

Transition elements

A-Level Chemistry 9701 · Topic 28 revision notes

Everything from the 7 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

- | | |
|--|--|
| 1. <u>Physical properties of transition elements</u> | 4. <u>Variable oxidation states and redox</u> |
| 2. <u>Complex ions and ligands</u> | 5. <u>Colour of complexes</u> |
| 3. <u>Ligand exchange</u> | 6. <u>Stereoisomerism in complexes</u> |
| | 7. <u>Stability constants, K_{stab}</u> |

1 Physical properties of transition elements

Syllabus 28.1

A **transition element** is a d-block element that forms **one or more stable ions with an incomplete d subshell**. Scandium (only Sc^{3+} , $3d^0$) and zinc (only Zn^{2+} , $3d^{10}$) are d-block elements but **not** transition elements. Across Ti to Cu, electrons enter the inner 3d subshell, so the extra nuclear charge is largely shielded: **atomic radii and first ionisation energies stay very similar**. When ions form, the **4s electrons are lost first**. **Chromium** ($3d^5 4s^1$) and **copper** ($3d^{10} 4s^1$) are exceptions to the filling order. Transition elements show **variable oxidation states**, act as **catalysts**, form **coloured compounds** and form **complex ions**.

		3d	4s	red = exception						
Ti	[Ar]	<table><tr><td>↑</td><td>↑</td><td></td><td></td><td></td></tr></table>	↑	↑				<table><tr><td>↑↓</td></tr></table>	↑↓	$3d^2 4s^2$
↑	↑									
↑↓										
Cr	[Ar]	<table><tr><td>↑</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr></table>	↑	↑	↑	↑	↑	<table><tr><td>↑</td></tr></table>	↑	$3d^5 4s^1$
↑	↑	↑	↑	↑						
↑										
Fe	[Ar]	<table><tr><td>↑↓</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr></table>	↑↓	↑	↑	↑	↑	<table><tr><td>↑↓</td></tr></table>	↑↓	$3d^6 4s^2$
↑↓	↑	↑	↑	↑						
↑↓										
Fe ³⁺	[Ar]	<table><tr><td>↑</td><td>↑</td><td>↑</td><td>↑</td><td>↑</td></tr></table>	↑	↑	↑	↑	↑	<table><tr><td></td></tr></table>		$3d^5$
↑	↑	↑	↑	↑						
Cu	[Ar]	<table><tr><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td></tr></table>	↑↓	↑↓	↑↓	↑↓	↑↓	<table><tr><td>↑</td></tr></table>	↑	$3d^{10} 4s^1$
↑↓	↑↓	↑↓	↑↓	↑↓						
↑										
Cu ²⁺	[Ar]	<table><tr><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑</td></tr></table>	↑↓	↑↓	↑↓	↑↓	↑	<table><tr><td></td></tr></table>		$3d^9$
↑↓	↑↓	↑↓	↑↓	↑						

Fig. 1: electrons in boxes for some period 4 transition metals and their ions

Definition, configurations, properties.

- ✓ **Definition:** stable ion with an incomplete d subshell.
- ✓ **Ions:** remove 4s before 3d.
- ✓ **Exceptions:** Cr $3d^5 4s^1$, Cu $3d^{10} 4s^1$.
- ✓ **Properties:** variable oxidation states, catalysts, coloured, complexes.

Watch out!

When forming ions, remove the **4s electrons first**: Fe^{2+} is $[Ar]3d^6$, not $[Ar]3d^4 4s^2$. Chromium is $3d^5 4s^1$ and copper $3d^{10} 4s^1$. Zinc is in the d block but is **not** a transition element, because Zn^{2+} has a full 3d subshell; scandium is excluded because Sc^{3+} has no d electrons.

