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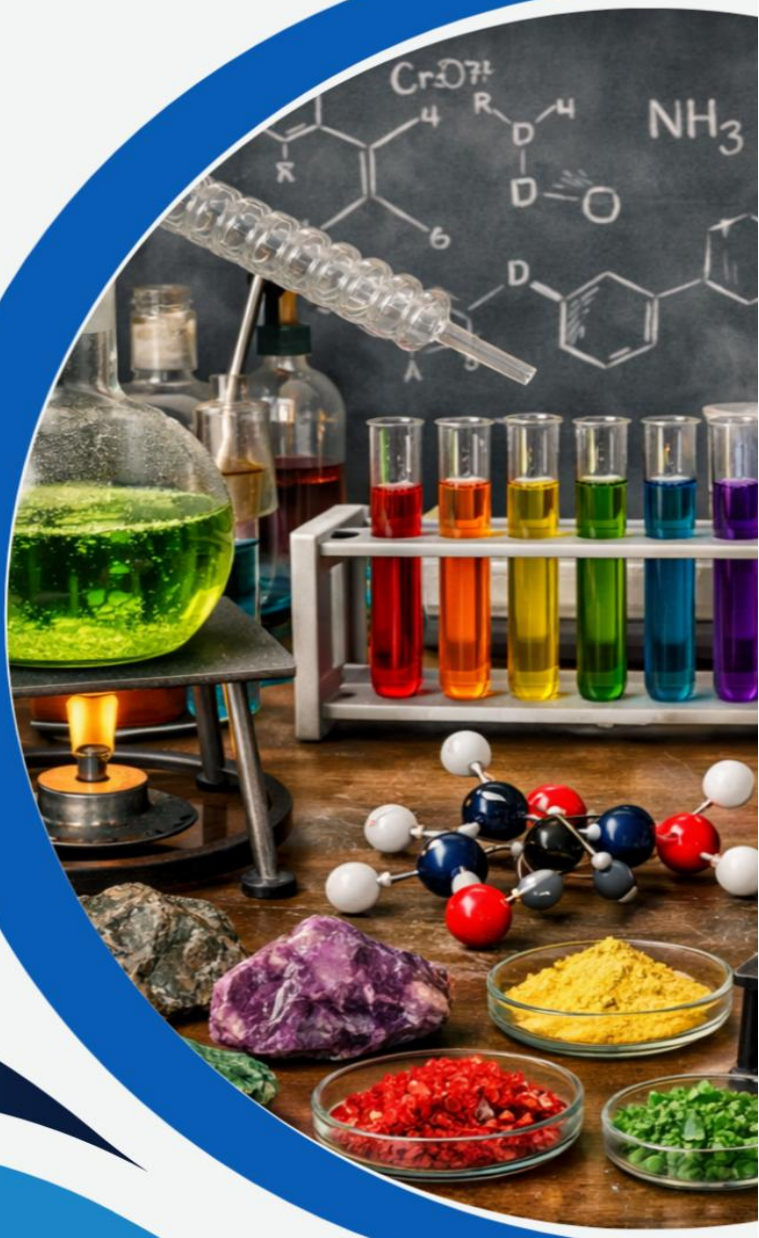
CHM212

INORGANIC CHEMISTRY I



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Course code: CHM 212

Course title: Inorganic Chemistry I

Course Unit: 2 Units C: LH 30

Series 1: Chemistry of First-Row Transition Metals

Series 2: Coordination Chemistry and Crystal Field Theory

Series 3: Comparative Chemistry of Selected Main Group Elements

Series 4: Fundamentals of Organometallic Chemistry

Series 5: Roles of Metals in Biochemical Systems and Redox Concepts

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Suggested Outline

Part 1.1: Introduction to First-Row Transition Metals

Sub-Part 1.1.1: Position in the periodic table and general characteristics
Sub-Part 1.1.2: Common oxidation states and variable valency
Sub-Part 1.1.3: General physical and chemical properties

Part 1.2: Electronic Configurations and Magnetic Properties

Sub-Part 1.2.1: d-orbital occupancy and electronic structures
Sub-Part 1.2.2: Magnetic behaviour and paramagnetism
Sub-Part 1.2.3: Trends across the first-row transition series

Part 1.3: Coordination and Complex Formation

Sub-Part 1.3.1: Nature of transition metal complexes
Sub-Part 1.3.2: Examples of common coordination compounds
Sub-Part 1.3.3: Importance in industrial and biological systems

Part 1.4: Applications and Significance of Transition Metals

Sub-Part 1.4.1: Catalytic roles in industry
Sub-Part 1.4.2: Use in materials and alloys
Sub-Part 1.4.3: Biological importance of selected transition metals

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Introduction

Transition metals are often described as the workhorses of inorganic chemistry because of their wide-ranging properties and applications. The first-row transition metals, stretching from scandium to zinc, are particularly important as they display variable oxidation states, form colourful compounds, and play key roles in catalysis and biological systems. By studying them, you will gain insight into the fundamental principles that underpin much of modern chemistry, from industrial processes to materials science.

The aim of this Series is to introduce you to the chemistry of the first-row transition metals, focusing on their structures, properties, and applications. It is designed to help you appreciate how these elements behave and why they are so significant in both theoretical and practical contexts.

We shall commence this Series by examining the position of the first-row transition metals in the periodic table, their general characteristics, and their common oxidation states. Next, we will explore their electronic configurations and magnetic properties, paying attention to trends across the series. Following that, we will consider their ability to form coordination compounds and complexes, with examples drawn from industry and biology. Finally, we will wrap up by discussing their applications, including their catalytic roles, use in alloys, and biological importance, thereby rounding off a comprehensive overview of this fascinating group of elements.

Series Learning Outcomes

Upon completing this Series, you should be able to:

SLO 1.1 define the position and general characteristics of the first-row transition metals in the periodic table,
SLO 1.2 explain the common oxidation states and variable valency of first-row transition metals,
SLO 1.3 analyse the electronic configurations and magnetic properties of first-row transition metals,
SLO 1.4 describe the trends in physical and chemical properties across the first-row transition series,
SLO 1.5 illustrate the nature of coordination and complex formation in first-row transition metals with relevant examples, and
SLO 1.6 evaluate the industrial, material, and biological applications of first-row transition metals.

1.1 Introduction to First-Row Transition Metals

1.1.1 Position in the periodic table and general characteristics

The **first-row transition metals** are the elements from scandium (Sc) to zinc (Zn) in the periodic table. They are located in period 4 and occupy the d-block, meaning their distinguishing feature is the gradual filling of the 3d orbitals. These elements are known for their ability to form coloured compounds, exhibit variable oxidation states, and act as catalysts in chemical reactions. Their position in the periodic table makes them a bridge between the s-block and p-block elements, displaying properties of both metals and non-metals.

Fill in the blank: The first-row transition metals occupy the _____ block of the periodic table.

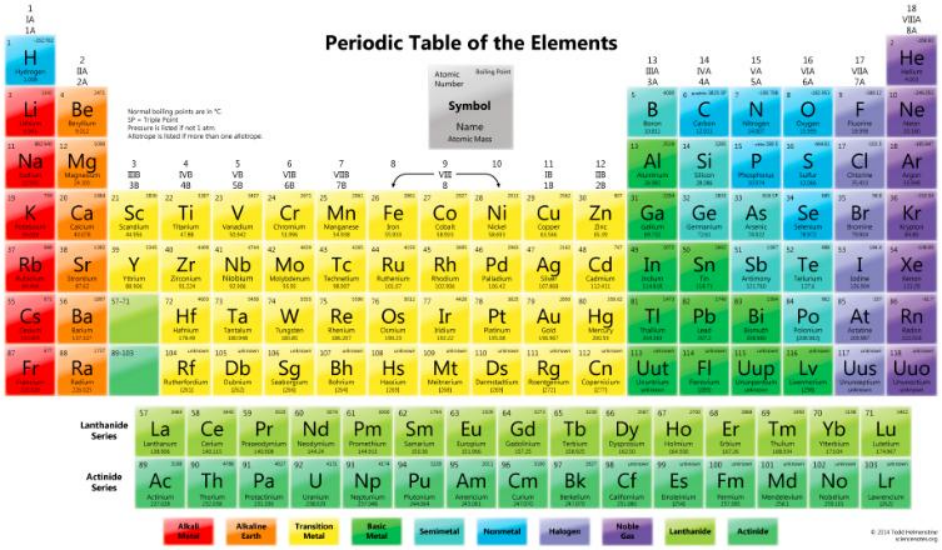

Figure 1.1: Position of first-row transition metals in the periodic table

1.1.2 Common oxidation states and variable valency

A defining feature of transition metals is their ability to exhibit **variable oxidation states**, which means they can lose different numbers of electrons depending on the chemical environment. For example, iron can exist as Fe^{2+} or Fe^{3+}, while **manganese** can show oxidation states ranging from +2 to +7. This variability arises from the close energy levels of the 3d and 4s orbitals, allowing electrons to be removed from both.

Fill in the blank: The variability in oxidation states of transition metals arises because the _____ and _____ orbitals have similar energy levels.

Element	Symbol	Atomic Number	Common Oxidation States	Most Stable/Frequent
Scandium	Sc	21	+3	+3
Titanium	Ti	22	+2, +3, +4	+4
Vanadium	V	23	+2, +3, +4, +5	+4, +5
Chromium	Cr	24	+2, +3, +6	+3, +6
Manganese	Mn	25	+2, +3, +4, +6, +7	+2, +4, +7
Iron	Fe	26	+2, +3	+2, +3
Cobalt	Co	27	+2, +3	+2
Nickel	Ni	28	+2, +3	+2
Copper	Cu	29	+1, +2	+2
Zinc	Zn	30	+2	+2

Table 1.1: Common oxidation states of selected first-row transition metals

1.1.3 General physical and chemical properties

The first-row transition metals share several **physical properties**, such as high melting points, high densities, and metallic lustre. Their **chemical properties** include the ability to form complexes, catalytic activity, and the tendency to produce compounds with vivid colours. For instance, **copper(II) sulphate** is bright blue, while **chromium(III) chloride** is green.

These properties make them essential in both industrial and biological contexts. Their catalytic behaviour is exploited in processes such as the Haber process (iron catalyst) and the Contact process (vanadium catalyst). Biologically, transition metals are found in enzymes and proteins that sustain life.

Fill in the blank: The colourful nature of transition metal compounds is often due to _____ electronic transitions.

Plate 1.1: Colourful compounds of first-row transition metals

Pilot questions 1.1

The first-row transition metals occupy the _____ block of the periodic table.

A. s-block
B. p-block
C. d-block
D. f-block

Which oxidation states are most common for iron?

A. +1 and +2
B. +2 and +3
C. +3 and +4
D. +4 and +5

The variability in oxidation states of transition metals arises because the _____ and _____ orbitals have similar energy levels.

A. 2p and 3p
B. 3d and 4s
C. 4p and 5s
D. 3s and 3p

The colourful nature of transition metal compounds is often due to _____ electronic transitions.

A. s–p
B. p–d
C. d–d
D. f–d

Which property is typical of first-row transition metals compared to s-block elements?

A. Low melting points

B. Softness
C. High density and hardness
D. Lack of catalytic activity

1.2 Electronic Configurations and Magnetic Properties

1.2.1 d-orbital occupancy and electronic structures

The **electronic configuration** of an element describes the arrangement of its electrons in orbitals. For the **first-row transition metals**, the distinguishing electrons enter the **3d orbitals** after the 4s orbital has been filled. For example, **scandium (Sc)** has the configuration [Ar] $3d^1$ $4s^2$, while **zinc (Zn)** has [Ar] $3d^{10}$ $4s^2$.

Because the 3d and 4s orbitals are close in energy, electrons can be lost from either, leading to the variable oxidation states typical of transition metals. This flexibility in electron occupancy is the foundation of their rich chemistry.

Fill in the blank: The first-row transition metals are characterised by the gradual filling of the _____ orbitals.

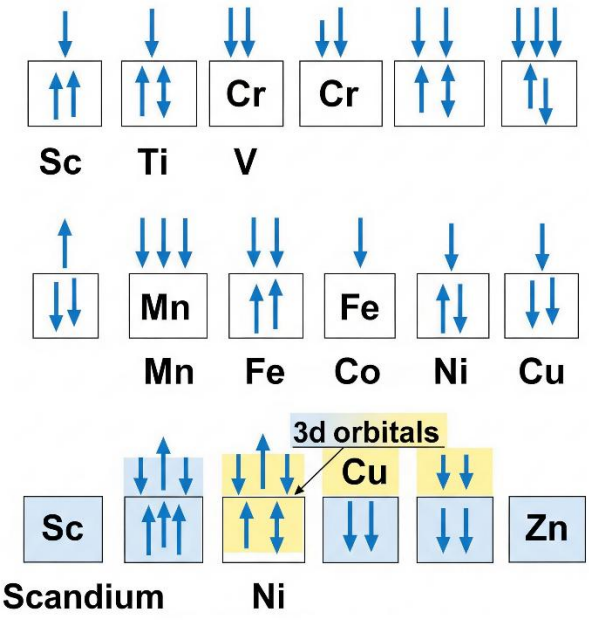

Figure 1.2: Progressive filling of 3d orbitals in first-row transition metals

1.2.2 Magnetic behaviour and paramagnetism

The **magnetic properties** of transition metals depend on the presence of **unpaired electrons** in their d-orbitals. A substance with unpaired electrons exhibits **paramagnetism**, meaning it is weakly attracted to a magnetic field. Conversely, if all d-orbitals are paired, the substance is **diamagnetic**, showing weak repulsion from a magnetic field.

For example, **manganese(II)** with a $3d^5$ configuration has five unpaired electrons and is strongly paramagnetic, while **zinc(II)** with a $3d^{10}$ configuration has no unpaired electrons and is diamagnetic.

Fill in the blank: Transition metals with completely filled d-orbitals, such as zinc, are described as _____.

Electronic Configuration and Magnetic Properties (Sc to Zn)

Element	Symbol	Atomic Number	Electronic Configuration	Unpaired Electrons	Magnetic Behavior
Scandium	Sc	21	[Ar]$3d^1 4s^2$	1	Paramagnetic
Titanium	Ti	22	[Ar]$3d^2 4s^2$	2	Paramagnetic
Vanadium	V	23	[Ar]$3d^3 4s^2$	3	Paramagnetic
Chromium	Cr	24	[Ar]$3d^5 4s^1$	6	Strongly Paramagnetic
Manganese	Mn	25	[Ar]$3d^5 4s^2$	5	Paramagnetic
Iron	Fe	26	[Ar]$3d^6 4s^2$	4	Ferromagnetic / Paramagnetic
Cobalt	Co	27	[Ar]$3d^7 4s^2$	3	Ferromagnetic / Paramagnetic
Nickel	Ni	28	[Ar]$3d^8 4s^2$	2	Ferromagnetic / Paramagnetic
Copper	Cu	29	[Ar]$3d^{10} 4s^1$	1	Paramagnetic
Zinc	Zn	30	[Ar]$3d^{10} 4s^2$	0	Diamagnetic

Table 1.2: Magnetic behaviour of selected first-row transition metals

Element	Electronic configuration	Magnetic behaviour
Sc	[Ar] $3d^1 4s^2$	Paramagnetic
Mn	[Ar] $3d^5 4s^2$	Strongly paramagnetic
Fe	[Ar] $3d^6 4s^2$	Paramagnetic
Cu	[Ar] $3d^{10} 4s^1$	Weakly paramagnetic
Zn	[Ar] $3d^{10} 4s^2$	Diamagnetic

1.2.3 Trends across the first-row transition series

Across the series from Sc to Zn, several **trends** can be observed:

Number of unpaired electrons increases from Sc to Mn, then decreases towards Zn.

Magnetic moment follows this trend, peaking around Mn(II).

Stability of oxidation states varies, with early elements favouring higher oxidation states and later ones favouring lower states.

Colour of compounds is linked to d-d electron transitions, which depend on the number of d electrons and the ligand environment.

These trends help explain why transition metals show such diverse chemistry and why their compounds are often vividly coloured and magnetically active.

Fill in the blank: The transition metal with the highest magnetic moment in the first row is _____.

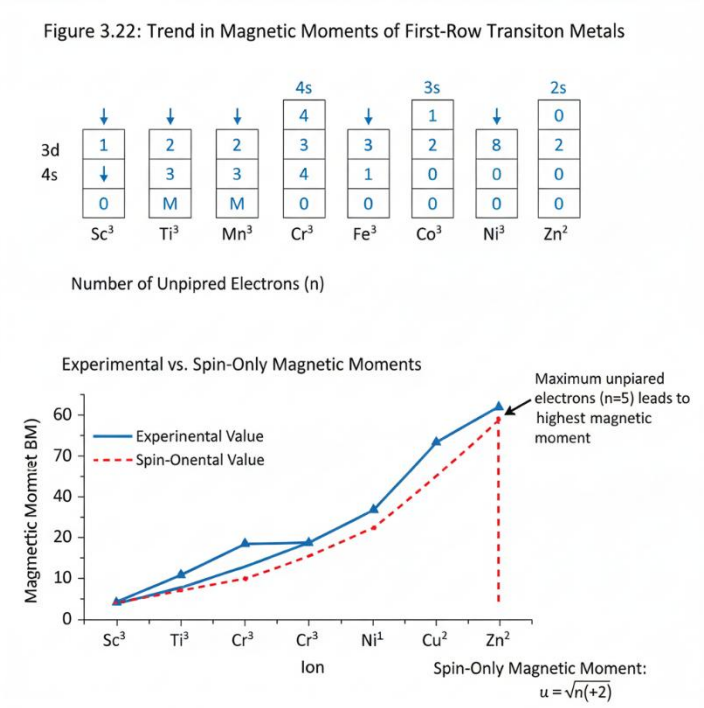

Plate 1.2: Magnetic moment trend across the first-row transition metals

Pilot questions 1.2

The first-row transition metals are characterised by the gradual filling of the _____ orbitals.

A. 2p
B. 3d
C. 4p
D. 4f

Transition metals with completely filled d-orbitals, such as zinc, are described as _____.

A. Paramagnetic
B. Diamagnetic

C. Ferromagnetic
D. Antimagnetic

Which element in the first-row transition metals has the highest magnetic moment?
A. Scandium
B. Iron
C. Manganese
D. Zinc

The magnetic properties of transition metals arise from the presence of _____ in the d-orbitals.
A. Paired electrons
B. Unpaired electrons
C. Empty orbitals
D. Hybridised orbitals

Copper, with the configuration [Ar] $3d^{10}$ $4s^{1}$, is described as _____ paramagnetic.
A. Strongly
B. Weakly
C. Not
D. Diamagnetic

1.3 Coordination and Complex Formation

1.3.1 Nature of transition metal complexes

A **complex** is a chemical species formed when a central **transition metal ion** binds to surrounding molecules or ions called **ligands**. A **ligand** is any species that donates a pair of electrons to the metal ion, forming a coordinate bond. Common ligands include water, ammonia, and chloride ions.

Complexes are important because they explain many of the unique properties of transition metals, such as their colours, magnetic behaviour, and ability to act as catalysts. The geometry of a complex (for example octahedral, tetrahedral, or square planar) depends on the number and type of ligands attached to the metal.

Fill in the blank: The molecules or ions that donate electron pairs to a central metal ion in a complex are called _____.

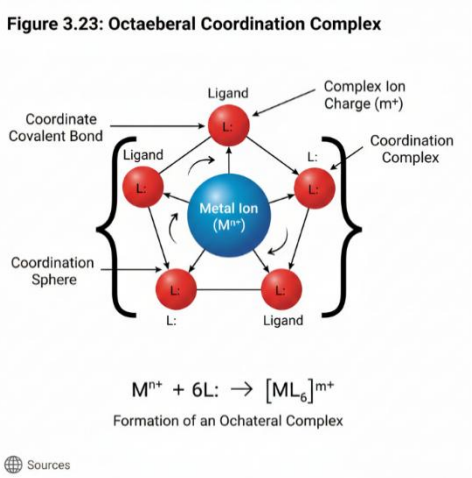

Figure 1.3: General structure of a transition metal complex

1.3.2 Examples of common coordination compounds

Transition metals form a wide variety of coordination compounds. For instance, **$[Cu(H_2O)_6]^{2+}$** is a simple hydrated copper(II) complex, while **$[Fe(CN)_6]^{3-}$** is a hexacyanoferrate(III) complex. These compounds often display vivid colours due to **d-d transitions**, where electrons move between d-orbitals of different energies in the presence of ligands.

The stability of complexes depends on factors such as the charge on the metal ion, the nature of the ligands, and the geometry of the complex. Chelating ligands, such as **ethylenediamine**, form more stable complexes because they bind through multiple donor atoms.

Fill in the blank: The deep blue colour of aqueous copper(II) sulphate solution is due to the formation of the _____ complex.

Common Coordination Compounds and Their Colours

Metal	Example Complex Ion	IUPAC Name	Observed Colour
Scandium (Sc)	$[Sc(H_2O)_6]^{3+}$	Hexaaquascandium(III)	Colourless (d^0)
Titanium (Ti)	$[Ti(H_2O)_6]^{3+}$	Hexaaquatitanium(III)	Purple/Violet
Vanadium (V)	$[V(H_2O)_6]^{2+}$	Hexaaquavanadium(II)	Violet
	$[V(H_2O)_6]^{3+}$	Hexaaquavanadium(III)	Blue-green
	$[VO(H_2O)_5]^{2+}$	Pentaaquavanadyl(IV)	Blue
Chromium (Cr)	$[Cr(H_2O)_6]^{3+}$	Hexaaquachromium(III)	Green/Violet
	$[Cr(NH_3)_6]^{3+}$	Hexaamminechromium(III)	Purple
Manganese (Mn)	$[Mn(H_2O)_6]^{2+}$	Hexaaquamanganese(II)	Pale Pink

Table 1.3: Examples of common coordination compounds of first-row transition metals

Compound	Complex formed	Colour
$CuSO_4$ (aq)	$[Cu(H_2O)_4]^{2+}$	Blue
$FeCl_3$ (aq)	$[Fe(H_2O)_6]^{3+}$	Yellow
$K_3[Fe(CN)_6]$	$[Fe(CN)_6]^{3-}$	Orange-red
$Ni(NH_3)_6Cl_2$	$[Ni(NH_3)_6]^{2+}$	Violet

1.3.3 Importance in industrial and biological systems

Complex formation is central to both industry and biology. In industry, complexes are used as **catalysts**, such as **$[PtCl_2(NH_3)_2]$** in hydrogenation reactions. In biology, complexes are vital for life: **haemoglobin** is an iron complex that transports oxygen in blood, while **chlorophyll** is a magnesium complex that enables photosynthesis.

These examples show how coordination chemistry bridges inorganic chemistry with real-world applications. Understanding complexes helps explain why transition metals are indispensable in technology, medicine, and the environment.

Fill in the blank: The iron-containing complex responsible for oxygen transport in blood is called _____.

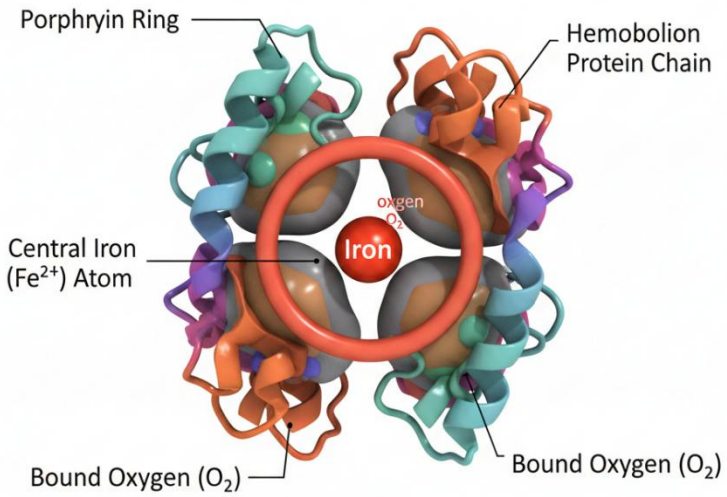

Plate 1.3: Biological importance of transition metal complexes

Pilot questions 1.3

The molecules or ions that donate electron pairs to a central metal ion in a complex are called _____.

A. Bases
B. Ligands
C. Catalysts
D. Radicals

The deep blue colour of aqueous copper(II) sulphate solution is due to the formation of the _____ complex.

A. $[CuCl_4]^{2-}$
B. $[Cu(H_2O)_4]^{2+}$
C. $[Cu(NH_3)_6]^{2+}$
D. $[Cu(CN)_4]^{2-}$

Which of the following is an example of a hexacyanoferrate complex?

A. $[Fe(H_2O)_6]^{3+}$
B. $[Fe(CN)_6]^{3-}$
C. $[FeCl_4]^{2-}$
D. $[Fe(NH_3)_6]^{2+}$

The chemotherapy drug cisplatin has the formula _____.

A. $[PtCl_4]^{2-}$
B. $[PtCl_2(NH_3)_2]$
C. $[Pt(NH_3)_4]^{2+}$
D. $[PtCl_6]^{2-}$

The iron-containing complex responsible for oxygen transport in blood is called _____.

A. Myoglobin
B. Haemoglobin
C. Chlorophyll
D. Cytochrome

1.4 Applications and Significance of Transition Metals

1.4.1 Catalytic roles in industry

Transition metals are widely used as **catalysts**, which are substances that increase the rate of a chemical reaction without being consumed. Their ability to adopt multiple **oxidation states** and form complexes makes them ideal for facilitating reactions. For example, **iron** is used in the Haber process to synthesise ammonia, while **vanadium(V) oxide** acts as a catalyst in the Contact process for producing sulphuric acid.

Catalysts lower the activation energy of reactions, making industrial processes more efficient and cost-effective. This is one of the reasons transition metals are indispensable in modern chemical industries.

Fill in the blank: The Haber process for ammonia production uses _____ as a catalyst.

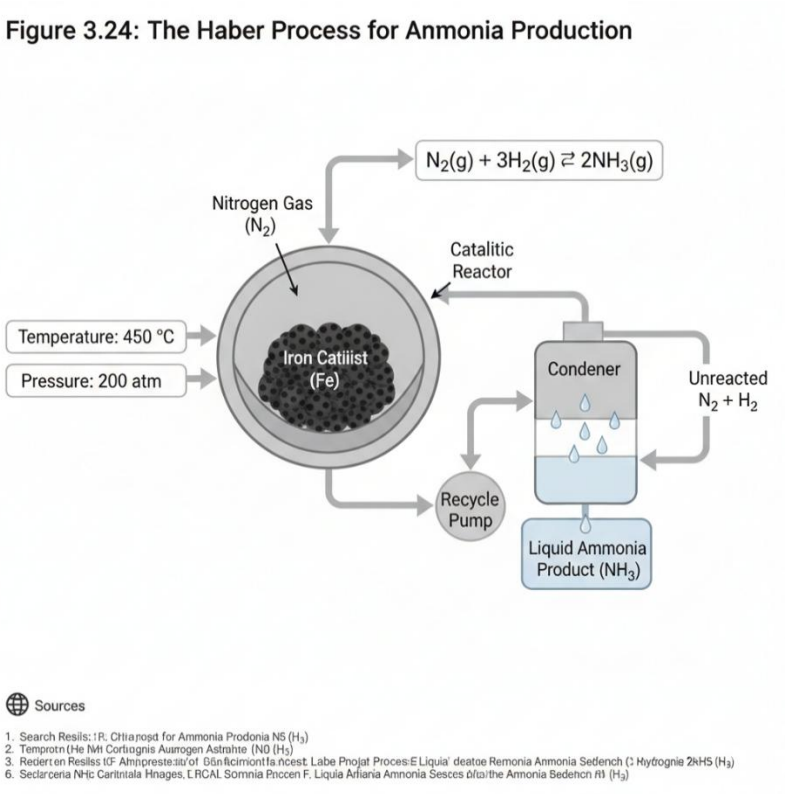

Figure 1.4: Catalytic role of iron in the Haber process

1.4.2 Use in materials and alloys

Transition metals are essential in the production of **alloys**, which are mixtures of metals designed to improve strength, durability, or resistance to corrosion. For example, **steel** is an alloy of iron and carbon, often enhanced with chromium or nickel to produce stainless steel. **Copper alloys**, such as bronze and brass, have been used for centuries in tools, coins, and decorative items.

The versatility of transition metals in alloy formation arises from their ability to form metallic bonds with other elements, resulting in materials with tailored properties for specific applications.

