

Chemistry of transition elements

A-Level Chemistry

Transition elements

A **transition element** 过渡元素 is a d-block element that forms one or more stable ions with **incomplete d orbitals**. (Scandium and zinc are in the d-block but are not transition elements, because their stable ions have empty or full d orbitals.)

The 3d **orbitals** 轨道 have set shapes: the $3d_{xy}$ orbital has four lobes pointing between the axes, and the $3d_{z^2}$ orbital has two lobes along the z -axis with a ring around the middle.

Four key properties (and why)

Property	Reason
variable oxidation state 氧化态	the 3d and 4s sub-shells are close in energy, so similar small amounts of energy remove different numbers of electrons
act as a catalyst 催化剂	they have more than one stable oxidation state, and vacant d orbitals that can form dative bonds
form complex ions	vacant d orbitals can accept lone pairs
form coloured compounds	electrons move between split d orbitals (see below)

variable oxidation states

act as catalysts

form complex ions

coloured compounds

The four key properties of the transition elements



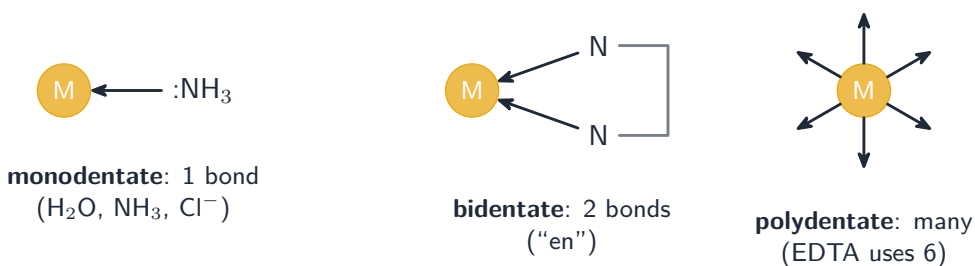
A ruby is red because of transition-metal (chromium) ions held in its crystal lattice

Ligands and complexes

A transition metal ion can be surrounded by **complex ions** 配离子. The species attached are ligands.

A **ligand** 配体 is a species with a lone pair of electrons that forms a **dative covalent bond** 配位键 to the central metal ion. (The **lone pair** 孤对电子 is what it donates.) Ligands are grouped by how many such bonds they can form:

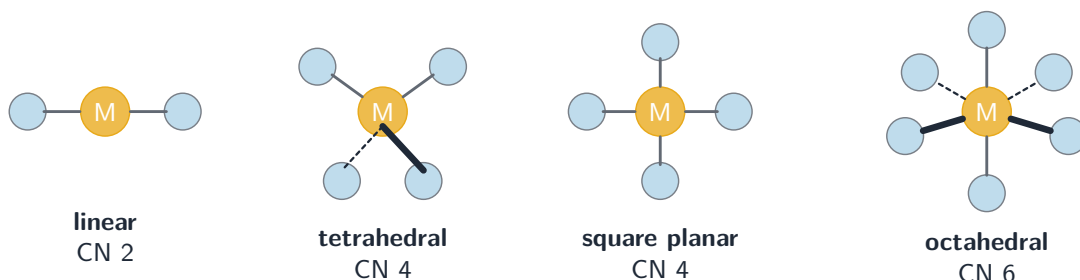
- **monodentate** 单齿: one bond (H_2O , NH_3 , Cl^- , CN^-).
- **bidentate** 双齿: two bonds (1,2-diaminoethane "en", and the ethanedioate ion $\text{C}_2\text{O}_4^{2-}$).
- **polydentate** 多齿: many bonds (EDTA^{4-} , which uses six).



Ligands are grouped by how many dative bonds they form: monodentate (one), bidentate (two) or polydentate (many, like EDTA's six)

A **complex** 配合物 is a central metal atom or ion surrounded by one or more ligands. Its shape can be **linear** 直线形, **square planar** 平面正方形, **tetrahedral** 四面体形 or **octahedral** 八面体形.

The **coordination number** 配位数 is the number of dative bonds from the ligands to the central ion (6 → octahedral, 4 → tetrahedral or square planar, 2 → linear). To predict the charge of a complex, add the metal's charge and all the ligand charges.



