

28.2 Ligands and complexes

Name: _____ Class: _____ Date: _____

Total: 33 marks

KEY WORDS ligand 配体 • coordination number 配位数 • monodentate 单齿
• octahedral 八面体形 • tetrahedral 四面体形

Objective

Build the skills to answer exam questions on **ligands and complexes** 配体和配合物 — **denticity** 齿数, complex shapes, **coordination number** 配位数, and **ligand exchange** 配体交换.

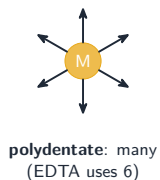
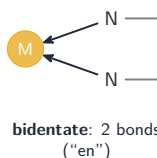
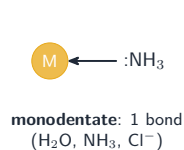
You must be able to:

- define a ligand and classify ligands as mono-, bi- or polydentate
- describe complex shapes and deduce coordination number and charge
- describe the ligand-exchange reactions of copper(II) and cobalt(II)

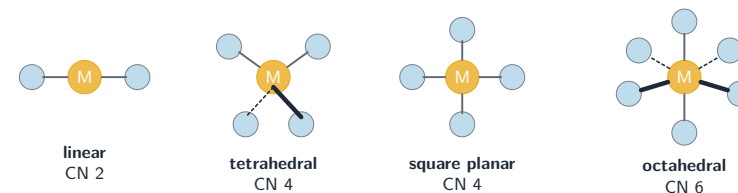
1 Worked examples

■ Ligands and complexes

A **ligand** has a lone pair that forms a **dative covalent bond** to the central metal ion.

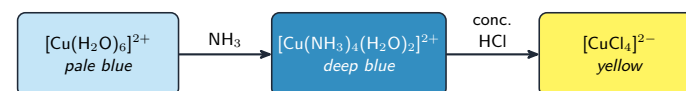


Monodentate (1 bond: H_2O , NH_3 , Cl^- , CN^-); bidentate (2: en, $\text{C}_2\text{O}_4^{2-}$); polydentate (EDTA^{4-} , 6)



Coordination number $\rightarrow$ shape: 2 linear, 4 tetrahedral or square planar, 6 octahedral

■ Ligand exchange



Ligand exchange changes colour: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (pale blue) $\rightarrow$ $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ (deep blue) $\rightarrow$ $[\text{CuCl}_4]^{2-}$ (yellow)

■ Ligands, denticity and the charge on a complex

A **ligand** 配体 is a molecule or ion with a **lone pair** that it donates into a vacant orbital of a metal ion, forming a **dative (coordinate) bond** 配位键. The metal ion is the electron-pair **acceptor**, the ligand the **donor** — a Lewis acid and a Lewis base.

Denticity 齿数 is how many dative bonds one ligand forms:

Denticity	Examples	Bonds per ligand
monodentate 单齿	H_2O , NH_3 , Cl^- , CN^- , OH^-	1
bidentate 双齿	1,2-diaminoethane ("en"), ethanedioate $\text{C}_2\text{O}_4^{2-}$	2
polydentate 多齿	EDTA^{4-}	6

Coordination number 配位数 is the number of **dative bonds**, not the number of ligands — three bidentate ligands give a coordination number of 6, not 3. Coordination number decides the shape: **6** $\rightarrow$ **octahedral** (90° bond angles), **4** $\rightarrow$ **tetrahedral** (109.5°) or **square planar** (90°), **2** $\rightarrow$ **linear** (180°).

Working out the overall charge, which is a mark in almost every question on this topic:

$$\text{charge on complex} = \text{oxidation number of metal} + \sum (\text{charges on ligands})$$

Worked example. Give the coordination number, shape and overall charge of the complex formed when Cr^{3+} bonds to four water molecules and two chloride ions.

1. Bonds: $4 + 2 = 6$, so the coordination number is 6 and the shape is **octahedral**.
2. Charges: +3 from chromium, 0 from each water, -1 from each chloride, giving $+3 + 0 - 2 = +1$.
3. Formula: $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$.

