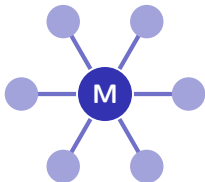


Transition Elements

A-Level Chemistry ■ Topic 28

A-Level Chemistry



What we will cover

- 1 Four key properties
- 2 Ligands & denticity
- 3 Complex shapes
- 4 Ligand exchange
- 5 Why complexes are coloured
- 6 Isomerism & stability



transition metals are colourful



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

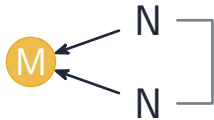
Ligands and denticity

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

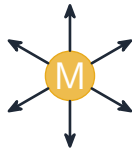
- **monodentate** – 1 bond (H_2O , NH_3)
- **bidentate** – 2 bonds (en)
- **polydentate** – many (EDTA: 6)



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



bidentate: 2 bonds
("en")



polydentate: many
(EDTA uses 6)

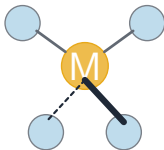
Complex shapes

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

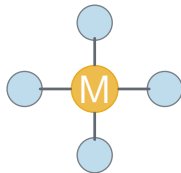
- 6 → **octahedral**
- 4 → tetrahedral or square planar
- 2 → linear



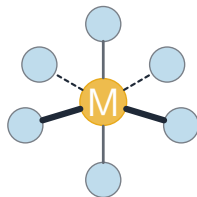
linear
CN 2



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

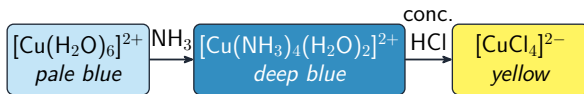
the ligand supplies both electrons to the bond with the metal ion

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 ($[\text{CuCl}_4]^{2-}$).



Why complexes are coloured



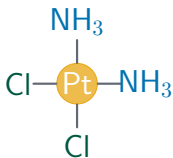
the complex absorbs light of energy ΔE , so we see the **complementary colour**

Ligands split the five **degenerate** d orbitals into two sets, a gap ΔE apart.

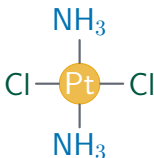
The complex absorbs light of energy ΔE ; we see the **complementary colour**. Different ligands give a different ΔE – so the colour changes.

Stereoisomerism in complexes

square planar $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$



cis (same side)



trans (opposite)

- **cis/trans** in square planar (e.g. $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$) & octahedral complexes
- **optical** in octahedral complexes with bidentate ligands

Isomerism in complexes, and predicting polarity

geometrical isomerism

cis and *trans* in square planar and octahedral complexes

optical isomerism

non-superimposable mirror images, in octahedral complexes with bidentate ligands

polarity

a *cis* form **may be polar**; the matching *trans* form is often **non-polar**, because its bond dipoles cancel

ligand exchange colours

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is blue; with concentrated HCl it becomes **yellow** $[\text{CuCl}_4]^{2-}$, and cobalt(II) behaves similarly

redox feasibility

use $E^\ominus$ values to predict whether a transition-metal redox reaction will go

The standard titrations to be able to calculate are MnO_4^- against Fe^{2+} , and thiosulfate against iodine. Both are asked most years.

Stability constants

K_{stab} : equilibrium for forming a complex

A **large stability constant** means a very stable complex – ligand exchange moves towards the larger K_{stab} .

Use $E^\ominus$ values to predict redox feasibility (e.g. $\text{MnO}_4^-/\text{Fe}^{2+}$ titrations, purple to colourless).

Four key properties (and why)

variable oxidation states

act as catalysts

form complex ions

coloured compounds

The four key properties of the transition elements

Exam tips

- Define a **transition element**: it forms at least one ion with a **partially filled d sub-shell** – so Sc and Zn are excluded.
- Colour comes from **d-d transitions** (ligands split the d orbitals); the colour seen is the complement of the light absorbed.
- State the **ligand and coordination number** and predict the shape (6 = octahedral, 4 = tetrahedral or square planar).
- **Ligand exchange** can change colour and coordination number; a larger stability constant = a more stable complex.



Worked example – a redox titration

25.0 cm³ of Fe²⁺ needs 22.0 cm³ of 0.0200 mol dm⁻³ KMnO₄ (ratio 1 : 5). Find [Fe²⁺].

■ Moles

$$\text{KMnO}_4 = \frac{22.0}{1000} \times 0.0200 = 4.40 \times 10^{-4}$$

■ Ratio 1 : 5, so moles

$$\text{Fe}^{2+} = 5 \times 4.40 \times 10^{-4} = 2.20 \times 10^{-3}$$

■ $[\text{Fe}^{2+}] = \frac{2.20 \times 10^{-3}}{25.0/1000} = 0.0880 \text{ mol dm}^{-3}$

Every titration is the same three steps: moles of the known → ratio from the equation → concentration of the unknown. KMnO₄ is self-indicating – the first permanent pink.

Topic 28 – key takeaways

1

Properties

variable states, catalysts,
complexes, colour

2

Ligands

donate a lone pair;
mono/bi/polydentate

3

Colour

split d orbitals; see the
complementary colour

4

Isomerism

cis/trans & optical; stability
constants

Check yourself

- 1 What does a bidentate ligand form?
- 2 What shape has coordination number 6?
- 3 Why are transition complexes coloured?
- 4 A large stability constant means what?



Answers 1. two dative bonds 2. octahedral 3. electrons jump split d orbitals 4. a very stable complex