CIE Chemistry A Level

12 : An Introduction to the Chemistry of Transition Elements
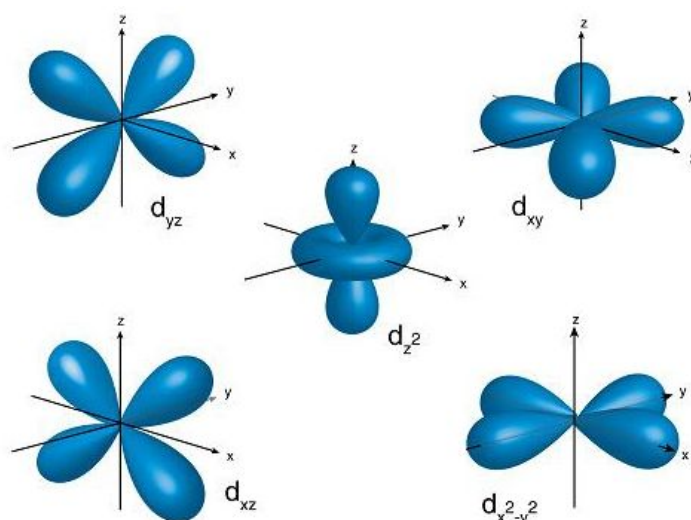
(A Level only)

Notes

General physical properties of the first row of transition elements, titanium to copper

Transition Elements

Transition elements are found in the **d-block** of the periodic table. Transition elements form **one or more stable ions** with **incomplete d orbitals.**
The d subshell can hold up to 10 electrons.

A **d orbital** looks like this:

Scandium and zinc

Scandium and **zinc** are in the d block of the periodic table but they are **not transition elements** because their ions do not have an incomplete d subshell.
Scandium forms one stable ion, Sc^{3+}, which has an empty d sub shell.
Electron configurations   Sc: $[Ar]3d^14s^2 \rightarrow Sc^{3+}$: $[Ar]$
Zinc also only forms one stable ion, Zn^{2+}, which has a full d sub shell.
Electron configurations   Zn: $[Ar]3d^{10}4s^2 \rightarrow Zn^{2+}$: $[Ar]3d^{10}$

Transition element	Atom electron configuration	Ion electron configuration
Titanium	Ti: $[Ar]3d^24s^2$	Ti^{2+}: $[Ar]3d^2$
Vanadium	V: $[Ar]3d^34s^2$	V^{2+}: $[Ar]3d^3$ also common: V^{3+}, V^{4+} and V^{5+}
Chromium	Cr: $[Ar]3d^54s^1$	Cr^{3+}: $[Ar]3d^3$ also common: Cr^{2+} and Cr^{6+}
Manganese	Mn: $[Ar]3d^54s^2$	Mn^{2+}: $[Ar]3d^5$ also common: Mn^{3+}, Mn^{4+}, Mn^{6+} and Mn^{7+}
Iron	Fe: $[Ar]3d^64s^2$	Fe^{2+}: $[Ar]3d^6$ also common: Fe^{3+}
Cobalt	Co: $[Ar]3d^74s^2$	Co^{2+}: $[Ar]3d^7$ also common Co^{3+}
Nickel	Ni: $[Ar]3d^84s^2$	Ni^{2+}: $[Ar]3d^8$ also common: Ni^+
Copper	Cu: $[Ar]3d^{10}4s^1$	Cu^{2+}: $[Ar]3d^{10}$ also common: Cu^+

It is important to remember that the **4s orbital is filled before the 3d** so the 4s electrons are **removed before the 3d electrons**. Also remember that the electron configurations of **copper** and **chromium** are different than expected as the 4s orbital only has one electron. This is so that the 3d subshell is filled for copper and half filled for chromium, as these are more stable electron configurations.

Melting points and densities
All transition metals have similar physical properties such as **high melting points** and **high densities**.

