

Exercise walk-through

28.2

General characteristic chemical properties of the first set of transition elements, titanium to copper

A-Level Chemistry

Four key properties

variable oxidation state

– 3d & 4s close in energy

complex ions

– vacant d orbitals accept lone pairs

catalyst

– more than one stable state, vacant d orbitals

coloured

compounds – electrons jump split d orbitals

A **transition element**

forms ions with **incomplete d orbitals** (so Sc and Zn don't count).



Ruby

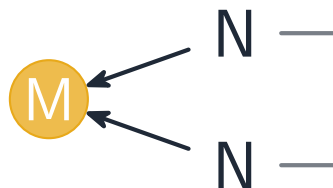
Ligands and denticity

A **ligand** donates a **lone pair** in a **dative bond** :

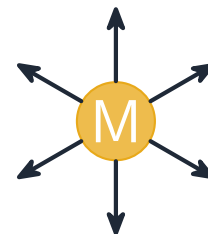
- **monodentate** – 1 bond (H_2O , NH_3)
- **bidentate** – 2 bonds (en)
- **polydentate** – many (EDTA: 6)



monodentate: 1 bond
(H_2O , NH_3 , Cl^-)



bidentate: 2 bonds
("en")



polydentate: many
(EDTA uses 6)

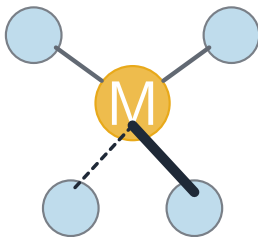
Complex shapes

The **coordination number** (dative bonds to the metal) sets the shape:

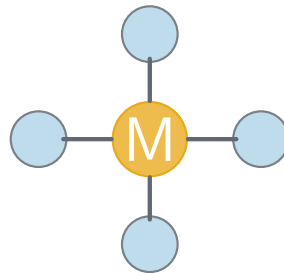
- 6 → **octahedral**
- 4 → tetrahedral or square planar
- 2 → linear



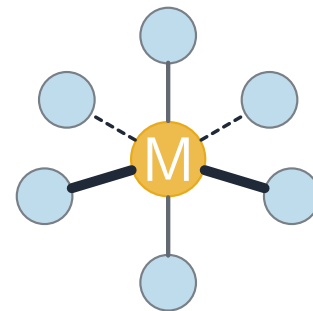
linear
CN 2



tetrahedral
CN 4



square planar
CN 4



octahedral
CN 6

The 3d orbitals, and the bond that makes a complex

the orbitals

the $3d_{xy}$ orbital has **four lobes pointing between** the axes; the $3d_{x^2-y^2}$ has four lobes pointing **along** them

why that matters

ligands approach along the axes, so those two sets are pushed up by **different amounts**

non-degenerate

the five 3d orbitals, equal in the free ion, split into two energy levels in a complex

a dative covalent bond

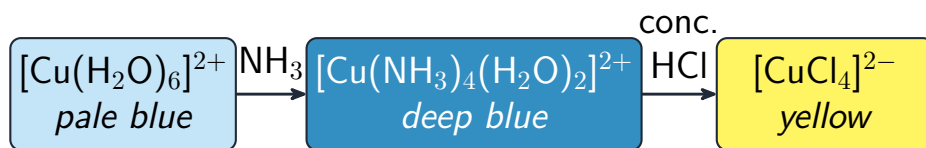
the ligand supplies **both** electrons to the bond with the metal ion

the colour

an electron absorbs light to jump the split, and the **complementary** colour is what we see

Change the ligand and you change the size of the split, so you change the colour. That is why ligand exchange is visible.

Ligand exchange



In **ligand exchange** one ligand replaces another, often with a colour change. Copper(II): pale blue (water) $\rightarrow$ deep blue (NH_3) $\rightarrow$ yellow ($[\text{CuCl}_4]^{2-}$).

Exercises 2.1-2.3

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]

Exercises 2.1-2.3

2.1 Define a **ligand**.

[2]

2.1

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

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

[2]

2.2

- coordination number 6; octahedral

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

[2]

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

Exercises 2.4·2.5

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]

Exercises 2.4·2.5

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

2.4

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

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

2.5

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

Exercises 3.1·3.2

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

Exercises 3.1·3.2

3.1 Which is a **bidentate** ligand?

[1]

☐

A H_2O

B Cl^-

C 1,2-diaminoethane (en)

D NH_3

3.1 C

- 1,2-diaminoethane (en) forms two dative bonds – bidentate

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

3.2 B

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

Exercise 3.3

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]

Exercise 3.3

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]

3.3

(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

Exercise 3.4

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

[2]

Exercise 3.4

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

[2]

3.4

- coordination number 4; tetrahedral

Exercise 3.5 (a)

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]

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(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

Exercise 3.5 (b)

3.5 Cobalt(II) forms a range of complexes.

(b) Complete the table for three cobalt complexes.

[6]

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

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(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+

Exercise 3.5 (c)

3.5 Cobalt(II) forms a range of complexes.

(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]

Exercise 3.5 (c)

3.5 Cobalt(II) forms a range of complexes.

(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]

(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

Exercise 3.5 (d)

3.5 Cobalt(II) forms a range of complexes.

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

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

(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