Fill in the blank: Stainless steel is an alloy of iron with _____ and _____.

Alloy	Principal Transition Metals	Other Components	Key Applications
Steel	Iron (Fe)	Carbon (C)	Construction, infrastructure, automobiles, and machinery.
Stainless Steel	Iron, Chromium (Cr), Nickel (Ni)	Carbon, Manganese	Cutlery, surgical instruments, kitchen appliances, and watches.
Brass	Copper (Cu), Zinc (Zn)	—	Musical instruments, plumbing fittings, and decorative items.
Bronze	Copper (Cu)	Tin (Sn)	Statues, medals, ship propellers, and bells.
Cupronickel	Copper (Cu), Nickel (Ni)	—	Marine engineering (corrosion resistance) and silver-coloured coinage.
Nichrome	Nickel (Ni), Chromium (Cr)	—	Heating elements in toasters, ovens, and hair dryers.

Table 1.4: Common alloys of transition metals and their uses

Alloy	Composition	Application
Steel	Iron + carbon	Construction, machinery
Stainless steel	Iron + chromium + nickel	Kitchenware, medical tools
Bronze	Copper + tin	Sculptures, coins
Brass	Copper + zinc	Musical instruments, fittings

1.4.3 Biological importance of selected transition metals

Transition metals also play vital roles in biological systems. **Iron** is central to haemoglobin, enabling oxygen transport in blood. **Copper** is found in enzymes such as cytochrome oxidase, which is essential for cellular respiration. **Zinc** is a cofactor in many enzymes, including those involved in DNA replication and protein synthesis.

These biological functions highlight the significance of transition metals beyond industry, showing how they are essential for life itself.

Fill in the blank: The transition metal at the centre of haemoglobin responsible for oxygen transport is _____.

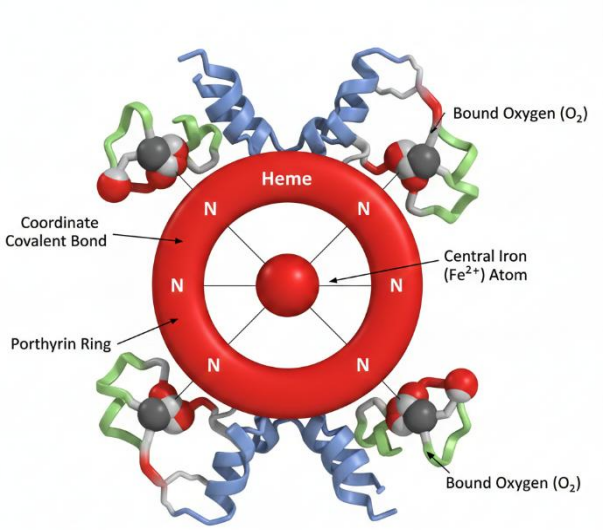

Figure 3.25: The Structure of Haumoloban with Iron-Porfhyrin Complex

Plate 1.4: Biological importance of transition metals

Pilot questions 1.4

The Haber process for ammonia production uses _____ as a catalyst.

A. Nickel
B. Iron
C. Copper
D. Zinc

Stainless steel is an alloy of iron with _____ and _____.

A. Carbon and copper
B. Chromium and nickel
C. Tin and zinc
D. Aluminium and magnesium

Which transition metal is central to haemoglobin and responsible for oxygen transport?

A. Copper
B. Zinc
C. Iron
D. Nickel

Vanadium(V) oxide is used as a catalyst in the _____ process.

A. Haber process
B. Contact process
C. Ostwald process
D. Solvay process

Brass is an alloy of copper and _____.

A. Tin
B. Zinc

C. Nickel
D. Carbon

Series Summary

Series Summary

This Series has introduced you to the chemistry of the first-row transition metals, emphasising their relevance in both scientific study and real-world applications. You began by considering their position in the periodic table and general characteristics, then explored how they exhibit common oxidation states and variable valency. From there, you analysed their electronic configurations and magnetic properties, before moving on to coordination and complex formation with illustrative examples. Finally, you examined their wide-ranging applications, including catalytic roles in industry, the development of alloys, and their essential biological functions.

By completing this Series, you should now be able to **define** the position and characteristics of the first-row transition metals (SLO 1.1), **explain** their oxidation states and variable valency (SLO 1.2), **analyse** their electronic structures and magnetic behaviour (SLO 1.3), **describe** trends in their physical and chemical properties (SLO 1.4), **illustrate** the principles of coordination and complex formation (SLO 1.5), and **evaluate** their industrial, material, and biological significance (SLO 1.6). These outcomes provide you with a strong foundation for understanding transition metal chemistry and applying it confidently in both academic and practical contexts.

Glossary of Terms

Alloy: A mixture of metals, or a metal combined with another element, designed to improve properties such as strength, durability, or resistance to corrosion.

Catalyst: A substance that increases the rate of a chemical reaction without being consumed, often by lowering the activation energy required.

Complex: A chemical species formed when a central transition metal ion binds to surrounding molecules or ions called ligands through coordinate bonds.

Coordination compound: A compound consisting of a transition metal ion bonded to ligands, often displaying distinctive colours and properties.

d-orbital: One of the five orbitals in the d subshell, which can hold up to ten electrons and is responsible for many of the unique properties of transition metals.

Diamagnetism: A weak repulsion from a magnetic field observed in substances where all electrons are paired.

Ligand: A molecule or ion that donates a pair of electrons to a transition metal ion, forming a coordinate bond.

Oxidation state: The number that represents how many electrons an atom has lost, gained, or shared in a compound; transition metals often show variable oxidation states.

Paramagnetism: A weak attraction to a magnetic field observed in substances with unpaired electrons.

Transition metal: An element that forms at least one stable ion with a partially filled d subshell, typically found in the central block of the periodic table.

Valency (variable valency): The ability of an element, especially transition metals, to exhibit different oxidation states depending on the chemical environment.

Zaitsev's rule: A principle stating that in elimination reactions, the more substituted alkene is usually formed as the major product.

Concept Check Questions [Series 1]

Objective Questions

Which of the following elements marks the beginning of the first-row transition metals?
A. Calcium
B. Scandium
C. Titanium
D. Zinc
(Linked to SLO 1.1)

Transition metals often exhibit variable _____, allowing them to form compounds in different oxidation states.
(Linked to SLO 1.2)

A transition metal ion with unpaired d-electrons will most likely show:
A. Diamagnetism
B. Paramagnetism
C. No magnetic behaviour
D. Metallic bonding only
(Linked to SLO 1.3)

Short-Answer Questions

Explain why manganese can display oxidation states ranging from +2 to +7.
(Linked to SLO 1.2)

State one industrial process that uses a transition metal catalyst and identify the metal involved.
(Linked to SLO 1.6)

What is a ligand, and why are ligands important in the formation of transition metal complexes?
(Linked to SLO 1.5)

Long-Answer Questions

Analyse the relationship between electronic configuration and magnetic properties across the first-row transition metals. Provide examples to illustrate your explanation.
(Linked to SLO 1.3)

Evaluate the significance of transition metals in both industrial and biological contexts, highlighting at least two examples from each area.
(Linked to SLO 1.6)

Answers to Concept Check Questions [Series 1]

Objective Questions

B. Scandium
Oxidation states
B. Paramagnetism

Short-Answer Questions

Manganese has both 3d and 4s electrons available for bonding, allowing it to lose different numbers of electrons depending on the chemical environment.
The Haber process uses iron as a catalyst to produce ammonia.
A ligand is a molecule or ion that donates a pair of electrons to a metal ion, forming a coordinate bond. Ligands are important because they stabilise complexes and influence their geometry and properties.

Long-Answer Questions

Question 1

Basic response: The magnetic properties of transition metals depend on the number of unpaired d-electrons. For example, Mn^{2+} with five unpaired electrons is strongly paramagnetic, while Zn^{2+} with a full d^{10} configuration is diamagnetic.
Value-added response: Beyond Series knowledge, learners may note that the magnetic moment can be calculated using the spin-only formula, and that ligand field effects can alter magnetic behaviour by pairing electrons in certain complexes.

Question 2

Basic response: Transition metals are significant in industry because they act as catalysts, such as iron in the Haber process and vanadium(V) oxide in the Contact process. Biologically, iron in haemoglobin transports oxygen, and zinc acts as a cofactor in enzymes.
Value-added response: Outstanding learners may add that transition metals are also used in advanced materials such as superconductors and in medical applications like cisplatin (a platinum complex used in cancer therapy). They may also highlight environmental roles, such as copper in photosynthetic electron transport.

Answers to Pilot Questions [Series 1]

Part 1.1

C. d-block
B. +2 and +3
B. 3d and 4s
C. d-d
C. High density and hardness

Part 1.2

B. 3d
B. Diamagnetic
C. Manganese
B. Unpaired electrons
C. Not

Part 1.3

B. Ligands
B. $[Cu(H_2O)_4]^{2+}$
B. $[Fe(CN)_6]^{3-}$
B. $[PtCl_2(NH_3)_2]$
B. Haemoglobin

Part 1.4

B. Iron
B. Chromium and nickel
C. Iron
B. Contact process
B. Zinc

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Skoog, D. A., Holler, F. J., & Crouch, S. R. (2014). *Fundamentals of Analytical Chemistry* (9th ed.). Cengage Learning.

Illustrations (Figures, Plates, Tables, Boxes)

Figure 1.1 Position of first-row transition metals in the periodic table

AI prompt: "Generate a labelled periodic table highlighting the first-row transition metals

from Sc to Zn."
Search string: "periodic table first-row transition metals diagram OER"

Table 1.1 Common oxidation states of selected first-row transition metals
AI prompt: "Generate a table showing common oxidation states of first-row transition metals from Sc to Zn."
Search string: "oxidation states of first-row transition metals table OER"

Plate 1.1 Colourful compounds of first-row transition metals
AI prompt: "Create an image showing colourful solutions of transition metal compounds such as copper sulphate and potassium dichromate."
Search string: "colourful transition metal compounds solutions OER"

Figure 1.2 Progressive filling of 3d orbitals in first-row transition metals
AI prompt: "Generate a labelled diagram showing the progressive filling of 3d orbitals from Sc to Zn."
Search string: "electronic configuration first-row transition metals diagram OER"

Table 1.2 Magnetic behaviour of selected first-row transition metals
AI prompt: "Generate a table showing electronic configurations and magnetic behaviour of selected first-row transition metals."
Search string: "magnetic properties first-row transition metals table OER"

Plate 1.2 Magnetic moment trend across the first-row transition metals
AI prompt: "Create an image showing the trend in magnetic moments across the first-row transition metals from Sc to Zn."
Search string: "magnetic moment trend first-row transition metals OER"

Figure 1.3 General structure of a transition metal complex
AI prompt: "Generate a labelled diagram showing a transition metal ion surrounded by ligands forming a coordination complex."
Search string: "transition metal complex diagram OER"

Table 1.3 Examples of common coordination compounds of first-row transition metals
AI prompt: "Generate a table showing examples of common coordination compounds of first-row transition metals with their colours."
Search string: "examples of coordination compounds transition metals OER"

Plate 1.3 Biological importance of transition metal complexes
AI prompt: "Create an image showing the haemoglobin molecule with iron at the centre of the porphyrin ring."
Search string: "haemoglobin iron complex structure OER"

Figure 1.4 Catalytic role of iron in the Haber process
AI prompt: "Generate a labelled diagram showing the Haber process with iron catalyst used for ammonia production."
Search string: "Haber process iron catalyst diagram OER"

Table 1.4 Common alloys of transition metals and their uses
AI prompt: "Generate a table showing common alloys of transition metals, their

composition, and applications."
Search string: "transition metal alloys uses table OER"

Plate 1.4 Biological importance of transition metals
AI prompt: "Create an image showing haemoglobin with iron at the centre of the porphyrin ring."
Search string: "haemoglobin iron complex structure OER"

Notes on Attribution

Where illustrations are AI-generated, prompts are recorded above and should be documented with the generation date and platform used.
Where OERs are used, ensure attribution complies with the licence terms of the source.
All references follow APA style for consistency.

Course code: CHM 212

Course title: Inorganic Chemistry I

Course Unit: 2 Units C: LH 30

Series 1: Chemistry of First-Row Transition Metals

Series 2: Coordination Chemistry and Crystal Field Theory

Series 3: Comparative Chemistry of Selected Main Group Elements

Series 4: Fundamentals of Organometallic Chemistry

Series 5: Roles of Metals in Biochemical Systems and Redox Concepts

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Suggested Outline

Part 2.1: Fundamentals of Coordination Chemistry

Sub-Part 2.1.1: Definition and classification of coordination compounds
Sub-Part 2.1.2: Types of ligands and coordination numbers
Sub-Part 2.1.3: Nomenclature of coordination compounds

Part 2.2: Structure and Bonding in Complexes

Sub-Part 2.2.1: Nature of coordinate bonds
Sub-Part 2.2.2: Geometries of coordination compounds
Sub-Part 2.2.3: Isomerism in complexes (structural and stereoisomerism)

Part 2.3: Crystal Field Theory (CFT)

Sub-Part 2.3.1: Basic assumptions of CFT
Sub-Part 2.3.2: Crystal field splitting in octahedral and tetrahedral complexes
Sub-Part 2.3.3: Factors affecting crystal field splitting (nature of ligands, oxidation state, geometry)

Part 2.4: Applications of Crystal Field Theory

Sub-Part 2.4.1: Explanation of colours in transition metal complexes
Sub-Part 2.4.2: Magnetic properties of complexes
Sub-Part 2.4.3: Role of CFT in predicting stability and reactivity

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Introduction

In the last Series, we explored the chemistry of the first-row transition metals, focusing on their properties, electronic structures, and applications. Building on that foundation, we now turn to one of the most fascinating aspects of inorganic chemistry: coordination chemistry and crystal field theory. These topics are central to understanding how transition metals interact with ligands, why their complexes exhibit such striking colours, and how their magnetic behaviours can be explained.

The aim of this Series is to introduce you to the principles of coordination chemistry and to equip you with the knowledge of crystal field theory needed to interpret the bonding, geometry, and properties of transition metal complexes.

We shall commence this Series by examining the fundamentals of coordination chemistry, including the definition of coordination compounds, types of ligands, and rules of nomenclature. Next, we will explore the structure and bonding in complexes, considering coordinate bonds, geometries, and isomerism. Following that, we will move on to crystal field theory, where we will study the splitting of d-orbitals in different geometries and the factors that influence this process. Finally, we will wrap up by applying crystal field theory to explain the colours, magnetic properties, and stability of transition metal complexes, thereby rounding off a comprehensive understanding of this essential area of inorganic chemistry.

Series Learning Outcomes

Upon completing this Series, you should be able to:

SLO 2.1 define coordination compounds and classify them based on ligands and coordination numbers,
SLO 2.2 apply the rules of nomenclature to correctly name coordination compounds,

SLO 2.3 explain the nature of coordinate bonds and describe common geometries of complexes,
SLO 2.4 analyse structural and stereoisomerism in coordination compounds,
SLO 2.5 outline the basic assumptions of crystal field theory and illustrate crystal field splitting in octahedral and tetrahedral complexes,
SLO 2.6 evaluate the factors that influence crystal field splitting, including ligand type, oxidation state, and geometry,
SLO 2.7 interpret the colours of transition metal complexes using crystal field theory,
SLO 2.8 assess the magnetic properties of complexes in relation to crystal field splitting, and
SLO 2.9 apply crystal field theory to predict the stability and reactivity of transition metal complexes.

2.1 Fundamentals of Coordination Chemistry

2.1.1 Definition and classification of coordination compounds

Coordination compounds are chemical substances in which a central metal atom or ion is bonded to surrounding molecules or ions, called ligands, through coordinate bonds. A **coordinate bond** is a type of covalent bond where both electrons in the bond are donated by the ligand. These compounds are important because they explain many properties of transition metals, such as colour, magnetism, and reactivity.

Coordination compounds can be classified based on:

The nature of the central metal ion (e.g., transition metals such as Fe, Cu, Co).

The type of ligands attached (neutral or charged).

Their applications (biological, industrial, or material science).

Fill in the blank: A coordination compound consists of a central metal atom or ion bonded to surrounding _____.

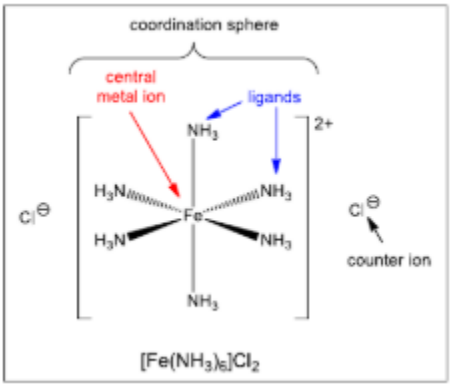


Figure 2.1: General structure of a coordination compound

2.1.2 Types of ligands and coordination numbers

A **ligand** is a molecule or ion that donates a pair of electrons to a central metal ion to form a coordinate bond. Ligands can be classified as:

Monodentate ligands: donate one pair of electrons (e.g., H_2O, NH_3, Cl^-).

Bidentate ligands: donate two pairs of electrons (e.g., ethylenediamine).

Polydentate ligands: donate multiple pairs of electrons (e.g., EDTA).

The **coordination number** refers to the number of ligand donor atoms directly bonded to the central metal ion. Common coordination numbers are 4 (tetrahedral or square planar) and 6 (octahedral).

Fill in the blank: The coordination number of iron in $[Fe(CN)_6]^{3-}$ is _____.

Common Ligands and Coordination Complexes

Ligand Name	Formula	Denticity	Example Complex
Ammine	NH_3	Monodentate	$[Co(NH_3)_6]^{3+}$
Aqua	H_2O	Monodentate	$[Ni(H_2O)_6]^{2+}$
Chlorido	Cl^-	Monodentate	$[PtCl_4]^{2-}$
Ethylenediamine (en)	$NH_2CH_2CH_2NH_2$	Bidentate	$[Ni(en)_3]^{2+}$
Oxalato (ox)	$C_2O_4^{2-}$	Bidentate	$[Fe(C_2O_4)_3]^{3-}$
Diethylenetriamine (dien)	$C_4H_{13}N_3$	Tridentate	$[Co(dien)_2]^{3+}$
EDTA	$C_{10}H_{12}N_2O_8^{4-}$	Hexadentate	$[Ca(EDTA)]^{2-}$

Table 2.1: Examples of ligands and their denticity

Ligand	Type	Denticity	Example complex
Water (H_2O)	Monodentate	1	$[Cu(H_2O)_4]^{2+}$
Ethylenediamine	Bidentate	2	$[Ni(en)_3]^{2+}$
EDTA	Polydentate	6	$[Fe(EDTA)]^-$

2.1.3 Nomenclature of coordination compounds

The **nomenclature of coordination compounds** follows specific rules set by IUPAC:

Name the ligands first, in alphabetical order, followed by the metal.

Use prefixes (di-, tri-, tetra-) to indicate the number of identical ligands.

For anionic complexes, the metal name ends with the suffix "-ate".

Oxidation state of the metal is indicated in Roman numerals in parentheses.

For example:

$[Cu(NH_3)_4]^{2+}$ is named **tetraamminecopper(II)**.

$[Fe(CN)_6]^{3-}$ is named **hexacyanoferrate(III)**.

Fill in the blank: The complex $[Co(NH_3)_6]^{3+}$ is named _____.

1. Order of Naming Ions
If the compound is a salt, name the **cation** first, then the **anion**, separated by a space.

2. Naming the Complex Entity
Within the coordination sphere, name the **ligands first** (in alphabetical order) followed by the **central metal**.

3. Alphabetical Order of Ligands
Ligands are listed alphabetically by their name, **ignoring numerical prefixes** (e.g., "tetraaqua" is alphabetized under "a" for aqua).

4. Ligand Name Endings

- **Anionic ligands** generally end in **-o** (e.g., chloride becomes *chlorido* or *chloro*, cyanide becomes *cyanido* or *cyano*).
- **Neutral ligands** usually keep their molecular names, with key exceptions: H_2O (**aqua**), NH_3 (**ammine**), CO (**carbonyl**), and NO (**nitrosyl**).

5. Numerical Prefixes

- Use **di-, tri-, tetra-, penta-, hexa-** for simple ligands.
- Use **bis-, tris-, tetrakis-** for complex ligands or those whose names already contain a numerical prefix (e.g., ethylenediamine), enclosing the ligand name in parentheses.

6. Metal Name and Oxidation State

- In **cationic or neutral** complexes, use the standard English name of the metal.
- In **anionic** complexes, add the suffix **-ate** to the metal's name (e.g., cobaltate). Some metals use their Latin roots: **ferrate** (iron), **cuprate** (copper), **argentate** (silver), **aurate** (gold), **stannate** (tin), and **plumbate** (lead).
- The metal's **oxidation state** is indicated by a Roman numeral in parentheses immediately following the metal's name

Box 2.1: Key rules for naming coordination compounds

• Name ligands before the metal.
• Use prefixes to indicate the number of ligands.
• For anionic complexes, add "-ate" to the metal name.
• Indicate the oxidation state of the metal in Roman numerals.

Pilot questions 2.1

A coordination compound consists of a central metal atom or ion bonded to surrounding _____.

A. Bases
B. Ligands

C. Catalysts
D. Radicals

The coordination number of iron in $[Fe(CN)_6]^{3-}$ is _____.
A. 4
B. 5
C. 6
D. 8

Which of the following is a bidentate ligand?
A. H_2O
B. NH_3
C. Ethylenediamine
D. CN^-

The complex $[Co(NH_3)_6]^{3+}$ is named _____.
A. Hexaamminecobalt(III) ion
B. Hexaamminecobaltate(III) ion
C. Cobalt hexammine ion
D. Hexacobaltammine ion

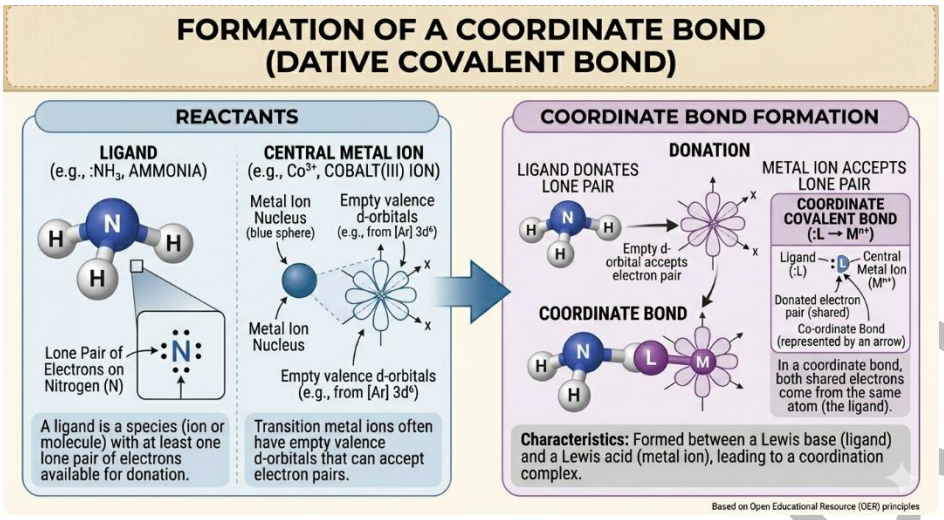
In naming coordination compounds, the ligands are listed _____ the metal.
A. After
B. Before
C. Randomly
D. Only if neutral

2.2 Structure And Bonding In Complexes

2.2.1 Nature of coordinate bonds

A **coordinate bond** is a type of covalent bond in which both electrons are donated by the same atom, usually a ligand, to a central metal ion. This bond is fundamental to coordination chemistry because it explains how ligands attach to metals to form stable complexes. Unlike ionic bonds, coordinate bonds involve electron sharing, but the donor atom provides both electrons.

Fill in the blank: A bond in which both electrons are donated by the same atom to a central metal ion is called a _____



Caption: Figure 2.2 Formation of a coordinate bond in a complex.

2.2.2 Geometries of coordination compounds

The **geometry** of a coordination compound refers to the spatial arrangement of ligands around the central metal ion. Common geometries include:

Octahedral (coordination number 6): six ligands arranged symmetrically around the metal ion.
Tetrahedral (coordination number 4): four ligands arranged at the corners of a tetrahedron.
Square planar (coordination number 4): four ligands arranged in a plane, common for d^8 metal ions such as Ni^{2+} and Pt^{2+}.

The geometry depends on factors such as the coordination number, the size of the ligands, and the electronic configuration of the metal ion.

Fill in the blank: A complex with six ligands arranged symmetrically around a central metal ion is described as having _____ geometry.

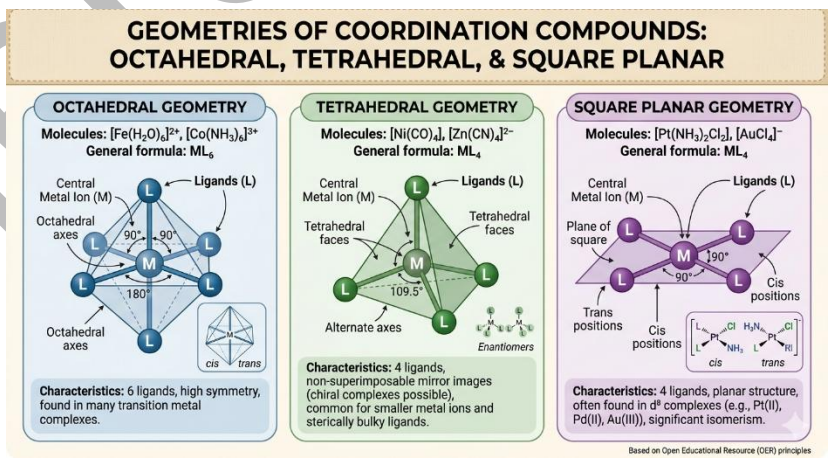


Figure 2.3 Common geometries of coordination compounds.

2.2.3 Isomerism in complexes (structural and stereoisomerism)

Isomerism in coordination compounds occurs when complexes with the same formula have different arrangements of atoms or ligands. There are two main types:

- **Structural isomerism:** arises from differences in how ligands are attached. Examples include linkage isomerism (ligand attaches through different donor atoms) and ionisation isomerism (different ions inside or outside the coordination sphere).
- **Stereoisomerism:** arises from differences in spatial arrangement. Examples include geometrical isomerism (cis/trans arrangements) and optical isomerism (mirror-image forms that are non-superimposable).

Fill in the blank: When ligands in a complex are arranged differently in space, leading to cis and trans forms, this is called _____ isomerism.

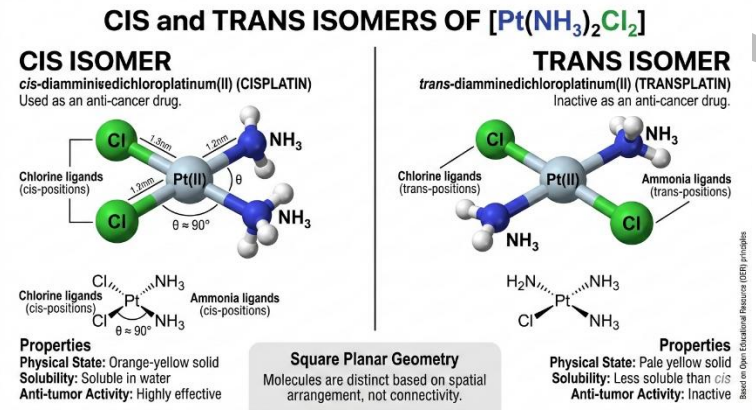


Plate 2.2 Geometrical isomerism in coordination compounds.

1. Structural Isomerism

Structural isomers have different connectivity between the metal center and the ligands.

Type	Definition	Example
Ionisation	Results from the exchange of a ligand in the coordination sphere with a counter ion.	$[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$
Linkage	Occurs with ambidentate ligands (like NO_2^- or SCN^-) that can bind via different atoms.	$[Co(NH_3)_5(NO_2)]^{2+}$ (nitro) and $[Co(NH_3)_5(ONO)]^{2+}$ (nitrito)
Coordination	Occurs in compounds containing both complex cations and anions; ligands are exchanged between centers.	$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
Solvate	Formed when the solvent (usually H_2O) acts as either a ligand or a free molecule in	$[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

2. Stereoisomerism

Stereoisomers have the same chemical bonds but different spatial orientations.

