and properties. Finally, we will conclude with physicochemical methods such as spectroscopy, magnetism, and X-ray crystallography, which provide experimental evidence for the structures of coordination compounds.

Series Learning Outcomes

Upon completing this Series, you should be able to:

- **SLO 3.1** explain the principles of Werner's theory of coordination compounds,
- **SLO 3.2** evaluate the strengths and limitations of Werner's theory,
- **SLO 3.3** describe the basic principles of valence bond theory,
- **SLO 3.4** apply valence bond theory to explain bonding in coordination complexes,
- **SLO 3.5** analyse the limitations of valence bond theory,
- **SLO 3.6** explain crystal field splitting in octahedral and tetrahedral complexes,
- **SLO 3.7** describe ligand field theory and its relationship to crystal field theory,
- **SLO 3.8** evaluate the advantages and limitations of crystal field and ligand field theories,
- **SLO 3.9** demonstrate how spectroscopic methods are used in structural elucidation of complexes,
- **SLO 3.10** interpret magnetic measurements in relation to bonding and structure,
- **SLO 3.11** explain the role of X-ray crystallography in determining the structures of coordination compounds.

3.1 Werner's Theory Of Coordination Compounds

3.1.1 Historical background and principles

Werner's theory was proposed by Alfred Werner in 1893 to explain the structures of coordination compounds. Before Werner, chemists struggled to understand why certain compounds, such as $CoCl_3 \cdot 6NH_3$, exhibited unusual properties. Werner suggested that metals in complexes have two types of valencies:

- **Primary valency**: Corresponds to the oxidation state of the metal and is satisfied by anions.
- **Secondary valency**: Refers to the coordination number, satisfied by ligands directly bonded to the metal.

This theory explained why compounds such as $[Co(NH_3)_6]Cl_3$ exist, where cobalt has a primary valency of +3 and a secondary valency of 6.

Fill in the blank: According to Werner, the primary valency corresponds to the ______ state of the metal.

Feature	Primary Valency	Secondary Valency
Nature	Ionizable	Non-ionizable
Satisfied by	Anions (negative ions)	Ligands (neutral/charged)
Relates to	Oxidation State	Coordination Number
Spatial Arrangement	Non-directional	Fixed geometry (e.g., octahedral)

Figure 3.1: Primary and secondary valencies in Werner's theory.

3.1.2 Strengths and limitations

Werner's theory was revolutionary because it explained the geometry and bonding of complexes at a time when atomic theory was still developing. Its strengths include:

- Providing a clear distinction between oxidation state and coordination number.
- Explaining the existence of isomers in coordination compounds.
- Laying the foundation for modern bonding theories.

However, Werner's theory also had limitations:

- It did not explain the nature of bonding between metals and ligands.
- It could not account for electronic structures or magnetic properties.
- Later theories such as valence bond theory and crystal field theory were needed to provide deeper insights.

Fill in the blank: One limitation of Werner's theory is that it did not explain the ______ structure of complexes.

Category	Strengths	Limitations
Bonding	Correctly identified that metal ions have two distinct types of bonding.	Could not explain the nature of the chemical bond (covalent vs. ionic).

Category	Strengths	Limitations
Geometry	Successfully predicted the existence of definite spatial arrangements (e.g., octahedral, square planar).	Could not account for the specific geometry or bond angles of various complexes.
Isomerism	Explained the existence of linkage and geometrical isomers.	Could not explain the relative stability of different isomers.
Magnetism	—	Failed to explain the magnetic properties (paramagnetism vs. diamagnetism).
Electronic Structure	—	Could not explain why coordination compounds exhibit characteristic colors or electronic spectra.

Box 3.1: Strengths and limitations of Werner's theory.

Pilot questions 3.1

1. Who proposed the theory of coordination compounds in 1893? a. Alfred Werner b. Linus Pauling c. Marie Curie d. Robert Boyle
2. Fill in the blank: According to Werner, the primary valency corresponds to the ______ state of the metal.
3. Which of the following best defines secondary valency? a. The oxidation state of the metal b. The coordination number satisfied by ligands c. The number of protons in the nucleus d. The charge of the complex
4. Fill in the blank: One limitation of Werner's theory is that it did not explain the ______ structure of complexes.
5. Which of the following is a strength of Werner's theory? a. Explaining isomerism in complexes b. Distinguishing oxidation state and coordination number c. Laying the foundation for modern bonding theories d. All of the above

3.2 Valence Bond Theory (VBT)

3.2.1 Basic principles of VBT

Valence Bond Theory (VBT) explains bonding in coordination compounds by considering the hybridisation of the central metal atom's orbitals. According to VBT, the metal ion provides vacant orbitals which hybridise to accommodate electron pairs donated by ligands. The resulting hybrid orbitals determine the geometry of the complex.

For example, in an octahedral complex such as $[Co(NH_3)_6]^{3+}$, the metal ion undergoes **d^2sp^3 hybridisation**, producing six equivalent orbitals that bond with six ligands.

Fill in the blank: In an octahedral complex such as $[Co(NH_3)_6]^{3+}$, the metal ion undergoes ______ hybridisation.

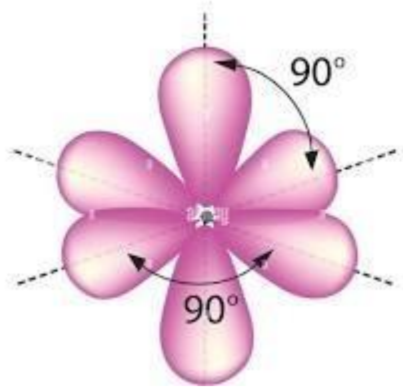


Figure 3.2: Hybridisation in Valence Bond Theory.

3.2.2 Applications to coordination complexes

VBT helps explain:

- **Geometry**: Predicts whether complexes are tetrahedral, square planar, or octahedral.
- **Magnetic properties**: Accounts for whether complexes are paramagnetic (unpaired electrons) or diamagnetic (all electrons paired).
- **Bonding**: Shows how ligands donate electron pairs to the central metal ion.

For instance, $[Ni(CN)_4]^{2-}$ is square planar due to dsp^2 hybridisation, while $[NiCl_4]^{2-}$ is tetrahedral due to sp^3 hybridisation.

Fill in the blank: $[Ni(CN)_4]^{2-}$ is square planar due to ______ hybridisation.

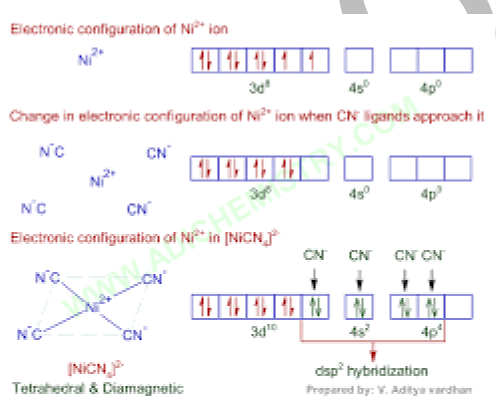


Plate 3.2: Geometrical predictions using VBT.

3.2.3 Limitations of VBT

Although VBT was a major advancement, it has limitations:

- It does not explain the colour of complexes.

- It cannot account for the quantitative values of magnetic moments.
- It does not consider the splitting of d-orbitals by ligands, which is explained by crystal field theory.

Thus, while VBT provides a useful starting point, more advanced theories are required for a complete understanding of coordination chemistry.

Fill in the blank: One limitation of VBT is that it does not explain the ______ of complexes.

Limitation	Description
Color Explanation	VBT cannot explain why most coordination compounds are brightly colored due to electronic transitions.
Magnetic Moments	While it predicts the *number* of unpaired electrons, it cannot provide precise values for magnetic moments or explain temperature-dependent magnetic behavior.
d-Orbital Splitting	It assumes the metal orbitals are equivalent until hybridization occurs; it fails to account for the energy separation (splitting) of d-orbitals caused by ligands.
Thermodynamic Stability	VBT does not explain the relative thermodynamic stabilities of different complexes or the kinetic factors influencing reaction rates.
Quantitative Data	It is largely a qualitative theory and cannot predict accurate bond energies or metal-ligand bond distances.
Spectra	It fails to provide information regarding the electronic absorption spectra of complex ions.

Box 3.2: Limitations of Valence Bond Theory.

Pilot questions 3.2

1. Which of the following best defines Valence Bond Theory? a. A theory explaining bonding through hybridisation of metal orbitals b. A theory explaining bonding through d-orbital splitting c. A theory explaining bonding through electrostatic attraction only d. A theory explaining bonding through resonance structures
2. Fill in the blank: In an octahedral complex such as $[Co(NH_3)_6]^{3+}$, the metal ion undergoes ______ hybridisation.
3. Which of the following complexes is square planar due to dsp^2 hybridisation? a. $[Ni(CN)_4]^{2-}$ b. $[NiCl_4]^{2-}$ c. $[Co(NH_3)_6]^{3+}$ d. $[Fe(H_2O)_6]^{2+}$
4. Fill in the blank: $[Ni(CN)_4]^{2-}$ is square planar due to ______ hybridisation.
5. Which of the following is a limitation of VBT? a. It does not explain colour of complexes b. It does not account for magnetic moments c. It does not consider d-orbital splitting d. All of the above

3.3 Crystal Field And Ligand Field Theories

3.3.1 Crystal field splitting in octahedral and tetrahedral complexes

Crystal Field Theory (CFT) explains the bonding in coordination compounds by considering the electrostatic interactions between the central metal ion and surrounding ligands. Ligands are treated as point charges or dipoles that affect the energy of the metal's d-orbitals.

In an **octahedral complex**, the five d-orbitals split into two sets:

- **t_2g orbitals** (dxy, dxz, dyz) with lower energy.
- **eg orbitals** (dz^2, $dx^2–y^2$) with higher energy.

In a **tetrahedral complex**, the splitting is reversed, with the eg orbitals lower in energy and the t_2g orbitals higher.

Fill in the blank: In an octahedral complex, the d-orbitals split into ______ and eg sets.