Melting point
Transition metals have higher melting points that metals found in the s-block, like calcium. This is because the transition metals have the **extra 3d electrons** so **metallic bonding is stronger**, requiring **more energy** to overcome.

Density
As you go across the periodic table, nuclear charge increases. This draws the electrons inwards slightly, decreases the **atomic radius**. **As a result,** transition metals have **higher densities** than metals in the s-block because the **atoms are smaller** so atoms fit into a given volume compared with s-block metal atoms. Density is also greater because **atomic mass increases** across the period.

Variable oxidation states
Transition metals can exist in **variable oxidation states**. For example, iron forms two common ions, Fe^{2+} (+2 oxidation state) and Fe^{3+} (+3 oxidation state).
Variable oxidation states form because the electrons in the **4s and 3d orbitals have very similar energies.** This means that a relatively similar amount of energy is required to gain or lose different numbers of electrons.

General characteristic chemical properties of the first set of transition elements, titanium to copper

Reactions with ligands to form complexes

- **Ligand**: a species that has a lone pair of electrons that forms a dative covalent bond with a central metal atom or ion. Monodentate ligands form one coordinate bond, bidentate ligands form two and polydentate ligands form more than two.
- **Complex**: a molecule containing a central metal atom or ion surrounded by one or more ligands.
- **Coordination number**: the number of dative bonds formed with the central metal ion.

Reactions with water:

Transition metal ions react with **monodentate** water ligands to form complexes.

$Cu^{2+} + 6H_2O \rightarrow [Cu(H_2O)_6]^{2+}$ Observation: **Blue** solution formed
$Co^{2+} + 6H_2O \rightarrow [Co(H_2O)_6]^{2+}$ Observation: **Pink** solution formed

Reactions with ammonia:

Metal aqua ions react with aqueous **ammonia** to form precipitates. Ammonia molecules are **monodentate ligands**.
Copper and **cobalt** undergo two reactions when ammonia is added to their metal aqua ion. The second reaction only occurs when there is an excess of ammonia.

Aqua ion	Equation	Observation sol=solution / ppt=precipitate
Cu^{2+}	$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$ Excess: $[Cu(H_2O)_4(OH)_2]+4NH_3 \rightarrow [Cu(H_2O)_2(NH_3)_4]+2H_2O+2OH^-$	Blue sol → light blue ppt Light blue ppt → dark blue sol
Co^{2+}	$[Co(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Co(H_2O)_4(OH)_2] + 2NH_4^+$ Excess: $[Co(H_2O)_4(OH)_2] + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 4H_2O + 2OH^-$	Pink sol → blue ppt Blue ppt → yellow brown sol

The ammonia ligands make Co(II) unstable so Co(II) is oxidised to Co(III) in air. $[Co(NH_3)_6]^{2+}$ becomes $[Co(NH_3)_6]^{3+}$ (red-brown solution).

Reactions with hydroxide ions

Metal aqua ions react with **hydroxide ions** to form precipitates. Hydroxide ions are **monodentate** ligands.

Aqua ion	Equation	Observation sol=solution / ppt=precipitate
Cu^{2+}	$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$	Blue sol → light blue ppt
Co^{2+}	$[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow [Co(H_2O)_4(OH)_2] + 2H_2O$	Pink sol → blue ppt

Reactions with chloride ions

Chloride ions act as **monodentate** ligands when they react with metal aqua ions. They are **charged** and **larger** so only four Cl⁻ ions are able to fit around the metal ion. This means the **coordination number** decreases from 6 to 4.

Aqua ion	Equation	Observation sol=solution / ppt=precipitate
Cu^{2+}	$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$	Blue sol → yellow sol
Co^{2+}	$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$	Pink sol → blue sol

Geometry of transition metal complexes

Transition metal complexes can be described as **linear**, **octahedral**, **tetrahedral** or **square planar**, depending on the ligands and the metal ions in the complex.