- **Geometrical Isomerism:**
  - **Cis/Trans:** Common in square planar and octahedral complexes (ML_2X_2 or ML_4X_2). **Cis** isomers have identical ligands adjacent (90°), while **Trans** isomers have them opposite (180°).
  - **Fac/Mer:** Found in octahedral MA_3B_3 complexes. **Facial (fac)** has three ligands on one face of the octahedron; **Meridional (mer)** has them around the "meridian."
- **Optical Isomerism:**
  - Occurs when molecules are non-superimposable mirror images (enantiomers). They are common in octahedral complexes with bidentate ligands, such as $[Co(en)_3]^{3+}$.

Box 2.2 Types of isomerism in coordination compounds.

2.3 Crystal Field Theory (CFT)

2.3.1 Basic assumptions of CFT

rystal Field Theory (CFT) is a model that explains the electronic structure, colour, and magnetism of transition metal complexes. It assumes that ligands are point charges (if ionic) or dipoles (if neutral) that interact electrostatically with the d-orbitals of the central metal ion. This interaction causes the d-orbitals to split into groups of different energies, depending on the geometry of the complex.

The key assumptions are:

Ligands are treated as point charges or dipoles.

The interaction between ligands and the central metal ion is purely electrostatic.

Splitting of d-orbitals depends on the arrangement of ligands around the metal ion.

Fill in the blank: Crystal Field Theory assumes that ligands interact with the central metal ion as _____ charges.

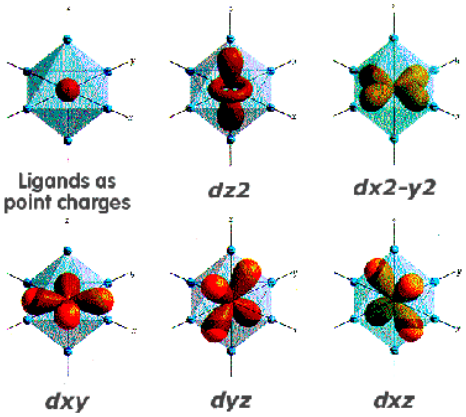


Figure 2.3: Basic assumptions of Crystal Field Theory

2.3.2 Crystal field splitting in octahedral and tetrahedral complexes

In an **octahedral complex**, six ligands surround the central metal ion. The d-orbitals split into two sets:

t_2g (dxy, dxz, dyz) orbitals at lower energy.

eg (dz^2, $dx^2–y^2$) orbitals at higher energy.

In a **tetrahedral complex**, four ligands surround the metal ion. The splitting is reversed compared to octahedral complexes:

eg orbitals are lower in energy.

t_2 orbitals are higher in energy.

The energy difference between the two sets of orbitals is called the **crystal field splitting energy (Δ)**.

Fill in the blank: In an octahedral complex, the higher-energy set of orbitals is called the _____ orbitals.

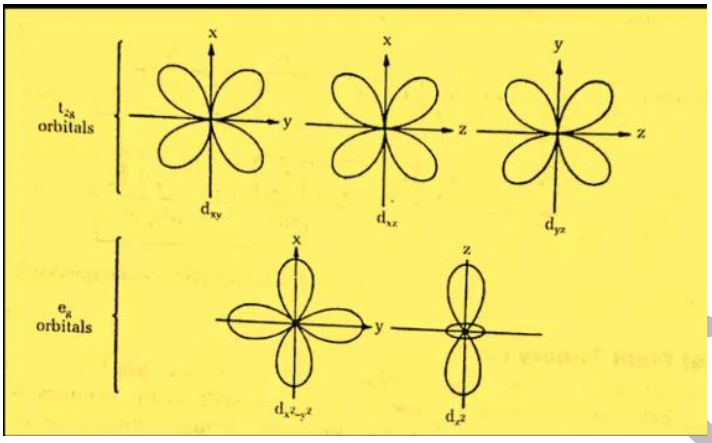


Plate 2.3: Crystal field splitting in octahedral and tetrahedral complexes

2.3.3 Factors affecting crystal field splitting

The magnitude of the **crystal field splitting energy (Δ)** depends on several factors:

- **Nature of the ligands**: Strong-field ligands (e.g., CN^-, CO) produce large splitting, while weak-field ligands (e.g., H_2O, Cl^-) produce small splitting.
- **Oxidation state of the metal**: Higher oxidation states increase the attraction between ligands and the metal, leading to larger splitting.
- **Geometry of the complex**: Octahedral complexes generally have larger splitting than tetrahedral ones.

These factors are summarised in the **spectrochemical series**, which ranks ligands according to their field strength.

Fill in the blank: Ligands such as CN^- and CO are described as _____-field ligands because they produce large splitting.

~ An ordering of ligands according to their ability to cause crystal field splittings.

➢ **Spectrochemical series for ligands**

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

Weak-field ligands (high spin) Intermediate-field ligands Strong-field ligands (low spin)

➢ **Spectrochemical series for metal ions**

$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < Fe^{3+} < Co^{3+} < Mn^{4+} < Pd^{4+} < Ir^{3+} < Pt^{4+}$

Box 2.2: The spectrochemical series (selected ligands from weak to strong field)

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

Pilot questions 2.3

Crystal Field Theory assumes that ligands interact with the central metal ion as _____ charges.

A. Neutral
B. Point
C. Dipole
D. Random

In an octahedral complex, the higher-energy set of orbitals is called the _____ orbitals.

A. t2g
B. eg
C. p
D. f

Which geometry produces larger crystal field splitting, octahedral or tetrahedral?

A. Octahedral
B. Tetrahedral
C. Both equal
D. Neither

Ligands such as CN^- and CO are described as _____-field ligands.

A. Weak
B. Strong
C. Neutral
D. Random

The energy difference between the split d-orbitals in a complex is called the _____.

A. Bond energy
B. Crystal field splitting energy (Δ)
C. Ionisation energy
D. Lattice energy

2.4 Applications of Crystal Field Theory

2.4.1 Explanation of colours in transition metal complexes

One of the most striking features of transition metal complexes is their vivid **colour**. Crystal Field Theory explains this by showing how electrons in the d-orbitals absorb light energy to move from lower-energy orbitals (t_2g) to higher-energy orbitals (eg). The energy difference between these orbitals corresponds to the wavelength of light absorbed. The colour we see is the complementary colour of the absorbed wavelength.

Fill in the blank: The colour observed in a transition metal complex is the _____ colour of the light absorbed.

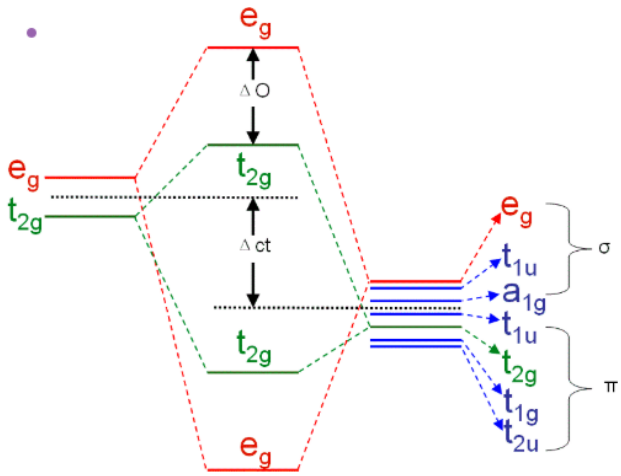


Figure 2.4: Electronic transitions explaining colour in transition metal complexes

2.4.2 Magnetic properties of complexes

The **magnetic properties** of transition metal complexes depend on the number of unpaired electrons in the d-orbitals. Crystal Field Theory helps predict whether a complex will be **high-spin** (more unpaired electrons) or **low-spin** (fewer unpaired electrons), depending on the strength of the ligands.

Weak field ligands (e.g., H_2O, Cl^-) produce small splitting, leading to high-spin complexes.

Strong field ligands (e.g., CN^-, CO) produce large splitting, leading to low-spin complexes.

Fill in the blank: Complexes with strong-field ligands often form _____-spin complexes due to electron pairing.

Configuration	Weak-Field (High-Spin)	Unpaired e^-	Strong-Field (Low-Spin)	Unpaired e^-
d^1	t_{2g}^1	1	t_{2g}^1	1
d^2	t_{2g}^2	2	t_{2g}^2	2
d^3	t_{2g}^3	3	t_{2g}^3	3
d^4	$t_{2g}^3 e_g^1$	4	t_{2g}^4	2
d^5	$t_{2g}^3 e_g^2$	5	t_{2g}^5	1
d^6	$t_{2g}^4 e_g^2$	4	t_{2g}^6 (Diamagnetic)	0
d^7	$t_{2g}^5 e_g^2$	3	$t_{2g}^6 e_g^1$	1
d^8	$t_{2g}^6 e_g^2$	2	$t_{2g}^6 e_g^2$	2
d^9	$t_{2g}^6 e_g^3$	1	$t_{2g}^6 e_g^3$	1
d^{10}	$t_{2g}^6 e_g^4$ (Diamagnetic)	0	$t_{2g}^6 e_g^4$ (Diamagnetic)	0

Table 2.3: Magnetic properties of octahedral complexes with different ligands

Complex	Ligand type	Spin state	Magnetic behaviour
$[Fe(H_2O)_6]^{2+}$	Weak-field	High-spin	Paramagnetic
$[Fe(CN)_6]^{4-}$	Strong-field	Low-spin	Diamagnetic
$[Co(NH_3)_6]^{3+}$	Intermediate	Variable	Paramagnetic/diamagnetic

2.4.3 Role of CFT in predicting stability and reactivity

Crystal Field Theory also helps explain the **stability** and **reactivity** of complexes. The arrangement of electrons in the split d-orbitals influences how stable a complex is and how it reacts with other substances.

Complexes with large splitting (Δ) are often more stable because electrons are held more tightly.

The distribution of electrons can explain why some complexes prefer certain geometries (octahedral vs. tetrahedral).

CFT helps predict substitution reactions, where ligands are replaced, by considering the relative stability of the initial and final complexes.

Fill in the blank: The measure of stabilisation provided by the arrangement of electrons in split d-orbitals is called _____.

Key Applications of Crystal Field Theory

Application	Description
Colours	Explains color through **d-d transitions**, where electrons absorb visible light to move between split d-orbitals. The observed color is **complementary** to the absorbed wavelength.
Magnetism	Predicts if a complex is **paramagnetic** (unpaired electrons) or **diamagnetic** (paired electrons). It distinguishes between **high-spin** (weak-field) and **low-spin** (strong-field) configurations.
Stability	Uses **Crystal Field Stabilization Energy (CFSE)** to quantify the net energy gain of a complex. Higher CFSE values typically correlate with increased **thermodynamic stability**.
Reactivity	Rationalizes **kinetic stability**; complexes with high CFSE are often **inert** (slow to react), while those with low or zero CFSE are **labile** (rapidly exchange ligands).
Geometry	Predicts preferred structures (e.g., **octahedral, tetrahedral,** or **square planar**) based on which arrangement maximizes electronic stabilization.

Box 2.3: Key applications of Crystal Field Theory

• Explains colours of transition metal complexes.
• Accounts for magnetic properties (high-spin vs. low-spin).
• Predicts stability through CFSE values.
• Helps rationalise preferred geometries and reactivity patterns.

Pilot questions 2.4

The colour observed in a transition metal complex is the _____ colour of the light absorbed.
A. Same
B. Complementary
C. Opposite
D. Neutral

Complexes with strong-field ligands often form _____-spin complexes.
A. High
B. Low
C. Neutral
D. Random

The measure of stabilisation provided by the arrangement of electrons in split d-orbitals is called _____.
A. Bond energy
B. Crystal Field Stabilisation Energy (CFSE)
C. Ionisation energy
D. Lattice energy

Which of the following complexes is diamagnetic due to strong-field ligands?
A. $[Fe(H_2O)_6]^{2+}$
B. $[Fe(CN)_6]^{4-}$
C. $[CoCl_4]^{2-}$
D. $[Ni(H_2O)_6]^{2+}$

The difference in magnetic behaviour between $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ is explained by _____.
A. Ligand size
B. Crystal field splitting
C. Oxidation state
D. Geometry

Series Summary

This Series explored **coordination chemistry and crystal field theory**, helping you understand how transition metals form complexes and how their properties can be explained through orbital interactions. You began by defining and classifying coordination compounds, identifying ligands and coordination numbers, and applying the rules of nomenclature. You then examined the nature of coordinate bonds, common geometries, and the different types of isomerism. Building on this structural knowledge, you studied the assumptions of crystal field theory, the splitting of d-orbitals in octahedral and tetrahedral complexes, and the factors that influence the magnitude

of splitting. Finally, you applied these ideas to explain the colours, magnetic properties, and stability of transition metal complexes.

By completing this Series, you should now be able to **define and classify coordination compounds (SLO 2.1)**, **apply nomenclature rules (SLO 2.2)**, **explain bonding and geometries (SLO 2.3)**, **analyse isomerism (SLO 2.4)**, **illustrate crystal field splitting (SLO 2.5)**, **evaluate factors influencing splitting (SLO 2.6)**, **interpret colours of complexes (SLO 2.7)**, **assess magnetic properties (SLO 2.8)**, and **apply crystal field theory to predict stability and reactivity (SLO 2.9)**. These outcomes ensure you can connect theoretical principles with practical applications, strengthening your understanding of transition metal chemistry.

Glossary of Terms

Coordinate bond: A type of covalent bond in which both electrons are donated by the same atom, usually a ligand, to a central metal ion.

Coordination compound: A chemical substance consisting of a central metal ion bonded to surrounding ligands through coordinate bonds.

Coordination number: The number of ligand donor atoms directly attached to the central metal ion in a complex.

Crystal field splitting: The separation of d-orbitals into groups of different energies when ligands interact with a central metal ion.

Crystal Field Theory (CFT): A model that explains the electronic structure, colour, and magnetism of transition metal complexes by considering electrostatic interactions between ligands and d-orbitals.

Geometrical isomerism: A type of stereoisomerism in coordination compounds where ligands are arranged differently in space, such as cis and trans forms.

Ligand: A molecule or ion that donates a pair of electrons to a central metal ion, forming a coordinate bond.

Monodentate ligand: A ligand that donates one pair of electrons to a central metal ion.

Polydentate ligand: A ligand that donates multiple pairs of electrons to a central metal ion, often forming stable chelate complexes.

Spectrochemical series: An arrangement of ligands in order of their ability to cause crystal field splitting, from weak field to strong field.

Stereoisomerism: Isomerism arising from different spatial arrangements of ligands in a complex, including geometrical and optical isomerism.

Structural isomerism: Isomerism in coordination compounds resulting from differences in how ligands are attached or arranged, such as linkage or ionisation isomerism.

Strong field ligand: A ligand that causes large splitting of d-orbitals, often leading to low-spin complexes.

Weak field ligand: A ligand that causes small splitting of d-orbitals, often leading to high-spin complexes.

This glossary consolidates the essential terms introduced in Series 2, providing clear and accessible definitions to support independent learning.

Concept Check Questions [Series 2]

Objective Questions

Which of the following best describes a coordination compound?
A. A compound formed only by ionic bonds
B. A compound with a central metal ion bonded to ligands through coordinate bonds
C. A compound consisting only of non-metals
D. A compound with no defined geometry
(Linked to SLO 2.1)

In the complex $[Fe(CN)_6]^{3-}$, the ligand CN^- is classified as:
A. Monodentate
B. Bidentate
C. Polydentate
D. Neutral
(Linked to SLO 2.1)

Which geometry is most common for complexes with coordination number 6?
A. Tetrahedral
B. Octahedral
C. Square planar
D. Linear
(Linked to SLO 2.3)

The cis and trans forms of $[Pt(NH_3)_2Cl_2]$ are examples of:
A. Structural isomerism
B. Geometrical isomerism
C. Optical isomerism
D. Linkage isomerism
(Linked to SLO 2.4)

Which ligands are considered strong field ligands in the spectrochemical series?
A. H_2O and Cl^-
B. CN^- and CO
C. NH_3 and OH^-
D. Br^- and I^-
(Linked to SLO 2.6)

Short-Answer Questions

Define a coordinate bond and explain how it differs from a normal covalent bond.
(Linked to SLO 2.3)

State the rules for naming coordination compounds according to IUPAC.
(Linked to SLO 2.2)

Explain the difference between structural isomerism and stereoisomerism in coordination compounds.
(Linked to SLO 2.4)

What is the spectrochemical series, and why is it important in crystal field theory?
(Linked to SLO 2.6)

Why do transition metal complexes often display vivid colours?
(Linked to SLO 2.7)

Long-Answer Questions

Analyse how crystal field theory explains the splitting of d-orbitals in octahedral and tetrahedral complexes. Provide examples to illustrate your explanation.
(Linked to SLO 2.5)

Evaluate the factors that influence crystal field splitting energy (Δ), and discuss how these factors affect the magnetic properties of complexes.
(Linked to SLO 2.6 and SLO 2.8)

Assess the role of crystal field theory in predicting the stability and reactivity of transition metal complexes, with reference to industrial or biological examples.
(Linked to SLO 2.9)

Answers to Concept Check Questions [Series 2]

Objective Questions

B. A compound with a central metal ion bonded to ligands through coordinate bonds
A. Monodentate
B. Octahedral
B. Geometrical isomerism
B. CN^- and CO

Short-Answer Questions

A coordinate bond is a covalent bond where both electrons are donated by the ligand. Unlike a normal covalent bond, the donor atom provides both electrons.

Ligands are named first in alphabetical order, followed by the metal. Prefixes indicate the number of ligands, and the oxidation state of the metal is shown in Roman numerals. For anionic complexes, the metal name ends with "-ate".

Structural isomerism arises from differences in how ligands are attached (e.g., linkage or ionisation), while stereoisomerism arises from differences in spatial arrangement (e.g., cis/trans or optical).

The spectrochemical series arranges ligands from weak field to strong field. It is important because it predicts the magnitude of crystal field splitting and whether complexes are high-spin or low-spin.

Transition metal complexes display colours because d-electrons absorb light energy to move between split orbitals. The observed colour is the complementary colour of the absorbed wavelength.

Long-Answer Questions

Question 1

Basic response: In octahedral complexes, d-orbitals split into t_2g (lower energy) and eg (higher energy). In tetrahedral complexes, the splitting is reversed, with eg orbitals lower and t_2 orbitals higher.
Value-added response: Learners may add that the magnitude of splitting (Δ) depends on ligand type and geometry, and can be measured using spectroscopy. They may also note that square planar complexes show unique splitting patterns, especially for d^8 metals.

Question 2

Basic response: Factors influencing Δ include ligand type (strong vs. weak field), oxidation state of the metal, and geometry of the complex. These factors determine whether a complex is high-spin or low-spin, and thus whether it is paramagnetic or diamagnetic.
Value-added response: Outstanding learners may discuss the spectrochemical series in detail, explain how Δ affects electronic transitions and magnetic susceptibility, and connect this to experimental techniques such as magnetic moment measurements.

Question 3

Basic response: Crystal field theory predicts stability by showing how electrons occupy split orbitals. Complexes with larger splitting are often more stable. It also explains ligand substitution reactions.
Value-added response: Learners may extend this by citing industrial examples such as the role of transition metal complexes in catalysis (e.g., platinum in hydrogenation) and biological examples such as haemoglobin, where iron's orbital interactions enable oxygen transport.

This set of concept check questions ensures coverage of all Series Learning Outcomes, encouraging learners to recall, explain, analyse, and evaluate the principles and applications of coordination chemistry and crystal field theory.

Answers to Pilot Questions [Series 2]

Part 2.1: Fundamentals of Coordination Chemistry

Ligands
6
Ethylenediamine
Hexaamminecobalt(III) ion
Before

Part 2.2: Structure and Bonding in Complexes

Coordinate bond

Octahedral
Square planar
Linkage isomerism
Optical isomerism

Part 2.3: Crystal Field Theory (CFT)

Point charges
eg orbitals
Octahedral
Strong
Crystal field splitting energy (Δ)

Part 2.4: Applications of Crystal Field Theory

Complementary
Low
Crystal Field Stabilisation Energy (CFSE)
$[Fe(CN)_6]^{4-}$
Crystal field splitting

References and Attributions [Series 2]

Textual Sources

Housecroft, C. E., & Sharpe, A. G. (2018). *Inorganic Chemistry* (5th ed.). Pearson.
Miessler, G. L., Fischer, P. J., & Tarr, D. A. (2014). *Inorganic Chemistry* (5th ed.). Pearson.
IUPAC. (1997). *Compendium of Chemical Terminology (the "Gold Book")*.
Cotton, F. A., Wilkinson, G., Murillo, C. A., & Bochmann, M. (1999). *Advanced Inorganic Chemistry* (6th ed.). Wiley.

Illustrations (Figures, Plates, Tables, Boxes)

Figure 2.1 General structure of a coordination compound
AI prompt: "Generate a labelled diagram showing a central transition metal ion surrounded by ligands forming a coordination complex."
Search string: "coordination compound diagram OER"

Table 2.1 Examples of ligands and their denticity
AI prompt: "Generate a table showing types of ligands (monodentate, bidentate, polydentate) with examples."
Search string: "types of ligands coordination chemistry table OER"

Box 2.1 Rules for naming coordination compounds
AI prompt: "Generate a text box summarising IUPAC rules for naming coordination compounds with examples."
Search string: "IUPAC rules nomenclature coordination compounds OER"

Figure 2.2 Formation of a coordinate bond in a complex

AI prompt: “Generate a labelled diagram showing a ligand donating a pair of electrons to a central metal ion to form a coordinate bond.”
Search string: “coordinate bond diagram transition metal complex OER”

Figure 2.3 Common geometries of coordination compounds

AI prompt: “Generate a labelled diagram showing octahedral, tetrahedral, and square planar geometries of coordination compounds.”
Search string: “geometries of coordination compounds diagram OER”

Plate 2.2 Geometrical isomerism in coordination compounds

AI prompt: “Create an image showing cis and trans isomers of $[Pt(NH_3)_2Cl_2]$.”
Search string: “cis trans isomerism coordination compounds OER”

Box 2.2 Types of isomerism in coordination compounds

AI prompt: “Generate a text box summarising types of isomerism in coordination compounds with examples.”
Search string: “isomerism coordination compounds table OER”

Figure 2.4 Basic concept of crystal field splitting

AI prompt: “Generate a labelled diagram showing how ligands cause splitting of d-orbitals in a transition metal complex.”
Search string: “crystal field theory d orbital splitting diagram OER”

Figure 2.5 Crystal field splitting in octahedral and tetrahedral complexes

AI prompt: “Generate a labelled diagram showing octahedral and tetrahedral crystal field splitting of d-orbitals.”
Search string: “octahedral tetrahedral crystal field splitting diagram OER”

Table 2.2 The spectrochemical series of ligands

AI prompt: “Generate a table showing the spectrochemical series of ligands from weak field to strong field.”
Search string: “spectrochemical series ligands table OER”

Box 2.3 Factors affecting crystal field splitting

AI prompt: “Generate a text box summarising factors affecting crystal field splitting with examples.”
Search string: “factors affecting crystal field splitting OER”

Figure 2.6 Origin of colour in transition metal complexes

AI prompt: “Generate a labelled diagram showing d-d transitions in an octahedral complex and the resulting colour absorption.”
Search string: “colour in transition metal complexes d-d transitions diagram OER”

Table 2.3 Magnetic properties of high-spin and low-spin complexes

AI prompt: “Generate a table comparing high-spin and low-spin complexes, showing ligand type, electron arrangement, and magnetic property.”
Search string: “high spin low spin complexes table OER”

Box 2.4 Applications of crystal field theory in stability and reactivity

AI prompt: “Generate a text box summarising applications of crystal field theory in

stability and reactivity of complexes."
Search string: "applications of crystal field theory stability reactivity OER"

Notes on Attribution

Where illustrations are AI-generated, prompts are recorded above and should be documented with the generation date and platform used.
Where OERs are used, attribution must comply with the licence terms of the source.
References are presented in APA style for consistency.

Course code: CHM 212

Course title: Inorganic Chemistry I

Course Unit: 2 Units C: LH 30

Series 1: Chemistry of First-Row Transition Metals

Series 2: Coordination Chemistry and Crystal Field Theory

Series 3: Comparative Chemistry of Selected Main Group Elements

Series 4: Fundamentals of Organometallic Chemistry

Series 5: Roles of Metals in Biochemical Systems and Redox Concepts

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Suggested Outline

Part 3.1: General Characteristics of Main Group Elements

Sub-Part 3.1.1: Position of main group elements in the periodic table
Sub-Part 3.1.2: Trends in atomic and physical properties across groups
Sub-Part 3.1.3: General reactivity patterns

Part 3.2: Comparative Chemistry of Group 1 and Group 2 Elements

Sub-Part 3.2.1: Alkali metals – properties, reactivity, and compounds
Sub-Part 3.2.2: Alkaline earth metals – properties, reactivity, and compounds
Sub-Part 3.2.3: Comparative trends between Group 1 and Group 2

Part 3.3: Comparative Chemistry of Groups 13 and 14 Elements

Sub-Part 3.3.1: Boron and aluminium – properties and compounds
Sub-Part 3.3.2: Carbon and silicon – properties and compounds
Sub-Part 3.3.3: Comparative trends between Group 13 and Group 14

Part 3.4: Comparative Chemistry of Groups 15 and 16 Elements

Sub-Part 3.4.1: Nitrogen and phosphorus – properties and compounds
Sub-Part 3.4.2: Oxygen and sulphur – properties and compounds
Sub-Part 3.4.3: Comparative trends between Group 15 and Group 16

Part 3.5: Applications and Significance of Main Group Elements

Sub-Part 3.5.1: Industrial uses of selected main group elements
Sub-Part 3.5.2: Biological importance of selected main group elements
Sub-Part 3.5.3: Environmental relevance and challenges

Introduction

In the last Series, we examined coordination chemistry and crystal field theory, focusing on how transition metals interact with ligands and how their properties can be explained through orbital splitting. We now turn our attention to the **main group elements**, which, although not transition metals, play equally vital roles in chemistry, industry, biology, and the environment. Understanding their comparative chemistry helps us appreciate periodic trends and the diverse applications of these elements in everyday life.

The aim of this Series is to provide you with a clear comparative study of selected main group elements, highlighting their properties, reactivity, and significance. By the end of this Series, you will be able to analyse similarities and differences across groups, explain their chemical behaviour, and connect these insights to practical applications.

We shall commence this Series by exploring the general characteristics of main group elements, including their positions in the periodic table and trends in properties. Next, we will compare the chemistry of Group 1 and Group 2 elements, followed by a study of Groups 13 and 14. Subsequently, we will move on to Groups 15 and 16, examining their properties and compounds. Finally, we will wrap up by considering the industrial, biological, and environmental significance of selected main group elements, thereby rounding off a comprehensive comparative perspective.

Series Learning Outcomes

Upon completing this Series, you should be able to:

SLO 3.1 define the general characteristics of main group elements and explain periodic trends in their properties,
SLO 3.2 describe the properties and reactivity of alkali metals and their compounds,
SLO 3.3 explain the properties and reactivity of alkaline earth metals and their compounds,
SLO 3.4 analyse comparative trends between Group 1 and Group 2 elements,

SLO 3.5 outline the properties and compounds of boron and aluminium,
SLO 3.6 explain the properties and compounds of carbon and silicon,
SLO 3.7 compare the chemistry of Group 13 and Group 14 elements,
SLO 3.8 describe the properties and compounds of nitrogen and phosphorus,
SLO 3.9 explain the properties and compounds of oxygen and sulphur,
SLO 3.10 analyse comparative trends between Group 15 and Group 16 elements,
SLO 3.11 evaluate the industrial applications of selected main group elements,
SLO 3.12 assess the biological importance of selected main group elements, and
SLO 3.13 discuss the environmental relevance and challenges associated with main group elements.

3.1 General Characteristics of Main Group Elements

3.1.1 Position of main group elements in the periodic table

The **main group elements** are those found in Groups 1, 2, and 13 to 18 of the periodic table. They include the alkali metals, alkaline earth metals, and the non-transition elements from Groups 13 to 18. These elements are characterised by having their valence electrons in the **s** and **p orbitals**, which largely determine their chemical behaviour. Their positions in the periodic table reflect recurring trends in properties such as atomic size, ionisation energy, and electronegativity.

Fill in the blank: The main group elements are found in Groups _____ of the periodic table.