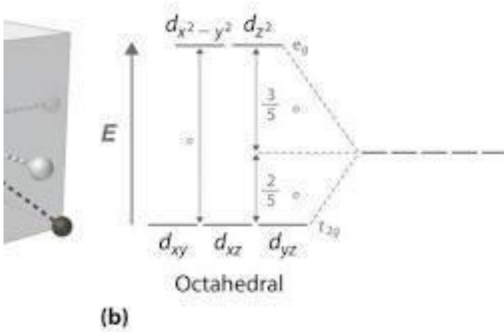


Figure 3.3: Crystal field splitting patterns.

3.3.2 Ligand field theory as an extension of CFT

Ligand Field Theory (LFT) combines aspects of crystal field theory and molecular orbital theory. Unlike CFT, which treats ligands as point charges, LFT considers the overlap of ligand orbitals with metal orbitals. This provides a more realistic description of bonding and explains properties such as:

- Covalent character in metal-ligand bonds.
- Electronic spectra of complexes.
- Magnetic behaviour more accurately than CFT alone.

Fill in the blank: Ligand Field Theory combines Crystal Field Theory with ______ Orbital Theory.

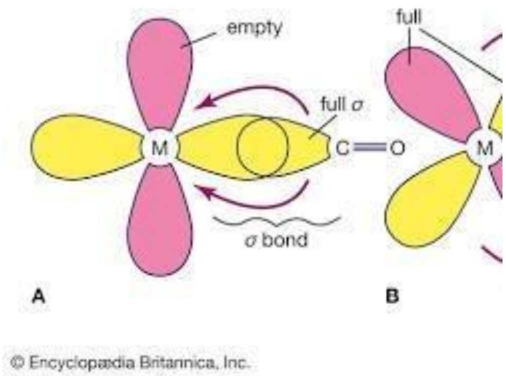


Plate 3.3: Orbital overlap in ligand field theory.

3.3.3 Advantages and limitations

Crystal field and ligand field theories have several advantages:

- They explain the colour of complexes due to d–d electronic transitions.
- They account for magnetic properties based on electron arrangements.
- They provide insight into stability and reactivity of complexes.

However, limitations include:

- CFT oversimplifies bonding by ignoring covalent interactions.
- LFT, while more advanced, requires complex calculations and is less intuitive.

Fill in the blank: One advantage of CFT is that it explains the ______ of complexes due to d–d transitions.

Feature	Crystal Field Theory (CFT)	Ligand Field Theory (LFT)
Primary Advantages	Predicts colour, magnetism, and splitting energy (Δ) using simple electrostatic models.	Provides a more accurate quantum mechanical description of metal-ligand bonding and covalency.
Explanation Capability	Excellent for understanding high-spin/low-spin states and spectral origins.	Explains nuances like the spectrochemical series and π-bonding effects.
Limitations	Oversimplifies bonding as purely ionic; ignores orbital overlap/covalent character.	Computationally complex and requires significant mathematical rigor to apply.

Box 3.3: Advantages and limitations of crystal field and ligand field theories.

Pilot questions 3.3

1. Which of the following best defines Crystal Field Theory? a. A theory explaining bonding through electrostatic interactions between ligands and metal ions b. A theory

explaining bonding through hybridisation of orbitals c. A theory explaining bonding through resonance structures d. A theory explaining bonding through covalent overlap only

2. Fill in the blank: In an octahedral complex, the d-orbitals split into ______ and eg sets.
3. Which of the following best defines Ligand Field Theory? a. A theory combining crystal field theory with molecular orbital theory b. A theory explaining bonding through hybridisation only c. A theory explaining bonding through electrostatic attraction only d. A theory explaining bonding through resonance structures
4. Fill in the blank: Ligand Field Theory combines Crystal Field Theory with ______ Orbital Theory.
5. Which of the following is an advantage of crystal field theory? a. Explains colour of complexes b. Accounts for magnetic properties c. Provides insight into stability d. All of the above

3.4 Physicochemical Methods Of Structural Elucidation

3.4.1 Spectroscopic methods (UV-Vis, IR, NMR)

Spectroscopy refers to techniques that study the interaction of matter with electromagnetic radiation. In coordination chemistry, spectroscopic methods are vital for determining the structure and properties of complexes.

- **UV-Vis spectroscopy**: Used to study electronic transitions, especially d–d transitions, which explain the colour of complexes.
- **Infrared (IR) spectroscopy**: Identifies functional groups and ligand bonding modes by detecting vibrational frequencies.
- **Nuclear Magnetic Resonance (NMR) spectroscopy**: Provides information about the environment of nuclei such as hydrogen or carbon, useful for complexes with organic ligands.

Fill in the blank: UV-Vis spectroscopy is particularly useful for studying ______ transitions in coordination complexes.

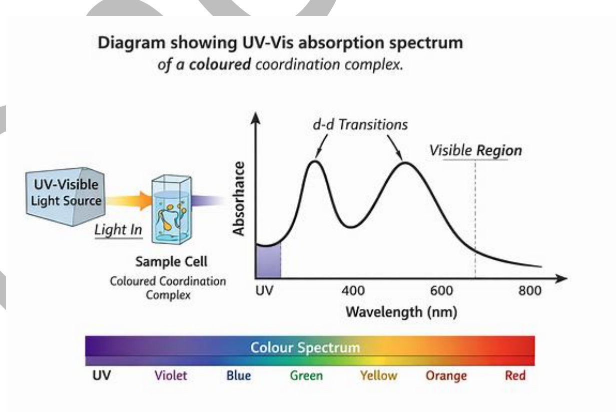


Figure 3.4: UV-Vis absorption spectrum of a coordination complex.

3.4.2 Magnetic measurements

Magnetic measurements help determine the number of unpaired electrons in a complex, which provides insight into its electronic configuration and geometry.

- Complexes with unpaired electrons are **paramagnetic**.
- Complexes with all electrons paired are **diamagnetic**.

For example, $[Fe(H_2O)_6]^{2+}$ is paramagnetic due to unpaired d-electrons, while $[Fe(CN)_6]^{4-}$ is diamagnetic because strong field ligands cause pairing of electrons.

Fill in the blank: Complexes with unpaired electrons are described as ______.

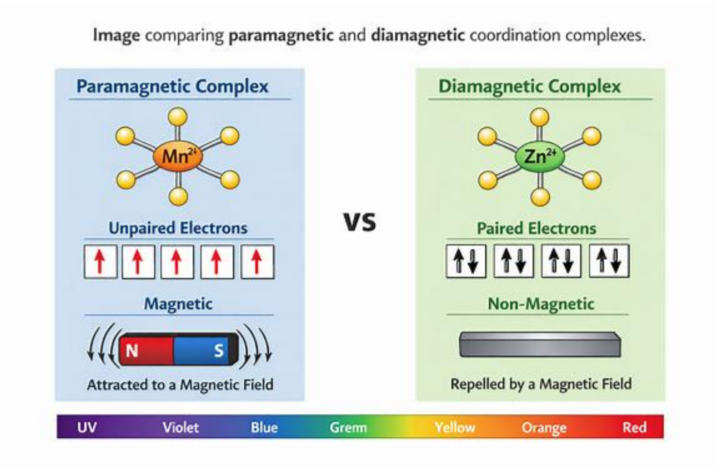


Plate 3.4: Magnetic behaviour of coordination complexes.

3.4.3 X-ray crystallography

X-ray crystallography is the most powerful method for determining the three-dimensional structures of coordination complexes. It involves directing X-rays at a crystal of the compound and analysing the diffraction pattern to reveal atomic positions. This technique provides precise information about bond lengths, bond angles, and overall geometry.

Fill in the blank: X-ray crystallography provides precise information about ______ lengths and angles in complexes.

Application	Description	Impact on Understanding
Bond Length Determination	Precision measurement of distance between metal center and ligand donor atoms.	Reveals strength of metal-ligand bonds and extent of covalent character.

Application	Description	Impact on Understanding
Bond Angle Mapping	Determination of the precise angles between ligands around the central ion.	Confirms coordination geometry (e.g., distorted vs. ideal octahedral).
Geometry Identification	Mapping the overall spatial arrangement of the complex.	Differentiates between isomers (e.g., *fac* vs. *mer*) and identifies structural motifs.
Solid-State Interactions	Visualization of intermolecular packing, hydrogen bonding, and π-stacking.	Explains crystal stability and bulk physical properties.

Box 3.4: Applications of X-ray crystallography.

Pilot questions 3.4

1. Which of the following spectroscopic methods is used to study d–d transitions in coordination complexes? a. UV-Vis spectroscopy b. IR spectroscopy c. NMR spectroscopy d. X-ray crystallography
2. Fill in the blank: UV-Vis spectroscopy is particularly useful for studying ______ transitions in coordination complexes.
3. Which of the following statements about magnetic measurements is correct? a. Complexes with unpaired electrons are diamagnetic b. Complexes with paired electrons are paramagnetic c. Complexes with unpaired electrons are paramagnetic d. Magnetic measurements cannot provide information about electronic configuration
4. Fill in the blank: Complexes with unpaired electrons are described as ______.
5. Which of the following techniques provides precise information about bond lengths and angles in complexes? a. UV-Vis spectroscopy b. IR spectroscopy c. Magnetic measurements d. X-ray crystallography

Series Summary

In this Series, we explored the **bonding theories and structural elucidation in coordination chemistry**. We began with Werner's theory, which introduced the concepts of primary and secondary valencies and laid the foundation for modern coordination chemistry. We then studied Valence Bond Theory (VBT), focusing on hybridisation, geometry, and magnetic properties, while noting its limitations. Following that, we examined Crystal Field Theory (CFT) and Ligand Field Theory (LFT), which explain d-orbital splitting, colour, magnetism, and covalent character in bonding. Finally, we considered physicochemical methods such as spectroscopy, magnetic measurements, and X-ray crystallography, which provide experimental evidence for the structures of complexes. Altogether, this Series has equipped learners with theoretical and practical tools to understand and analyse bonding and structures in coordination compounds.