Linear

A **linear** complex is most commonly formed by a **silver metal ion** with two coordinate bonds. The bond angles are **180°**.


Octahedral

An octahedral complex is formed when a metal ion has **6 coordinate bonds.** This happens with **water** and **ammonia** because they are small so 6 ligands are able to surround the central metal ion. Two octahedral complexes are shown below, one with a single type of ligand and the second with a mixture of ligands. The bond angles are **90°**.
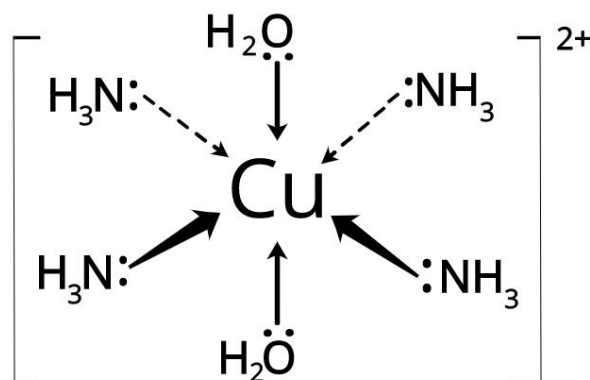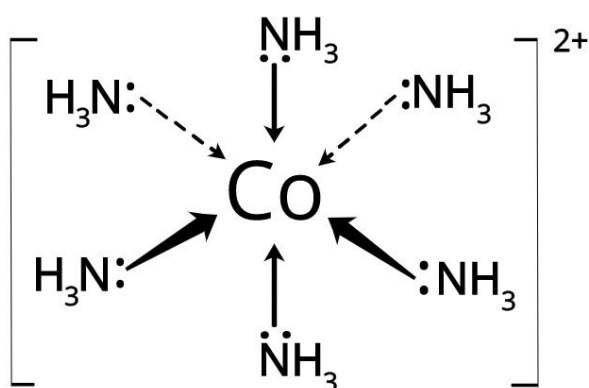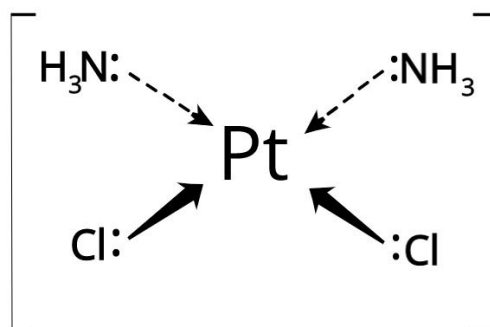
Tetrahedral

If there are **four coordinate bonds** in a complex, like $[CuCl_4]^{2-}$, the shape is usually tetrahedral. The bond angles are **109.5°**.
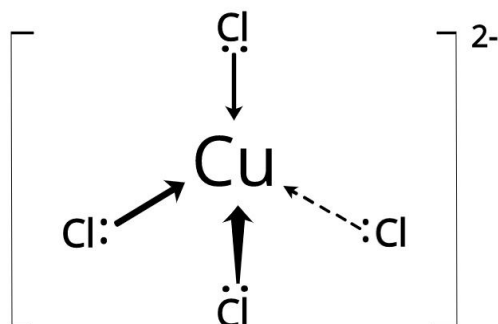

Square planar

Sometimes a square planar shape when there are **four coordinate bonds** instead of a tetrahedral shape. The bond angle is **90°.** The compound shown is **cisplatin**, an anti cancer drug.


Ligand exchange

When ligands **swap places** with one another, this is called ligand exchange or ligand substitution. The **coordination number** and **shape** of the ion stays the same if the ligands are a similar size and charge.