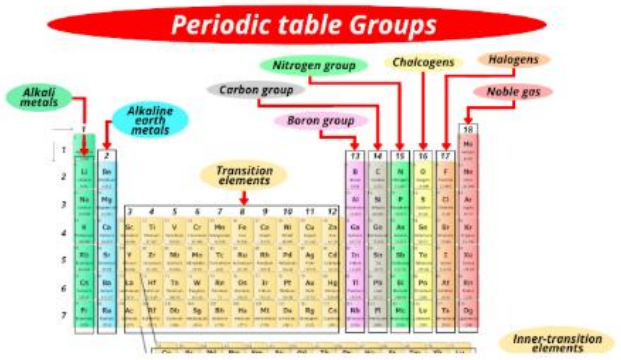

Figure 3.1: Position of main group elements in the periodic table

3.1.2 Trends in atomic and physical properties across groups

The **atomic radius** of main group elements increases down a group because additional electron shells are added. Across a period, the atomic radius decreases as nuclear charge increases, pulling electrons closer to the nucleus.

The **ionisation energy** decreases down a group because outer electrons are further from the nucleus and easier to remove. Across a period, ionisation energy increases due to stronger nuclear attraction.

The **electronegativity** generally decreases down a group and increases across a period, reflecting the tendency of atoms to attract electrons in a bond.

Fill in the blank: The atomic radius of main group elements generally _____ as you move down a group.

Periodic Trend	Across a Period (Left to Right)	Down a Group (Top to Bottom)	Reason
Atomic Radius	Decreases	Increases	More protons increase nuclear pull across a period; more shells increase size down a group.
Ionisation Energy	Increases	Decreases	Stronger nuclear pull makes removing electrons harder across; distance/shielding makes it easier down.
Electronegativity	Increases	Decreases	Higher nuclear charge attracts electrons more across; distance from nucleus reduces attraction down.
Melting/Boiling Points	Increases then Decreases	Varies by Group Type	Peak occurs at Group 14 (giant structures); decreases toward Group 18 (simple molecules).

Table 3.1: General periodic trends in main group elements

Property	Trend down a group	Trend across a period
Atomic radius	Increases	Decreases
Ionisation energy	Decreases	Increases
Electronegativity	Decreases	Increases
Melting/boiling pts	Variable	Variable

3.1.3 General reactivity patterns

The reactivity of main group elements is closely linked to their valence electron configurations:

Alkali metals (Group 1): Highly reactive, readily losing one electron to form +1 cations.
Alkaline earth metals (Group 2): Reactive, though less so than alkali metals, forming +2 cations.
Non-metals (Groups 15–17): Tend to gain electrons, forming anions or covalent bonds.
Noble gases (Group 18): Generally inert due to their complete valence shells, though some form compounds under extreme conditions.

Fill in the blank: The noble gases are generally _____ because they have complete valence shells.

- **Group 1 (Alkali Metals):** Highly reactive; they easily **lose one valence electron** to form **+1 cations**. Reactivity increases as you move down the group. LibreTexts Chemistry
- **Group 2 (Alkaline Earth Metals):** Reactive (though less so than Group 1); they **lose two valence electrons** to form **+2 cations**. PubChem - Alkaline Earth Metals
- **Groups 15–17 (Non-metals):** These elements tend to **gain or share electrons** to complete their outer shell. Group 17 (Halogens) are the most reactive non-metals, needing only one electron to form **-1 anions**. Britannica - Halogens
- **Group 18 (Noble Gases):** Mostly **inert and unreactive**. Their full valence shells provide exceptional stability, meaning they rarely participate in chemical reactions. ThoughtCo - Noble Gases

Box 3.1: Key points on reactivity of main group elements

• Group 1 elements lose one electron easily, forming +1 cations.
• Group 2 elements lose two electrons, forming +2 cations.
• Groups 15–17 elements tend to gain electrons or share them covalently.
• Group 18 elements are mostly inert due to stable electron configurations.

Pilot questions 3.1

The main group elements are found in Groups _____ of the periodic table.

A. 3–12
B. 1, 2, and 13–18
C. 1–8 only
D. 13–18 only

The atomic radius of main group elements generally _____ as you move down a group.

A. Decreases
B. Increases
C. Remains constant
D. Becomes irregular

Which group of main group elements is generally inert due to complete valence shells?

A. Group 1
B. Group 2
C. Group 17
D. Group 18

3.2 Comparative Chemistry of Group 1 and Group 2 Elements

3.2.1 Alkali metals – properties, reactivity, and compounds

Alkali metals are the elements of Group 1 in the periodic table (lithium, sodium, potassium, rubidium, caesium, and francium). They are soft, silvery metals with low melting points and densities. Their most distinctive feature is their high reactivity, especially with water, where they form hydroxides and release hydrogen gas.

For example, sodium reacts vigorously with water to form sodium hydroxide and hydrogen. Alkali metals typically form **ionic compounds**, such as NaCl, due to their tendency to lose one valence electron and form +1 cations.

Fill in the blank: The alkali metals are highly reactive because they have _____ valence electron in the s-orbital.

Element	Symbol	Atomic Number	Full Electron Configuration	Valence Shell (ns^1)
Lithium	Li	3	$1s^2 2s^1$	$2s^1$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s^1$	$3s^1$
Potassium	K	19	$[Ar] 4s^1$	$4s^1$
Rubidium	Rb	37	$[Kr] 5s^1$	$5s^1$
Cesium	Cs	55	$[Xe] 6s^1$	$6s^1$
Francium	Fr	87	$[Rn] 7s^1$	$7s^1$

Figure 3.2: Group 1 alkali metals and their valence electron configuration

3.2.2 Alkaline earth metals – properties, reactivity, and compounds

Alkaline earth metals are the elements of Group 2 (beryllium, magnesium, calcium, strontium, barium, and radium). They are harder and denser than alkali metals, with higher melting points. Their reactivity is lower compared to Group 1, but they still readily form compounds such as oxides and carbonates.

For example, calcium reacts with water less vigorously than sodium, producing calcium hydroxide and hydrogen gas. These metals typically form **+2 cations**, leading to compounds such as $CaCO_3$ and MgO.

Fill in the blank: Alkaline earth metals form _____ cations by losing two valence electrons.

Comparative Properties of Group 1 and Group 2 Elements

Property	Group 1: Alkali Metals	Group 2: Alkaline Earth Metals
Valence Electrons	1 (ns^1)	2 (ns^2)
Common Ion	+1 Cation	+2 Cation
Reactivity	**Extremely high**; increases down the group; stored under oil.	**High** (but lower than Group 1); increases down the group.
Solubility	Most salts (chlorides, sulfates, carbonates) are **highly soluble** in water.	Many salts (carbonates, phosphates, sulfates) are **insoluble or poorly soluble**.
Hardness/Density	Very soft (can be cut with a knife); low density.	Harder and denser than Group 1 metals.
Biological Roles	Sodium and Potassium are vital for **nerve impulses** and osmotic balance.	Magnesium and Calcium are essential for **structural support** (bones/teeth) and enzyme function.

Plate 3.1: Examples of alkaline earth metal compounds

3.2.3 Comparative trends between Group 1 and Group 2

When comparing Group 1 and Group 2 elements, several differences and similarities emerge:

Reactivity: Group 1 elements are more reactive than Group 2 due to their lower ionisation energy.
Compounds: Group 1 compounds are generally more soluble and strongly basic, while Group 2 compounds are less soluble and often form precipitates.
Physical properties: Group 2 metals are harder, denser, and have higher melting points compared to Group 1 metals.
Biological relevance: Sodium and potassium ions are essential for nerve function, while calcium and magnesium ions are crucial for bone structure and enzyme activity.

Fill in the blank: Group 1 elements are generally _____ reactive than Group 2 elements because of their lower ionisation energy.

Comparative Properties of Group 1 and Group 2 Elements

Property	Group 1: Alkali Metals	Group 2: Alkaline Earth Metals
Valence Electrons	**1** (ns^1)	**2** (ns^2)
Common Ion	**+1 Cation**	**+2 Cation**
Reactivity	**Extremely high**; increases down the group; stored under oil.	**High** (but lower than Group 1); increases down the group.
Solubility	Most salts (chlorides, sulfates, carbonates) are **highly soluble** in water.	Many salts (carbonates, phosphates, sulfates) are **insoluble or poorly soluble.**
Hardness/Density	Very soft (can be cut with a knife); low density.	Harder and denser than Group 1 metals.
Biological Roles	Sodium and Potassium are vital for **nerve impulses** and osmotic balance.	Magnesium and Calcium are essential for **structural support** (bones/teeth) and enzyme function.

Table 3.2: Comparative trends between Group 1 and Group 2 elements

Property	Group 1 (Alkali metals)	Group 2 (Alkaline earth metals)
Valence electrons	1	2
Typical cation	+1	+2
Reactivity	Very high	Moderate
Solubility of compounds	High	Lower, often forming precipitates
Biological role	Na^+, K^+ in nerve function	Ca^{2+}, Mg^{2+} in bones and enzymes

Pilot questions 3.2

The alkali metals are highly reactive because they have _____ valence electron in the s-orbital.

A. Two
B. One
C. Three
D. Four

Alkaline earth metals form _____ cations by losing two valence electrons.

A. +1
B. +2
C. +3
D. +4

Group 1 elements are generally _____ reactive than Group 2 elements because of their lower ionisation energy.

A. Less
B. More
C. Equally
D. Not

3.3 Comparative Chemistry of Groups 13 and 14 Elements

3.3.1 Boron and aluminium – properties and compounds

Boron is a metalloid, meaning it has properties of both metals and non-metals. It is hard, brittle, and does not conduct electricity well. Boron commonly forms covalent compounds, such as borates.

Aluminium, on the other hand, is a lightweight, silvery metal that conducts electricity and heat efficiently. It readily forms ionic compounds, such as aluminium oxide (Al_2O_3), and is widely used in packaging and construction due to its corrosion resistance.

Fill in the blank: Aluminium is protected from further reaction by a thin layer of _____ on its surface.

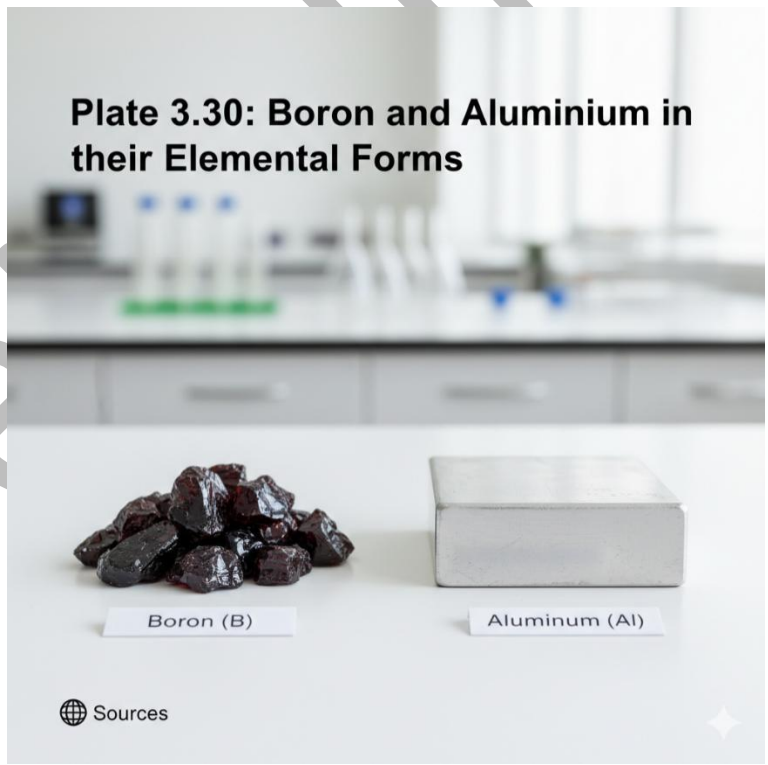

Plate 3.2: Boron and aluminium in their elemental forms

3.3.2 Carbon and silicon – properties and compounds

Carbon is a non-metal that forms the basis of organic chemistry. It can bond in multiple ways, producing compounds such as hydrocarbons, carbonates, and carbon dioxide. Carbon exists in several allotropes, including graphite and diamond.

Silicon is a metalloid, widely used in electronics as a semiconductor. It forms compounds such as silicon dioxide (SiO_2), found in sand and quartz. Silicon also forms silicates, which are the most abundant minerals in the Earth's crust.

Fill in the blank: The ability of carbon to bond with itself and form long chains is called _____.

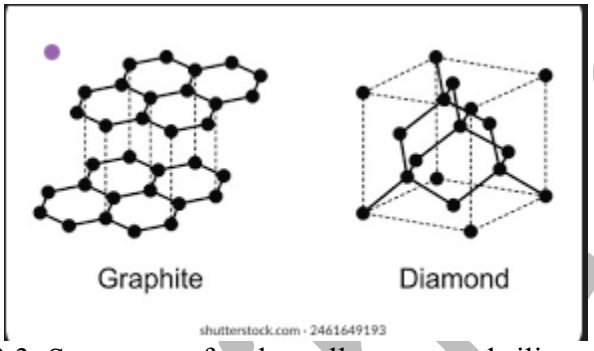

Figure 3.3: Structures of carbon allotropes and silicon dioxide

3.3.3 Comparative trends between Group 13 and Group 14

Comparing Groups 13 and 14 reveals important differences and similarities:

- **Bonding**: Group 13 elements tend to form compounds with +3 oxidation states, while Group 14 elements show +4 oxidation states and extensive covalent bonding.
- **Structures**: Group 13 elements are more metallic, (e.g., boron, aluminium) typically form **trivalent compounds**, whereas Group 14 elements range from non-metallic (carbon) to metalloid (silicon) and metallic (tin, lead), (e.g., carbon, silicon) typically form **tetravalent compounds**.
- **Applications**: Aluminium is widely used in construction and packaging, while silicon is essential in electronics. Carbon is the backbone of organic chemistry, and lead has historical uses in pipes and paints.

Fill in the blank: Group 14 elements typically exhibit the _____ oxidation state in their compounds.

Property	Group 13 (Boron Group)	Group 14 (Carbon Group)
Common Oxidation States	+3 and +1	+4, +2, and −4
Oxidation Trend	+3 is stable for lighter elements; **+1** becomes more stable down the group (Inert Pair Effect)	+4 is stable for lighter elements; **+2** becomes more stable down the group (Inert Pair Effect)
Bonding Type	Predominantly **covalent** (B, Al); transition to **ionic** for heavier metals (In, Tl)	Mostly **covalent** (C, Si, Ge); **metallic bonding** in Sn and Pb
Metallic Character	Increases down the group: Boron (metalloid), rest are metals	Increases down the group: C (non-metal), Si/Ge (metalloids), Sn/Pb (metals)
Catenation	Very limited; occurs in Boron clusters	Highly pronounced in **Carbon**; decreases rapidly down the group (Si > Ge > Sn)
Key Applications	**Al**: Aircraft, cans, wiring; **Ga**: LEDs; **B**: Glass, detergents	**Si/Ge**: Semiconductors; **C**: Steel (coke), organic chemistry; **Pb**: Batteries

Table 3.3: Comparative trends between Group 13 and Group 14 elements

Property	Group 13 (B, Al, etc.)	Group 14 (C, Si, etc.)
Typical oxidation state	+3	+4
Bonding type	Mostly ionic	Mostly covalent
Metallic character	More metallic	Ranges from non-metal to metallic
Key applications	Aluminium in packaging	Silicon in electronics, carbon in organic chemistry

Pilot questions 3.3

Aluminium is protected from further reaction by a thin layer of _____ on its surface.

A. Chloride
B. Oxide
C. Sulphide
D. Hydroxide

The ability of carbon to bond with itself and form long chains is called _____.

A. Polymerisation
B. Catenation
C. Crystallisation
D. Hybridisation

Group 14 elements typically exhibit the _____ oxidation state in their compounds.

A. +2
B. +3
C. +4
D. +5

3.4 Comparative Chemistry of Groups 15 and 16 Elements

3.4.1 Nitrogen and phosphorus – properties and compounds

Nitrogen is a non-metal found in Group 15. It exists naturally as a diatomic molecule (N_2), which is relatively inert due to its strong triple bond. Nitrogen forms compounds such as ammonia (NH_3) and nitrates, which are vital in agriculture.

Phosphorus, also in Group 15, exists in several allotropes, including white, red, and black phosphorus. It is more reactive than nitrogen and forms compounds such as phosphates, which are essential in fertilisers and biological molecules like DNA.

Fill in the blank: Nitrogen gas is relatively inert because of the strong _____ bond between its atoms.

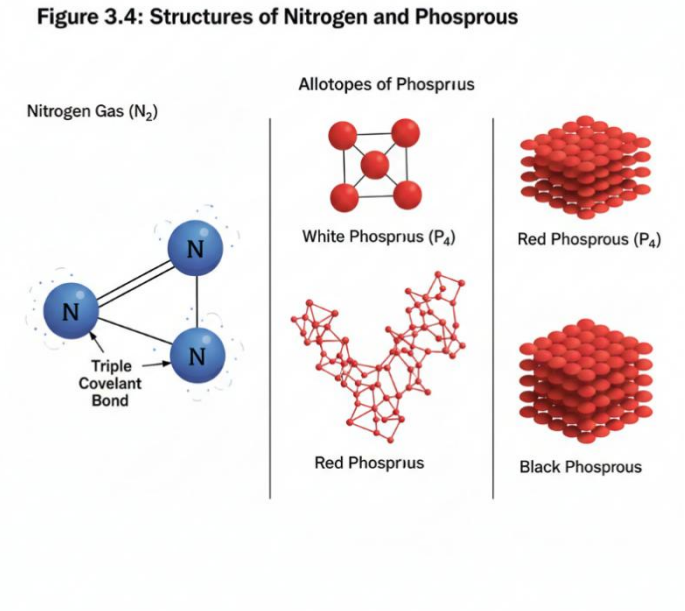

Figure 3.4: Structures of nitrogen and phosphorus

3.4.2 Oxygen and sulphur – properties and compounds

Oxygen is a Group 16 non-metal, existing naturally as a diatomic molecule (O_2). It is essential for respiration and combustion. Oxygen forms compounds such as oxides and peroxides.

Sulphur, also in Group 16, is a yellow solid that exists in several allotropes, the most common being rhombic sulphur. It forms compounds such as hydrogen sulphide (H_2S) and sulphur dioxide (SO_2), which are important in industry but can also contribute to environmental pollution

Fill in the blank: The most common allotrope of sulphur consists of _____ atoms arranged in a ring.

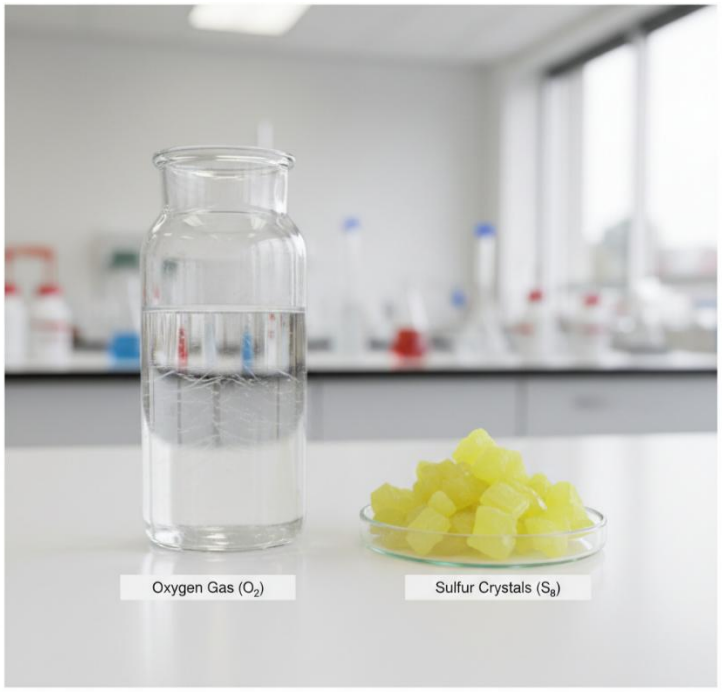

Plate 3.3: Oxygen and sulphur in their elemental forms

3.4.3 Comparative trends between Group 15 and Group 16

Comparing Groups 15 and 16 highlights important chemical differences:

Bonding: Group 15 elements typically form **trivalent compounds**, while Group 16 elements form **divalent compounds.**

Reactivity: Oxygen is more reactive than nitrogen due to weaker O=O bonds compared to N≡N bonds.

Biological importance: Nitrogen is crucial for proteins and nucleic acids, while oxygen is essential for respiration. Phosphorus is vital for energy transfer, and sulphur is important in amino acids and vitamins.

Industrial relevance: Nitrogen compounds are used in fertilisers and explosives, oxygen in steelmaking and medicine, phosphorus in detergents, and sulphur in sulphuric acid production.

Fill in the blank: Group 15 elements typically form _____ compounds, while Group 16 elements typically form divalent compounds.

Feature	Group 15 (Nitrogen Family)	Group 16 (Oxygen Family)
Valence Configuration	ns^2np^3 (Half-filled, extra stable)	ns^2np^4 (One electron pair in p-orbital)
Bonding	Forms up to **triple bonds** (e.g., $N \equiv N$). Typically trivalent (EH_3).	Forms up to **double bonds** (e.g., $O = O$). Typically divalent (H_2E).
Reactivity	Generally less reactive than Group 16; N_2 is inert. Reactivity varies; P_4 is highly reactive.	Generally **highly reactive**; Oxygen is a powerful oxidant. Reactivity decreases down the group.
Ionization Energy	**Higher** than Group 16 in the same period due to stable half-filled orbitals.	**Lower** than Group 15 due to electron-electron repulsion in the np^4 configuration.
Biological Roles	**Nitrogen:** Amino acids, proteins, DNA. **Phosphorus:** ATP, DNA/RNA, bone structure ($Ca_5(PO_4)_3OH$).	**Oxygen:** Cellular respiration, water. **Sulfur:** Amino acids (cysteine/methionine), vitamins. **Selenium:** Trace enzyme cofactor.
Industrial Uses	**Nitrogen:** Fertilizers (NH_3), explosives, cryogenics. **Phosphorus:** Detergents, pesticides, semiconductors.	**Oxygen:** Steel manufacturing, medical oxygen, rocket propellant. **Sulfur:** Sulfuric acid production, vulcanization of rubber.

Table 3.4: Comparative trends between Group 15 and Group 16 elements

Property	Group 15 (N, P, etc.)	Group 16 (O, S, etc.)
Typical bonding	Trivalent	Divalent
Reactivity	Moderate	High
Biological role	Proteins, nucleic acids	Respiration, amino acids
Industrial use	Fertilisers, explosives	Steelmaking, sulphuric acid

Pilot questions 3.4

Nitrogen gas is relatively inert because of the strong _____ bond between its atoms.

A. Single
B. Double
C. Triple
D. Ionic

The most common allotrope of sulphur consists of _____ atoms arranged in a ring.

A. 4
B. 6

C. 8
D. 12

Group 15 elements typically form _____ compounds, while Group 16 elements typically form divalent compounds.
A. Monovalent
B. Trivalent
C. Quadrivalent
D. Hexavalent

3.5 Applications and Significance of Main Group Elements

3.5.1 Industrial uses of selected main group elements

Main group elements play crucial roles in industry. **Sodium** and **potassium** compounds are widely used in glass manufacture, detergents, and fertilisers. **Calcium carbonate** is essential in cement and construction materials, while **aluminium** is valued for its strength-to-weight ratio in packaging, transport, and building. **Silicon** is indispensable in electronics, especially in semiconductors. **Sulphuric acid**, derived from sulphur, is one of the most important industrial chemicals, used in fertilisers, petroleum refining, and chemical synthesis.

Fill in the blank: The element that is indispensable in electronics, especially in semiconductors, is _____.

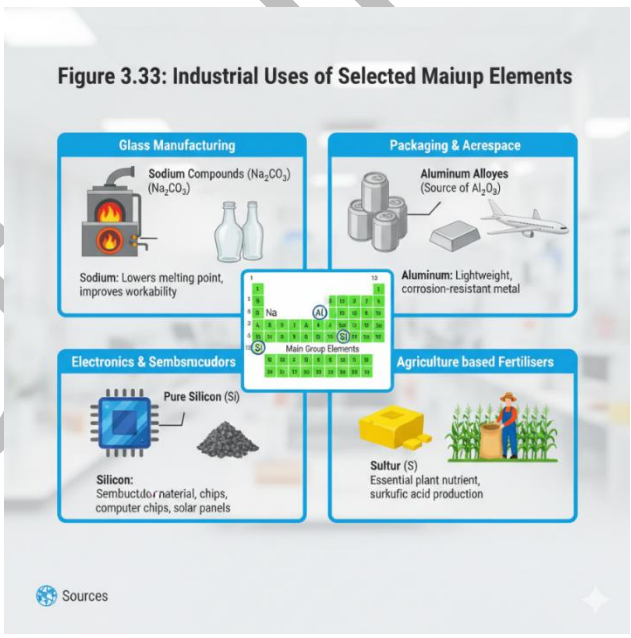

Figure 3.5: Industrial uses of selected main group elements

3.5.2 Biological importance of selected main group elements

Several main group elements are vital for life. **Sodium** and **potassium** ions regulate nerve impulses and muscle contraction. **Calcium** is essential for bone and teeth formation, as well as

blood clotting. **Phosphorus** is a key component of DNA, RNA, and ATP, which stores and transfers energy in cells. **Sulphur** is found in amino acids such as cysteine and methionine, contributing to protein structure. **Oxygen** is indispensable for respiration, enabling energy release from food molecules.

Fill in the blank: The element that forms part of DNA, RNA, and ATP, making it vital for energy transfer, is _____.

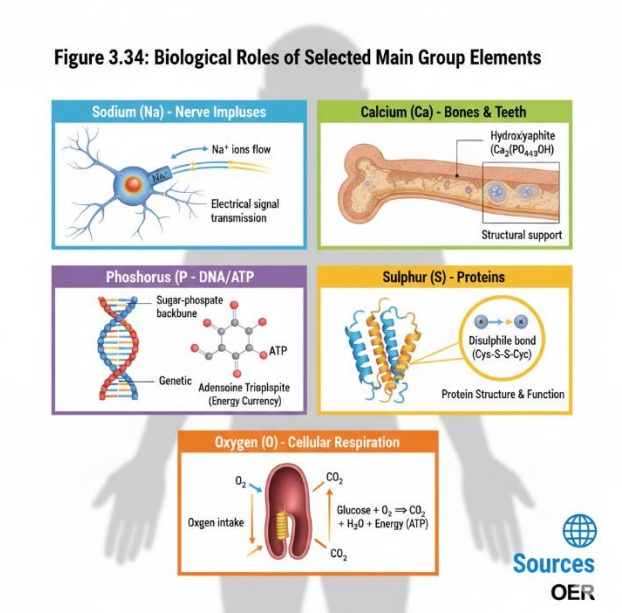

Plate 3.4: Biological importance of selected main group elements

3.5.3 Environmental relevance and challenges

Main group elements also have significant environmental impacts. **Nitrogen compounds** are essential for plant growth, but excessive fertiliser use can lead to water pollution and eutrophication. **Carbon dioxide**, a compound of carbon, is a major greenhouse gas contributing to climate change. **Sulphur dioxide**, released from burning fossil fuels, causes acid rain, which damages ecosystems and buildings. On the positive side, **oxygen** sustains life and supports ecological balance.

Fill in the blank: Excessive use of nitrogen fertilisers can lead to water pollution and _____.

Element / Compound	Primary Environmental Challenges	Impact on Ecosystems & Health
Nitrogen (N)	Eutrophication & Acidification	Causes "dead zones" in aquatic systems; loss of biodiversity; contributes to acid rain and smog.
Carbon Dioxide (CO_2)	Global Warming & Greenhouse Effect	Drives climate change, leading to rising sea levels, melting ice caps, and ocean acidification.
Sulphur Dioxide (SO_2)	Acid Rain & Air Pollution	Acidifies soil and water; damages forests and monuments; causes severe respiratory issues like bronchitis and asthma.
Oxygen (O_2)	Hypoxia & Ground-level Ozone	Depletion in water (hypoxia) leads to fish kills. In the form of ozone (O_3), it acts as a toxic pollutant at ground level.

