

Cambridge (CIE) A Level Chemistry



Colour of Complexes

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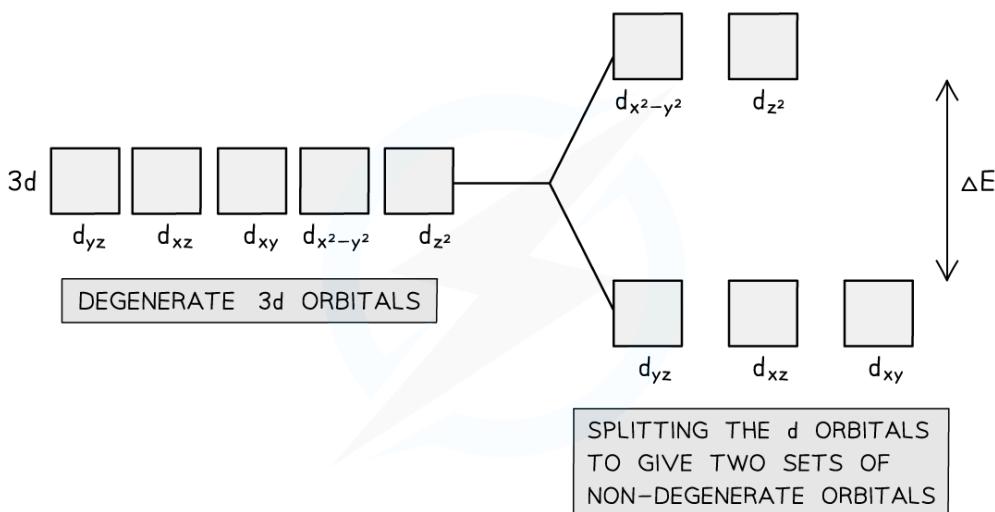
- * Degenerate & non-Degenerate d Orbitals
- * Coloured Complexes



Degenerate & non-Degenerate d Orbitals Definitions

- There are **five d orbitals** in an **isolated** transition element atom or ion
 - An isolated transition element is one that is not bonded to anything else
- These d orbitals are all at the same energy level (they are equal in energy) and are therefore said to be **degenerate orbitals**
- When ligands are attached, the transition element ion is **not** isolated anymore
- The dative bonding from the ligands causes the five d orbitals to split into two sets
- These two sets are **not** equal in energy and are described as being **non-degenerate orbitals**

Degenerate orbitals forming non-degenerate orbitals



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Upon binding to ligands, the d orbitals of the transition element ion split into two non-degenerate sets of orbitals

Degenerate d Orbital Splitting

- An isolated transition element has five **degenerate** 3d orbitals
- Upon dative covalently bonding to a ligand, these d orbitals are split into two sets of non-degenerate orbitals

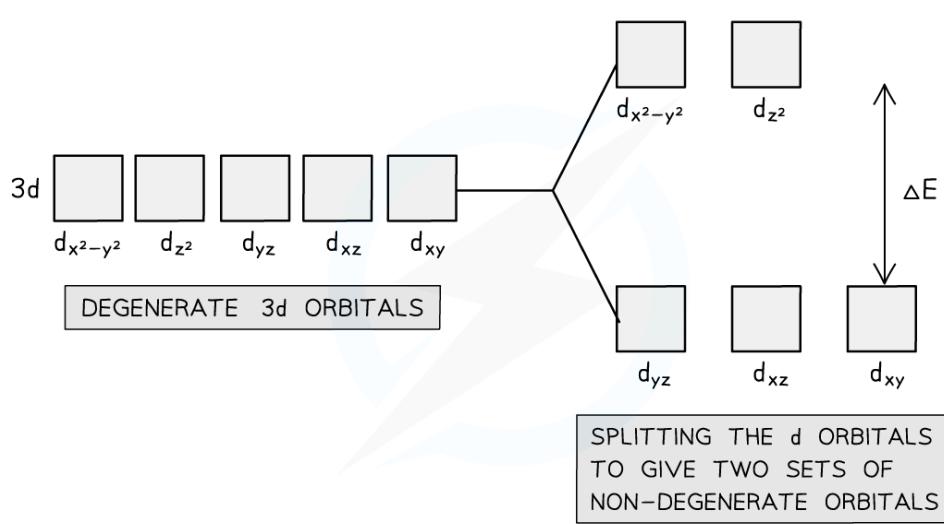
Splitting in octahedral complexes

- In **octahedral** complexes, there are six ligands arranged around the **central metal ion**



- The lone pairs of the ligands repel the electrons in the x^2-y^2 and z^2 orbitals of the metal ion **more than** they repel the electrons in the $3d_{yz}$, $3d_{xz}$, and $3d_{xy}$ orbitals
- This is because the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals line up with the dative bonds in the complex's octahedral shape
- This is because the ligands are attached to or approaching the central metal ion along the x, y and z axes, and the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals have lobes along these axes
- The electrons in these two orbitals are closer to the bonding electrons, so there is more **repulsion**
- This means that when the d orbitals split, the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are at a slightly higher energy level than the other three
- The difference in energy between the **non-degenerate** d orbitals is labelled as ΔE