Some examples of ligand substitution reactions are shown below:

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$$
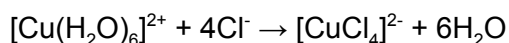
- **Blue** solution → **yellow** solution
- Octahedral → tetrahedral
- **Coordination number** reduces from **6 to 4** because of the change in size of the ligands.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)(H_2O)_2]^{2+} + 4H_2O$$
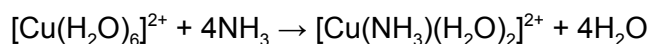
- This exchange only occurs with excess ammonia. If it is not in excess then $[Cu(H_2O)_4(OH)_2]$ precipitate forms.
- **Blue** solution → **dark blue** solution.
- Shape stays as octahedral.
- **Coordination number** remains at **6.**

Redox systems

Redox reactions can be used in **titrations**.

Potassium manganate(VII)

Potassium manganate(VII) contains the MnO_4^- ion and is an **oxidising agent** commonly used in redox titrations. The half equation for this redox system is shown below:
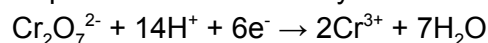
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
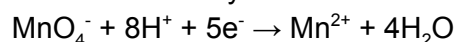
The titration:
- **Purple potassium manganate(VII)** is placed in a **burette**. The sample being analysed is placed in the conical flask with excess dilute **sulfuric acid.**
- As potassium manganate(VII) is added from the burette, a reaction occurs, forming **colourless Mn^{2+}.** The end point is when the solution is first **tinted pink**.

Potassium dichromate(VI)

Potassium dichromate(VI) solution can be acidified with dilute sulfuric acid. Potassium dichromate is an **oxidising agent**. The half equation for this redox system is shown below:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

The titration:
- **Orange potassium dichromate(VI)** is placed in a burette. The sample to be analysed is placed in the conical flask with excess dilute **sulfuric acid**.
- As potassium dichromate(VI) is added from the burette, a reaction occurs, forming **green Cr^{3+}**. The end point is when the $Cr_2O_7^{2-}$ stops reacting and doesn't turn green. This can be seen when the solution in the flask starts becoming **discoloured** due to the orange solution being added.

Conditions:

Acidic conditions are required for both oxidising agents to work so that **H^+ ions** are present.
Dilute **sulfuric acid** is chosen for several reasons:
- **Hydrochloric acid** can not be used because the oxidising agent will cause the formation of Cl_2. As Cl_2 is a gas, this will affect the volume of oxidising agent in the reaction mixture.
- **Concentrated sulfuric acid** or **concentrated nitric acid** can not be used because they are only weak oxidising agents.
- **Ethanoic acid** can not be used because it is a weak acid so not enough H^+ ions would be released.
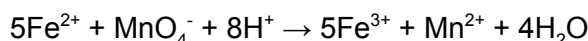
Fe^{2+}/Fe^{3+} can be analysed with acidified potassium manganate(VII)

The half equations: $\qquad\qquad Fe^{2+} \rightarrow Fe^{3+} + e^-$

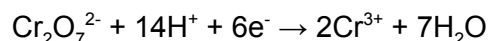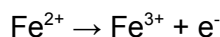$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
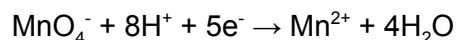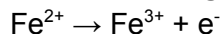
To write an overall equation, the first equation must be multiplied by 5 so that there are equal numbers of electrons in each equation. Combine the equations, cancelling out any terms which are the same on both sides:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Fe^{2+}/Fe^{3+} can be analysed with acidified potassium dichromate(VI)

The half equations: $\qquad\qquad Fe^{2+} \rightarrow Fe^{3+} + e^-$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

To write an overall equation, the first equation must be multiplied by 6 so that there are equal numbers of electrons in each equation. Combine the equations, cancelling out any terms which are the same on both sides:
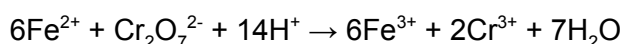
$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Predicting the likelihood of redox reactions

The **redox potential** of an ion tells you how **easily** it can be **reduced to a lower oxidation state**. The **smaller the redox potential, the more stable the ion** is so the less likely it will be reduced. E.g.