Box 3.2: Environmental challenges linked to main group elements

• Nitrogen fertilisers → eutrophication of water bodies
• Carbon dioxide → greenhouse effect and climate change
• Sulphur dioxide → acid rain formation
• Oxygen → sustains life and ecological balance

Pilot questions 3.5

The element that is indispensable in electronics, especially in semiconductors, is _____.

A. Aluminium
B. Silicon
C. Sulphur
D. Calcium

The element that forms part of DNA, RNA, and ATP, making it vital for energy transfer, is _____.

A. Nitrogen
B. Phosphorus
C. Oxygen
D. Sulphur

Excessive use of nitrogen fertilisers can lead to water pollution and _____.

A. Acid rain
B. Eutrophication
C. Greenhouse effect
D. Desertification

Series Summary

Series Summary

This Series introduced you to the comparative chemistry of selected main group elements, highlighting their positions in the periodic table, periodic trends, and characteristic reactivity. You explored the properties and compounds of alkali and alkaline earth metals, compared their behaviour, and then examined the chemistry of boron, aluminium, carbon, and silicon. Building on this, you analysed the similarities and differences between Groups 13 and 14, and then studied nitrogen, phosphorus, oxygen, and sulphur, before comparing the overall trends in Groups 15 and 16. The Series concluded with a focus on the industrial, biological, and environmental significance of these elements, linking theory to real-world applications.

By completing this Series, you should now be able to **define the general characteristics of main group elements and explain periodic trends (SLO 3.1)**, **describe and compare the properties and reactivity of Groups 1 and 2 (SLOs 3.2–3.4)**, **outline the chemistry of Groups 13 and 14 (SLOs 3.5–3.7)**, **explain the properties and compounds of Groups 15 and 16 (SLOs 3.8–3.10)**, and **evaluate their industrial, biological, and environmental significance (SLOs 3.11–3.13)**. These outcomes ensure you can connect periodic trends with practical uses and challenges, strengthening your understanding of how main group elements shape both everyday life and global sustainability.

Glossary of Terms

Acid rain: Rainfall made acidic by gases such as sulphur dioxide and nitrogen oxides, which can damage ecosystems and buildings.

Alkaline earth metals: Group 2 elements (e.g., calcium, magnesium) that are harder and less reactive than alkali metals, forming +2 cations in compounds.

Alkali metals: Group 1 elements (e.g., sodium, potassium) that are soft, highly reactive metals forming +1 cations in compounds.

Allotrope: Different structural forms of the same element, such as diamond and graphite for carbon, or white and red phosphorus.

Carbon dioxide (CO_2): A greenhouse gas produced by respiration and combustion, contributing to climate change.

Electronegativity: A measure of how strongly an atom attracts electrons in a chemical bond.

Ionisation energy: The energy required to remove an electron from an atom or ion.

Main group elements: Elements in Groups 1, 2, and 13–18 of the periodic table, including s-block and p-block elements.

Metalloid: An element with properties of both metals and non-metals, such as boron or silicon.

Nitrogen cycle: The natural process by which nitrogen moves through the atmosphere, soil, and living organisms.

Periodic trends: Predictable changes in properties such as atomic radius, ionisation energy, and electronegativity across the periodic table.

Phosphates: Compounds containing phosphorus and oxygen, important in fertilisers and biological molecules like DNA.

Rhombic sulphur: The most stable allotrope of sulphur, appearing as yellow crystals.

Semiconductor: A material, such as silicon, that conducts electricity under certain conditions and is used in electronics.

Valency: The combining capacity of an element, determined by the number of electrons it can lose, gain, or share.

This glossary consolidates the essential terms introduced in Series 3, providing clear and accessible definitions to support independent learning.

Concept Check Questions [Series 3]

Objective Questions

Main group elements are located in which groups of the periodic table?
A. 1, 2, and 13–18
B. 3–12
C. Only Group 1
D. Only Group 18
(Linked to SLO 3.1)

Which Group 1 element reacts vigorously with water to form hydroxide and hydrogen gas?
A. Calcium
B. Sodium
C. Aluminium
D. Carbon
(Linked to SLO 3.2)

Group 2 elements typically form cations with what charge?
A. +1
B. +2
C. +3
D. +4
(Linked to SLO 3.3)

Which Group 14 element is widely used in semiconductors?
A. Carbon
B. Silicon
C. Tin
D. Lead
(Linked to SLO 3.6)

The most common allotrope of sulphur found in nature is:
A. White sulphur
B. Rhombic sulphur
C. Red sulphur
D. Black sulphur
(Linked to SLO 3.9)

Short-Answer Questions

Define the term **metalloid** and give one example from the main group elements.
(Linked to SLO 3.5 and SLO 3.6)

Explain why alkali metals are more reactive than alkaline earth metals.
(Linked to SLO 3.4)

State one industrial use of aluminium and one biological role of phosphorus.
(Linked to SLO 3.11 and SLO 3.12)

Describe how sulphur dioxide contributes to environmental pollution.
(Linked to SLO 3.13)

Long-Answer Questions

Compare the chemistry of boron and aluminium, highlighting their differences in bonding and applications.
(Linked to SLO 3.5)

Analyse the similarities and differences between carbon and silicon, and discuss their significance in organic chemistry and electronics.
(Linked to SLO 3.6)

Evaluate the environmental relevance of carbon dioxide, sulphur dioxide, and nitrogen compounds, and suggest possible strategies to mitigate their negative impacts.
(Linked to SLO 3.13)

Answers to Concept Check Questions [Series 3]

Objective Questions

A. 1, 2, and 13–18
B. Sodium
B. +2
B. Silicon
B. Rhombic sulphur

Short-Answer Questions

A metalloid is an element with properties of both metals and non-metals. Example: Boron or Silicon.
Alkali metals are more reactive because they have only one valence electron, which is easily lost, while alkaline earth metals have two.
Aluminium is used in packaging and construction; phosphorus is part of DNA and ATP.
Sulphur dioxide dissolves in rainwater to form acids, leading to acid rain that damages ecosystems and structures.

Long-Answer Questions

Question 1

Basic response: Boron is a metalloid forming covalent compounds, while aluminium is a metal forming ionic compounds. Boron is used in glass and detergents, aluminium in packaging and construction.
Value-added response: Learners may add that boron's electron deficiency leads to unusual bonding (e.g., boranes), while aluminium's amphoteric oxide behaviour makes it useful in catalysis and industrial processes.

Question 2

Basic response: Carbon is a non-metal forming organic compounds, while silicon is a metalloid forming silicates and silicon dioxide. Carbon is central to life, silicon to electronics.
Value-added response: Outstanding learners may discuss carbon allotropes (diamond, graphite, graphene) and silicon's role in semiconductors, solar cells, and nanotechnology.

Question 3

Basic response: Carbon dioxide contributes to climate change, sulphur dioxide causes acid rain, and nitrogen compounds pollute water.
Value-added response: Learners may propose mitigation strategies such as reducing fossil fuel use, employing scrubbers in power plants, promoting renewable energy, and improving agricultural practices to reduce nitrate runoff.

Answers to Pilot Questions [Series 3]

Part 3.1: General Characteristics of Main Group Elements

Groups 1, 2, and 13–18
Increases
Inert

Part 3.2: Comparative Chemistry of Group 1 and Group 2 Elements

One
+2
More

Part 3.3: Comparative Chemistry of Groups 13 and 14 Elements

Oxide
Catenation
+4

Part 3.4: Comparative Chemistry of Groups 15 and 16 Elements

Triple

8
Trivalent

Part 3.5: Applications and Significance of Main Group Elements

Silicon
Phosphorus
Eutrophication

References and Attributions [Series 3]

Textual Sources

Housecroft, C. E., & Sharpe, A. G. (2018). *Inorganic Chemistry* (5th ed.). Pearson.
Miessler, G. L., Fischer, P. J., & Tarr, D. A. (2014). *Inorganic Chemistry* (5th ed.). Pearson.
IUPAC. (1997). *Compendium of Chemical Terminology (the "Gold Book")*.
Cotton, F. A., Wilkinson, G., Murillo, C. A., & Bochmann, M. (1999). *Advanced Inorganic Chemistry* (6th ed.). Wiley.

Illustrations (Figures, Plates, Tables, Boxes)

Figure 3.1 Position of main group elements in the periodic table
AI prompt: "Generate a labelled periodic table highlighting Groups 1, 2, and 13–18 as main group elements."
Search string: "periodic table main group elements diagram OER"

Table 3.1 Trends in atomic and physical properties of main group elements
AI prompt: "Generate a table showing trends in atomic radius, ionisation energy, and electronegativity across main group elements."
Search string: "atomic properties trends main group elements table OER"

Box 3.1 Reactivity patterns of main group elements
AI prompt: "Generate a text box summarising the reactivity patterns of main group elements with examples."
Search string: "reactivity patterns main group elements OER"

Figure 3.2 Reaction of an alkali metal with water
AI prompt: "Generate a labelled diagram showing sodium reacting with water to form sodium hydroxide and hydrogen gas."
Search string: "alkali metals reaction with water diagram OER"

Plate 3.1 Calcium carbonate in limestone
AI prompt: "Create an image showing limestone as a natural source of calcium carbonate."
Search string: "calcium carbonate limestone OER"

Box 3.2 Comparative trends between Group 1 and Group 2 elements
AI prompt: "Generate a text box summarising comparative trends between Group 1 and

Group 2 elements."
Search string: "comparative chemistry group 1 and group 2 OER"

Figure 3.3 Properties and compounds of boron and aluminium
AI prompt: "Generate a labelled diagram comparing boron and aluminium, showing borates and aluminium oxide as examples."
Search string: "boron aluminium properties compounds diagram OER"

Plate 3.2 Quartz crystals containing silicon dioxide
AI prompt: "Create an image showing quartz crystals as a natural source of silicon dioxide."
Search string: "silicon dioxide quartz crystals OER"

Box 3.3 Comparative trends between Group 13 and Group 14 elements
AI prompt: "Generate a text box summarising comparative trends between Group 13 and Group 14 elements."
Search string: "comparative chemistry group 13 and group 14 OER"

Figure 3.4 Properties and compounds of nitrogen and phosphorus
AI prompt: "Generate a labelled diagram showing nitrogen as a diatomic molecule and phosphorus allotropes with examples of their compounds."
Search string: "nitrogen phosphorus properties compounds diagram OER"

Plate 3.3 Rhombic sulphur crystals
AI prompt: "Create an image showing rhombic sulphur crystals as the common allotrope of sulphur."
Search string: "rhombic sulphur crystals OER"

Box 3.4 Comparative trends between Group 15 and Group 16 elements
AI prompt: "Generate a text box summarising comparative trends between Group 15 and Group 16 elements with examples."
Search string: "comparative chemistry group 15 and group 16 OER"

Figure 3.5 Industrial uses of selected main group elements
AI prompt: "Generate a labelled diagram showing aluminium in packaging, silicon in electronics, sodium in detergents, and calcium in cement production."
Search string: "industrial uses of aluminium silicon sodium calcium OER"

Plate 3.4 Biological importance of calcium and phosphorus
AI prompt: "Create an image showing calcium in bones and phosphorus in DNA structure."
Search string: "calcium bones phosphorus DNA OER"

Box 3.5 Environmental relevance of main group elements
AI prompt: "Generate a text box summarising the environmental relevance of carbon dioxide, sulphur dioxide, and nitrogen compounds."
Search string: "environmental relevance carbon sulphur nitrogen OER"

Notes on Attribution

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References are presented in APA style for consistency.

Course code: CHM 212

Course title: Inorganic Chemistry I

Course Unit: 2 Units C: LH 30

Series 1: Chemistry of First-Row Transition Metals

Series 2: Coordination Chemistry and Crystal Field Theory

Series 3: Comparative Chemistry of Selected Main Group Elements

Series 4: Fundamentals of Organometallic Chemistry

Series 5: Roles of Metals in Biochemical Systems and Redox Concepts

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Suggested Outline

4.1 Introduction to Organometallic Chemistry

Definition and scope of organometallic compounds
Historical development and significance
General applications in industry and research

4.2 Bonding and Structure in Organometallic Compounds

Nature of metal–carbon bonds
Types of ligands in organometallic chemistry (alkyl, aryl, carbonyl, etc.)
Structural features and stability factors

4.3 Classification of Organometallic Compounds

Alkyl and aryl complexes
Carbonyl complexes

Metallocenes and sandwich compounds
Organometallic clusters

4.4 Reactions of Organometallic Compounds

Oxidative addition and reductive elimination
Insertion and elimination reactions
Ligand substitution and rearrangements
Catalytic cycles involving organometallic intermediates

4.5 Applications of Organometallic Chemistry

Industrial catalysis (e.g., polymerisation, hydroformylation)
Role in organic synthesis
Environmental and biological relevance

Introduction

Organometallic chemistry is a fascinating branch of chemistry that bridges the gap between organic and inorganic disciplines. It focuses on compounds containing direct bonds between metals and carbon, which play a central role in catalysis, materials science, and industrial processes. Building on the comparative chemistry of main group elements studied in the previous Series, this Series introduces you to the fundamentals of organometallic chemistry, preparing you to appreciate its theoretical foundations and practical applications.

The aim of this Series is to provide you with a clear understanding of the bonding, classification, and reactivity of organometallic compounds, while also highlighting their importance in industry, research, and everyday life.

We shall commence this Series by introducing the scope and significance of organometallic chemistry. Next, we will explore bonding and structural features, followed by a study of the classification of organometallic compounds. Subsequently, we will examine their characteristic reactions, including processes such as oxidative addition and catalytic cycles. Finally, we will conclude by considering the wide-ranging applications of organometallic chemistry in industrial catalysis, organic synthesis, and environmental contexts.

Series Learning Outcomes

Upon completing this Series, you should be able to:

SLO 4.1 define the scope and significance of organometallic chemistry,
SLO 4.2 explain the nature of metal–carbon bonds and describe the structural features of organometallic compounds,
SLO 4.3 classify organometallic compounds into categories such as alkyl, aryl, carbonyl, metallocenes, and clusters,

SLO 4.4 analyse key reactions of organometallic compounds including oxidative addition, reductive elimination, insertion, and ligand substitution,
SLO 4.5 evaluate the role of organometallic compounds in catalytic cycles,
SLO 4.6 assess the industrial applications of organometallic chemistry in processes such as polymerisation and hydroformylation, and
SLO 4.7 discuss the environmental and biological relevance of organometallic compounds.

4.1 Introduction to Organometallic Chemistry

4.1.1 Definition and scope of organometallic compounds

Organometallic compounds are chemical substances that contain at least one direct bond between a metal atom and a carbon atom of an organic group. This unique bonding arrangement allows them to combine properties of both organic and inorganic chemistry. Their scope extends across catalysis, materials science, and biological systems, making them central to modern chemical research and industry.

Fill in the blank: Organometallic compounds are characterised by having a direct bond between a _____ atom and a carbon atom.

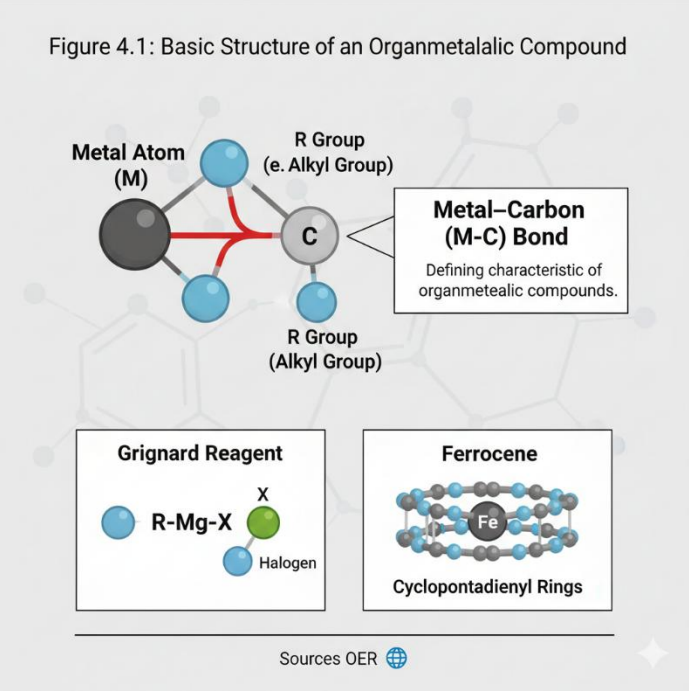

Figure 4.1: Basic structure of an organometallic compound

4.1.2 Historical development and significance

The study of organometallic chemistry began in the 19th century with discoveries such as **Zeise's salt**, one of the first known organometallic compounds. Later, the synthesis of **ferrocene** in the 20th century revolutionised the field, demonstrating the stability of sandwich compounds.

These milestones highlighted the importance of organometallic chemistry in understanding bonding and reactivity, and paved the way for its use in catalysis and industrial processes.

Fill in the blank: The discovery of _____ in the 20th century demonstrated the stability of sandwich compounds in organometallic chemistry.

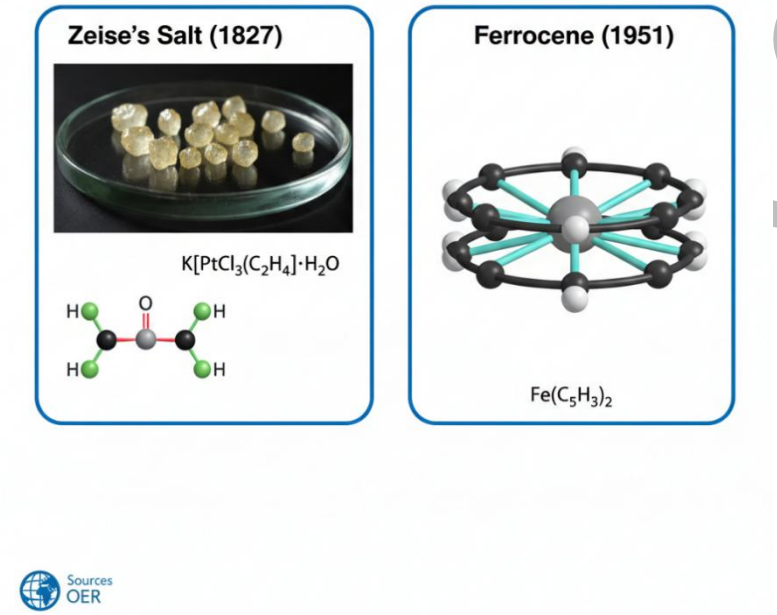

Plate 4.1: Historical milestones in organometallic chemistry

4.1.3 General applications in industry and research

Organometallic compounds are widely used in industry and research. In **industrial catalysis**, they enable processes such as polymerisation, hydroformylation, and hydrogenation. In **organic synthesis**, they provide pathways for forming carbon–carbon and carbon–heteroatom bonds. Organometallic chemistry also has **biological relevance**, with compounds such as cisplatin used in cancer treatment, and **environmental significance**, where catalysts help reduce harmful emissions.

Fill in the blank: Organometallic compounds are widely used as _____ in industrial processes such as polymerisation and hydroformylation.

Application Area	Primary Use	Key Examples & Mechanisms
Industrial Polymerization	Production of plastics and elastomers.	**Ziegler-Natta Catalysts:** Titanium-based organometallics used to produce polyethylene and polypropylene with precise structural control.
Hydroformylation	Converting alkenes into aldehydes.	**Rhodium/Cobalt Carbonyls:** Used in the "Oxo process" to create precursors for detergents, plasticizers, and fragrances.
Pharmaceutical Development	Cross-coupling reactions to build complex molecules.	**Palladium Catalysts:** (e.g., Suzuki or Heck reactions) Essential for "stitching" carbon atoms together to form the specific frameworks of modern medicines.
Advanced Materials	Chemical Vapor Deposition (CVD).	**Trimethylgallium:** An organometallic precursor used to create thin films for semiconductors, LEDs, and high-efficiency solar cells.
Mechanistic Research	"Probing" how chemical reactions occur.	**Organometallic Intermediates:** Scientists isolate unstable metal-carbon species to map out reaction pathways, allowing for the design of faster, "greener" reactions.

Box 4.1: Selected applications of organometallic compounds

- Catalysts in polymerisation and hydroformylation
- Tools for studying reaction mechanisms
- Precursors for advanced materials
- Agents in pharmaceutical development

Pilot questions 4.1

Organometallic compounds are characterised by having a direct bond between a _____ atom and a carbon atom.

A. Oxygen
B. Metal
C. Nitrogen
D. Hydrogen

The discovery of _____ in the 20th century demonstrated the stability of sandwich compounds in organometallic chemistry.

A. Zeise's salt
B. Ferrocene
C. Ammonia
D. Methane

Organometallic compounds are widely used as _____ in industrial processes such as polymerisation and hydroformylation.

A. Reactants
B. Catalysts
C. Solvents
D. Inhibitors

4.2 Bonding and Structure in Organometallic Compounds

4.2.1 Nature of metal–carbon bonds

The defining feature of organometallic compounds is the **metal–carbon bond**, which can vary in character depending on the metal and the organic group attached. In some cases, the bond is largely ionic, with the carbon acting as a negatively charged centre. In other cases, the bond is covalent, involving shared electron density between the metal and carbon. Transition metals often form bonds that are partly covalent and partly ionic, giving rise to unique reactivity patterns.

Fill in the blank: The defining feature of organometallic compounds is the presence of a _____ bond.

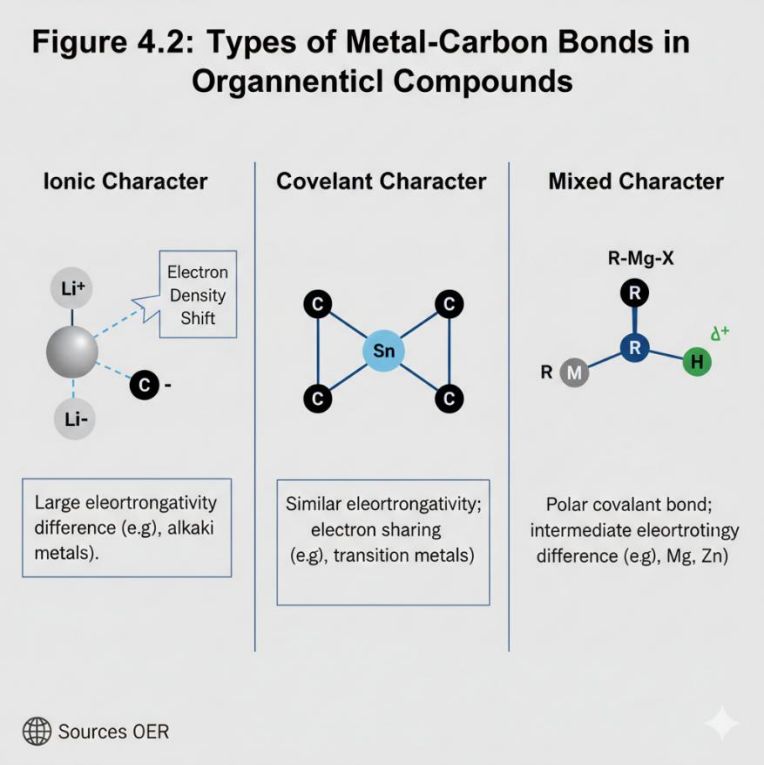

Figure 4.2: Types of metal–carbon bonds in organometallic compounds

4.2.2 Types of ligands in organometallic chemistry

Ligands are molecules or ions that donate electrons to a central metal atom. In organometallic chemistry, common ligands include:

Alkyl ligands: carbon chains bonded directly to the metal.

Aryl ligands: aromatic rings such as phenyl groups.

Carbonyl ligands: carbon monoxide molecules bonded to the metal, stabilising complexes through back-bonding.

Other ligands: such as cyclopentadienyl (Cp) rings in metallocenes.

Fill in the blank: In organometallic chemistry, _____ ligands stabilise metals through backbonding interactions.

Ligand Type	Examples	Bonding Characteristics	Effect on Stability/Reactivity
Carbonyls	Carbon Monoxide (CO)	Strong **π-acceptor;** stabilizes metals in low oxidation states.	Increases stability of electron-rich metals; makes the metal center more electrophilic.
Phosphines	Triphenylphosphine (PPh_3)	Good **σ-donor** and tunable π-acceptor.	Sterically "bulky" phosphines prevent unwanted side reactions and stabilize coordinatively unsaturated intermediates.
Hydrides	Hydrogen (H^-)	Small, strong σ-donor.	Highly reactive; essential for **hydrogenation** and **hydroformylation** catalytic cycles.
Alkenes	Ethylene (C_2H_4)	π-donor and π-acceptor (Dewar-Chatt-Duncanson model).	Generally labile (easily displaced), making them excellent "leaving groups" to open up active sites for catalysis.

Table 4.1: Common ligands in organometallic chemistry and their effects

Ligand type	Example	Effect on compound stability/reactivity
Alkyl	$-CH_3$	Increases reactivity
Aryl	$-C_6H_5$	Provides stability through resonance
Carbonyl	CO	Stabilises via backbonding
Cyclopentadienyl	$C_5H_5^-$	Forms stable sandwich compounds

4.2.3 Structural features and stability factors

The **structure** of organometallic compounds depends on the type of ligands and the bonding interactions. Some compounds, such as **metallocenes**, adopt sandwich structures where a metal atom is bound between two aromatic rings. Stability is influenced by factors such as electron count, ligand type, and geometry. The **18-electron rule** is often used to predict stability, stating that transition metal complexes are most stable when the sum of their valence electrons and donated electrons equals 18.

Fill in the blank: Transition metal organometallic complexes are often most stable when they obey the _____ rule.

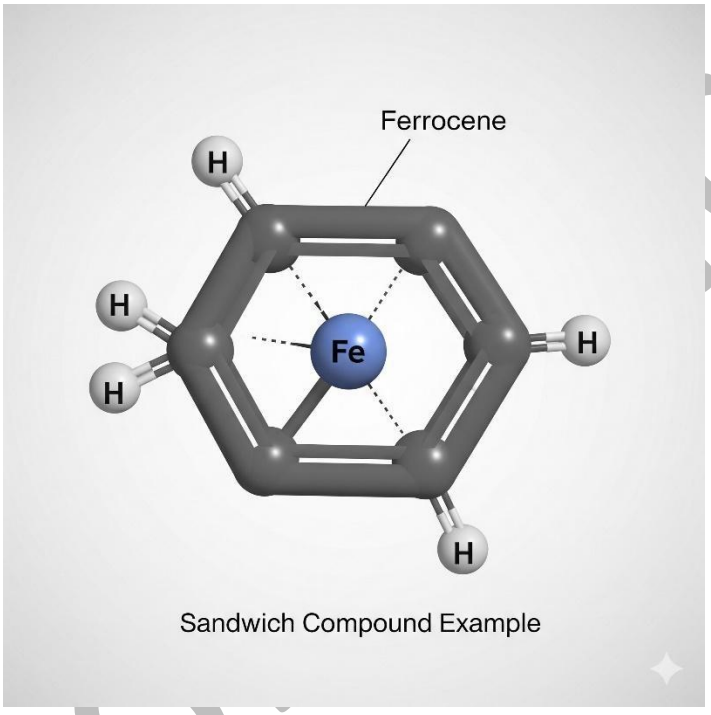

Plate 4.2: Structure of ferrocene illustrating sandwich bonding

Pilot questions 4.2

The defining feature of organometallic compounds is the presence of a _____ bond.

A. Hydrogen–oxygen
B. Metal–carbon
C. Nitrogen–hydrogen
D. Carbon–carbon

In organometallic chemistry, _____ ligands stabilise metals through backbonding interactions.

A. Alkyl
B. Aryl
C. Carbonyl
D. Cyclopentadienyl

Transition metal organometallic complexes are often most stable when they obey the _____ rule.

A. Octet
B. 18-electron
C. 12-electron
D. 24-electron

4.3 Classification of Organometallic Compounds

4.3.1 Alkyl and aryl complexes

Alkyl complexes are organometallic compounds where a metal is directly bonded to an alkyl group (–CH_3, –C_2H_5, etc.). These complexes are often highly reactive because the carbon–metal bond can undergo insertion or elimination reactions. **Aryl complexes**, in contrast, involve a metal bonded to an aromatic ring such as phenyl (–C_6H_5). The resonance stabilisation of the aromatic ring often makes aryl complexes more stable than alkyl complexes.

Fill in the blank: Organometallic compounds where a metal is bonded to an aromatic ring are called _____ complexes.