Glossary of Terms

- **Werner's theory**: Early theory distinguishing primary valency (oxidation state) and secondary valency (coordination number).
- **Valence Bond Theory (VBT)**: A bonding theory based on orbital hybridisation of the central metal ion.
- **Hybridisation**: Mixing of atomic orbitals to form new orbitals suitable for bonding.
- **Crystal Field Theory (CFT)**: A theory explaining bonding through electrostatic interactions between ligands and metal d-orbitals.
- **Ligand Field Theory (LFT)**: An extension of CFT incorporating molecular orbital concepts and orbital overlap.
- **t_2g orbitals**: Lower-energy set of d-orbitals in an octahedral crystal field.
- **eg orbitals**: Higher-energy set of d-orbitals in an octahedral crystal field.
- **Spectroscopy**: Study of matter using electromagnetic radiation (UV-Vis, IR, NMR).
- **Magnetic measurements**: Techniques used to determine the number of unpaired electrons in complexes.
- **X-ray crystallography**: Experimental method for determining three-dimensional structures of compounds.

Concept Check Questions 3

Objective questions

1. According to Werner, the primary valency corresponds to the ______ state of the metal. (Linked to SLO 3.1)
2. In an octahedral complex, the metal ion undergoes ______ hybridisation. (Linked to SLO 3.4)
3. In an octahedral crystal field, the d-orbitals split into ______ and eg sets. (Linked to SLO 3.6)
4. Ligand Field Theory combines Crystal Field Theory with ______ Orbital Theory. (Linked to SLO 3.7)
5. Complexes with unpaired electrons are described as ______. (Linked to SLO 3.10)

Short-answer questions

6. Explain the distinction between primary and secondary valencies in Werner's theory. (Linked to SLO 3.1)

7. Describe how Valence Bond Theory predicts the geometry of coordination complexes. (Linked to SLO 3.3, 3.4)

8. Explain the difference in d-orbital splitting between octahedral and tetrahedral complexes. (Linked to SLO 3.6)

9. Describe how UV-Vis spectroscopy helps in structural elucidation of coordination complexes. (Linked to SLO 3.9)

Long-answer questions

10. Evaluate the strengths and limitations of Werner's theory, Valence Bond Theory, and Crystal Field Theory. (Linked to SLO 3.2, 3.5, 3.8)

11. Analyse the role of Ligand Field Theory in explaining covalent character and electronic spectra of complexes. (Linked to SLO 3.7, 3.8)

12. Discuss the applications of physicochemical methods such as spectroscopy, magnetic measurements, and X-ray crystallography in structural elucidation of coordination compounds. (Linked to SLO 3.9, 3.10, 3.11)

Answers To Pilot Questions 3

Part 3.1: 1.a, 2.oxidation, 3.b, 4.electronic, 5.d **Part 3.2**: 1.a, 2.d^2sp^3, 3.a, 4.dsp^2, 5.d **Part 3.3**: 1.a, 2.$t_{2}g$, 3.a, 4.Molecular, 5.d **Part 3.4**: 1.a, 2.d–d, 3.c, 4.paramagnetic, 5.d

References And Attributions 3

- Figures 3.1–3.4: Suggested AI prompts for diagrams showing valencies, hybridisation, crystal field splitting, and UV-Vis spectra.
- Plates 3.2–3.4: Suggested AI prompts for images comparing geometries, magnetic behaviour, and orbital overlap.
- Boxes 3.1–3.4: Suggested AI prompts for tables summarising strengths/limitations, hybridisation, advantages/limitations, and applications of structural elucidation methods.
- Open Educational Resources (OER) suggested search strings:
  - "OER diagram Werner's theory coordination chemistry"
  - "OER diagram valence bond theory hybridisation coordination chemistry"
  - "OER diagram crystal field splitting coordination chemistry"
  - "OER image ligand field theory orbital overlap chemistry"
  - "OER image magnetic properties coordination complexes"
  - "OER table valence bond theory limitations chemistry"
  - "OER table crystal field ligand field theory advantages limitations chemistry"
  - "OER table X-ray crystallography applications coordination chemistry"
- Attribution style: APA (institutional standard assumed). Example: OpenStax. (2016). *Chemistry*. OpenStax CNX. Retrieved from https://openstax.org/books/chemistry

Course code: CHM 424
Course title: Coordination Chemistry
Course credit load: 2 Units
Series 1: Foundations Of Coordination Chemistry

Series 2: Nomenclature, Isomerism And Stereochemistry Of Complexes

Series 3: Theories Of Bonding And Structural Elucidation

Series 4: Spectral And Magnetic Properties Of Complexes

Series 5: Stability, Reactions And Technological Applications Of Complexes

Proposed Outline Series 4

4.1 Electronic Spectra Of Complexes

- 4.1.1 Origin of colour in complexes
- 4.1.2 d–d transitions and charge transfer transitions
- 4.1.3 Applications of electronic spectra

4.2 Magnetic Properties Of Complexes

- 4.2.1 Paramagnetism and diamagnetism
- 4.2.2 Magnetic susceptibility measurements
- 4.2.3 Correlation with electronic configuration

4.3 Spectrochemical Series And Crystal Field Stabilisation Energy (CFSE)

- 4.3.1 Spectrochemical series of ligands
- 4.3.2 CFSE in octahedral and tetrahedral complexes
- 4.3.3 Applications of CFSE in stability and reactivity

Introduction

In the last Series, we examined bonding theories and structural elucidation, learning how coordination compounds form and how their structures are determined experimentally. Building on that foundation, we now turn to the spectral and magnetic properties that give complexes their distinctive colours, behaviours, and reactivities.

The aim of this Series is to explain the origin of colour and magnetism in coordination complexes, to introduce the spectrochemical series, and to show how crystal field stabilisation energy influences stability and reactivity.

We shall commence this Series by exploring electronic spectra of complexes, focusing on d–d transitions and charge transfer processes. Next, we will study magnetic properties, considering paramagnetism, diamagnetism, and how magnetic measurements correlate with electronic configurations. Finally, we will conclude with the spectrochemical series and crystal field stabilisation energy, highlighting their applications in predicting stability and reactivity of complexes.

Series Learning Outcomes

Upon completing this Series, you should be able to:

- **SLO 4.1** explain the origin of colour in coordination complexes,
- **SLO 4.2** describe d–d transitions and charge transfer transitions in electronic spectra,
- **SLO 4.3** analyse applications of electronic spectra in coordination chemistry,
- **SLO 4.4** define paramagnetism and diamagnetism in complexes,
- **SLO 4.5** demonstrate how magnetic susceptibility measurements are used to determine electronic configurations,
- **SLO 4.6** correlate magnetic properties with electronic arrangements in complexes,
- **SLO 4.7** explain the spectrochemical series of ligands,
- **SLO 4.8** calculate crystal field stabilisation energy (CFSE) in octahedral and tetrahedral complexes,
- **SLO 4.9** evaluate the applications of CFSE in predicting stability and reactivity of complexes.

4.1 Electronic Spectra Of Complexes

4.1.1 Origin of colour in complexes

The striking colours of coordination complexes arise from **electronic transitions**, where electrons move between energy levels in the d-orbitals of the central metal ion. When light strikes the complex, certain wavelengths are absorbed, and the remaining wavelengths are transmitted or reflected, giving the compound its characteristic colour.

The energy difference between d-orbitals depends on the type of ligands and the geometry of the complex, as explained by crystal field theory.

Fill in the blank: The colours of coordination complexes arise because certain wavelengths of ______ are absorbed during electronic transitions.

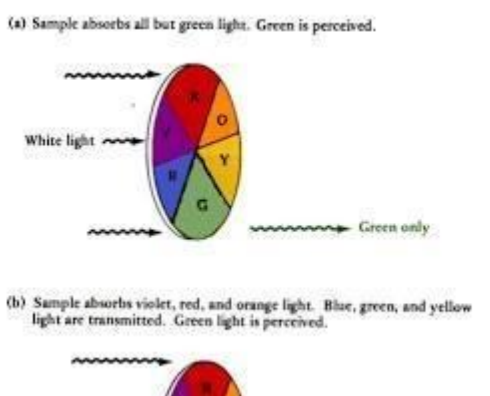


Figure 4.1: Origin of colour in coordination complexes.

4.1.2 d–d transitions and charge transfer transitions

d–d transitions occur when an electron moves between d-orbitals of different energies within the same metal ion. These transitions are responsible for many of the colours observed in transition metal complexes.

Charge transfer transitions involve the movement of an electron between the metal and a ligand. They are often more intense than d–d transitions and can produce vivid colours. For example, in $[Fe(SCN)]^{2+}$ complexes, charge transfer transitions give a deep red colour.

Fill in the blank: Charge transfer transitions involve the movement of an electron between the ______ and a ligand.

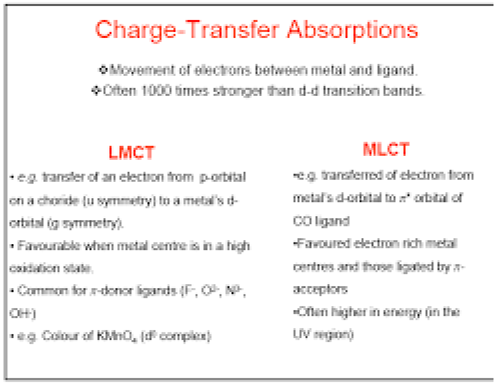


Plate 4.1: Types of electronic transitions in complexes.

4.1.3 Applications of electronic spectra

Electronic spectra provide valuable information about coordination complexes:

- **Identification of complexes**: Spectral patterns help distinguish different complexes.
- **Determination of geometry**: The type of transitions observed can indicate whether a complex is octahedral, tetrahedral, or square planar.
- **Study of ligand strength**: Spectra reveal the position of ligands in the spectrochemical series.
- **Analysis of stability**: Spectral data can be used to calculate crystal field stabilisation energy (CFSE).

Fill in the blank: Electronic spectra can be used to determine the ______ of a coordination complex.

Application	Insight Provided
Identification	Unique absorption "fingerprints" allow for the characterization and identification of specific coordination species in solution.
Geometry Determination	The number and intensity of absorption bands reflect the symmetry of the complex (e.g., octahedral vs. tetrahedral), acting as a probe for geometry.
Ligand Strength	The magnitude of splitting (Δ) calculated from spectra allows for the ranking of ligands in the Spectrochemical Series.
Stability Analysis	Shifts in spectral peaks over time can indicate complex dissociation, ligand exchange reactions, or changes in oxidation states, signaling thermodynamic or kinetic stability.