Ligand exchange replaces one ligand with another, often with a **colour change** — the exam's evidence that a reaction happened. Adding concentrated HCl to pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ gives blue $[\text{CoCl}_4]^{2-}$: both the colour and the coordination number change, from 6 (octahedral) to 4 (tetrahedral), because chloride is the larger ligand and fewer fit around the ion.

2 Practice

2.1 Define a **ligand**. [2]

2.2 State the coordination number and shape of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. [2]

2.3 Define a ligand, and state the type of bond it forms with the metal ion. [2]

2.4 Give the coordination number and shape of $[\text{Ni}(\text{en})_3]^{2+}$, where en is bidentate. [2]

2.5 Deduce the overall charge on the complex formed by Fe^{3+} with six cyanide ions. [2]

3 Exam-style questions

3.1 Which is a **bidentate** ligand? [1]

- A H_2O
- B Cl^-
- C 1,2-diaminoethane (en)
- D NH_3

3.2 The overall charge on $[\text{CuCl}_4]^{2-}$ shows copper is in oxidation state: [1]

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

3.3 (a) Write the formula and state the colour of the complex formed when excess ammonia is added to $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. [2]

(b) State what is meant by **ligand exchange**. [2]

3.4 Deduce the coordination number and shape of $[\text{CuCl}_4]^{2-}$. [2]

3.5 Cobalt(II) forms a range of complexes.

- (a) Define the term ligand, and explain why a ligand must have a lone pair. [3]

- (b) Complete the table for three cobalt complexes. [6]

Complex	Coordination number	Shape	Overall charge
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ from Co^{2+}			
$[\text{CoCl}_4]^{2-}$ from Co^{2+}			
$[\text{Co}(\text{en})_3]^{3+}$ from Co^{3+}			

- (c) Concentrated hydrochloric acid is added to a pink solution of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and the solution turns blue. Explain what has happened, including the change in coordination number. [4]

- (d) Explain why 1,2-diaminoethane is described as bidentate while ammonia is monodentate. [2]

Solutions

2.1 a species with a lone pair of electrons that forms a dative (coordinate) bond to a central metal ion.

2.2 coordination number 6; octahedral.

2.3 A ligand is a molecule or ion that donates a lone pair of electrons to a metal ion; the bond formed is a dative, or coordinate, bond.

2.4 Three bidentate ligands form six dative bonds, so the coordination number is 6; the shape is octahedral.

2.5 $+3 + 6(-1) = -3$; the complex is $[\text{Fe}(\text{CN})_6]^{3-}$.

3.1 C. 1,2-diaminoethane (en) forms two dative bonds — bidentate.

3.2 B. $x + 4(-1) = -2 \Rightarrow x = +2$.

3.3 (a) $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$; deep blue.

(b) one ligand is replaced by another ligand around the central metal ion, often with a colour change.

3.4 coordination number 4; tetrahedral.

3.5 (a) A ligand is a molecule or ion that donates a lone pair of electrons to a metal ion, forming a dative bond; it must have a lone pair because the metal ion supplies no electrons to the bond — both electrons come from the ligand.

(b) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$: 6, octahedral, 2+. $[\text{CoCl}_4]^{2-}$: 4, tetrahedral, 2-. $[\text{Co}(\text{en})_3]^{3+}$: 6, octahedral, 3+.

(c) Ligand exchange has occurred: chloride ions have replaced the water ligands; the coordination number falls from 6 to 4 because chloride is a larger ligand and fewer fit around the ion; the shape changes from octahedral to tetrahedral, which is what changes the colour from pink to blue.

(d) 1,2-diaminoethane has two nitrogen atoms, each with a lone pair, so one molecule forms two dative bonds to the same metal ion; ammonia has only one nitrogen with one lone pair, so it forms one bond.