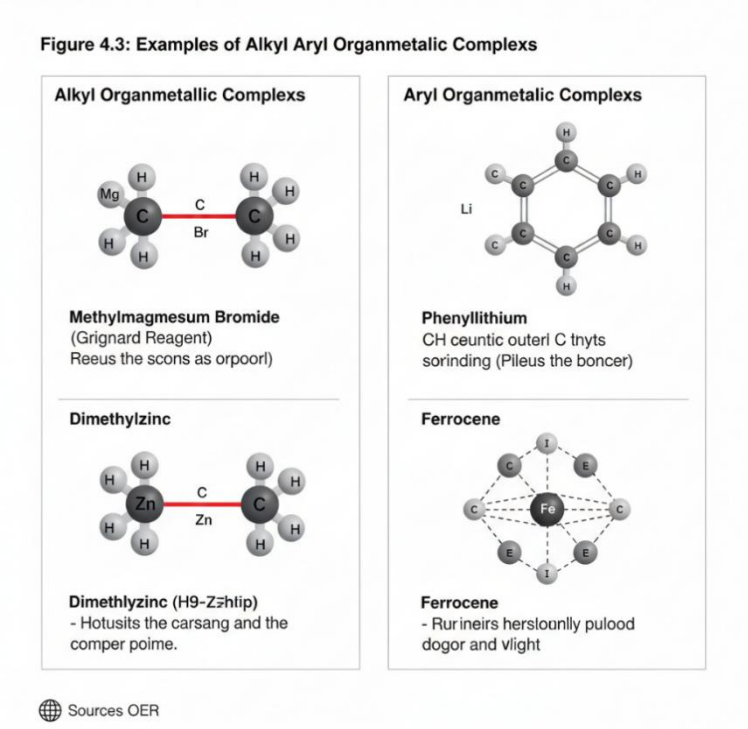

Figure 4.3: Alkyl and aryl complexes in organometallic chemistry

4.3.2 Carbonyl complexes

Carbonyl complexes are compounds where carbon monoxide (CO) acts as a ligand, bonding to a metal through its carbon atom. These complexes are stabilised by **backbonding**, where

electrons from the metal are donated into the antibonding orbitals of CO. Carbonyl complexes are important in catalysis, particularly in processes such as hydroformylation and carbonylation.

Fill in the blank: Carbonyl complexes are stabilised by a process known as _____, where electrons are donated from the metal into CO orbitals.

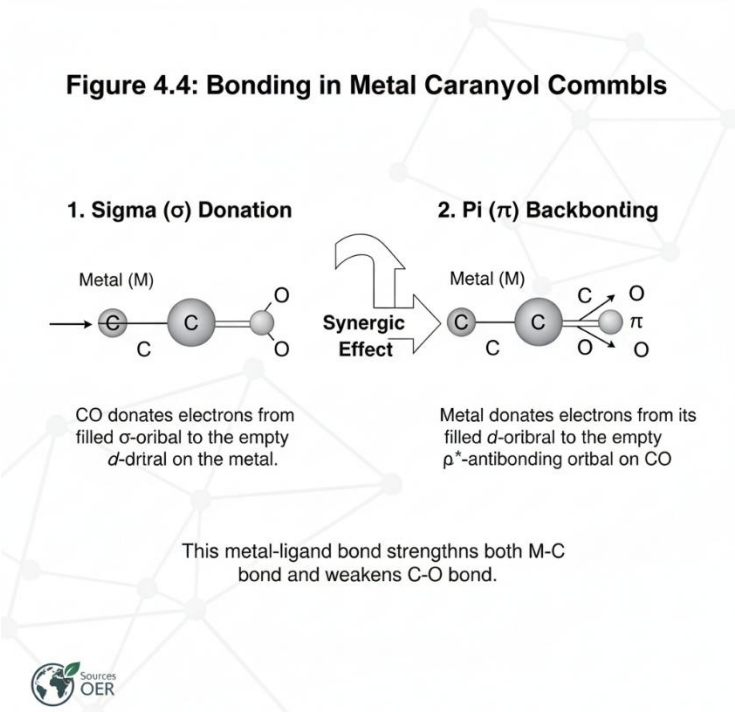

Plate 4.3: Bonding in carbonyl complexes

4.3.3 Metallocenes and sandwich compounds

Metallocenes are a class of organometallic compounds where a metal atom is sandwiched between two cyclopentadienyl (Cp) rings. The most famous example is **ferrocene**, which demonstrated remarkable stability and led to significant advances in organometallic chemistry.

Sandwich compounds extend this concept to other ligands, where the metal is positioned between two planar groups.

Fill in the blank: The most famous example of a metallocene is _____, which consists of an iron atom between two cyclopentadienyl rings.

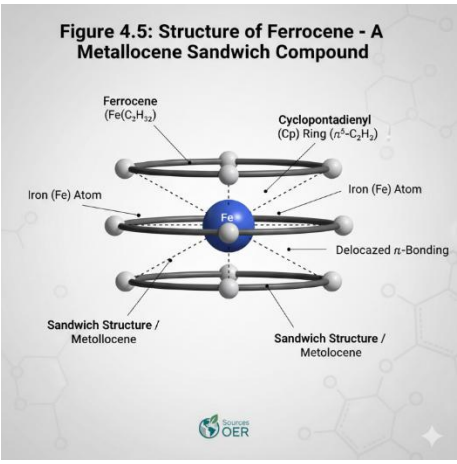

Figure 4.4: Structure of ferrocene as a metallocene

4.3.4 Organometallic clusters

Organometallic clusters are compounds containing two or more metal atoms bonded together, often with bridging ligands such as carbonyls or hydrides. These clusters can exhibit unique electronic and structural properties, making them useful in catalysis and materials science. Their bonding is often complex, involving both metal–metal and metal–ligand interactions.

Fill in the blank: Organometallic clusters often contain _____ metal atoms bonded together with bridging ligands.

Cluster Formula	Metal Framework	Key Features	Biological/Industrial Relevance
Triiron Dodecacarbonyl $[Fe_3(CO)_{12}]$	**Triangular (** Fe_3)	Features unique **bridging CO ligands**; serves as a precursor for generating highly reactive iron species.	Used in organic synthesis to desulfurize molecules and reduce nitro groups.
Tetrarhodium Dodecacarbonyl $[Rh_4(CO)_{12}]$	**Tetrahedral (** Rh_4)	A stable, "closed-shell" cluster; high catalytic activity due to the noble metal centers.	Studied as a model for **hydroformylation** catalysts (converting alkenes to aldehydes).
Triosmium Dodecacarbonyl $[Os_3(CO)_{12}]$	**Triangular (** Os_3)	Extremely robust M-M bonds; often used as a "scaffold" to study how organic molecules bind to metal surfaces.	Used to model the **Fischer-Tropsch** process (converting CO/H_2 into liquid fuels).

Table 4.2: Examples of organometallic clusters

Cluster type	Example	Key feature
Carbonyl cluster	$Fe_3(CO)_{12}$	Bridging carbonyl ligands

Cluster type	Example	Key feature
Hydride cluster	$Ru_3H(CO)_9$	Bridging hydride ligands
Mixed-metal cluster	$CoMo(CO)_{10}$	Metal–metal bonding with mixed metals

Pilot questions 4.3

Organometallic compounds where a metal is bonded to an aromatic ring are called _____ complexes.

A. Alkyl
B. Aryl
C. Carbonyl
D. Sandwich

Carbonyl complexes are stabilised by a process known as _____.

A. Resonance
B. Backbonding
C. Hybridisation
D. Substitution

The most famous example of a metallocene is _____.

A. Zeise's salt
B. Ferrocene
C. Methane
D. Benzene

Organometallic clusters often contain _____ metal atoms bonded together with bridging ligands.

A. Single
B. Two or more
C. Four only
D. None

4.4 Reactions of Organometallic Compounds

4.4.1 Oxidative addition and reductive elimination

Oxidative addition is a reaction where a metal complex increases its oxidation state and coordination number by adding new ligands, often breaking a bond in the added molecule. For example, a metal may insert into a hydrogen–halogen bond, forming two new metal–ligand bonds.

Reductive elimination is the reverse process, where two ligands on a metal combine and are released as a molecule, reducing the oxidation state and coordination number of the metal. Together, these reactions form a fundamental pair in catalytic cycles.

Fill in the blank: The process in which a metal complex increases its oxidation state by adding new ligands is called _____.

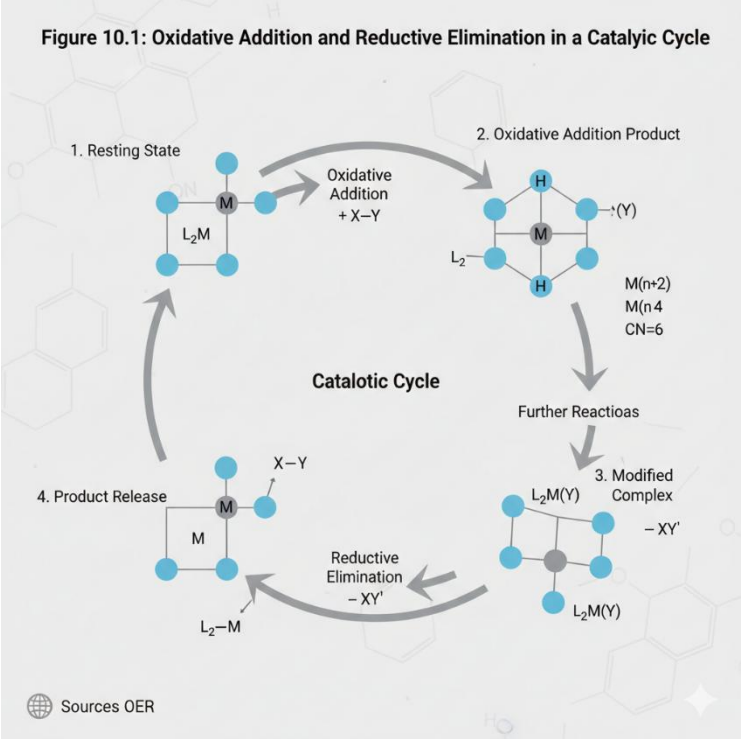

Figure 4.5: Oxidative addition and reductive elimination in organometallic chemistry

4.4.2 Insertion and elimination reactions

Insertion reactions occur when a ligand such as CO or an alkene inserts itself between the metal and another ligand, forming a new bond. This is a common step in processes like hydroformylation.

Elimination reactions involve the removal of a ligand from the metal complex, often producing small molecules such as H_2 or alkenes. These reactions are important for rearranging ligands and generating useful products.

Fill in the blank: When a ligand such as CO inserts itself between the metal and another ligand, the process is called _____.

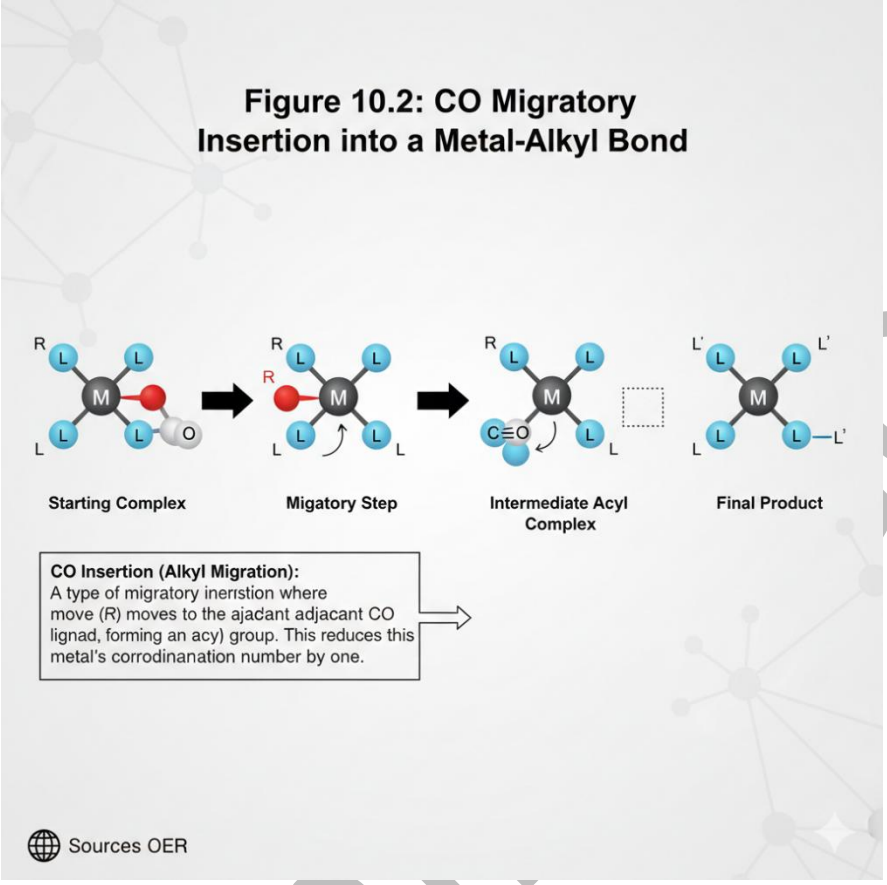

Plate 4.4: Example of an insertion reaction in organometallic chemistry

4.4.3 Ligand substitution and rearrangements

Ligand substitution involves replacing one ligand in a metal complex with another. This can occur through associative mechanisms (where the new ligand attaches before the old one leaves) or dissociative mechanisms (where the old ligand leaves first).

Rearrangements occur when ligands change their positions around the metal centre, often altering the geometry of the complex. These processes are important in fine-tuning the reactivity and selectivity of catalysts.

Fill in the blank: In ligand substitution, if the new ligand attaches before the old one leaves, the mechanism is called _____.

Feature	Associative (S_N2 type)	Dissociative (S_N1 type)
Step 1	The entering ligand (L') binds to the metal **before** the leaving group (L) departs.	The leaving group (L) departs **be** the entering ligand (L') binds.
Intermediate	Formation of a **higher-coordinate** intermediate (e.g., 5-coord → 6-coord).	Formation of a **lower-coordinate** intermediate (e.g., 6-coord → 5-coord).
Rate-Determining Step	The arrival of the new ligand.	The departure of the old ligand.
Favoured By	**16-electron** complexes (square planar) or unsaturated centers.	**18-electron** complexes (octahed that are electronically "full."
Example Reaction	**Vaska's Complex:** $[IrCl(CO)(PPh_3)_2] + L \rightarrow [IrCl(CO)(PPh_3)_2L]$	**Nickel Tetracarbonyl:** $[Ni(CO)_4] + L \rightarrow [Ni(CO)_3L]$
Steric Influence	Hindered by bulky ligands around the metal.	Accelerated by bulky ligands (crowding forces the leaving grou out).

Table 4.3: Mechanisms of ligand substitution

Mechanism type	Description	Example reaction
Associative	New ligand attaches before old one leaves	Substitution in square-planar complexes
Dissociative	Old ligand leaves before new one attaches	Substitution in octahedral complexes

4.4.4 Catalytic cycles involving organometallic intermediates

Catalytic cycles are sequences of reactions in which organometallic complexes act as catalysts, facilitating transformations without being consumed. These cycles often involve oxidative addition, insertion, and reductive elimination steps. A well-known example is the **hydroformylation reaction**, where alkenes are converted into aldehydes using a metal carbonyl catalyst. Catalytic cycles are central to industrial processes, as they enable efficient production of chemicals with minimal waste.

Fill in the blank: In hydroformylation, alkenes are converted into _____ using a metal carbonyl catalyst.

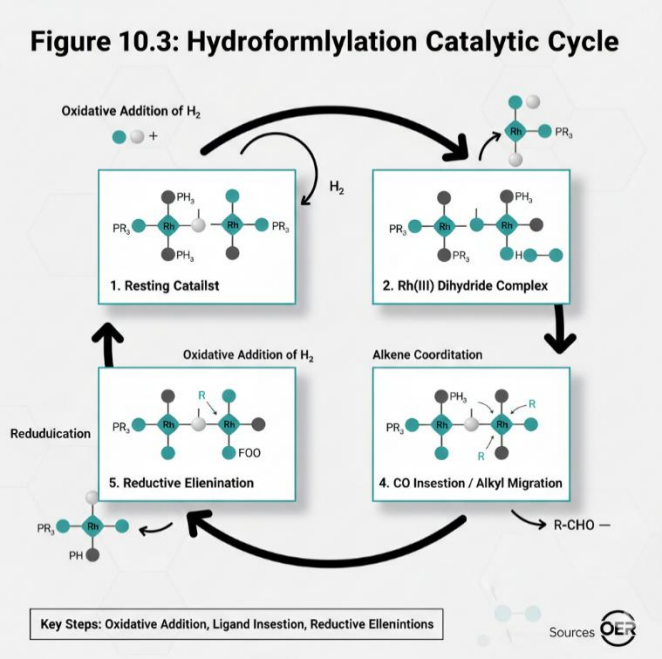

Figure 4.6: Hydroformylation catalytic cycle involving organometallic intermediates

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Pilot questions 4.4

The process in which a metal complex increases its oxidation state by adding new ligands is called _____.

A. Reductive elimination
B. Oxidative addition
C. Insertion
D. Substitution

When a ligand such as CO inserts itself between the metal and another ligand, the process is called _____.

A. Elimination
B. Insertion
C. Substitution
D. Rearrangement

In ligand substitution, if the new ligand attaches before the old one leaves, the mechanism is called _____.

A. Dissociative
B. Associative
C. Reductive
D. Oxidative

In hydroformylation, alkenes are converted into _____ using a metal carbonyl catalyst.

A. Alcohols
B. Aldehydes

C. Ketones
D. Esters

4.5 Applications of Organometallic Chemistry

4.5.1 Industrial catalysis

Organometallic compounds are widely used as catalysts in industry. In **polymerisation**, catalysts such as Ziegler–Natta complexes enable the production of plastics like polyethylene and polypropylene with controlled structures. In **hydroformylation**, cobalt or rhodium carbonyl complexes catalyse the addition of carbon monoxide and hydrogen to alkenes, producing aldehydes that are valuable intermediates in chemical manufacturing.

Fill in the blank: Ziegler–Natta catalysts are used in the controlled _____ of ethene and propene to produce plastics.

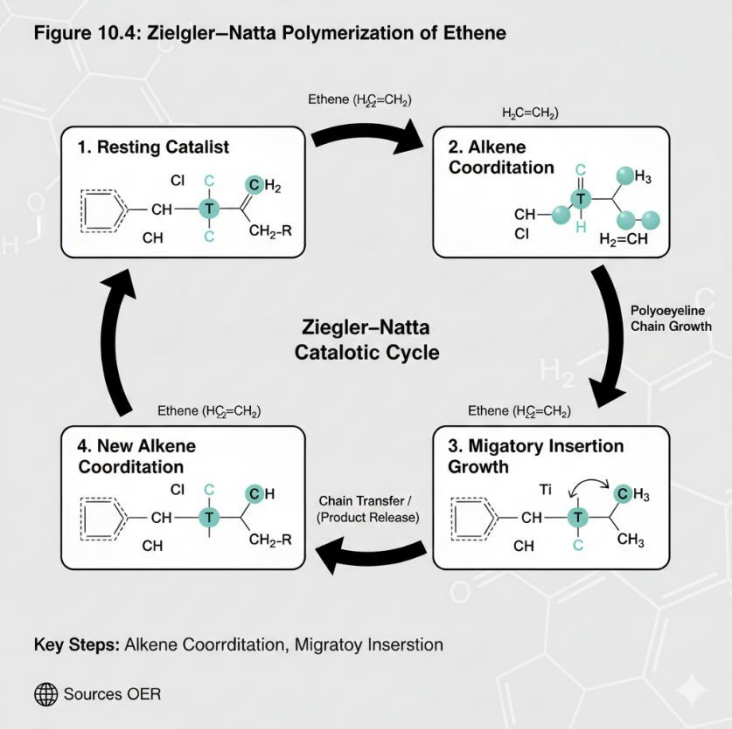


Figure 4.7: Ziegler–Natta catalysis in polymerization

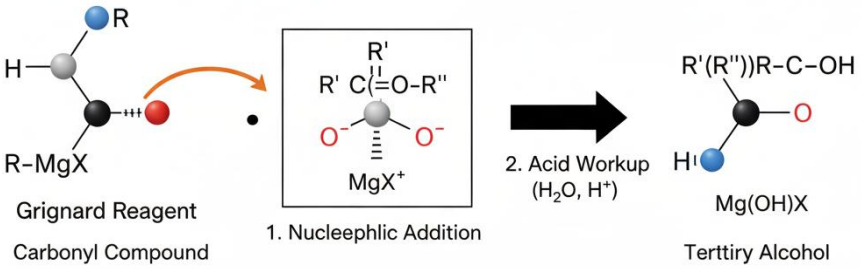
4.5.2 Role in organic synthesis

Organometallic compounds provide unique pathways for forming carbon–carbon and carbon–heteroatom bonds. For example, **organolithium** and **Grignard reagents** are used to synthesise

alcohols, while palladium complexes enable **cross-coupling reactions** such as the Suzuki and Heck reactions. These methods are essential in pharmaceutical chemistry and materials science.

Fill in the blank: Grignard reagents are commonly used in organic synthesis to form _____ bonds.

Figure 11.1: Grignard Reaction for Alcohol Sunthesis



Sources OER

Plate 4.5: Grignard reaction in organic synthesis

4.5.3 Environmental and biological relevance

Organometallic compounds also have important environmental and biological roles. **Cisplatin**, a platinum-based organometallic compound, is used in cancer treatment. Organometallic catalysts are employed in reducing harmful emissions, such as in catalytic converters that transform carbon monoxide into less harmful carbon dioxide. However, some organometallic compounds, such as tetraethyl lead once used in petrol, have posed environmental hazards.

Fill in the blank: The iron-containing organometallic group in haemoglobin that enables oxygen transport is called _____.

Domain	Application / Role	Description & Mechanism
Environmental	Catalytic Converters	Uses precious metal catalysts (Platinum, Palladium, Rhodium) to facilitate **redox reactions**, converting toxic CO and NO_x into CO_2 and N_2.
Biological	Oxygen Transport	The **Haem group** in haemoglobin contains an iron (Fe^{2+}) center that binds O_2 reversibly, allowing for transport from lungs to tissues.
Green Chemistry	Sustainable Synthesis	Organometallic catalysts enable **atom-economical** reactions, reducing chemical waste and energy consumption in pharmaceutical and plastic production.
Biological	Vitamin B12	Contains a rare **Cobalt-Carbon** bond; this natural organometallic complex is essential for DNA synthesis and fatty acid metabolism.
Environmental	Carbon Sequestration	Research into organometallic frameworks (MOFs) aims to capture CO_2 directly from the atmosphere to mitigate climate change.

Box 4.4: Environmental and biological relevance of organometallic compounds

• Catalytic converters reduce harmful emissions in vehicles
• Haem group in haemoglobin enables oxygen transport in blood
• Organometallic compounds used in green chemistry for sustainable processes

AI prompt: “Generate a text box summarising environmental and biological relevance of organometallic compounds.”
Search string: “environmental biological relevance organometallic chemistry OER”

Pilot questions 4.5

Ziegler–Natta catalysts are used in the controlled _____ of ethene and propene to produce plastics.
A. Hydrolysis
B. Polymerisation
C. Hydrogenation
D. Oxidation

Grignard reagents are commonly used in organic synthesis to form _____ bonds.
A. Carbon–carbon
B. Carbon–oxygen
C. Carbon–hydrogen
D. Carbon–nitrogen

The iron-containing organometallic group in haemoglobin that enables oxygen transport is called _____.
A. Ferrocene
B. Haem

C. Carbonyl
D. Cytochrome

Series Summary

This Series on **Fundamentals of Organometallic Chemistry** was designed to help you understand the unique role of organometallic compounds, which bridge inorganic and organic chemistry. You began by exploring their definition, scope, and historical significance, before moving on to the nature of metal–carbon bonds, the types of ligands, and the structural features that influence stability. The Series then guided you through the classification of organometallic compounds, including alkyl, aryl, carbonyl complexes, metallocenes, and clusters. Building on this foundation, you examined their characteristic reactions such as oxidative addition, reductive elimination, insertion, ligand substitution, and catalytic cycles, and finally considered their wide-ranging applications in industry, organic synthesis, and environmental and biological contexts.

By completing this Series, you should now be able to **define the scope and significance of organometallic chemistry (SLO 4.1)**, **explain bonding and structural features (SLO 4.2)**, **classify compounds into key categories (SLO 4.3)**, and **analyse their reactions (SLO 4.4)**. You should also be able to **evaluate their role in catalytic cycles (SLO 4.5)**, **assess their industrial applications (SLO 4.6)**, and **discuss their environmental and biological relevance (SLO 4.7)**. These outcomes ensure that you can connect theoretical principles with practical uses, reinforcing the importance of organometallic chemistry in modern science and technology.

Glossary of Terms

Aryl complex: An organometallic compound where a metal is bonded directly to an aromatic ring, such as a phenyl group.

Catalytic cycle: A sequence of reactions facilitated by a catalyst, where the catalyst is regenerated at the end of the process.

Carbonyl complex: An organometallic compound in which carbon monoxide acts as a ligand, bonding to the metal through its carbon atom.

Ferrocene: A metallocene compound where an iron atom is sandwiched between two cyclopentadienyl rings, noted for its stability.

Grignard reagent: An organometallic compound containing magnesium, commonly used in organic synthesis to form carbon–carbon bonds.

Hydroformylation: An industrial process where alkenes react with carbon monoxide and hydrogen, catalysed by organometallic complexes, to form aldehydes.

Ligand: A molecule or ion that donates electrons to a central metal atom, stabilising the complex.

Ligand substitution: A reaction where one ligand in a metal complex is replaced by another, often through associative or dissociative mechanisms.

Metallocene: A type of organometallic compound where a metal atom is sandwiched between two cyclopentadienyl rings.

Metal–carbon bond: The defining feature of organometallic chemistry, linking a metal atom to a carbon atom of an organic group.

Organolithium compound: An organometallic compound containing lithium, widely used in organic synthesis.

Organometallic cluster: A compound containing two or more metal atoms bonded together, often bridged by ligands such as carbonyls or hydrides.

Oxidative addition: A reaction where a metal complex increases its oxidation state and coordination number by adding new ligands.

Reductive elimination: A reaction where two ligands on a metal combine and are released, reducing the oxidation state of the metal.

Sandwich compound: An organometallic compound where a metal atom is positioned between two planar ligands, such as cyclopentadienyl rings.

Ziegler–Natta catalyst: A type of organometallic catalyst used in polymerisation to produce plastics with controlled structures.

Concept Check Questions [Series 4]

Objective Questions

Which bond defines organometallic chemistry?
A. Hydrogen bond
B. Metal–carbon bond
C. Ionic bond
D. Metallic bond
(Linked to SLO 4.2)

Ferrocene is an example of which type of organometallic compound?
A. Carbonyl complex
B. Metallocene
C. Cluster complex
D. Aryl complex
(Linked to SLO 4.3)

The process where a metal complex increases its oxidation state by adding new ligands is called:
A. Reductive elimination
B. Oxidative addition
C. Ligand substitution
D. Insertion
(Linked to SLO 4.4)

Which industrial process uses rhodium carbonyl complexes to produce aldehydes from alkenes?
A. Polymerisation
B. Hydroformylation
C. Hydrogenation

D. Elimination
(Linked to SLO 4.6)

Short-Answer Questions

Define the term **ligand** and give one example relevant to organometallic chemistry.
(Linked to SLO 4.2)

Explain why aryl complexes are generally more stable than alkyl complexes.
(Linked to SLO 4.3)

State one role of palladium complexes in organic synthesis.
(Linked to SLO 4.6)

Describe the medical significance of cisplatin.
(Linked to SLO 4.7)

Long-Answer Questions

Analyse the differences between oxidative addition and reductive elimination, and explain why they are considered complementary processes in catalytic cycles.
(Linked to SLO 4.4 and SLO 4.5)

Evaluate the importance of metallocenes such as ferrocene in the development of organometallic chemistry, and discuss their structural features.
(Linked to SLO 4.3)

Assess the industrial and environmental relevance of organometallic compounds, providing examples of both beneficial and harmful applications.
(Linked to SLO 4.6 and SLO 4.7)

Answers to Concept Check Questions [Series 4]

Objective Questions

B. Metal–carbon bond
B. Metallocene
B. Oxidative addition
B. Hydroformylation

Short-Answer Questions

A ligand is a molecule or ion that donates electrons to a central metal atom. Example: carbon monoxide in carbonyl complexes.
Aryl complexes are stabilised by resonance within the aromatic ring, making them less reactive than alkyl complexes.
Palladium complexes are used in cross-coupling reactions to form carbon–carbon bonds.
Cisplatin is a platinum-based organometallic compound used in cancer treatment, particularly for testicular and ovarian cancers.