Application	Insight Provided
Electronic Structure	Provides direct evidence of d-d transitions and charge transfer, confirming the oxidation state and electronic configuration of the metal center.

Box 4.1: Applications of electronic spectra.

Pilot questions 4.1

1. Which of the following best explains the origin of colour in coordination complexes? a. Reflection of all wavelengths of light b. Absorption of specific wavelengths due to electronic transitions c. Emission of light from ligands d. Presence of impurities in the compound
2. Fill in the blank: The colours of coordination complexes arise because certain wavelengths of ______ are absorbed during electronic transitions.
3. Which of the following transitions are responsible for the colours of many transition metal complexes? a. d–d transitions b. Charge transfer transitions c. Both a and b d. None of the above
4. Fill in the blank: Charge transfer transitions involve the movement of an electron between the ______ and a ligand.
5. Which of the following is an application of electronic spectra? a. Identification of complexes b. Determination of geometry c. Study of ligand strength d. All of the above

4.2 Magnetic Properties Of Complexes

4.2.1 Paramagnetism and diamagnetism

Magnetic properties of coordination complexes depend on the presence or absence of unpaired electrons in the d-orbitals of the central metal ion.

- **Paramagnetism**: Complexes with one or more unpaired electrons are attracted to a magnetic field.
- **Diamagnetism**: Complexes with all electrons paired are weakly repelled by a magnetic field.

For example, $[Fe(H_2O)_6]^{2+}$ is paramagnetic due to unpaired d-electrons, while $[Fe(CN)_6]^{4-}$ is diamagnetic because strong field ligands cause electron pairing.

Fill in the blank: Complexes with all electrons paired are described as ______.

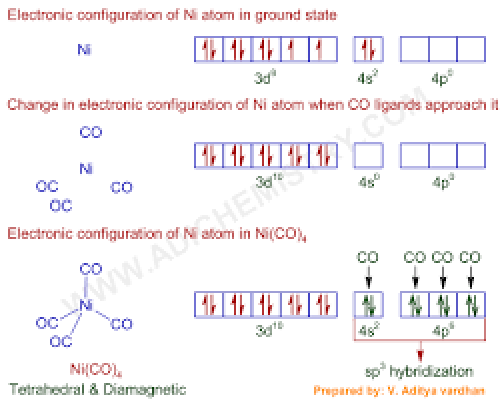


Figure 4.2: Paramagnetism and diamagnetism in coordination complexes.

4.2.2 Magnetic susceptibility measurements

Magnetic susceptibility is a measure of how strongly a substance is attracted to or repelled by a magnetic field. In coordination chemistry, these measurements are used to determine the number of unpaired electrons in a complex.

The experimental values can be compared with theoretical predictions based on electronic configurations. This helps chemists deduce whether a complex is high-spin or low-spin, depending on the strength of the ligands.

Fill in the blank: Magnetic susceptibility measurements help determine the number of ______ electrons in a complex.

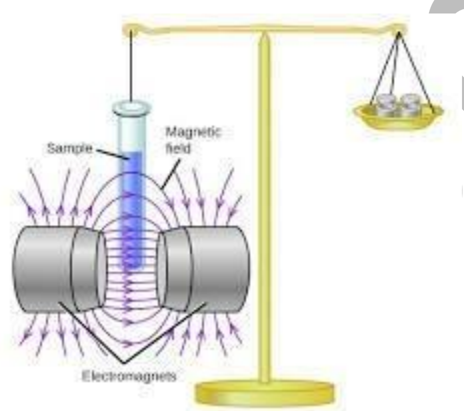


Plate 4.2: Magnetic susceptibility measurement in complexes.

4.2.3 Correlation with electronic configuration

The magnetic properties of complexes correlate directly with their **electronic configuration**.

- Weak field ligands (e.g., H_2O, Cl^-) often produce high-spin complexes with more unpaired electrons.
- Strong field ligands (e.g., CN^-, CO) produce low-spin complexes with fewer or no unpaired electrons.

This correlation is explained by crystal field theory and is essential for predicting the behaviour of complexes in magnetic fields.

Fill in the blank: Strong field ligands such as CN^- usually produce ______-spin complexes.

Feature	Weak Field Ligands	Strong Field Ligands
Spectrochemical Series	Low end (e.g., $\ce{I^-, Br^-, Cl^-, F^-}$)	High end (e.g., $\ce{CN^-, CO, en, NH3}$)
Splitting Energy (Δ)	Small splitting	Large splitting
Spin State	High Spin	Low Spin
Electron Pairing	Pairing is unfavorable ($\Delta < P$)	Pairing is favorable ($\Delta > P$)
Magnetic Property	Usually paramagnetic	Often diamagnetic (or fewer unpaired electrons)

Box 4.2: Correlation of magnetic properties with electronic configuration.

Pilot questions 4.2

1. Which of the following best defines paramagnetism? a. Complexes with all electrons paired, weakly repelled by a magnetic field b. Complexes with unpaired electrons, attracted to a magnetic field c. Complexes with no electrons in d-orbitals d. Complexes with strong field ligands only
2. Fill in the blank: Complexes with all electrons paired are described as ______.
3. Which of the following is measured to determine the number of unpaired electrons in a complex? a. Magnetic susceptibility b. UV-Vis absorption c. Infrared vibrations d. X-ray diffraction
4. Fill in the blank: Magnetic susceptibility measurements help determine the number of ______ electrons in a complex.
5. Which of the following ligands usually produce low-spin complexes? a. H_2O b. Cl^- c. CN^- d. Br^-

4.3 Spectrochemical Series And Crystal Field Stabilisation Energy (CFSE)

4.3.1 Spectrochemical series of ligands

The **spectrochemical series** is an arrangement of ligands based on their ability to split the d-orbitals of the central metal ion. Strong field ligands cause large splitting, while weak field ligands cause small splitting.

Typical order (from weak to strong field): $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < en < CN^- < CO$

This series helps predict whether a complex will be high-spin or low-spin, and therefore whether it will be paramagnetic or diamagnetic.

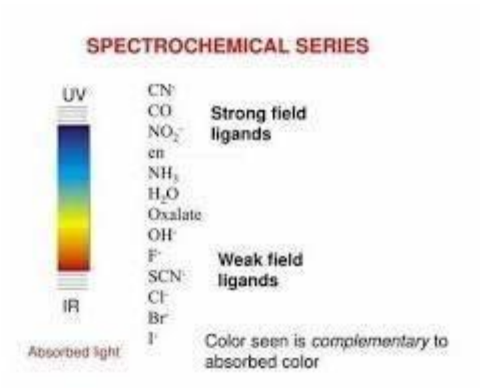


Figure 4.3: Spectrochemical series of ligands.

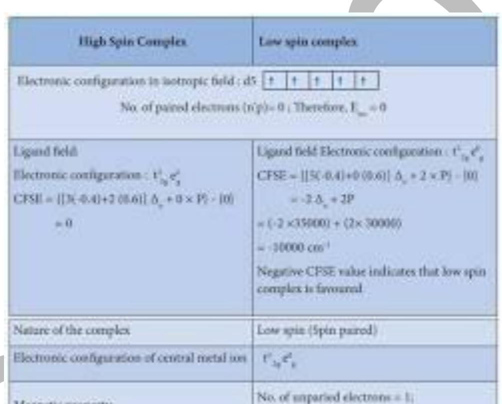
4.3.2 CFSE in octahedral and tetrahedral complexes

Crystal Field Stabilisation Energy (CFSE) is the energy gained by a complex due to the splitting of d-orbitals in a crystal field.

- In **octahedral complexes**, electrons occupy t_2g and eg orbitals depending on ligand strength.
- In **tetrahedral complexes**, the splitting is smaller, and electrons occupy eg and t_2g orbitals in reverse order compared to octahedral.

CFSE influences the stability, colour, and magnetic properties of complexes.

Fill in the blank: CFSE is greater in ______ complexes compared to tetrahedral complexes.



High Spin Complex	Low spin complex
Electronic configuration in isotropic field : d5 ↑ ↑ ↑ ↑ ↑ No. of paired electrons (n'p) = 0 ; Therefore, E_{pe} = 0	
Ligand field Electronic configuration : $t^3_{2g}e^2_g$ CFSE = [[3(-0.4)+2 (0.6)] Δ_o + 0 × P] - [0] = 0	Ligand field Electronic configuration : $t^5_{2g}e^0_g$ CFSE = [[5(-0.4)+0 (0.6)] Δ_o + 2 × P] - [0] = -2 Δ_o + 2P = (-2 × 35000) + (2× 30000) = -10000 cm^{-1} Negative CFSE value indicates that low spin complex is favoured
Nature of the complex	Low spin (Spin paired)
Electronic configuration of central metal ion	$t^5_{2g}e^0_g$
Magnetic property	No. of unparied electrons = 1;

Plate 4.3: CFSE in octahedral and tetrahedral complexes.

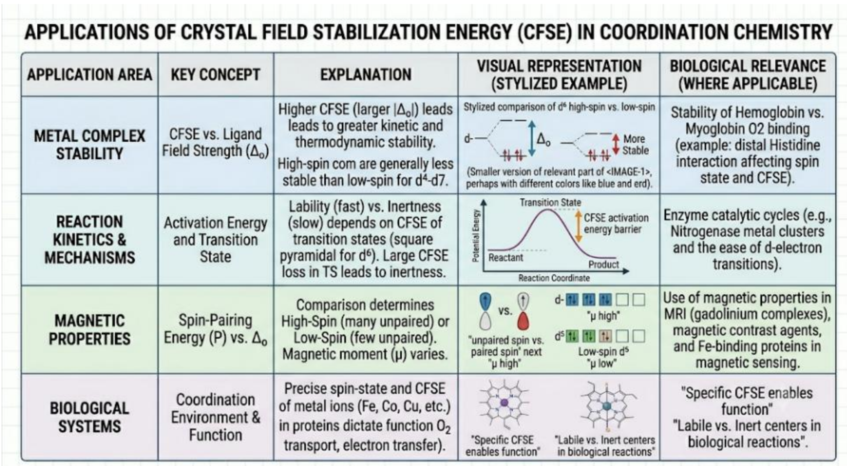
4.3.3 Applications of CFSE in stability and reactivity

CFSE has several important applications:

- **Stability**: Complexes with higher CFSE are generally more stable.
- **Reactivity**: CFSE influences substitution reactions and ligand exchange rates.