Half equation	Standard electrode potential, $E^\ominus$ (V)
$Cu^{2+} + e^- \rightarrow Cu^+$	+0.15
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.41

For the table above, the Cr^{3+} has a **smaller redox potential so it is more stable**. This means Cu^{2+} will be reduced because it is **more unstable** since it is a **larger value of $E^\ominus$**. The species with the **smaller/ more negative $E^\ominus$** value will **always** be **oxidised** so Cr^{2+} is oxidised in the example above. This means that Cu^{2+} will react with Cr^{2+} but Cr^{3+} will not react with Cu^+.

Colour of complexes

Splitting of degenerate d orbitals

Degenerate orbitals are electron orbitals that have the same energy level. In an isolated metal atom or ion the **five d orbitals** are **degenerate** because they all have the **same energy level**. When ligands join to a metal ion, the electric fields of the ligands **repel** the d orbitals, causing the energy levels of the d orbitals to split. They gain/ lose different amounts of energy as some d orbitals are closer to the ligands so they experience more repulsion meaning their energy level is increased more than those further away from the ligands.

In a tetrahedral complex none of the orbitals point directly to the ligands so the splitting energy is less than that of octahedral complexes.

The diagram on the right is a simple representation of how the d orbitals, originally at the same level in the centre, split for both **tetrahedral and octahedral complexes.** Another example of this can be seen in the diagram below for Ni^{2+}.

Tetrahedral

Octahedral

Energy gap

Energy gap
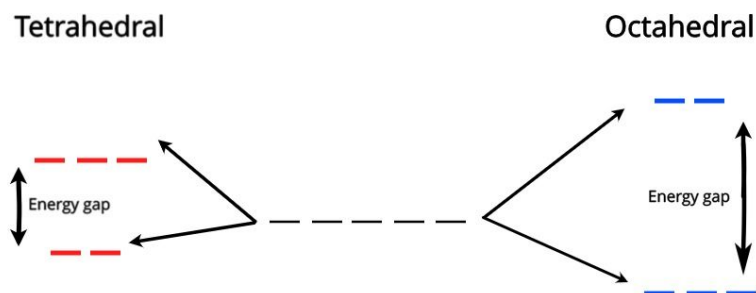
Origin of coloured complexes

When **visible light** hits a transition metal ion, **electrons are excited** to higher energy levels. Some **frequencies** of the visible light is **absorbed** when electrons jump up to the higher orbitals. The rest of the frequencies of visible light are **transmitted or reflected**. These frequencies combine to make the complement of the **colour** of the absorbed frequencies. This causes the colour of the complex seen.

d orbital of Ni^{2+} without ligands

Energy gap

Ground state

Electron excited

Excited state
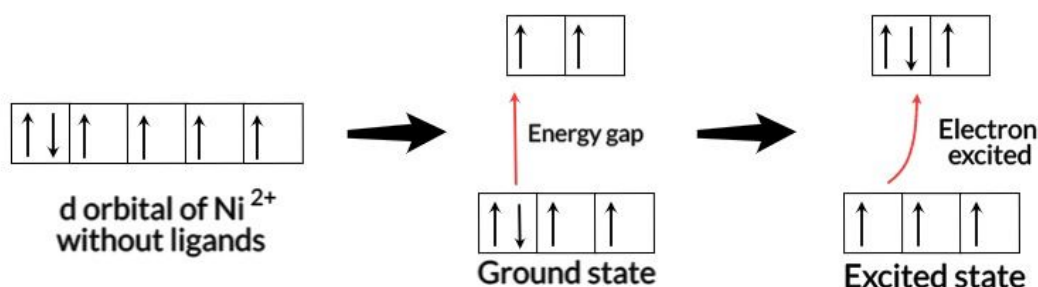
Effect of ligands on absorption

Different ligands cause **different amounts of visible light** to be absorbed. This means that different ligands in metal complexes cause **different colours** to be seen. The frequencies of light absorbed depend on the size of the energy gap, $\square E$. Each ligand produces an **energy gap with a different size**, which depends on the repulsion that the d orbitals experience from the ligands. This can be seen with **coloured complexes** containing copper ions. For the example of $[Cu(H_2O)_6]^{2+}$, ions absorb light from the red part of the visible light spectrum, so blue is the colour seen as it is the complementary colour formed from the remaining frequencies.

