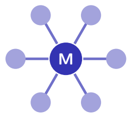
Transition Elements

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

1 Properties and complexes

Four key properties

variable oxidation state 氧化态 – 3d & 4s close in energy

complex ions 配离子 – vacant d orbitals accept lone pairs

catalyst 催化剂 – more than one stable state, vacant d orbitals

coloured 有色 compounds – electrons jump split d orbitals

A **transition element** 过渡元素 forms ions with incomplete d orbitals (so Sc and Zn don't count).

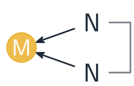
Ruby

Ligands and denticity

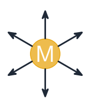
A **ligand** 配体 donates a **lone pair** 孤对电子 in a **dative bond** 配位键:

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

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



bidentate: 2 bonds
("en")



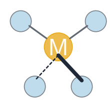
polydentate: many
(EDTA uses 6)

Complex shapes

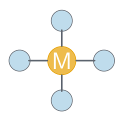
The **coordination number** 配位数 (dative bonds to the metal) sets the shape:

- 6 → **octahedral** 八面体形
- 4 → tetrahedral or square planar
- 2 → linear

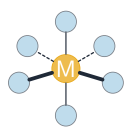
linear
CN 2



tetrahedral
CN 4



square planar
CN 4



octahedral
CN 6

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

the orbitals 轨道	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 非简并	the five 3d orbitals, equal in the free ion, split into two energy levels in a complex
a dative covalent bond 配位键	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.

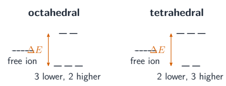
Ligand exchange

$[Cu(H_2O)_6]^{2+}$ *pale blue* $\xrightarrow{NH_3}$ $[Cu(NH_3)_4(H_2O)_2]^{2+}$ *deep blue* $\xrightarrow{\text{conc. HCl}}$ $[CuCl_4]^{2-}$ *yellow*

In **ligand exchange** 配体交换 one ligand replaces another, often with a colour change. Copper(II): pale blue (water) → deep blue (NH_3) → yellow ($[CuCl_4]^{2-}$).

2 Colour and isomerism

Why complexes are coloured



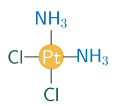
the complex absorbs light of energy ΔE, so we see the **complementary colour**

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

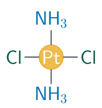
> The complex absorbs light of energy ΔE; we see the **complementary colour** 互补色. Different ligands give a different ΔE – so the colour changes.

Stereoisomerism in complexes

square planar $[Pt(NH_3)_2Cl_2]$



cis (same side)



trans (opposite)

- **cis/trans** 顺反异构 in square planar (e.g. $Pt(NH_3)_2Cl_2$) & octahedral complexes
- **optical** 旋光异构 in octahedral complexes with bidentate ligands

Isomerism in complexes, and predicting polarity

geometrical isomerism 几何异构	*cis* and *trans* in square planar and octahedral complexes
optical isomerism 光学异构	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	$[Cu(H_2O)_6]^{2+}$ is blue; with concentrated HCl it becomes yellow $[CuCl_4]^{2-}$, 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** 稳定常数 means a very stable complex – ligand exchange moves towards the larger K_{stab}.

Use $E^{\ominus}$ values to predict redox feasibility (e.g. MnO_4^-/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.

3 Recap

Worked example – a redox titration

$25.0\,\text{cm}^3$ of Fe^{2+} needs $22.0\,\text{cm}^3$ of $0.0200\,\text{mol dm}^{-3}$ $KMnO_4$ (ratio $1:5$). Find [Fe^{2+}].

- Moles $KMnO_4 = \dfrac{22.0}{1000} \times 0.0200 = 4.40 \times 10^{-4}$
- Ratio $1:5$, so moles $Fe^{2+} = 5 \times 4.40 \times 10^{-4} = 2.20 \times 10^{-3}$
- $[Fe^{2+}] = \dfrac{2.20 \times 10^{-3}}{25.0/1000} = 0.0880\,\text{mol dm}^{-3}$

Every titration is the same three steps: moles of the known → ratio from the equation → concentration of the unknown. $KMnO_4$ is self-indicating – the first permanent pink.

Topic 28 – key takeaways

1 Properties
variable states, catalysts, complexes, colour

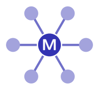
2 Ligands
donate a lone pair; mono/bi/polydentate

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