- **Magnetic properties**: CFSE determines whether complexes are high-spin or low-spin.
- **Biological relevance**: CFSE helps explain the behaviour of metalloproteins and enzymes.

Fill in the blank: Complexes with higher CFSE are generally more ______.



APPLICATIONS OF CRYSTAL FIELD STABILIZATION ENERGY (CFSE) IN COORDINATION CHEMISTRY

APPLICATION AREA	KEY CONCEPT	EXPLANATION	VISUAL REPRESENTATION (STYLIZED EXAMPLE)	BIOLOGICAL RELEVANCE (WHERE APPLICABLE)
METAL COMPLEX STABILITY	CFSE vs. Ligand Field Strength (Δ_o)	Higher CFSE (larger $\lvert\Delta_o\rvert$) leads leads to greater kinetic and thermodynamic stability. High-spin com are generally less stable than low-spin for d^4-d7.	Stylized comparison of d^6 high-spin vs. low-spin; d-; Δ_o; More Stable; (Smaller version of relevant part of <IMAGE-1>, perhaps with different colors like blue and erd).	Stability of Hemoglobin vs. Myoglobin 02 binding (example: distal Histidine interaction affecting spin state and CFSE).
REACTION KINETICS & MECHANISMS	Activation Energy and Transition State	Lability (fast) vs. Inertness (slow) depends on CFSE of transition states (square pyramidal for d^6). Large CFSE loss in TS leads to inertness.	Transition State; CFSE activation energy barrier; Potential Energy; Reactant; Product; Reaction Coordinate	Enzyme catalytic cycles (e.g., Nitrogenase metal clusters and the ease of d-electron transitions).
MAGNETIC PROPERTIES	Spin-Pairing Energy (P) vs. Δ_o	Comparison determines High-Spin (many unpaired) or Low-Spin (few unpaired). Magnetic moment (μ) varies.	vs.; "unpaired spin vs. paired spin" next "μ high"; d- "μ high"; d^5 Low-spin d^5 "μ low"	Use of magnetic properties in MRI (gadolinium complexes), magnetic contrast agents, and Fe-binding proteins in magnetic sensing.
BIOLOGICAL SYSTEMS	Coordination Environment & Function	Precise spin-state and CFSE of metal ions (Fe, Co, Cu, etc.) in proteins dictate function O_2 transport, electron transfer).	"Specific CFSE enables function"; "Labile vs. Inert centers in biological reactions"	"Specific CFSE enables function" "Labile vs. Inert centers in biological reactions".

Box 4.3: Applications of CFSE.

Pilot questions 4.3

1. Which of the following best defines the spectrochemical series? a. Arrangement of ligands based on their size b. Arrangement of ligands based on their ability to split d-orbitals c. Arrangement of ligands based on their charge d. Arrangement of ligands based on their geometry
2. Fill in the blank: In the spectrochemical series, CN^- is considered a ______ field ligand.
3. Which of the following complexes has greater CFSE? a. Octahedral b. Tetrahedral c. Both equal d. None of the above
4. Fill in the blank: CFSE is greater in ______ complexes compared to tetrahedral complexes.
5. Which of the following is an application of CFSE? a. Determining stability of complexes b. Predicting reactivity c. Explaining magnetic properties d. All of the above

Series Summary

In this Series, we explored the **spectral and magnetic behaviour of coordination complexes**. We began with electronic spectra, learning how colours arise from d–d transitions and charge transfer processes, and how these spectra can be applied to identify complexes, determine geometry, and assess ligand strength. We then examined magnetic properties, distinguishing between paramagnetism and diamagnetism, and studied how magnetic susceptibility measurements reveal the number of unpaired electrons and correlate with electronic configurations. Finally, we considered the spectrochemical series and crystal field stabilisation energy (CFSE), which explain ligand strength, spin states, and the stability and reactivity of complexes. Altogether, this Series has provided learners with both theoretical and experimental insights into the spectral and magnetic characteristics of coordination compounds.

Glossary of Terms

- **Electronic spectra**: Patterns of light absorption or emission that reveal electronic transitions in complexes.
- **d–d transitions**: Electronic transitions between d-orbitals of different energies in a metal ion.
- **Charge transfer transitions**: Movement of electrons between a metal and a ligand, producing intense colours.
- **Paramagnetism**: Property of complexes with unpaired electrons, attracted to a magnetic field.
- **Diamagnetism**: Property of complexes with all electrons paired, weakly repelled by a magnetic field.
- **Magnetic susceptibility**: Measure of how strongly a substance is attracted to or repelled by a magnetic field.
- **Spectrochemical series**: Arrangement of ligands based on their ability to split d-orbitals.
- **Crystal Field Stabilisation Energy (CFSE)**: Energy gained by a complex due to d-orbital splitting in a crystal field.
- **High-spin complex**: Complex with maximum unpaired electrons due to weak field ligands.
- **Low-spin complex**: Complex with fewer unpaired electrons due to strong field ligands.

Concept Check Questions 4

Objective questions

1. The colours of coordination complexes arise because certain wavelengths of ______ are absorbed during electronic transitions. (Linked to SLO 4.1)
2. Charge transfer transitions involve the movement of an electron between the ______ and a ligand. (Linked to SLO 4.2)
3. Complexes with all electrons paired are described as ______. (Linked to SLO 4.4)
4. Magnetic susceptibility measurements help determine the number of ______ electrons in a complex. (Linked to SLO 4.5)
5. In the spectrochemical series, CN^- is considered a ______ field ligand. (Linked to SLO 4.7)

Short-answer questions

6. Explain the difference between d–d transitions and charge transfer transitions. (Linked to SLO 4.2)

7. Describe how magnetic susceptibility measurements are used to determine electronic configurations. (Linked to SLO 4.5, 4.6)

8. Explain the significance of the spectrochemical series in predicting spin states of complexes. (Linked to SLO 4.7)

9. Calculate CFSE for an octahedral complex with a d^3 configuration. (Linked to SLO 4.8)

Long-answer questions

10. Analyse the applications of electronic spectra in coordination chemistry, including identification, geometry determination, and ligand strength. (Linked to SLO 4.3)

11. Evaluate the correlation between magnetic properties and electronic configurations in complexes, with examples of high-spin and low-spin states. (Linked to SLO 4.6)

12. Discuss the role of CFSE in determining stability, reactivity, and biological relevance of coordination complexes. (Linked to SLO 4.9)

Answers To Pilot Questions 4

Part 4.1: 1.b, 2.light, 3.c, 4.metal, 5.d **Part 4.2**: 1.b, 2.diamagnetic, 3.a, 4.unpaired, 5.c **Part 4.3**: 1.b, 2.strong, 3.a, 4.octahedral, 5.d

References And Attributions 4

- Figures 4.1–4.3: Suggested AI prompts for diagrams showing origin of colour, paramagnetism vs diamagnetism, and spectrochemical series.
- Plates 4.1–4.3: Suggested AI prompts for images comparing d–d vs charge transfer transitions, magnetic susceptibility setups, and CFSE in geometries.
- Boxes 4.1–4.3: Suggested AI prompts for tables summarising applications of spectra, correlation of magnetic properties, and CFSE applications.
- Open Educational Resources (OER) suggested search strings:
    - “OER diagram origin of colour coordination complexes”
    - “OER image d-d transitions charge transfer coordination complexes”
    - “OER diagram paramagnetism diamagnetism coordination complexes”
    - “OER image magnetic susceptibility measurement chemistry”
    - “OER diagram spectrochemical series ligands coordination chemistry”
    - “OER image CFSE octahedral tetrahedral complexes”
    - “OER table CFSE applications coordination chemistry”

- Attribution style: APA (institutional standard assumed). Example: OpenStax. (2016). *Chemistry*. OpenStax CNX. Retrieved from https://openstax.org/books/chemistry

Course code: CHM 424
Course title: Coordination Chemistry
Course credit load: 2 Units
Series 1: Foundations Of Coordination Chemistry

Series 2: Nomenclature, Isomerism And Stereochemistry Of Complexes

Series 3: Theories Of Bonding And Structural Elucidation

Series 4: Spectral And Magnetic Properties Of Complexes

Series 5: Stability, Reactions And Technological Applications Of Complexes

Proposed Outline Series 5

5.1 Stability Of Complexes

- 5.1.1 Thermodynamic stability
- 5.1.2 Kinetic stability
- 5.1.3 Factors influencing stability

5.2 Reactions Of Complexes

- 5.2.1 Substitution reactions
- 5.2.2 Redox reactions
- 5.2.3 Acid-base reactions of complexes

5.3 Technological And Biological Applications Of Complexes

- 5.3.1 Industrial applications (catalysis, metallurgy, materials)
- 5.3.2 Biological applications (metalloproteins, medicine)
- 5.3.3 Environmental and technological relevance

Introduction

In the last Series, we examined the spectral and magnetic behaviour of complexes, learning how their colours, spin states, and magnetic properties arise from electronic transitions and orbital splitting. Building on that knowledge, we now turn to the stability, reactivity, and practical applications of coordination compounds.

The aim of this Series is to explain the factors that determine the stability of complexes, to explore the types of reactions they undergo, and to highlight their technological and biological importance.

We shall commence this Series by discussing the stability of complexes, considering both thermodynamic and kinetic aspects. Next, we will examine the reactions of complexes, including substitution, redox, and acid-base processes. Finally, we will conclude with technological and biological applications, focusing on their roles in industry, medicine, and environmental systems.

Series Learning Outcomes

Upon completing this Series, you should be able to:

- **SLO 5.1** explain the concepts of thermodynamic and kinetic stability in coordination complexes,
- **SLO 5.2** analyse the factors influencing stability of complexes,
- **SLO 5.3** describe substitution reactions in coordination chemistry,
- **SLO 5.4** explain redox reactions involving coordination complexes,
- **SLO 5.5** demonstrate how acid-base reactions occur in complexes,
- **SLO 5.6** evaluate industrial applications of coordination complexes such as catalysis and metallurgy,
- **SLO 5.7** explain biological applications of complexes in medicine and metalloproteins,
- **SLO 5.8** assess the environmental and technological relevance of coordination complexes.

