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)

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

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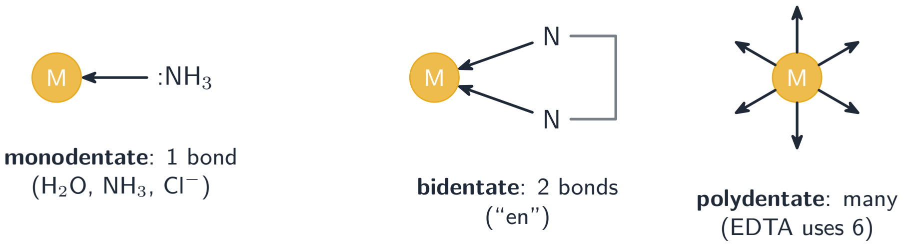
Ligands and complexes

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^-).

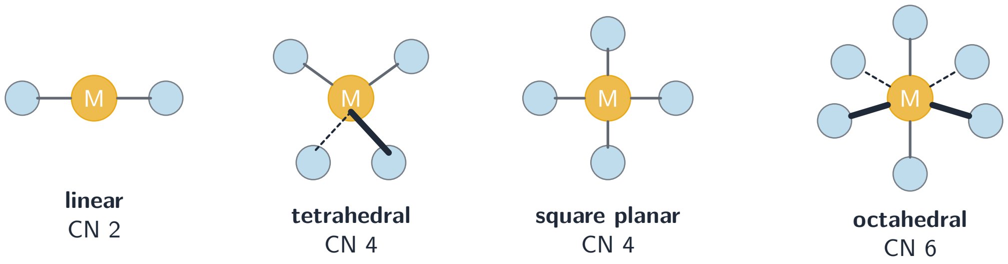
- **bidentate** 双齿: two bonds (1,2-diaminoethane ”en”, and the ethanedioate ion $C_2O_4^{2-}$).
- **polydentate** 多齿: many bonds ($EDTA^{4-}$, which uses six).



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.



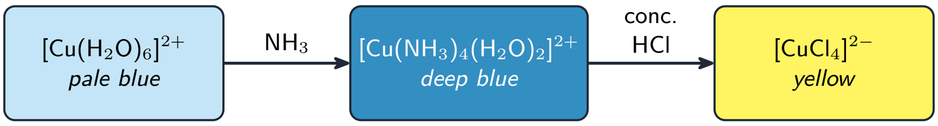
Complex shapes follow the coordination number: 2 is linear, 4 is tetrahedral or square planar, 6 is octahedral

Ligand exchange

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

$$[Cu(H_2O)_6]^{2+}\text{ (pale blue) }\xrightarrow{NH_3}[Cu(NH_3)_4(H_2O)_2]^{2+}\text{ (deep blue)}$$

With concentrated HCl it becomes yellow $[CuCl_4]^{2-}$; 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

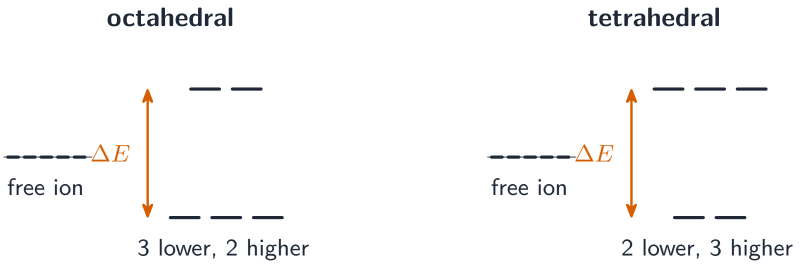
Use $E^\ominus$ values to predict whether a redox reaction is feasible. Common titrations you should be able to calculate include $MnO_4^-/C_2O_4^{2-}$ and MnO_4^-/Fe^{2+} in acid (purple to colourless), and Cu^{2+}/I^- (which makes iodine, then titrated with thiosulfate).

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)

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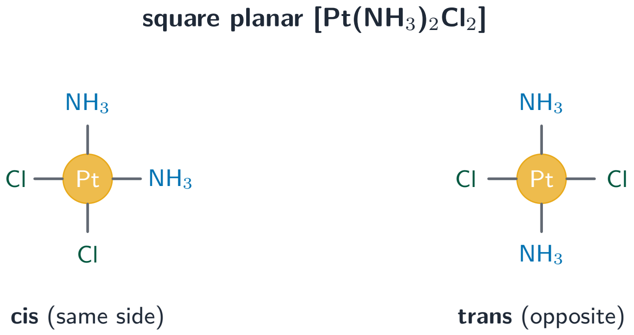
Stereoisomerism in complexes

- **geometrical isomerism** 几何异构 (**cis** 顺式 / **trans** 反式) appears in square planar complexes such as $[Pt(NH_3)_2Cl_2]$, and in octahedral complexes such as $[Co(NH_3)_4(H_2O)_2]^{2+}$.



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 $[Ni(en)_3]^{2+}$, 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.