$[Cu(H_2O)_6]^{2+} \rightarrow$ **Blue** solution.
$[CuCl_4]^{2-} \rightarrow$ **Yellow** solution.
$[Cu(NH_3)_4(H_2O)_2]^{2+} \rightarrow$ **Dark blue** solution.

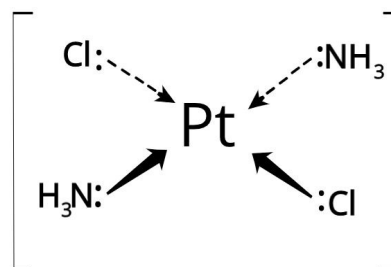# Stereoisomerism in transition metal complexes

Stereoisomerism

Cis-trans isomerism

Square planar complexes with two pairs of ligands show cis-trans isomerism. A trans isomer is when the two paired ligands are opposite each other in the complex. A cis isomer is when the pair of ligands are next to each other. The image below shows cis-platin and trans-platin:
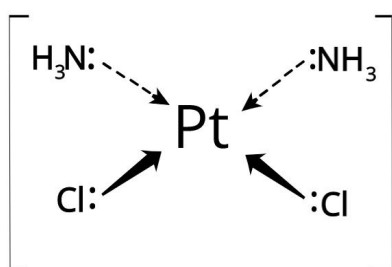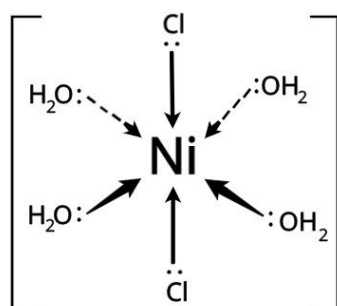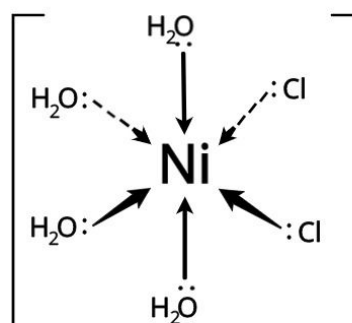

CISPLATIN   **TRANSPLATIN**

Octahedral complexes with two monodentate ligands of one type and four monodente ligands of another type also show cis-trans isomerism:
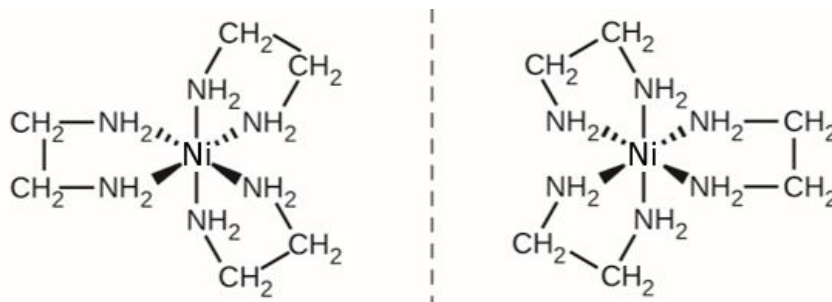

Trans-[NiCl$_2$(H$_2$O)$_4$]   **Cis-[NiCl$_2$(H$_2$O)$_4$]**

Optical isomerism

Optical isomerism is where an ion can exist in two forms which are **non-superimposable mirror images**. This occurs in **octahedral complexes** with **three bidentate ligands**. For example when Ni^{2+} bonds with the bidentate ligand $NH_2CH_2CH_2NH_2$.