thelucidstem.com

2 Complex ions and ligands

Syllabus 28.2

A **complex** is a central metal atom or ion surrounded by **ligands**. A ligand is a species with at least one **lone pair** that forms a **dative covalent (coordinate) bond** to the metal. **Monodentate** ligands (H_2O , NH_3 , Cl^- , CN^- , OH^-) form one bond; **bidentate** ligands (1,2-diaminoethane, en, and ethanedioate, $\text{C}_2\text{O}_4^{2-}$) form two; **polydentate** EDTA^{4-} forms six. The **coordination number** is the number of dative bonds to the metal. Coordination number 6 gives an **octahedral** complex, 4 gives **tetrahedral** (large ligands such as Cl^-) or **square planar** (Pt^{2+} , as in cisplatin), and 2 gives **linear**, as in $[\text{Ag}(\text{NH}_3)_2]^+$. The overall charge is the metal's oxidation state plus the charges of the ligands.

coordination number decides the shape

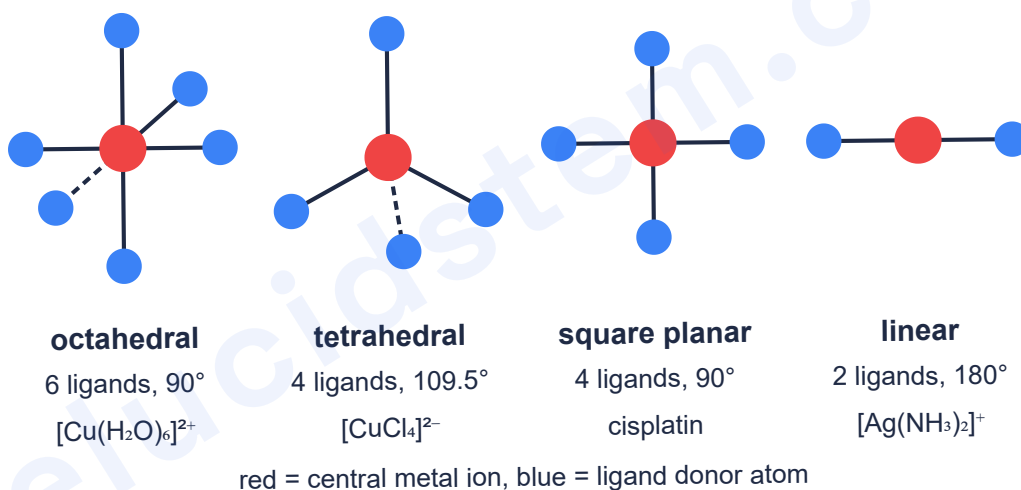


Fig. 1: the four geometries of complexes you need, with examples

Ligand, coordination number, shape, charge.

- ✓ **Ligand:** lone pair donor, forms a dative bond.
- ✓ **Denticity:** mono (H_2O), bi (en, $\text{C}_2\text{O}_4^{2-}$), hexa (EDTA^{4-}).
- ✓ **Shape:** 6 octahedral; 4 tetrahedral or square planar; 2 linear.
- ✓ **Charge:** metal oxidation state + ligand charges.

Watch out!