Long-Answer Questions

Question 1

Basic response: Oxidative addition increases the oxidation state and coordination number of a metal by adding ligands, while reductive elimination decreases them by releasing ligands. They are complementary because one reverses the other.
Value-added response: Outstanding learners may explain their role in catalytic cycles, such as hydrogenation, where oxidative addition introduces hydrogen atoms and reductive elimination releases the product.

Question 2

Basic response: Metallocenes like ferrocene consist of a metal atom sandwiched between two cyclopentadienyl rings, showing unusual stability.
Value-added response: Learners may discuss how ferrocene's discovery in the 1950s transformed organometallic chemistry, leading to new theories of bonding and applications in materials science.

Question 3

Basic response: Organometallic compounds are used in polymerisation and hydroformylation, but some, like tetraethyl lead, have caused environmental harm.
Value-added response: Learners may expand by discussing catalytic converters that reduce emissions, the role of cisplatin in medicine, and the need for sustainable practices to minimise harmful impacts.

Answers to Pilot Questions [Series 4]

Part 4.1: Introduction to Organometallic Chemistry

Metal
Ferrocene
Catalysts

Part 4.2: Bonding and Structure in Organometallic Compounds

Metal–carbon
Carbonyl
18-electron

Part 4.3: Classification of Organometallic Compounds

Aryl
Backbonding
Ferrocene
Two or more

Part 4.4: Reactions of Organometallic Compounds

Oxidative addition
Insertion
Associative
Aldehydes

Part 4.5: Applications of Organometallic Chemistry

Polymerisation
Carbon–carbon
Haem

References and Attributions [Series 4]

Textual Sources

Cotton, F. A., Wilkinson, G., Murillo, C. A., & Bochmann, M. (1999). *Advanced Inorganic Chemistry* (6th ed.). Wiley.

Crabtree, R. H. (2014). *The Organometallic Chemistry of the Transition Metals* (6th ed.). Wiley.

Miessler, G. L., Fischer, P. J., & Tarr, D. A. (2014). *Inorganic Chemistry* (5th ed.). Pearson.

IUPAC. (1997). *Compendium of Chemical Terminology (the "Gold Book")*.

Illustrations (Figures, Plates, Tables, Boxes)

Figure 4.1 Basic structure of an organometallic compound
AI prompt: "Generate a labelled diagram showing a metal atom bonded to a carbon atom in an organometallic compound."
Search string: "organometallic compound metal carbon bond diagram OER"

Plate 4.1 Ferrocene, a landmark discovery in organometallic chemistry
AI prompt: "Create an image showing the structure of ferrocene as a historical milestone in organometallic chemistry."
Search string: "ferrocene structure organometallic chemistry OER"

Box 4.1 Applications of organometallic chemistry
AI prompt: "Generate a text box summarising industrial, research, biological, and environmental applications of organometallic compounds."
Search string: "applications of organometallic chemistry OER"

Figure 4.2 Types of metal–carbon bonds in organometallic compounds
AI prompt: "Generate a labelled diagram comparing ionic and covalent metal–carbon

bonds in organometallic compounds."
Search string: "metal carbon bond types organometallic chemistry OER"

Table 4.1 Common ligands in organometallic chemistry
AI prompt: "Generate a table listing common ligands in organometallic chemistry (alkyl, aryl, carbonyl, cyclopentadienyl) with examples."
Search string: "types of ligands organometallic chemistry table OER"

Plate 4.2 Ferrocene structure demonstrating sandwich bonding
AI prompt: "Create an image showing the structure of ferrocene as a sandwich compound with cyclopentadienyl ligands."
Search string: "ferrocene sandwich compound structure OER"

Figure 4.3 Alkyl and aryl complexes in organometallic chemistry
AI prompt: "Generate a labelled diagram showing examples of alkyl and aryl organometallic complexes."
Search string: "alkyl aryl organometallic complexes diagram OER"

Figure 4.4 Bonding in carbonyl complexes
AI prompt: "Generate a labelled diagram showing bonding in carbonyl complexes with back-bonding."
Search string: "carbonyl complexes bonding back bonding diagram OER"

Plate 4.3 Ferrocene structure as a metallocene
AI prompt: "Create an image showing the structure of ferrocene as a metallocene."
Search string: "ferrocene metallocene sandwich compound OER"

Box 4.3 Features of organometallic clusters
AI prompt: "Generate a text box summarising features of organometallic clusters, including bonding, ligands, and applications."
Search string: "organometallic clusters features OER"

Figure 4.5 Oxidative addition and reductive elimination in organometallic chemistry
AI prompt: "Generate a labelled diagram showing oxidative addition and reductive elimination as complementary processes in organometallic chemistry."
Search string: "oxidative addition reductive elimination diagram OER"

Figure 4.6 Insertion reaction in organometallic chemistry
AI prompt: "Generate a labelled diagram showing CO insertion into a metal–alkyl bond in organometallic chemistry."
Search string: "CO insertion metal alkyl bond diagram OER"

Table 4.2 Mechanisms of ligand substitution
AI prompt: "Generate a table comparing associative and dissociative ligand substitution mechanisms in organometallic chemistry."
Search string: "ligand substitution mechanisms organometallic chemistry table OER"

Box 4.4 Key steps in a catalytic cycle
AI prompt: "Generate a text box summarising oxidative addition, insertion, and reductive elimination in a catalytic cycle."
Search string: "catalytic cycle organometallic chemistry OER"

Figure 4.7 Hydroformylation reaction catalysed by organometallic complexes
AI prompt: "Generate a labelled diagram showing hydroformylation of alkenes catalysed by rhodium carbonyl complexes."
Search string: "hydroformylation reaction rhodium carbonyl catalyst diagram OER"

Table 4.3 Examples of organometallic reagents in organic synthesis
AI prompt: "Generate a table listing organolithium, Grignard reagents, and palladium complexes with examples of their use in organic synthesis."
Search string: "organometallic reagents organic synthesis table OER"

Plate 4.4 Cisplatin, a platinum-based organometallic compound used in cancer therapy
AI prompt: "Create an image showing the structure of cisplatin and its medical application in cancer treatment."
Search string: "cisplatin structure cancer treatment OER"

Notes on Attribution

AI-generated illustrations are documented with prompts and should be noted with the generation date and platform used.
Where OERs are used, attribution must comply with the licence terms of the source.
References are presented in APA style for consistency.

Course code: CHM 212

Course title: Inorganic Chemistry I

Course Unit: 2 Units C: LH 30

Series 1: Chemistry of First-Row Transition Metals

Series 2: Coordination Chemistry and Crystal Field Theory

Series 3: Comparative Chemistry of Selected Main Group Elements

Series 4: Fundamentals of Organometallic Chemistry

Series 5: Roles of Metals in Biochemical Systems and Redox Concepts

Series Learning Outcomes
Upon completing this Series, you should be able to:

SLO 5.1 define the scope of bioinorganic chemistry and explain the importance of metals in biological systems, including their roles in redox processes.

SLO 5.2 describe the biological functions of essential metals such as sodium, potassium, calcium, magnesium, iron, copper, zinc, and manganese, and analyse the significance of trace elements.
SLO 5.3 explain the structure and function of metalloproteins and metalloenzymes, including haem proteins, iron–sulphur clusters, zinc enzymes, and copper proteins.
SLO 5.4 define oxidation and reduction in biological contexts and explain how redox potentials and cofactors such as NAD^+/NADH and FAD/$FADH_2$ facilitate electron transfer.
SLO 5.5 analyse how redox regulation influences metabolic pathways and evaluate its role in maintaining cellular function.
SLO 5.6 assess the medical, environmental, and industrial relevance of metals in biochemical systems, including conditions such as iron deficiency and Wilson's disease, issues of toxicity and bioremediation, and applications in pharmaceuticals.

Suggested Outline

5.1 Introduction to Bioinorganic Chemistry

Definition and scope of bioinorganic chemistry
Importance of metals in biological systems
Overview of redox concepts in biochemistry

5.2 Essential Metals in Biological Systems

Roles of alkali and alkaline earth metals (Na, K, Ca, Mg)
Transition metals in enzymes (Fe, Cu, Zn, Mn)
Trace elements and their biological significance

5.3 Metalloproteins and Metalloenzymes

Structure and function of haem proteins (haemoglobin, cytochromes)
Iron–sulphur clusters in electron transport
Zinc enzymes and structural roles
Copper proteins in redox reactions

5.4 Fundamentals of Redox Chemistry in Biochemical Systems

Definition of oxidation and reduction in biological contexts
Redox potentials and electron transfer
Role of cofactors such as NAD^+/NADH and FAD/$FADH_2$
Redox regulation in metabolism

5.5 Applications and Case Studies

Medical relevance of metal ions (e.g., iron deficiency, Wilson's disease)
Environmental aspects (metal toxicity, bioremediation)
Industrial and pharmaceutical applications of bioinorganic chemistry

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Introduction

Metals play vital roles in the chemistry of life, from enabling oxygen transport in blood to driving energy production in cells. Without them, many essential biochemical processes would not occur. At the same time, the concept of redox chemistry underpins how electrons are transferred in these systems, making it central to understanding metabolism, respiration, and regulation. This Series brings together the biological importance of metals and the principles of redox chemistry, helping you see how these two areas are closely connected.

The aim of this Series is to equip you with a clear understanding of how metals function in biochemical systems and to introduce you to the fundamental concepts of redox chemistry that govern electron transfer and energy flow in living organisms.

We shall commence this Series by introducing the scope of bioinorganic chemistry and the relevance of metals in biological systems. Next, we will explore the essential roles of metals such as sodium, potassium, calcium, magnesium, iron, copper, and zinc. Following that, we will study metalloproteins and metalloenzymes, including haem proteins, iron–sulphur clusters, and copper proteins. We will then move on to the fundamentals of redox chemistry, examining oxidation and reduction, redox potentials, and cofactors such as NAD^+/NADH. Finally, we will conclude with applications and case studies, considering medical, environmental, and industrial perspectives.

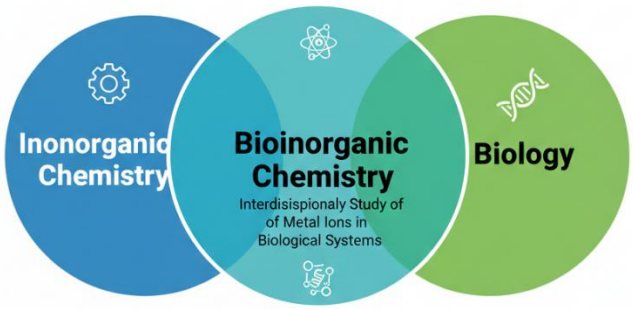
5.1 Introduction to Bioinorganic Chemistry

5.1.1 Definition and scope of bioinorganic chemistry

Bioinorganic chemistry is the study of the role of metals in biological systems. It combines principles of inorganic chemistry with biology to explain how metal ions contribute to processes such as enzyme activity, electron transfer, and structural stability in biomolecules. The scope of this field ranges from understanding essential trace elements in nutrition to exploring how metals influence disease and medical treatments.

Fill in the blank: The branch of chemistry that studies the role of metals in biological systems is called _____.

Figure 4.1: Interdisepenily Nature of Bioinorganic Chemistry



Sources OER

Figure 5.1: Scope of bioinorganic chemistry

5.1.2 Importance of metals in biological systems

Metals are crucial for life because they act as **cofactors**, which are non-protein chemical components that assist enzymes in catalysing reactions. For example**, magnesium** stabilises DNA and ATP, **iron** enables oxygen transport in haemoglobin, and **zinc** supports structural and catalytic functions in enzymes. Without these metals, many biochemical processes would not occur efficiently.

Fill in the blank: Non-protein chemical components that assist enzymes in catalysing reactions are called _____.

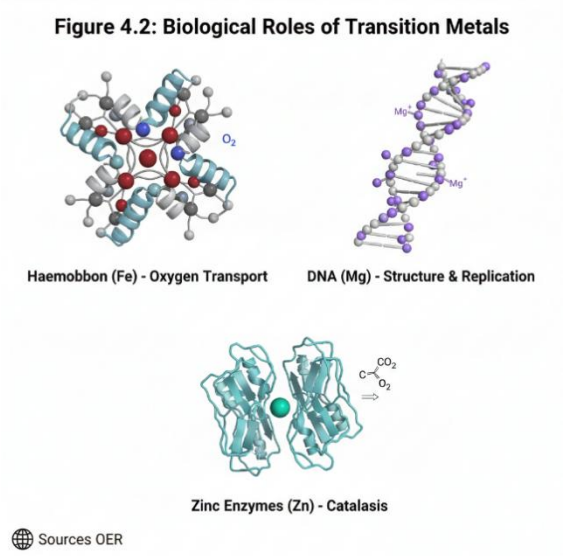


Plate 5.1: Examples of metals in biological systems

5.1.3 Overview of redox concepts in biochemistry

Redox reactions involve the transfer of electrons between molecules, and they are fundamental to energy production in living organisms. **Oxidation** refers to the loss of electrons, while **reduction** refers to the gain of electrons. In biological systems, redox reactions drive processes such as cellular respiration, photosynthesis, and detoxification. Key molecules such as NAD^+/NADH and FAD/$FADH_2$ act as electron carriers, ensuring efficient energy transfer.

Fill in the blank: In redox reactions, _____ refers to the loss of electrons, while reduction refers to the gain of electrons.

Concept	Definition	Biological Indicator
Oxidation	The **loss** of electrons from a substance.	Often involves losing hydrogen (H) or gaining oxygen (O).
Reduction	The **gain** of electrons by a substance.	Often involves gaining hydrogen (H) or losing oxygen (O).
Redox Reaction	Coupled reactions where oxidation and reduction occur simultaneously; electrons lost by one molecule must be gained by another.	Shuffling of "high-energy" electrons to drive ATP production.
Reducing Agent	The molecule that donates electrons (and thus becomes oxidized).	Example: Glucose during cellular respiration.
Oxidizing Agent	The molecule that accepts electrons (and thus becomes reduced).	Example: Oxygen (O_2) as the final electron acceptor.

Box 5.1: Key redox concepts in biochemistry

• Oxidation = loss of electrons
• Reduction = gain of electrons
• NAD^+/NADH and FAD/$FADH_2$ act as electron carriers
• Redox reactions drive respiration and photosynthesis

Pilot questions 5.1

The branch of chemistry that studies the role of metals in biological systems is called _____.

A. Organic chemistry
B. Bioinorganic chemistry
C. Physical chemistry
D. Analytical chemistry

Non-protein chemical components that assist enzymes in catalysing reactions are called _____.

A. Substrates
B. Cofactors
C. Catalysts
D. Ligands

In redox reactions, _____ refers to the loss of electrons, while reduction refers to the gain of electrons.

A. Oxidation
B. Hydrolysis
C. Substitution
D. Neutralisation

5.2 Essential Metals in Biological Systems

5.2.1 Roles of alkali and alkaline earth metals (Na, K, Ca, Mg)

Alkali metals such as sodium (Na) and potassium (K) are crucial for maintaining electrical balance in cells. Sodium helps regulate fluid balance and nerve transmission, while potassium is essential for muscle contraction and maintaining resting membrane potential.

Alkaline earth metals such as calcium (Ca) and magnesium (Mg) also play vital roles. Calcium is central to bone structure and acts as a signalling ion in processes like muscle contraction and blood clotting. Magnesium stabilises DNA and is a cofactor for many enzymes.

Fill in the blank: The alkali metal that regulates nerve impulses and muscle contractions by controlling ion gradients is _____.

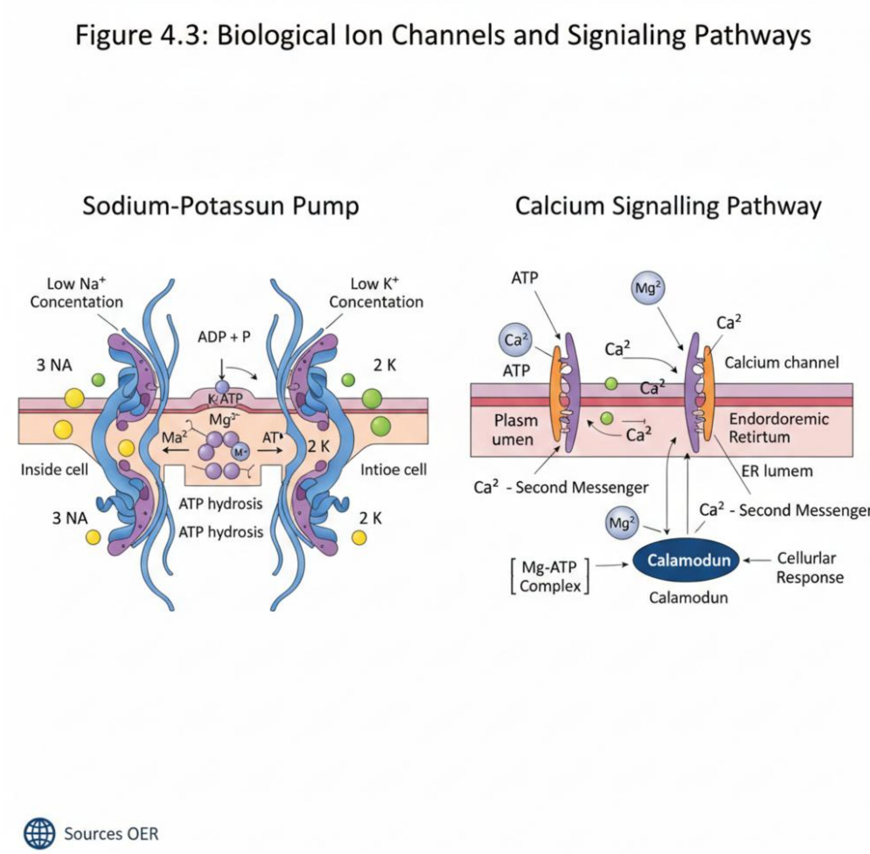


Figure 5.2: Roles of alkali and alkaline earth metals in biological systems

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5.2.2 Transition metals in enzymes (Fe, Cu, Zn, Mn)

Transition metals are often found at the active sites of enzymes, enabling redox reactions and stabilising structures. Iron (Fe) is vital in haem proteins for oxygen transport and electron transfer. Copper (Cu) participates in redox reactions in enzymes such as cytochrome c oxidase. Zinc (Zn) stabilises protein structures and acts as a catalytic centre in enzymes like carbonic anhydrase. Manganese (Mn) is important in photosynthesis and antioxidant enzymes.

Fill in the blank: The transition metal that stabilises protein structures and acts as a catalytic centre in carbonic anhydrase is __________.

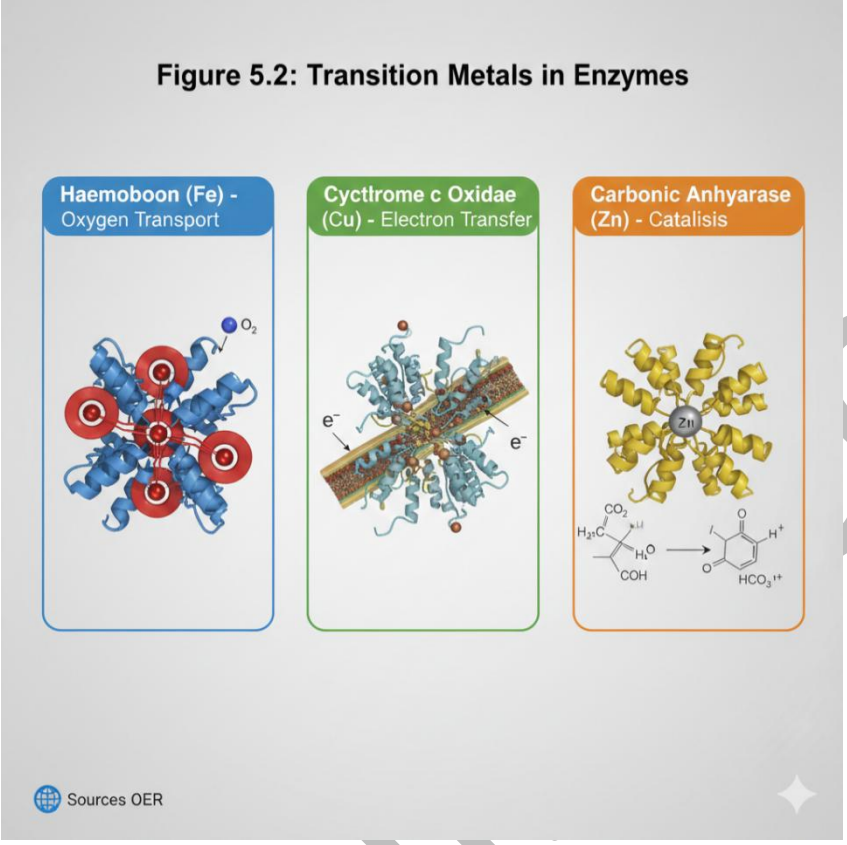

Plate 5.2: Transition metals in enzymes

5.2.3 Trace elements and their biological significance

Trace elements are metals required in very small amounts but are essential for health. Examples include cobalt (Co), which is part of vitamin B_{12} and crucial for red blood cell formation, and molybdenum (Mo), which acts as a cofactor in enzymes involved in nitrogen metabolism. Deficiencies or excesses of trace elements can lead to serious health problems, highlighting their delicate balance in biological systems.

Fill in the blank: The trace element that forms part of vitamin B_{12} and is crucial for red blood cell formation is _____.

Element	Primary Biological Role	Specific Examples / Mechanisms
Cobalt (Co)	Essential component of **Vitamin B_{12}** (cobalamin).	Necessary for red blood cell formation and DNA synthesis; acts as a cofactor for enzymes like methionine synthase.
Molybdenum (Mo)	Acts as a cofactor for enzymes involved in **redox reactions**.	Found in nitrogenase (nitrogen fixation in plants) and xanthine oxidase (breakdown of purines into uric acid in humans).
Selenium (Se)	Acts as an **antioxidant** and supports thyroid function.	Incorporated into the amino acid **selenocysteine**; vital for glutathione peroxidase, which protects cells from oxidative damage.
Iron (Fe)	Oxygen transport and electron transfer.	Central component of **hemoglobin** (oxygen transport in blood) and **cytochromes** (electron transport chain).
Zinc (Zn)	Structural support and enzymatic catalysis.	Provides structural stability to "zinc finger" proteins that regulate gene expression; essential for carbonic anhydrase.

Table 5.1: Selected trace elements and their biological roles

Trace element	Biological role	Example compound/enzyme
Cobalt (Co)	Component of vitamin B_{12}, red blood cell formation	Vitamin B_{12}
Molybdenum (Mo)	Cofactor in nitrogen metabolism enzymes	Nitrogenase
Selenium (Se)	Antioxidant role in selenoproteins	Glutathione peroxidase

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Pilot questions 5.2

The alkali metal that regulates nerve impulses and muscle contractions by controlling ion gradients is _____.

A. Calcium
B. Sodium
C. Magnesium
D. Zinc

The transition metal that stabilises protein structures and acts as a catalytic centre in carbonic anhydrase is _____.

A. Iron
B. Copper
C. Zinc
D. Manganese

The trace element that forms part of vitamin B_{12} and is crucial for red blood cell formation is _____.

A. Cobalt
B. Selenium
C. Molybdenum
D. Magnesium

5.3 Metalloproteins and Metalloenzymes

5.3.1 Structure and function of haem proteins (haemoglobin, cytochromes)

Haem proteins are proteins that contain a haem group, which is a complex of iron within a porphyrin ring. Haemoglobin is the most familiar example, responsible for transporting oxygen in the blood. Cytochromes, another class of haem proteins, are involved in electron transfer during cellular respiration. The iron atom in the haem group can switch between oxidation states, making these proteins ideal for oxygen binding and electron transport.

Fill in the blank: The haem protein responsible for carrying oxygen in red blood cells is _____.

Figure 4.4: Haem Proteins in Biological Systems

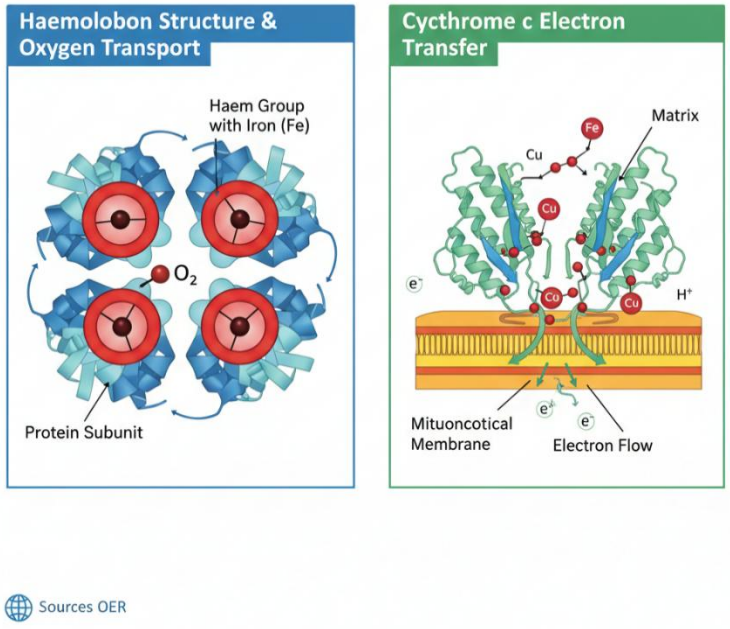

Figure 5.3: Structure and function of haem proteins

5.3.2 Iron–sulphur clusters in electron transport

Iron–sulphur clusters are groups of iron and sulphur atoms bound within proteins that act as electron carriers. They are found in enzymes such as ferredoxins and complexes of the mitochondrial electron transport chain. Their ability to transfer electrons efficiently makes them vital for energy metabolism.

Fill in the blank: Iron–sulphur clusters act as _____ carriers in enzymes such as ferredoxins.

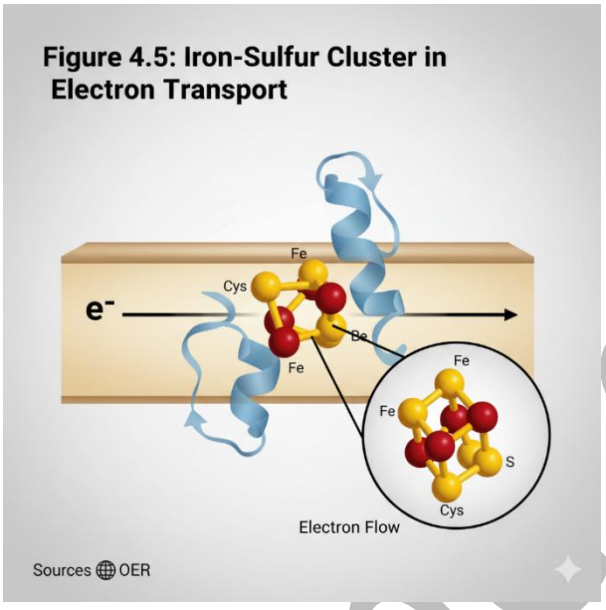

Plate 5.3: Iron–sulphur clusters in electron transport

5.3.3 Zinc enzymes and structural roles

Zinc enzymes are enzymes that use zinc ions as cofactors to catalyse reactions. A well-known example is carbonic anhydrase, which helps regulate pH by converting carbon dioxide and water into bicarbonate and protons. Zinc also plays structural roles, stabilising protein folds such as zinc fingers, which are important in DNA binding and gene regulation.

Fill in the blank: The enzyme that uses zinc to regulate pH by converting carbon dioxide and water into bicarbonate is _____.