5.1 Stability Of Complexes

5.1.1 Thermodynamic stability

Thermodynamic stability refers to how favourable the formation of a coordination complex is in terms of energy. A complex is thermodynamically stable if it has a low free energy, meaning it is less likely to decompose into its constituent parts. Stability is often expressed using the **stability constant (K)**, which measures the equilibrium between the complex and its dissociated ions.

For example, $[Cu(NH_3)_4]^{2+}$ has a high stability constant, indicating that it is strongly favoured over free Cu^{2+} and NH_3 molecules.

Fill in the blank: Thermodynamic stability of a complex is often expressed using the ______ constant.

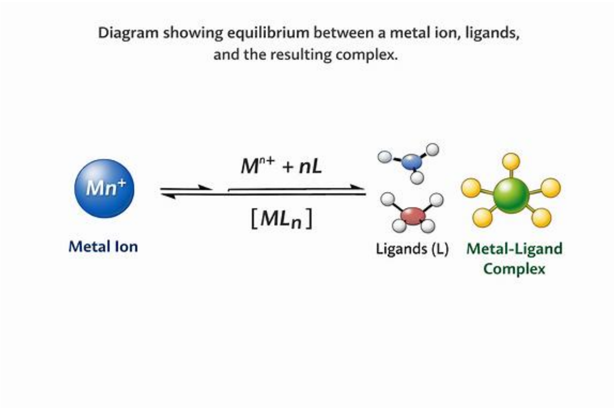


Figure 5.1: Thermodynamic stability of complexes.

5.1.2 Kinetic stability

Kinetic stability refers to how quickly or slowly a complex undergoes reactions such as ligand substitution. A complex may be thermodynamically stable but kinetically unstable if it reacts rapidly. Conversely, some complexes are kinetically inert, meaning they resist substitution even if they are not highly stable thermodynamically.

For example, $[Co(NH_3)_6]^{3+}$ is kinetically inert, while $[Cu(H_2O)_6]^{2+}$ is labile and undergoes substitution quickly.

Fill in the blank: A complex that resists substitution reactions is described as kinetically ______.

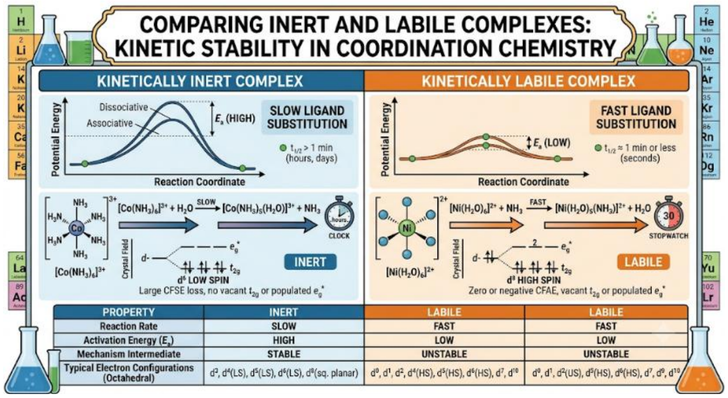


Plate 5.1: Kinetic stability of complexes.

5.1.3 Factors influencing stability

Several factors influence the stability of coordination complexes:

- **Nature of the metal ion**: Charge density, size, and electronic configuration affect stability.
- **Nature of the ligands**: Strong field ligands (e.g., CN^-, CO) form more stable complexes than weak field ligands (e.g., H_2O, Cl^-).
- **Chelate effect**: Complexes with multidentate ligands (chelates) are more stable due to entropic and enthalpic advantages.
- **Steric effects**: Bulky ligands may reduce stability by hindering effective bonding.

Fill in the blank: Complexes with multidentate ligands are more stable due to the ______ effect.

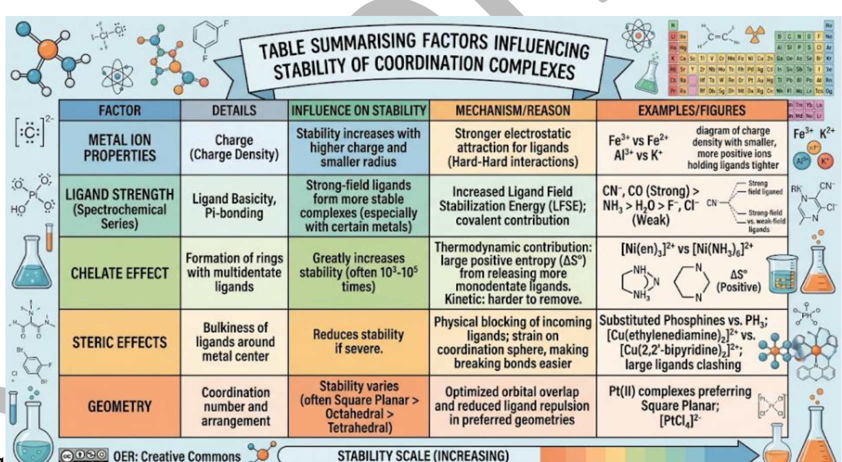


TABLE SUMMARISING FACTORS INFLUENCING STABILITY OF COORDINATION COMPLEXES

FACTOR	DETAILS	INFLUENCE ON STABILITY	MECHANISM/REASON	EXAMPLES/FIGURES
METAL ION PROPERTIES	Charge (Charge Density)	Stability increases with higher charge and smaller radius	Stronger electrostatic attraction for ligands (Hard-Hard interactions)	Fe^{3+} vs Fe^{2+} Al^{3+} vs K^+ diagram of charge density with smaller, more positive ions holding ligands tighter
LIGAND STRENGTH (Spectrochemical Series)	Ligand Basicity, Pi-bonding	Strong-field ligands form more stable complexes (especially with certain metals)	Increased Ligand Field Stabilization Energy (LFSE); covalent contribution	CN^-, CO (Strong) > NH_3 > H_2O > F^-, Cl^- (Weak)
CHELATE EFFECT	Formation of rings with multidentate ligands	Greatly increases stability (often 10^3-10^5 times)	Thermodynamic contribution: large positive entropy (ΔS°) from releasing more monodentate ligands. Kinetic: harder to remove.	$[Ni(en)_3]^{2+}$ vs $[Ni(NH_3)_6]^{2+}$ ΔS° (Positive)
STERIC EFFECTS	Bulkiness of ligands around metal center	Reduces stability if severe.	Physical blocking of incoming ligands; strain on coordination sphere, making breaking bonds easier	Substituted Phosphines vs. PH_3; $[Cu(ethylenediamine)_2]^{2+}$ vs. $[Cu(2,2'\text{-}bipyridine)_2]^{2+}$; large ligands clashing
GEOMETRY	Coordination number and arrangement	Stability varies (often Square Planar > Octahedral > Tetrahedral)	Optimized orbital overlap and reduced ligand repulsion in preferred geometries	Pt(II) complexes preferring Square Planar; $[PtCl_4]^{2-}$

q

Box 5.1: Factors influencing stability of complexes.

Pilot questions 5.1

1. Which of the following best defines thermodynamic stability? a. Resistance of a complex to substitution reactions b. Favourability of complex formation in terms of energy c. Rate at which a complex reacts d. Size of the ligands in a complex

2. Fill in the blank: Thermodynamic stability of a complex is often expressed using the ______ constant.
3. Which of the following complexes is kinetically inert? a. $[Cu(H_2O)_6]^{2+}$ b. $[Co(NH_3)_6]^{3+}$ c. $[Fe(CN)_6]^{3-}$ d. $[NiCl_4]^{2-}$
4. Fill in the blank: A complex that resists substitution reactions is described as kinetically ______.
5. Which of the following factors increases stability of complexes? a. Chelate effect b. Strong field ligands c. High charge density of metal ion d. All of the above

5.2 Reactions Of Complexes

5.2.1 Substitution reactions

Substitution reactions occur when one ligand in a coordination complex is replaced by another. These reactions can be classified as:

- **Ligand substitution**: Exchange of one ligand for another, e.g., $[Co(NH_3)_6]^{3+}$ reacting with Cl^- to form $[Co(NH_3)_5Cl]^{2+}$.
- **Solvent exchange**: Replacement of a solvent molecule acting as a ligand, e.g., $[Ni(H_2O)_6]^{2+}$ exchanging H_2O for NH_3.

The rate of substitution depends on the kinetic stability of the complex. Labile complexes undergo substitution quickly, while inert complexes resist substitution.

Fill in the blank: A substitution reaction involves the replacement of one ______ by another in a coordination complex.

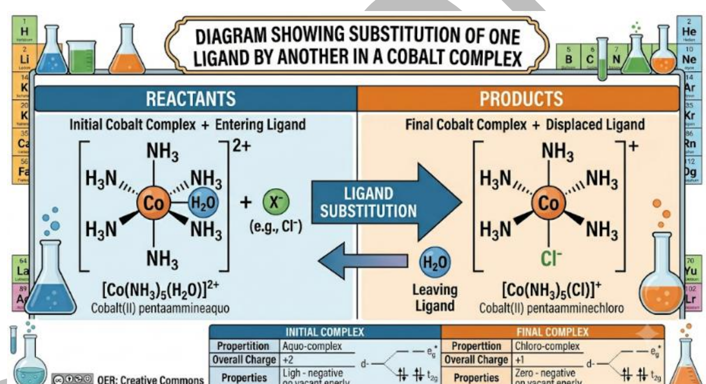


Figure 5.2: Ligand substitution in coordination complexes.

5.2.2 Redox reactions

Redox reactions in coordination chemistry involve changes in the oxidation state of the central metal ion. These reactions are important in biological systems and industrial processes.

- Example: $[Fe(CN)_6]^{3-}$ can be reduced to $[Fe(CN)_6]^{4-}$.
- Example: $[Co(NH_3)_6]^{2+}$ can be oxidised to $[Co(NH_3)_6]^{3+}$.

Such reactions often occur with electron transfer between the metal ion and external reagents.