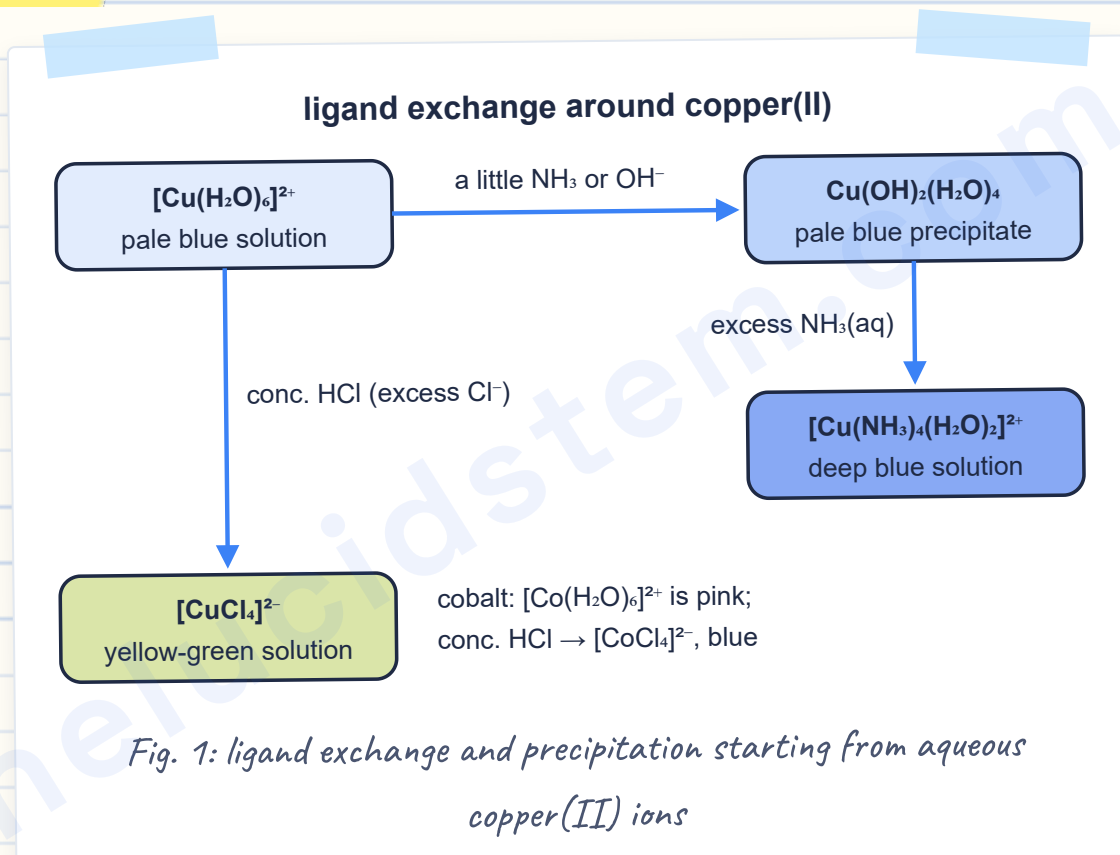
The coordination number counts **dative bonds**, not ligands:

$[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ is 6-coordinate. Neutral ligands (H_2O , NH_3 , en) add nothing to the charge, so $[\text{Co}(\text{NH}_3)_6]^{3+}$ contains Co(+3). Four ligands can mean **tetrahedral or square planar**; Pt(II) complexes are square planar.

3 Ligand exchange

Syllabus 28.2

In **ligand exchange** one ligand in a complex is replaced by another. Pale blue $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ reacts with **excess aqueous ammonia** to give deep blue $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$; NH_3 and H_2O are similar in size, so the coordination number stays 6. With **concentrated HCl** it gives yellow-green $[\text{CuCl}_4]^{2-}$; the large Cl^- ions change the coordination number to 4 and the shape to tetrahedral. Pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ similarly gives blue $[\text{CoCl}_4]^{2-}$. Adding a **little $\text{NaOH}(\text{aq})$ or $\text{NH}_3(\text{aq})$** removes H^+ from water ligands and precipitates the **neutral hydroxide**, e.g. blue $\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4$; some precipitates redissolve in excess reagent.



Ammonia, chloride, hydroxide.

- ✓ **Excess NH_3 :** Cu^{2+} deep blue $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.
- ✓ **Conc. HCl:** $[\text{CuCl}_4]^{2-}$ yellow-green, $[\text{CoCl}_4]^{2-}$ blue, CN 4.
- ✓ **A little OH^- :** neutral hydroxide precipitates.
- ✓ **Colours:** Cu blue, Fe(II) green, Fe(III) red-brown, Mn off-white, Cr grey-green.

Watch out!

A **little** ammonia acts as a **base** and gives the hydroxide precipitate; only **excess** ammonia acts as a **ligand** and gives the deep blue solution. Concentrated HCl changes the coordination number from 6 to 4 because Cl^- is large. $[\text{CuCl}_4]^{2-}$ has a 2- charge $(+2 + 4 \times -1)$.