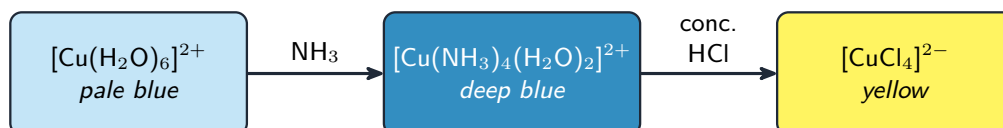
Complex shapes follow the coordination number: 2 is linear, 4 is tetrahedral or square planar, 6 is octahedral

Ligand exchange

In **ligand exchange** 配体交换 one ligand replaces another, often with a colour change. For copper(II):



With concentrated HCl it becomes yellow $[\text{CuCl}_4]^{2-}$; cobalt(II) behaves in a similar way.



Ligand exchange changes the colour of copper(II): pale blue with water, deep blue with ammonia, yellow with concentrated HCl

Redox reactions of transition ions

Use $E^\ominus$ values to predict whether a redox reaction is feasible. Common titrations you should be able to calculate include $\text{MnO}_4^-/\text{C}_2\text{O}_4^{2-}$ and $\text{MnO}_4^-/\text{Fe}^{2+}$ in acid (purple to colourless), and $\text{Cu}^{2+}/\text{I}^-$ (which makes iodine, then titrated with thiosulfate).

Worked example. In acid, MnO_4^- reacts with Fe^{2+} in the ratio 1 : 5 (see the balanced equation above). A 25.0 cm^3 sample of Fe^{2+} solution needs 22.0 cm^3 of $0.0200\text{ mol dm}^{-3}$ KMnO_4 to reach the end point. Find the concentration of the Fe^{2+} .

Moles of MnO_4^- used = $0.0200 \times \frac{22.0}{1000} = 4.40 \times 10^{-4}\text{ mol}$. Each mole of MnO_4^- reacts with 5 moles of Fe^{2+} , so moles of $\text{Fe}^{2+} = 5 \times 4.40 \times 10^{-4} = 2.20 \times 10^{-3}\text{ mol}$. This was in 25.0 cm^3 , so

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

Why complexes are coloured

In a free ion the five d orbitals are **degenerate** 简并 — they have the same energy. When ligands come close, they split the d orbitals into two **non-degenerate** 非简并 sets, separated by an energy gap ΔE :

- **octahedral**: three lower and two higher orbitals.
- **tetrahedral**: two lower and three higher orbitals.

A complex absorbs light whose frequency matches ΔE , promoting an electron from a lower to a higher d orbital. The colour you **see** is the **complementary colour** 互补色 of the light absorbed. Different ligands give a different ΔE , so they change the frequency absorbed and hence the colour — which is why ligand exchange changes the colour.



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

Ligands split the five d orbitals into two sets separated by a gap ΔE ; the complex absorbs light of that energy, so we see the complementary colour

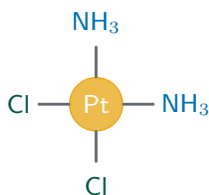


Different metals and oxidation states give different colours: cobalt(II) (red), dichromate (orange), chromate (yellow), nickel(II) (green), copper(II) (blue) and permanganate (violet)

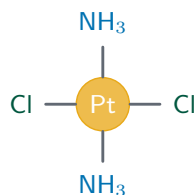
Stereoisomerism in complexes

- **geometrical isomerism** 几何异构 (**cis** 顺式 / **trans** 反式) appears in square planar complexes such as $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, and in octahedral complexes such as $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

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



cis (same side)



trans (opposite)

Geometrical isomerism in a square planar complex: the two identical ligands are adjacent (cis) or opposite (trans)

- **optical isomerism** 旋光异构 appears in octahedral complexes with bidentate ligands, such as $[\text{Ni}(\text{en})_3]^{2+}$, which has two non-superimposable mirror images.

You can also deduce the polarity of a complex: a *cis* form may be polar, while the matching *trans* form is often non-polar because its dipoles cancel.

Stability constants

The **stability constant** 稳定常数 (K_{stab}) is the equilibrium constant for forming a complex ion from the metal ion and its ligands in solution (water is left out of the expression).

A **large** K_{stab} means a very stable complex. In a ligand exchange, the position moves towards the complex with the larger K_{stab} — that is why a ligand that forms a more stable complex can push out a weaker one.

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.