Fill in the blank: Redox reactions in complexes involve changes in the ______ state of the central metal ion.

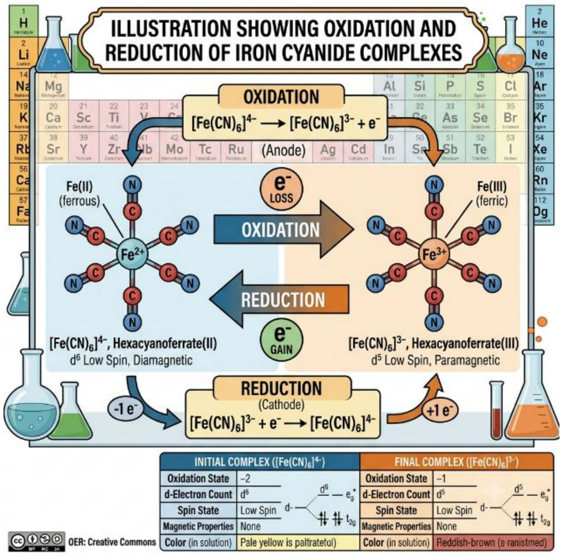


Plate 5.2: Redox reactions in coordination complexes.

5.2.3 Acid-base reactions of complexes

Acid-base reactions in coordination chemistry occur when complexes act as acids or bases.

- **Lewis acid behaviour**: Metal ions act as electron pair acceptors.
- **Lewis base behaviour**: Ligands act as electron pair donors.

For example, $[Al(H_2O)_6]^{3+}$ can act as a Lewis acid, while NH_3 acts as a Lewis base. These interactions are fundamental to the formation and reactivity of complexes.

Fill in the blank: In acid-base reactions, metal ions in complexes act as Lewis ______.

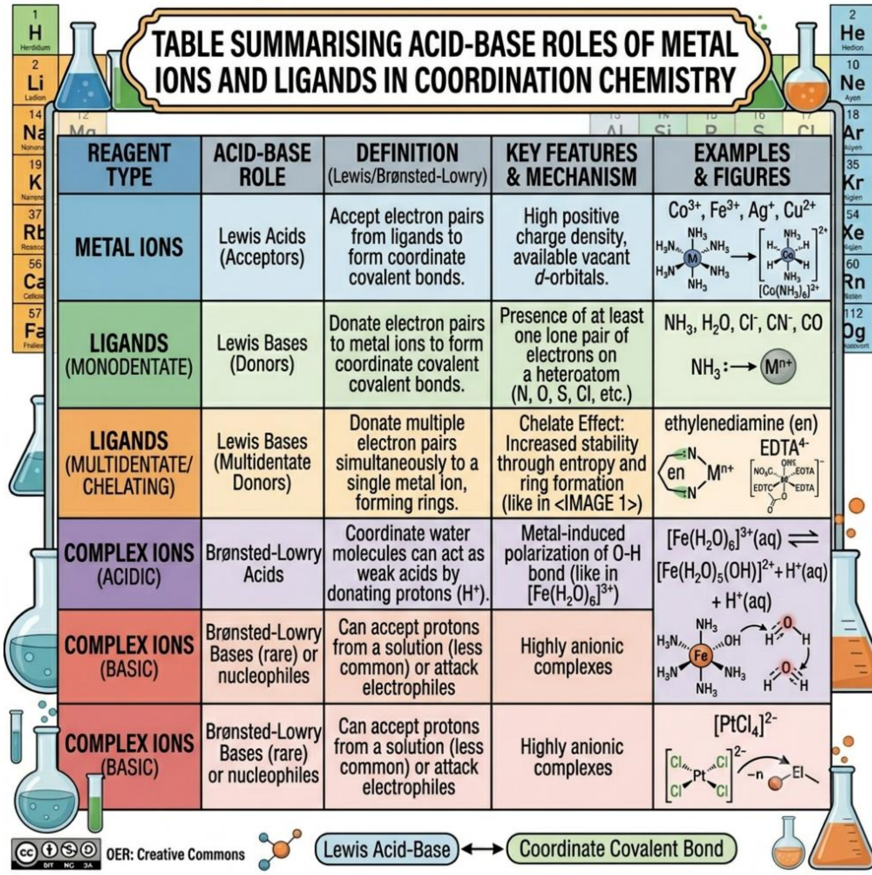


TABLE SUMMARISING ACID-BASE ROLES OF METAL IONS AND LIGANDS IN COORDINATION CHEMISTRY

REAGENT TYPE	ACID-BASE ROLE	DEFINITION (Lewis/Brønsted-Lowry)	KEY FEATURES & MECHANISM	EXAMPLES & FIGURES
METAL IONS	Lewis Acids (Acceptors)	Accept electron pairs from ligands to form coordinate covalent bonds.	High positive charge density, available vacant *d*-orbitals.	Co^{3+}, Fe^{3+}, Ag^{+}, Cu^{2+}; $[Co(NH_3)_6]^{2+}$
LIGANDS (MONODENTATE)	Lewis Bases (Donors)	Donate electron pairs to metal ions to form coordinate covalent covalent bonds.	Presence of at least one lone pair of electrons on a heteroatom (N, O, S, Cl, etc.)	NH_3, H_2O, Cl^-, CN^-, CO; $NH_3: \rightarrow M^{n+}$
LIGANDS (MULTIDENTATE/ CHELATING)	Lewis Bases (Multidentate Donors)	Donate multiple electron pairs simultaneously to a single metal ion, forming rings.	Chelate Effect: Increased stability through entropy and ring formation (like in <IMAGE 1>)	ethylenediamine (en); $EDTA^{4-}$
COMPLEX IONS (ACIDIC)	Brønsted-Lowry Acids	Coordinate water molecules can act as weak acids by donating protons (H^+).	Metal-induced polarization of O-H bond (like in $[Fe(H_2O)_6]^{3+}$)	$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+(aq)$
COMPLEX IONS (BASIC)	Brønsted-Lowry Bases (rare) or nucleophiles	Can accept protons from a solution (less common) or attack electrophiles	Highly anionic complexes	
COMPLEX IONS (BASIC)	Brønsted-Lowry Bases (rare) or nucleophiles	Can accept protons from a solution (less common) or attack electrophiles	Highly anionic complexes	$[PtCl_4]^{2-}$

Box 5.2: Acid-base behaviour of complexes.

Pilot questions 5.2

1. Which of the following best defines a substitution reaction in coordination chemistry? a. Replacement of one ligand by another b. Change in oxidation state of the metal ion c. Exchange of protons between ligands d. Formation of chelates
2. Fill in the blank: A substitution reaction involves the replacement of one ______ by another in a coordination complex.
3. Which of the following is an example of a redox reaction in complexes? a. $[Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{4-}$ b. $[Co(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{2+}$ c. Both a and b d. None of the above
4. Fill in the blank: Redox reactions in complexes involve changes in the ______ state of the central metal ion.
5. In acid-base reactions, metal ions in complexes act as: a. Lewis bases b. Lewis acids c. Neutral molecules d. None of the above

5.3 Technological And Biological Applications Of Complexes

5.3.1 Industrial applications (catalysis, metallurgy, materials)

Coordination complexes play a vital role in industry.

- **Catalysis**: Complexes such as [$PtCl_2(NH_3)_2$] are used in catalytic processes, including hydrogenation and polymerisation. Transition metal complexes often serve as catalysts because they can easily change oxidation states and coordinate with reactants.
- **Metallurgy**: Complexes are used in extraction and purification of metals. For example, cyanide complexes are employed in gold extraction.
- **Materials science**: Complexes contribute to the development of dyes, pigments, and advanced materials with specific optical or magnetic properties.

Fill in the blank: Transition metal complexes are widely used as ______ because they can change oxidation states easily.

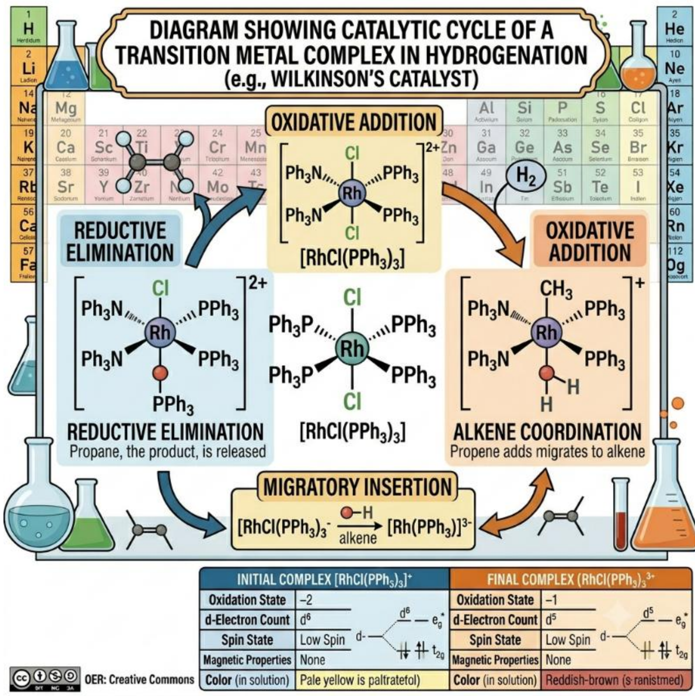


Figure 5.3: Catalytic role of coordination complexes.

5.3.2 Biological applications (metalloproteins, medicine)

Complexes are essential in biological systems:

- **Metalloproteins**: Haemoglobin contains an iron complex that binds oxygen, while chlorophyll contains a magnesium complex that captures light energy.
- **Medicine**: Complexes such as cisplatin are used in cancer treatment, while silver complexes have antimicrobial properties.
- **Nutrition**: Complexes of iron, zinc, and copper are vital for enzyme activity and metabolic processes.

Fill in the blank: Haemoglobin contains an ______ complex that binds oxygen in the blood.