4 Variable oxidation states and redox

Syllabus 28.2

Transition elements have **variable oxidation states** because the 3d and 4s electrons are close in energy. **Acidified manganate(VII)**, MnO_4^- , is reduced to Mn^{2+} (purple to colourless) and is its own indicator: the end point is the **first permanent pale pink**. It reacts with Fe^{2+} in a **1 : 5** ratio and with ethanedioate in a **2 : 5** ratio. **Acidified dichromate(VI)**, $\text{Cr}_2\text{O}_7^{2-}$, is reduced to Cr^{3+} (orange to green) and reacts with Fe^{2+} in a **1 : 6** ratio. **$E^\ominus$ values** predict feasibility: a reaction is feasible if $E^\ominus_{\text{cell}}$ is positive. Cu^{2+} oxidises I^- to I_2 , which is titrated with thiosulfate: overall **$n(\text{Cu}^{2+}) = n(\text{S}_2\text{O}_3^{2-})$** .

more positive $E^\ominus$: stronger oxidising agent on the left

	$E^\ominus / \text{V}$
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.52
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.54
$\text{S}_4\text{O}_6^{2-} + 2\text{e}^- \rightleftharpoons 2\text{S}_2\text{O}_3^{2-}$	+0.09

a species oxidises the right-hand side of any half-equation below it

Fig. 1: standard electrode potentials of the half-cells used in transition metal titrations

Ratios, indicators, acids.

- ✓ **$\text{MnO}_4^- : \text{Fe}^{2+}$ 1 : 5; $\text{MnO}_4^- : \text{C}_2\text{O}_4^{2-}$ 2 : 5.**
- ✓ **$\text{Cr}_2\text{O}_7^{2-} : \text{Fe}^{2+}$ 1 : 6.**
- ✓ **$\text{Cu}^{2+} : \text{S}_2\text{O}_3^{2-}$ 1 : 1** (via I_2 , starch indicator).
- ✓ **Acidify** with H_2SO_4 ; $E^\ominus_{\text{cell}}$ positive means feasible.

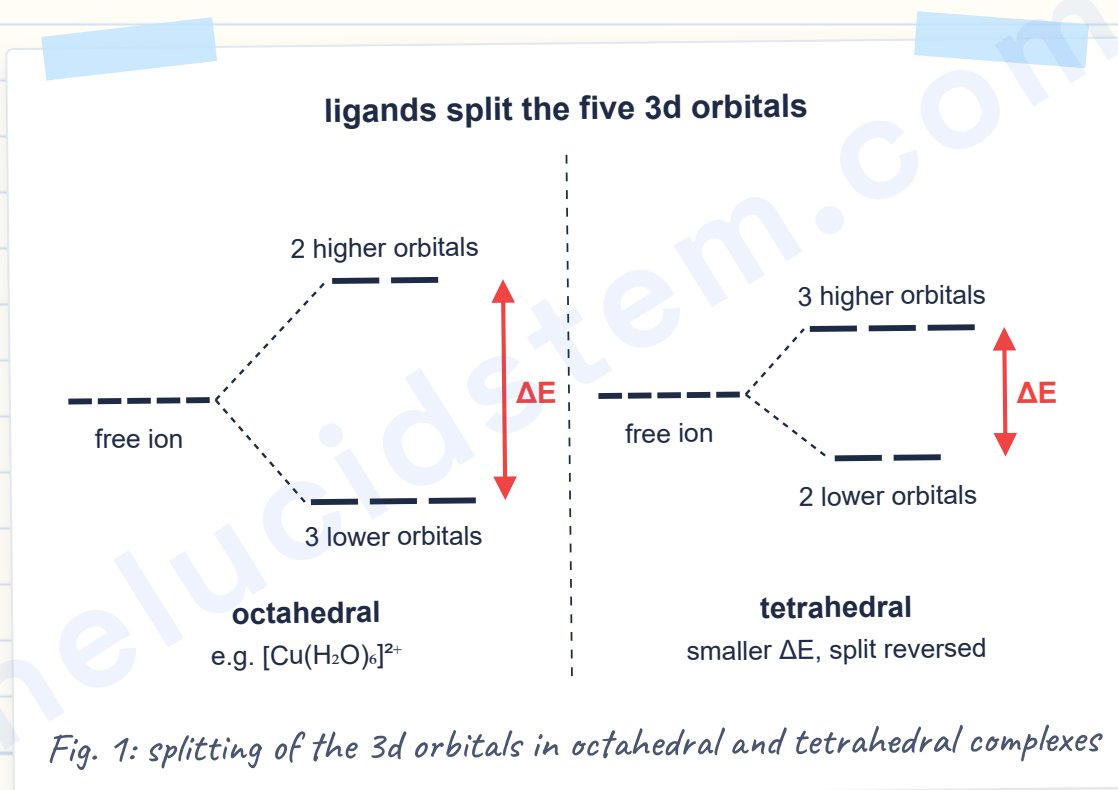
Watch out!