Cisplatin

Cisplatin is a complex of platinum(II) containing **two ammonia ligands** and **two chloride ion ligands**. It has a **square planar** shape, shown on the previous page.

Cisplatin is used as an **anticancer drug.**
Cancer is caused by cells dividing uncontrollably, forming tumours. Cisplatin **binds to DNA**, causing kinks in the DNA helix. This stops the DNA being copied properly which in turn **stops cancerous cells reproducing**.

How it works:
- DNA contains bases, one of which is **guanine**. A **nitrogen atom** in guanine forms a coordinate bond with the platinum ion in cisplatin, **replacing a chloride ion ligand**.
- A **second nitrogen** from a different guanine base bonds to the platinum ion, replacing the other chloride ion ligand.
- The **cisplatin has bonded to the DNA strands,** creating a kink in the strands and preventing correct cell replication.

Issues:
- Cisplatin can also **bind to DNA in healthy cells**. This is a problem for cells which replicate frequently, like hair cells and blood cells. This is why the drugs can cause **hair loss** and why it can **suppress the immune system**.
- The drug can also cause **kidney damage**.

The issues with the drug are minimised by giving patients **small dosages** and by **targeting** the tumour directly.
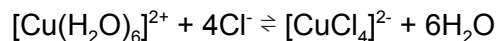
Stability constants, K_{stab}

Ligand exchange in terms of competing equilibria

When there is competing equilibria in ligand exchange reactions, the reaction which forms the **most stable complex will be prioritised**.

Example
The two equilibria reactions below are being carried out in the same system:
$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$
$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$
$[Cu(NH_3)_4(H_2O)_2]^{2+}$ is the **most stable product** so the solution will eventually **turn dark blue**. The $[Cu(H_2O)_6]^{2+}$ ions will react with the ammonia to form the more stable product.

The stability constant, K_{stab}
The stability constant, K_{stab}, is the **equilibrium constant** (K_c) for the formation of the complex ion in a solvent from its constituent ions or molecules.

- *Calculating **overall stability**:*

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

$$K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2^{2+}]}{[Cu(H_2O)_6^{2+}][NH_3]^4}$$

As can be seen from the stability expression on the left, it has a similar layout to the **equilibrium constant, K_c**.
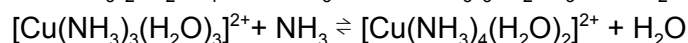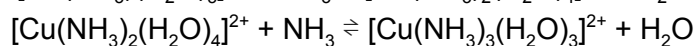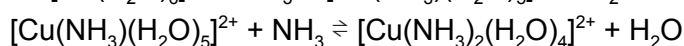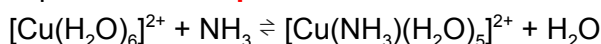
The square brackets of the complex have been removed so the square brackets in the expression indicate **concentrations in mol dm^{-3}**.
The concentration of **water also is not included** on the top of the equation as one of the products. This is because everything is dissolved in water so **water is in excess**. The water produced as a product is minimal by comparison.

- *Calculating **individual stability constants**:*

This is the overall equation: $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

However, this reaction takes part in **four steps**:
$$[Cu(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+} + H_2O$$
$$[Cu(NH_3)(H_2O)_5]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + H_2O$$
$$[Cu(NH_3)_2(H_2O)_4]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3(H_2O)_3]^{2+} + H_2O$$
$$[Cu(NH_3)_3(H_2O)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + H_2O$$

The stability constant for the first reaction can be called K_1:

$$K_1 = \frac{[Cu(NH_3)(H_2O)_5^{2+}]}{[Cu(H_2O)_6^{2+}][NH_3]}$$

K_2, K_3 and K_4 can also be found for the reactions that follow.

The **larger** the value of K_{stab}, the **more stable** the complex ion formed.
The **larger** the value of K_{stab}, the **further right** of the equilibrium the reaction lies.