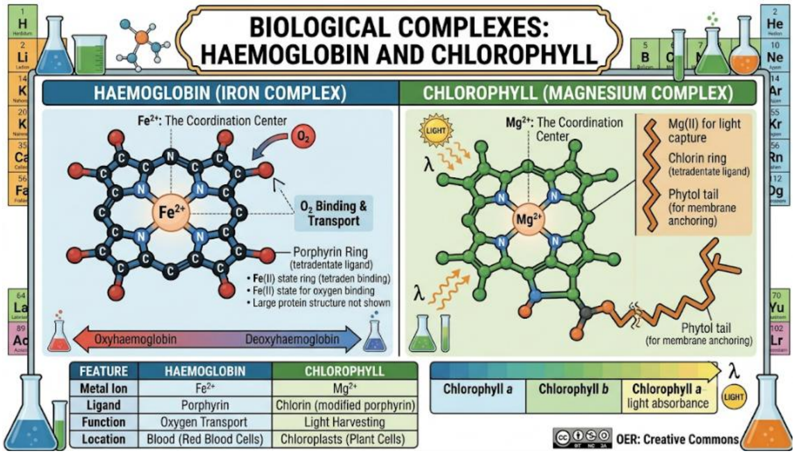


Plate 5.3: Biological importance of coordination complexes.

5.3.3 Environmental and technological relevance

Coordination complexes also have environmental and technological significance:

- **Environmental chemistry**: Complexes are used in water treatment, for example, chelating agents remove heavy metals from contaminated water.
- **Sensors and devices**: Complexes with specific optical or magnetic properties are used in sensors, batteries, and electronic devices.
- **Green chemistry**: Complexes are employed in sustainable catalytic processes that reduce waste and energy consumption.

Fill in the blank: Chelating agents are used in water treatment to remove ______ metals from contaminated water.

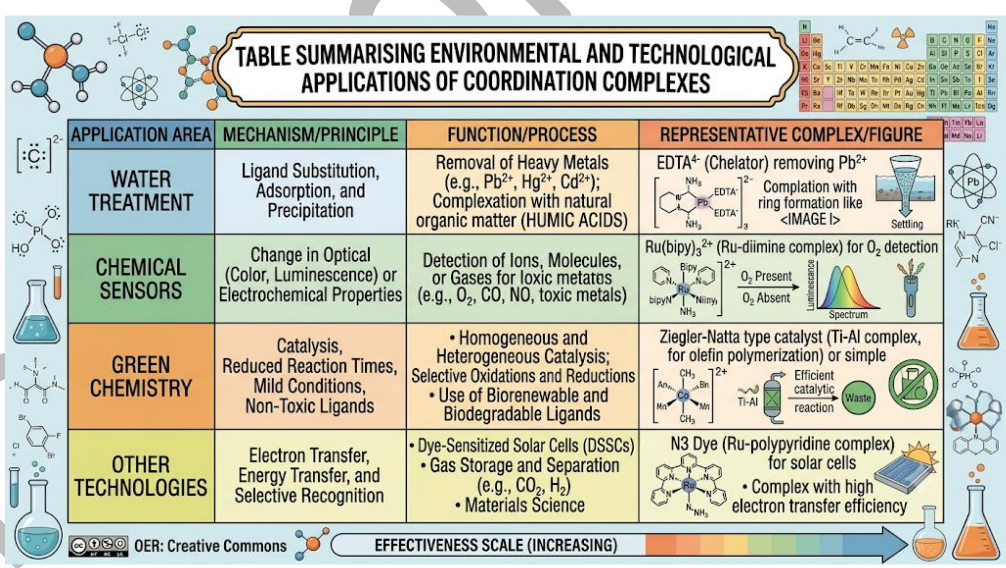


TABLE SUMMARISING ENVIRONMENTAL AND TECHNOLOGICAL APPLICATIONS OF COORDINATION COMPLEXES

APPLICATION AREA	MECHANISM/PRINCIPLE	FUNCTION/PROCESS	REPRESENTATIVE COMPLEX/FIGURE
WATER TREATMENT	Ligand Substitution, Adsorption, and Precipitation	Removal of Heavy Metals (e.g., Pb^{2+}, Hg^{2+}, Cd^{2+}); Complexation with natural organic matter (HUMIC ACIDS)	$EDTA^{4-}$ (Chelator) removing Pb^{2+}; Complation with ring formation like <IMAGE I>; Settling
CHEMICAL SENSORS	Change in Optical (Color, Luminescence) or Electrochemical Properties	Detection of Ions, Molecules, or Gases for loxic metatos (e.g., O_2, CO, NO, toxic metals)	$Ru(bipy)_3^{2+}$ (Ru-diimine complex) for O_2 detection; O_2 Present; O_2 Absent; Luminescence; Spectrum
GREEN CHEMISTRY	Catalysis, Reduced Reaction Times, Mild Conditions, Non-Toxic Ligands	• Homogeneous and Heterogeneous Catalysis; Selective Oxidations and Reductions • Use of Biorenewable and Biodegradable Ligands	Ziegler-Natta type catalyst (Ti-Al complex, for olefin polymerization) or simple; Ti-Al; Efficient catalytic reaction; Waste
OTHER TECHNOLOGIES	Electron Transfer, Energy Transfer, and Selective Recognition	• Dye-Sensitized Solar Cells (DSSCs) • Gas Storage and Separation (e.g., CO_2, H_2) • Materials Science	N3 Dye (Ru-polypyridine complex) for solar cells • Complex with high electron transfer efficiency

OER: Creative Commons
EFFECTIVENESS SCALE (INCREASING)

Box 5.3: Environmental and technological applications of complexes.

Pilot questions 5.3

1. Which of the following is an industrial application of coordination complexes? a. Catalysis b. Metallurgy c. Materials science d. All of the above
2. Fill in the blank: Transition metal complexes are widely used as ______ because they can change oxidation states easily.
3. Which of the following biological molecules contains a metal complex? a. Haemoglobin b. Chlorophyll c. Both a and b d. None of the above
4. Fill in the blank: Haemoglobin contains an ______ complex that binds oxygen in the blood.
5. Which of the following is an environmental application of complexes? a. Water treatment using chelating agents b. Use in sensors and devices c. Green chemistry processes d. All of the above

Series Summary

In this Series, we examined the **stability, reactivity, and applications of coordination complexes**. We began with stability, distinguishing between thermodynamic stability, which depends on energy favourability, and kinetic stability, which relates to the rate of ligand substitution. We then explored the factors influencing stability, including the nature of the metal ion, ligand strength, chelate effect, and steric hindrance. Next, we studied the reactions of complexes, focusing on substitution, redox, and acid–base processes. Finally, we considered the technological and biological applications of complexes, highlighting their roles in catalysis, metallurgy, medicine, nutrition, and environmental chemistry. Altogether, this Series has shown how coordination complexes are not only scientifically fascinating but also practically indispensable in industry, biology, and technology.

Glossary of Terms

- **Thermodynamic stability**: The favourability of complex formation based on energy considerations.
- **Stability constant (K)**: A numerical measure of the equilibrium between a complex and its dissociated ions.
- **Kinetic stability**: The resistance of a complex to ligand substitution reactions.
- **Inert complex**: A complex that resists substitution reactions.
- **Labile complex**: A complex that undergoes substitution reactions rapidly.
- **Substitution reaction**: Replacement of one ligand by another in a complex.

- **Redox reaction**: A reaction involving a change in the oxidation state of the central metal ion.
- **Acid–base reaction**: Interaction where metal ions act as Lewis acids and ligands act as Lewis bases.
- **Chelate effect**: Increased stability of complexes formed with multidentate ligands.
- **Metalloproteins**: Proteins containing metal complexes, such as haemoglobin and chlorophyll.
- **Cisplatin**: A platinum-based complex used in cancer treatment.

Concept Check Questions 5

Objective questions

1. Thermodynamic stability of a complex is often expressed using the ______ constant. (Linked to SLO 5.1)
2. A complex that resists substitution reactions is described as kinetically ______. (Linked to SLO 5.1)
3. Substitution reactions involve the replacement of one ______ by another in a coordination complex. (Linked to SLO 5.3)
4. Redox reactions in complexes involve changes in the ______ state of the central metal ion. (Linked to SLO 5.4)
5. Haemoglobin contains an ______ complex that binds oxygen in the blood. (Linked to SLO 5.7)

Short-answer questions

6. Explain the difference between thermodynamic and kinetic stability of complexes. (Linked to SLO 5.1)

7. Describe how substitution reactions occur in coordination chemistry with an example. (Linked to SLO 5.3)

8. Explain the role of redox reactions in biological systems involving complexes. (Linked to SLO 5.4)

9. Discuss the acid–base behaviour of complexes using Lewis theory. (Linked to SLO 5.5)

Long-answer questions

10. Analyse the factors influencing stability of complexes, including the chelate effect and steric hindrance. (Linked to SLO 5.2)

11. Evaluate the industrial and biological applications of coordination complexes, with examples from catalysis and medicine. (Linked to SLO 5.6, 5.7)

12. Assess the environmental and technological relevance of complexes in water treatment, sensors, and green chemistry. (Linked to SLO 5.8)

Answers To Pilot Questions 5

Part 5.1: 1.b, 2.stability, 3.b, 4.inert, 5.d **Part 5.2**: 1.a, 2.ligand, 3.c, 4.oxidation, 5.b **Part 5.3**: 1.d, 2.catalysts, 3.c, 4.iron, 5.d

References And Attributions 5

- Figures 5.1–5.3: Suggested AI prompts for diagrams showing equilibrium stability, substitution reactions, and catalytic cycles.
- Plates 5.1–5.3: Suggested AI prompts for images comparing inert vs labile complexes, redox reactions, and biological complexes.
- Boxes 5.1–5.3: Suggested AI prompts for tables summarising stability factors, acid–base behaviour, and environmental applications.
- Open Educational Resources (OER) suggested search strings:
    - "OER diagram thermodynamic stability coordination complexes"
    - "OER image kinetic stability inert labile complexes"
    - "OER diagram ligand substitution coordination chemistry"
    - "OER image redox reactions coordination complexes"
    - "OER table acid-base reactions coordination complexes"
    - "OER image haemoglobin chlorophyll coordination complexes"
    - "OER table environmental technological applications coordination complexes"
- Attribution style: APA (institutional standard assumed). Example: OpenStax. (2016). *Chemistry*. OpenStax CNX. Retrieved from https://openstax.org/books/chemistry