Get the **ratios** right: $\text{MnO}_4^- : \text{Fe}^{2+} = 1 : 5$, $\text{MnO}_4^- : \text{C}_2\text{O}_4^{2-} = 2 : 5$, $\text{Cr}_2\text{O}_7^{2-} : \text{Fe}^{2+} = 1 : 6$, $\text{Cu}^{2+} : \text{S}_2\text{O}_3^{2-} = 1 : 1$. Acidify manganate(VII) with **sulfuric acid**, never hydrochloric. The manganate(VII) end point is the **first permanent pale pink**, not colourless.

5 Colour of complexes

Syllabus 28.3

In a free ion the five 3d orbitals are **degenerate** (equal in energy). Ligand lone pairs repel the d electrons unequally, so the orbitals become **non-degenerate**: in an **octahedral** complex they split into **three lower and two higher** orbitals; in a **tetrahedral** complex into **two lower and three higher**, with a smaller gap. When white light passes through, an electron is promoted from a lower to a higher d orbital, absorbing a photon of energy $\Delta E = hf$. The **colour seen is the complementary colour** of the light absorbed. Ions with an **empty (d^0) or full (d^{10})** d subshell cannot make this transition, so they are colourless. A different **ligand, oxidation state or coordination number** changes ΔE and so changes the colour.



Split, absorb, see the complement.

- ✓ **Octahedral:** 3 lower, 2 higher.
Tetrahedral: 2 lower, 3 higher, smaller ΔE .
- ✓ $\Delta E = hf = hc/\lambda$; per mole multiply by L .
- ✓ **Colour seen** = complementary to colour absorbed.
- ✓ **d^0 and d^{10}** ions are colourless.

Watch out!

The colour you see is **not** the colour absorbed: a blue solution absorbs **red-orange** light.

Octahedral splitting is **3 lower, 2 upper**; tetrahedral is the reverse, **2 lower, 3 upper**, with a smaller ΔE .

Electrons are promoted **within the 3d subshell**, not from 3d to 4s.

Colour needs a **partly filled d** subshell, so Zn^{2+} and Sc^{3+} compounds are white.

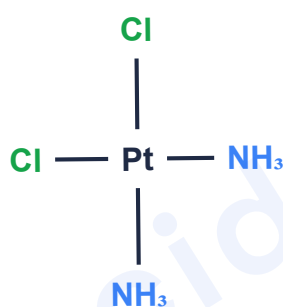
6 Stereoisomerism in complexes

Syllabus 28.4

Stereoisomers have the same structural formula but a different arrangement of atoms in space. **Cis-trans isomerism** occurs in **square planar** complexes of the type MA_2B_2 , such as $Pt(NH_3)_2Cl_2$, and in **octahedral** complexes of the type MA_4B_2 , such as $[Co(NH_3)_4Cl_2]^+$: in the **cis** isomer the two identical ligands are at **90°** , in the **trans** isomer at **180°** .

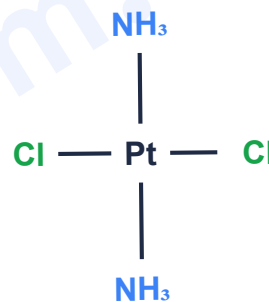
Optical isomerism occurs when a complex is **chiral**: its mirror image is non-superimposable. Octahedral complexes with **three bidentate ligands**, such as $[Ni(en)_3]^{2+}$, or two bidentate ligands in a cis arrangement, exist as a pair of **enantiomers**. **Cisplatin** is an anticancer drug: it loses its Cl^- ligands and **binds to nitrogen atoms on DNA**, stopping cancer cells from dividing.