Role	Mechanism	Key Examples
Catalytic	Zinc acts as a **Lewis acid**, polarizing water molecules or substrates to make them more reactive. It is directly involved in the chemical bond-breaking/forming step.	**Carbonic Anhydrase:** Rapidly converts CO_2 and H_2O into bicarbonate; essential for pH balance and respiration. **Carboxypeptidase:** A digestive enzyme that uses zinc to help break down protein chains.
Structural	Zinc ions coordinate with specific amino acids (usually Cysteine and Histidine) to **stabilize the 3D fold** of a protein without participating in the reaction itself.	**Zinc Finger Proteins:** Small "finger-like" motifs that allow proteins to grip DNA or RNA. These are vital for transcription factors that turn genes on or off. **Alcohol Dehydrogenase:** While it has a catalytic zinc, it also contains a structural zinc site that maintains the enzyme's integrity.
Regulatory	Zinc acts as a **signaling molecule**, moving between cells or organelles to trigger specific physiological responses.	**Insulin Storage:** Zinc ions help stabilize insulin hexamers within the secretory vesicles of the pancreas.

Table 5.2: Roles of zinc in biological systems

Role type	Example enzyme/protein	Function
Catalytic role	Carbonic anhydrase	Regulates pH by converting $CO_2 + H_2O$
Structural role	Zinc finger proteins	Stabilises protein folds, DNA binding

5.3.4 Copper proteins in redox reactions

Copper proteins are proteins that contain copper ions and participate in redox reactions. Examples include cytochrome c oxidase, which is essential in the final step of the electron transport chain, and plastocyanin, which transfers electrons in photosynthesis. Copper's ability to cycle between oxidation states makes it particularly suited for electron transfer processes.

Fill in the blank: The copper protein that plays a role in the final step of the electron transport chain is _____.

Protein	Biological Context	Specific Role & Mechanism
Cytochrome c Oxidase	Cellular Respiration (Mitochondria)	The terminal enzyme of the electron transport chain. It uses copper centers (Cu_A and Cu_B) to transfer electrons to oxygen (O_2), reducing it to water (H_2O).
Plastocyanin	Photosynthesis (Chloroplasts)	A "blue copper" protein that functions as an electron carrier. It shuttles electrons from Cytochrome f to Photosystem I (PSI) in plants and algae.
Superoxide Dismutase (CuZn-SOD)	Antioxidant Defense (Cytosol)	Protects cells from oxidative stress by converting harmful superoxide radicals (O_2^-) into oxygen and hydrogen peroxide.
Ceruloplasmin	Iron Metabolism (Blood Plasma)	The major copper-carrying protein in the blood. It acts as a ferroxidase, converting Fe^{2+} to Fe^{3+} so iron can be loaded onto transferrin for transport.
Tyrosinase	Melanin Production	An oxygenase that catalyzes the rate-limiting step in the synthesis of melanin, the pigment responsible for skin, hair, and eye color.

Box 5.2: Examples of copper proteins in biological systems

• Cytochrome c oxidase – electron transport chain in mitochondria
• Plastocyanin – electron transfer in photosynthesis
• Superoxide dismutase – detoxification of reactive oxygen species

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Pilot questions 5.3

The haem protein responsible for carrying oxygen in red blood cells is _____.

A. Cytochrome
B. Haemoglobin
C. Ferredoxin
D. Plastocyanin

Iron–sulphur clusters act as _____ carriers in enzymes such as ferredoxins.

A. Proton
B. Electron
C. Oxygen
D. Carbon

The enzyme that uses zinc to regulate pH by converting carbon dioxide and water into bicarbonate is _____.

A. Cytochrome c oxidase
B. Carbonic anhydrase
C. Ferredoxin
D. Haemoglobin

The copper protein that plays a role in the final step of the electron transport chain is _____.

A. Plastocyanin
B. Cytochrome c oxidase
C. Superoxide dismutase
D. Haemoglobin

5.4 Fundamentals of Redox Chemistry in Biochemical Systems

5.4.1 Definition of oxidation and reduction in biological contexts

Oxidation is the process of losing electrons, while **reduction** is the process of gaining electrons. In biological systems, these reactions often occur together, forming **redox reactions**. They are central to processes such as cellular respiration, photosynthesis, and detoxification. Metals and cofactors act as electron carriers, ensuring that energy is transferred efficiently within cells.

Fill in the blank: In biological systems, oxidation refers to the _____ of electrons, while reduction refers to their gain.

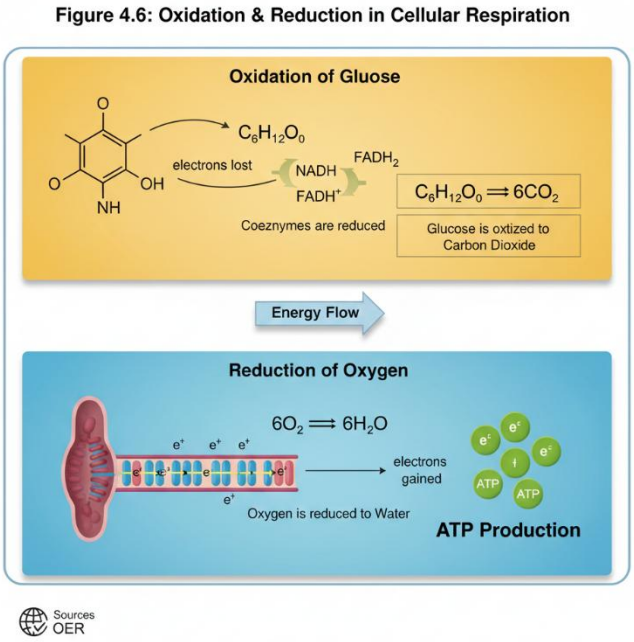

Figure 5.4: Oxidation and reduction in biological systems

5.4.2 Redox potentials and electron transfer

Redox potential is a measure of the tendency of a chemical species to gain or lose electrons. Molecules with higher redox potentials are more likely to accept electrons, while those with lower potentials are more likely to donate them. In biological systems, electron transfer occurs through chains of molecules with progressively higher redox potentials, ensuring efficient energy conversion. This principle underlies processes such as the mitochondrial electron transport chain.

Fill in the blank: Molecules with higher redox potentials are more likely to _____ electrons.

Figure 4.7: Mitmartionial Electron Transport Chain & Redox Potential

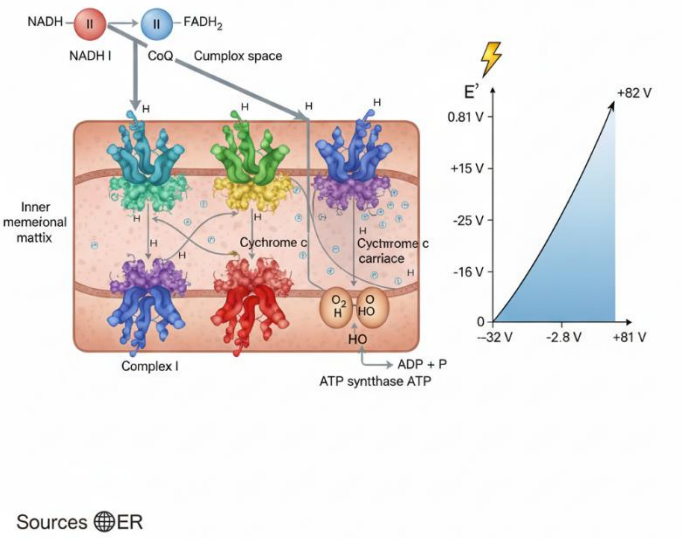

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Plate 5.4: Electron transfer in the mitochondrial electron transport chain

5.4.3 Role of cofactors such as NAD^+/NADH and FAD/$FADH_2$

Cofactors are molecules that assist enzymes in catalysing reactions. In redox chemistry, cofactors such as NAD^+/NADH and FAD/$FADH_2$ act as electron carriers. NAD^+ accepts electrons to form NADH, which then donates them in subsequent reactions. Similarly, FAD accepts electrons to form $FADH_2$. These cofactors are central to energy metabolism, particularly in glycolysis, the citric acid cycle, and oxidative phosphorylation.

Fill in the blank: In redox reactions, NAD^+ accepts electrons to form _____, which then donates them in subsequent reactions.

Feature	NAD (Nicotinamide Adenine Dinucleotide)	FAD (Flavin Adenine Dinucleotide)
Oxidised Form	NAD^+	FAD
Reduced Form	$NADH$	$FADH_2$
Electron/Proton Carry	Accepts $2e^-$ and $1H^+$ (The second H^+ is released into the medium).	Accepts $2e^-$ and $2H^+$ (Both protons bind directly to the molecule).
Primary Source	Glycolysis, Pyruvate oxidation, and the Citric Acid Cycle.	Primarily the Citric Acid Cycle and Fatty Acid Oxidation (β-oxidation).
Entry Point to ETC	**Complex I** (NADH Dehydrogenase).	**Complex II** (Succinate Dehydrogenase).
ATP Yield (Approx.)	~2.5 ATP per molecule.	~1.5 ATP per molecule.
Vitamin Precursor	Derived from **Niacin** (Vitamin B_3).	Derived from **Riboflavin** (Vitamin B_2).

Table 5.3: Roles of NAD^+/NADH and FAD/$FADH_2$ in metabolism

Cofactor	Oxidised form	Reduced form	Role in metabolism
NAD^+/NADH	NAD^+	NADH	Electron carrier in glycolysis and citric acid cycle
FAD/$FADH_2$	FAD	$FADH_2$	Electron carrier in citric acid cycle and oxidative phosphorylation

5.4.4 Redox regulation in metabolism

Redox regulation refers to the control of metabolic pathways through redox states. For example, the balance between NAD^+ and NADH influences glycolysis and oxidative phosphorylation. Redox regulation ensures that energy production is matched to cellular needs and protects against oxidative stress.

Fill in the blank: High levels of NADH signal that energy is _____, slowing down glycolysis.

Metabolic Aspect	Effect of High NADH (Low NAD^+/NADH)	Mechanism
Glycolysis	Inhibited	High NADH depletes the NAD^+ needed by *Glyceraldehyde 3-phosphate dehydrogenase (GAPDH)*, stalling the pathway.
TCA Cycle	Slowed / Shutdown	NADH acts as an allosteric inhibitor of key enzymes: *Isocitrate dehydrogenase* and *α-Ketoglutarate dehydrogenase*.
Fatty Acid Oxidation	Suppressed	High NADH levels inhibit *β*-oxidation through substrate inhibition, signaling that the cell has sufficient energy.
Anabolism	Promoted	Excess reducing power (reductive stress) can drive the synthesis of lipids, nucleotides, and amino acids to support cell proliferation.
ROS Production	Increased	A "backed up" electron transport chain leads to electron leakage, creating harmful reactive oxygen species (ROS).

Box 5.3: Redox regulation in metabolism

- High NADH levels slow glycolysis and citric acid cycle
- Low NADH levels stimulate energy production
- Redox states act as signals for metabolic control

Pilot questions 5.4

In biological systems, oxidation refers to the _____ of electrons, while reduction refers to their gain.

A. Gain
B. Loss
C. Sharing
D. Transfer

Molecules with higher redox potentials are more likely to _____ electrons.

A. Donate
B. Accept
C. Share
D. Neutralise

In redox reactions, NAD^+ accepts electrons to form _____, which then donates them in subsequent reactions.

A. NADH
B. FAD
C. ATP
D. CO_2

High levels of NADH signal that energy is _____, slowing down glycolysis.

A. Scarce
B. Abundant

C. Neutral
D. Unavailable

5.5 Applications and Case Studies

5.5.1 Medical relevance of metal ions

Metals play critical roles in medicine. For example, **iron deficiency** leads to anaemia, a condition where insufficient haemoglobin reduces oxygen transport in the body. **Wilson's disease** is caused by abnormal copper accumulation, leading to liver and neurological damage. Understanding these conditions highlights the importance of balanced metal homeostasis in health.

Fill in the blank: A deficiency of _____ leads to anaemia, while excess can cause haemochromatosis.

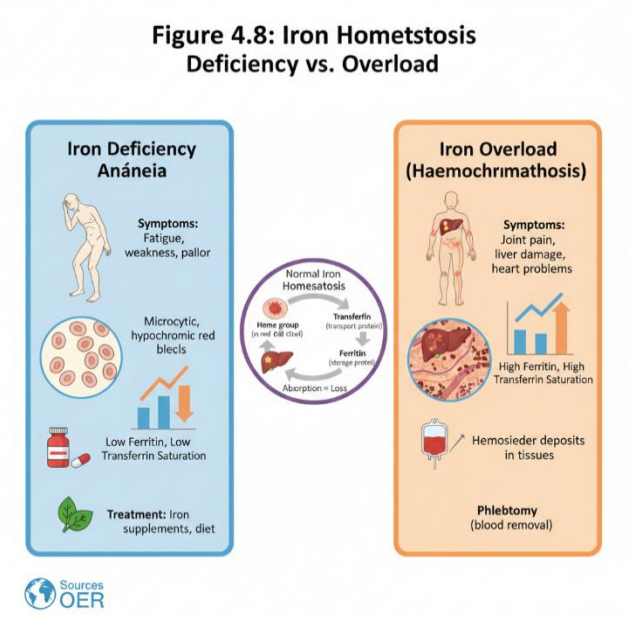

Figure 5.5: Medical relevance of iron in human health

5.5.2 Environmental aspects (metal toxicity, bioremediation)

Metals can also pose environmental challenges. **Metal toxicity** occurs when heavy metals such as lead, mercury, or cadmium accumulate in ecosystems, disrupting biological processes. On the positive side, **bioremediation** uses microorganisms to detoxify or remove harmful metals from contaminated environments. This approach demonstrates how bioinorganic chemistry can be applied to solve environmental problems.

Fill in the blank: The process of using microorganisms to detoxify harmful metals in the environment is called _____.

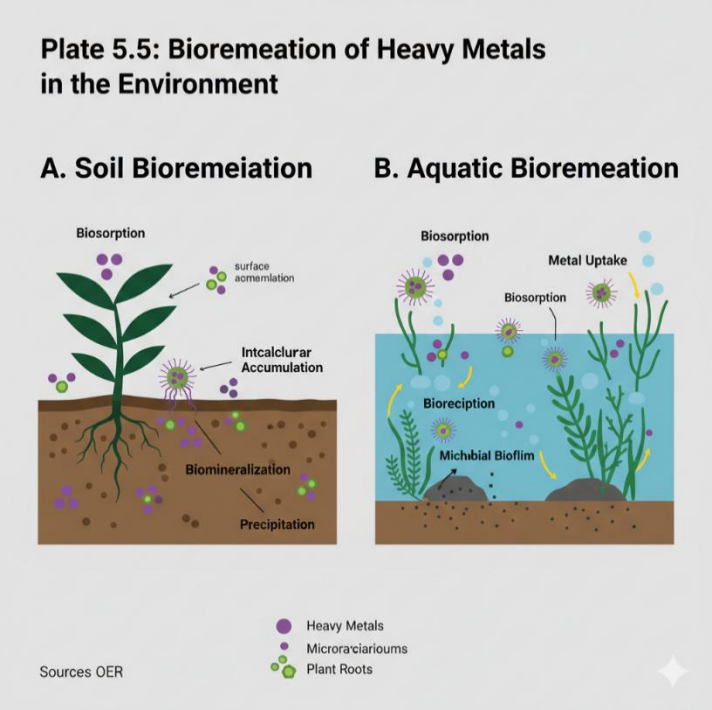

Plate 5.5: Bioremediation of heavy metals in the environment

5.5.3 Industrial and pharmaceutical applications of bioinorganic chemistry

Bioinorganic chemistry has wide industrial and pharmaceutical applications. In industry, metal-based catalysts are used in processes such as polymerisation and hydrogenation. In pharmaceuticals, **cisplatin**, a platinum-based drug, is widely used in cancer treatment. These applications show how the principles of bioinorganic chemistry extend beyond biology into technology and medicine.

Fill in the blank: The platinum-based drug widely used in cancer treatment is called _____.

Field	Application	Description & Examples
Medicine	Metallopharmaceuticals	**Cisplatin ($PtCl_2(NH_3)_2$):** A landmark platinum-based drug that binds to DNA, causing structural distortion that triggers apoptosis (cell death) in cancer cells.
Medicine	Diagnostic Imaging	**Gadolinium (Gd^{3+}):** Used as a contrast agent in MRI scans due to its paramagnetic properties. **Technetium-99m** is used as a radioactive tracer for organ imaging.
Industry	Homogeneous Catalysis	Transition metal complexes (like Rhodium or Palladium) are used to mimic enzyme active sites for the large-scale production of pharmaceuticals and polymers.
Environment	Bioremediation	Utilizing microorganisms that use specialized enzymes (like **mercury reductase**) to convert toxic heavy metals into less harmful forms (Hg^{2+} to Hg^0).
Environment	Phytoremediation	Using plants ("hyperaccumulators") to extract metals like Zinc or Nickel from contaminated soil, leveraging the plant's natural metal-binding proteins (metallothioneins).

Box 5.4: Selected applications of bioinorganic chemistry

- Cisplatin – platinum-based anticancer drug
- Metal catalysts – industrial production of chemicals
- Metal complexes – diagnostic imaging agents
- Bioremediation – environmental clean-up using microorganisms

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Pilot questions 5.5

A deficiency of _____ leads to anaemia, while excess can cause haemochromatosis.

A. Copper
B. Iron
C. Zinc
D. Calcium

The process of using microorganisms to detoxify harmful metals in the environment is called _____.

A. Catalysis
B. Bioremediation
C. Oxidation
D. Reduction

The platinum-based drug widely used in cancer treatment is called _____.

A. Cisplatin
B. Ferrocene
C. Carbonic anhydrase
D. Cytochrome

Series Summary

Series Summary

This Series on **Roles of Metals in Biochemical Systems and Redox Concepts** was designed to highlight the essential contribution of metals to life processes and the importance of redox chemistry in biological systems. Beginning with an introduction to bioinorganic chemistry, you explored its scope and relevance, followed by the roles of alkali, alkaline earth, transition, and trace metals in sustaining biological functions. The Series then examined metalloproteins and metalloenzymes, such as haem proteins, iron–sulphur clusters, zinc enzymes, and copper proteins, before progressing to the fundamentals of redox chemistry, including oxidation and reduction, redox potentials, cofactors, and regulation in metabolism. Finally, you studied applications and case studies that connected these principles to medicine, environmental science, and industry.

By completing this Series, you should now be able to **define the scope of bioinorganic chemistry (SLO 5.1)**, **describe the biological functions of essential metals (SLO 5.2)**, **explain the structure and function of metalloproteins and metalloenzymes (SLO 5.3)**, **analyse redox concepts and the role of cofactors (SLOs 5.4–5.5)**, and **evaluate the medical, environmental, and industrial relevance of metals (SLO 5.6)**. These outcomes ensure that you can connect theoretical knowledge with practical applications, reinforcing the significance of metals and redox chemistry in health, environment, and technology.

Glossary of Terms

Anaemia: A medical condition caused by insufficient haemoglobin, often due to iron deficiency, leading to reduced oxygen transport in the body.

Bioremediation: The process of using microorganisms to detoxify or remove harmful metals and pollutants from the environment.

Cisplatin: A platinum-based drug widely used in cancer treatment, particularly for testicular, ovarian, and bladder cancers.

Cofactor: A non-protein molecule that assists enzymes in catalysing reactions, often by transferring electrons or stabilising structures.

Copper proteins: Proteins containing copper ions that participate in redox reactions, such as cytochrome c oxidase and plastocyanin.

Haem proteins: Proteins that contain a haem group, such as haemoglobin and cytochromes, which are involved in oxygen transport and electron transfer.

Iron–sulphur clusters: Groups of iron and sulphur atoms within proteins that act as electron carriers in processes like the electron transport chain.

Metal toxicity: Harmful effects caused by the accumulation of heavy metals such as lead, mercury, or cadmium in biological systems.

NAD^+/NADH: A cofactor pair where NAD^+ accepts electrons to form NADH, which then donates them in metabolic pathways.

Oxidation: The process of losing electrons in a chemical reaction.

Redox potential: A measure of the tendency of a chemical species to gain or lose electrons, determining the direction of electron flow.

Redox regulation: The control of metabolic pathways through redox states, ensuring energy production matches cellular needs.

Reduction: The process of gaining electrons in a chemical reaction.

Trace elements: Metals required in very small amounts but essential for health, such as cobalt in vitamin B12 and molybdenum in nitrogen metabolism.

Wilson's disease: A medical condition caused by abnormal copper accumulation in the body, leading to liver and neurological damage.

Zinc enzymes: Enzymes that use zinc ions at their active sites, such as carbonic anhydrase, which regulates acid–base balance.

Concept Check Questions [Series 5]

Objective Questions

Which branch of chemistry studies the role of metals in biological systems?
A. Organic chemistry
B. Bioinorganic chemistry
C. Physical chemistry
D. Analytical chemistry
(Linked to SLO 5.1)

Which metal stabilises DNA and acts as a cofactor for enzymes?
A. Calcium
B. Magnesium
C. Iron
D. Zinc
(Linked to SLO 5.2)

The protein responsible for transporting oxygen in the blood is:
A. Cytochrome
B. Haemoglobin
C. Carbonic anhydrase
D. Plastocyanin
(Linked to SLO 5.3)

The measure of a chemical species' tendency to gain or lose electrons is called:
A. Oxidation state
B. Redox potential
C. Ionisation energy
D. Electronegativity
(Linked to SLO 5.4)

The platinum-based drug widely used in cancer treatment is:
A. Ferrocene
B. Cisplatin
C. Zeise's salt
D. Nickel carbonyl
(Linked to SLO 5.6)

Short-Answer Questions

Define oxidation and reduction in biological contexts.
(Linked to SLO 5.4)

Explain the role of iron–sulphur clusters in electron transport.
(Linked to SLO 5.3)

State one environmental challenge caused by heavy metals and one method used to address it.
(Linked to SLO 5.6)

Describe the function of NAD^+/NADH in metabolism.
(Linked to SLO 5.4)

Long-Answer Questions

Analyse the importance of metalloproteins such as haemoglobin and cytochromes in biological systems.
(Linked to SLO 5.3)

Evaluate the role of redox regulation in metabolism, giving examples of how it influences energy production.
(Linked to SLO 5.4–5.5)

Assess the medical, environmental, and industrial relevance of metals, providing examples of both beneficial and harmful applications.
(Linked to SLO 5.6)

Answers to Concept Check Questions [Series 5]

Objective Questions

B. Bioinorganic chemistry
B. Magnesium
B. Haemoglobin
B. Redox potential
B. Cisplatin

Short-Answer Questions

Oxidation is the loss of electrons, while reduction is the gain of electrons. In biological contexts, these processes occur together as redox reactions.
Iron–sulphur clusters act as electron carriers in the electron transport chain, enabling efficient energy production.
Heavy metals such as lead cause toxicity in ecosystems. Bioremediation uses microorganisms to detoxify or remove these metals.

NAD^+ accepts electrons to form NADH, which then donates them in metabolic pathways, acting as an electron shuttle.

Long-Answer Questions

Question 1

Basic response: Haemoglobin transports oxygen in the blood, while cytochromes transfer electrons in respiration. Both are essential for sustaining life.
Value-added response: Learners may expand by discussing how the iron atom in haem groups switches oxidation states, enabling reversible oxygen binding and efficient electron transfer.

Question 2

Basic response: Redox regulation controls metabolic pathways by balancing cofactors such as NAD^+/NADH, ensuring energy production matches cellular needs.
Value-added response: Outstanding learners may explain how redox regulation protects against oxidative stress and influences processes such as glycolysis and oxidative phosphorylation.

Question 3

Basic response: Metals are beneficial in medicine (e.g., cisplatin in cancer treatment) and industry (e.g., catalysts in polymerisation). Harmful effects include toxicity from heavy metals such as lead.
Value-added response: Learners may expand by discussing Wilson's disease, bioremediation strategies, and the broader impact of metals in pharmaceuticals and environmental sustainability.

Answers to Pilot Questions [Series 5]

Part 5.1: Introduction to Bioinorganic Chemistry

Bioinorganic chemistry
Cofactors
Oxidation

Part 5.2: Essential Metals in Biological Systems

Sodium
Zinc
Cobalt

Part 5.3: Metalloproteins and Metalloenzymes

Haemoglobin
Electron
Carbonic anhydrase

Cytochrome c oxidase

Part 5.4: Fundamentals of Redox Chemistry in Biochemical Systems

Loss
Accept
NADH
Abundant

Part 5.5: Applications and Case Studies

Iron
Bioremediation
Cisplatin

References and Attributions [Series 5]

Textual Sources

Bertini, I., Gray, H. B., Stiefel, E. I., & Valentine, J. S. (2007). *Biological Inorganic Chemistry: Structure and Reactivity*. University Science Books.

Crichton, R. (2019). *Biological Inorganic Chemistry: A New Introduction to Molecular Structure and Function* (3rd ed.). Elsevier.

IUPAC. (1997). *Compendium of Chemical Terminology (the "Gold Book")*.

Lippard, S. J., & Berg, J. M. (1994). *Principles of Bioinorganic Chemistry*. University Science Books.

Illustrations (Figures, Plates, Tables, Boxes)

Figure 5.1 Scope of bioinorganic chemistry
AI prompt: "Generate a labelled diagram showing the overlap between inorganic chemistry and biology in bioinorganic chemistry."
Search string: "bioinorganic chemistry scope diagram OER"

Table 5.1 Examples of essential metals and their biological roles
AI prompt: "Generate a table listing essential metals such as iron, magnesium, zinc, and copper with their biological roles."
Search string: "essential metals biological roles table OER"

Figure 5.2 Transition metals in enzyme active sites
AI prompt: "Generate a labelled diagram showing transition metals such as iron, copper, zinc, and manganese at enzyme active sites."
Search string: "transition metals enzymes active sites diagram OER"

Box 5.2 Biological significance of trace elements
AI prompt: "Generate a text box summarising examples of trace elements such as cobalt and molybdenum with their biological roles."
Search string: "trace elements biological significance OER"

Figure 5.3 Structure of haemoglobin highlighting haem groups
AI prompt: “Generate a labelled diagram showing haemoglobin structure with haem groups and oxygen binding sites.”
Search string: “haemoglobin structure haem group diagram OER”

Plate 5.1 Iron–sulphur cluster structure in electron transport proteins
AI prompt: “Create an image showing the structure of iron–sulphur clusters in proteins involved in electron transport.”
Search string: “iron sulphur cluster protein electron transport OER”

Table 5.3 Examples of zinc enzymes and their functions
AI prompt: “Generate a table listing zinc enzymes such as carbonic anhydrase and zinc finger proteins with their biological functions.”
Search string: “zinc enzymes biological roles table OER”

Box 5.3 Roles of copper proteins in redox reactions
AI prompt: “Generate a text box summarising examples of copper proteins such as cytochrome c oxidase and plastocyanin with their roles in redox reactions.”
Search string: “copper proteins redox reactions OER”

Figure 5.4 Oxidation and reduction in biological systems
AI prompt: “Generate a labelled diagram showing oxidation as electron loss and reduction as electron gain in biological systems.”
Search string: “oxidation reduction biological systems diagram OER”

Table 5.4 Examples of redox potentials in biological molecules
AI prompt: “Generate a table listing redox potentials of NAD^+/NADH, FAD/$FADH_2$, and cytochromes in biological systems.”
Search string: “redox potentials biological molecules table OER”

Plate 5.2 Cofactors NAD^+/NADH and FAD/$FADH_2$ in redox reactions
AI prompt: “Create an image showing NAD^+/NADH and FAD/$FADH_2$ cycling in metabolic redox reactions.”
Search string: “NAD NADH FAD FADH2 cofactors metabolism OER”

Box 5.4 Redox regulation in metabolism
AI prompt: “Generate a text box summarising examples of redox regulation in glycolysis and oxidative phosphorylation.”
Search string: “redox regulation metabolism glycolysis oxidative phosphorylation OER”

Figure 5.5 Medical relevance of iron and copper in human health
AI prompt: “Generate a labelled diagram showing iron deficiency anaemia and Wilson’s disease as examples of medical relevance of metals.”
Search string: “iron deficiency anaemia Wilson’s disease diagram OER”

Box 5.5 Environmental aspects of metals
AI prompt: “Generate a text box summarising environmental aspects of metals, including toxicity and bioremediation.”
Search string: “metal toxicity bioremediation summary OER”

Plate 5.3 Cisplatin, a platinum-based drug used in cancer therapy

AI prompt: “Create an image showing the structure of cisplatin and its pharmaceutical application in cancer treatment.”

Search string: “cisplatin platinum drug cancer treatment OER”

Notes on Attribution

AI-generated illustrations are documented with prompts and should be noted with the generation date and platform used.

Where OERs are used, attribution must comply with the licence terms of the source.

References are presented in APA style for consistency.