$Pt(NH_3)_2Cl_2$: square planar, two isomers



cis (cisplatin)

Cl-Pt-Cl angle 90°
anticancer drug



trans

Cl-Pt-Cl angle 180°
not an effective drug

Fig. 1: cis and trans isomers of the square planar complex $Pt(NH_3)_2Cl_2$

Cis, trans, chiral.

- ✓ **Cis-trans:** square planar MA_2B_2 or octahedral MA_4B_2 .
- ✓ **Cis** 90° , **trans** 180° .
- ✓ **Optical:** three bidentate ligands, or cis- $[M(en)_2X_2]$.
- ✓ **Cisplatin:** binds DNA, stops cell division.

Watch out!

Cis-trans isomerism needs **square planar or octahedral** geometry; a tetrahedral MA_2B_2 complex has **no** geometrical isomers. Cis means the identical ligands are at **90°** , trans at **180°** . In $[Co(en)_2Cl_2]^+$ only the **cis** isomer is chiral, giving **three** stereoisomers in total. It is **cisplatin** that is the drug.

thelucidstem.com

7 Stability constants, K_{stab}

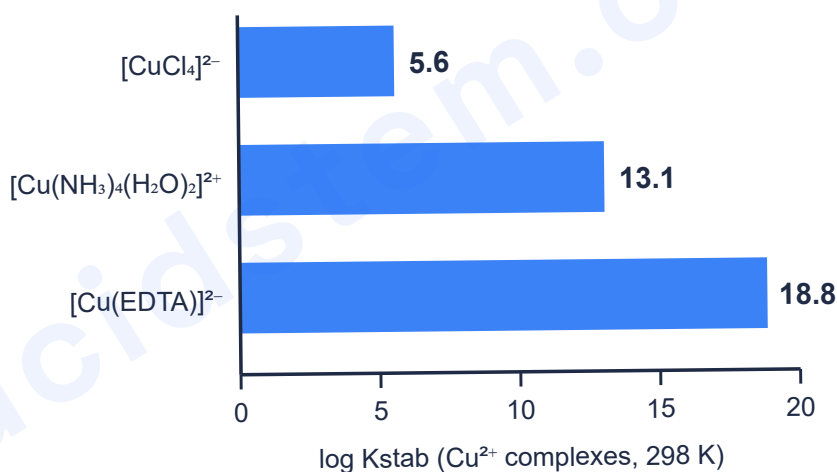
Syllabus 28.5

The **stability constant**, K_{stab} , is the **equilibrium constant for the formation of a complex ion** in a solvent from its constituent ions or molecules. For $\text{Cu}^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$, $K_{stab} = [\text{complex}] / ([\text{Cu}^{2+}][\text{NH}_3]^4)$, units $\text{mol}^{-4} \text{dm}^3$.

Water is left out because it is the solvent and its concentration is effectively constant. Values are huge, so they are often quoted as **$\log K_{stab}$** . A ligand exchange happens if the **new complex has a larger K_{stab}** ; the larger the value, the more stable the complex.

Multidentate ligands such as EDTA^{4-} form very stable complexes (the **chelate effect**) because one ligand releases several water molecules, so the number of particles and the **entropy increase**.

larger $\log K_{stab}$: the more stable complex wins



each forms from $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ by ligand exchange

Fig. 1: $\log K_{stab}$ for three complexes of copper(II)

Expression, units, compare, entropy.

- ✓ $K_{stab} = [\text{complex}] / ([M^{n+}][L]^x)$, water left out.
- ✓ **Units** from the powers: 4 ligands give $\text{mol}^{-4} \text{ dm}^3$.
- ✓ **Larger K_{stab}** = more stable; exchange goes towards it.
- ✓ **Chelate effect:** more particles, ΔS positive.

Watch out!

Leave **water out** of K_{stab} expressions. Units depend on the number of ligands: four monodentate ligands give $\text{mol}^{-4} \text{ dm}^3$, but one EDTA^{4-} gives $\text{mol}^{-1} \text{ dm}^3$. A **larger K_{stab}** means a **more stable** complex, and ligand exchange goes towards it. The chelate effect is mainly an **entropy** effect, not a stronger bond.