Splitting of 3d orbitals in an octahedral complex



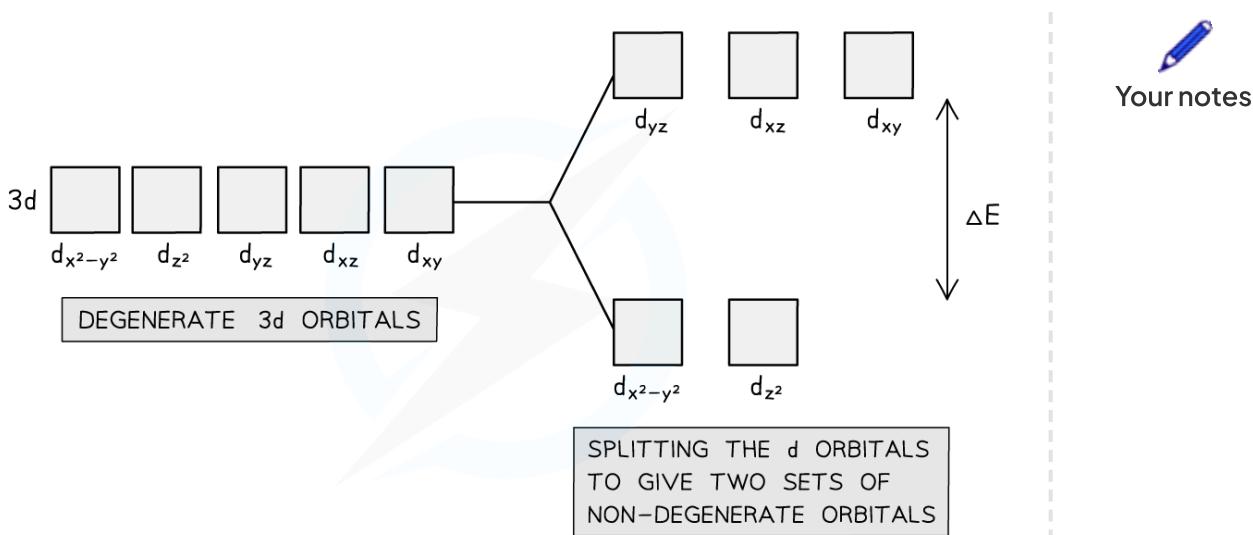
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The $3d_{x^2-y^2}$ and $3d_{z^2}$ non-degenerate orbitals are slightly higher in energy than the $3d_{yz}$, $3d_{xz}$ and $3d_{xy}$ non-degenerate orbitals

Splitting in tetrahedral complexes

- In **tetrahedral** complexes, there are four ligands arranged around the central metal ion
- The bonding pair of electrons from the four ligands now line up with the $3d_{yz}$, $3d_{xz}$, and $3d_{xy}$ orbitals of the central metal ion
- Now, the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals lie between the metal-ligand bonds
- Therefore, there is less repulsion with the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals
- When the d orbitals split this time, the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are at **lower and more stable** energy level than the other three

Splitting of 3d orbitals in a tetrahedral complex



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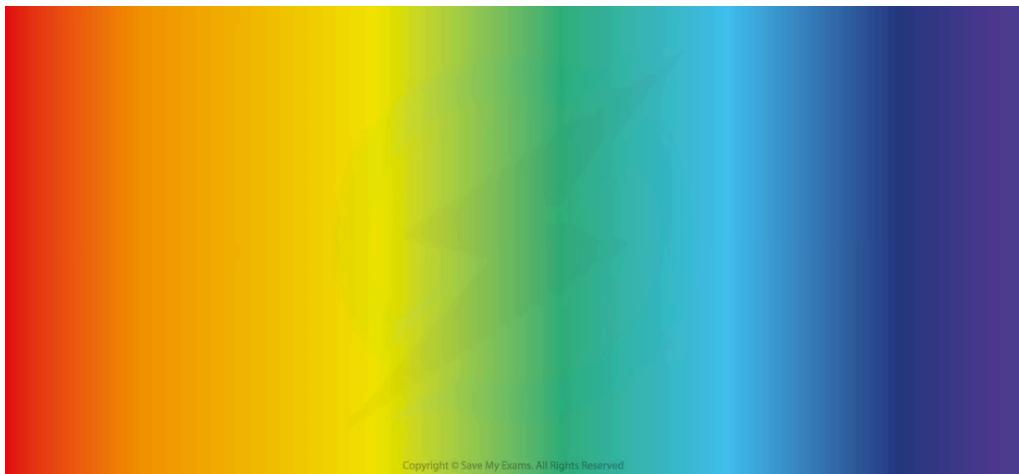
The $3d_{yz}$, $3d_{xz}$ and $3d_{xy}$ non-degenerate orbitals are slightly higher in energy than the $3d_{x^2-y^2}$ and $3d_{z^2}$ non-degenerate orbitals



Coloured Compounds & Electron Promotion

- Most transition element complexes are **coloured**
- A transition element complex solution which is coloured, **absorbs** part of the electromagnetic spectrum in the visible light region
- The observed colour is the **complementary colour** which is made up of light with frequencies that are **not** absorbed
 - For example, copper(II) ions absorb light from the **red** end of the spectrum
 - The complementary colour observed is therefore **pale blue** (cyan)

The visible light region of the electromagnetic spectrum



The visible light region ranges from red to violet

Electron promotion

- In an **isolated transition element ion** (which is not bonded to any ligands), all of the 3d orbitals are **degenerate**
- However, when ligands are attached to the central metal ion through dative covalent bonds, these orbitals are split into two sets of **non-degenerate orbitals**
- The difference in energy between these two sets of orbitals is ΔE
- When light shines on a solution containing a transition element complex, an electron will absorb this exact amount of energy (ΔE)
- The amount of energy absorbed can be worked out by the equation:

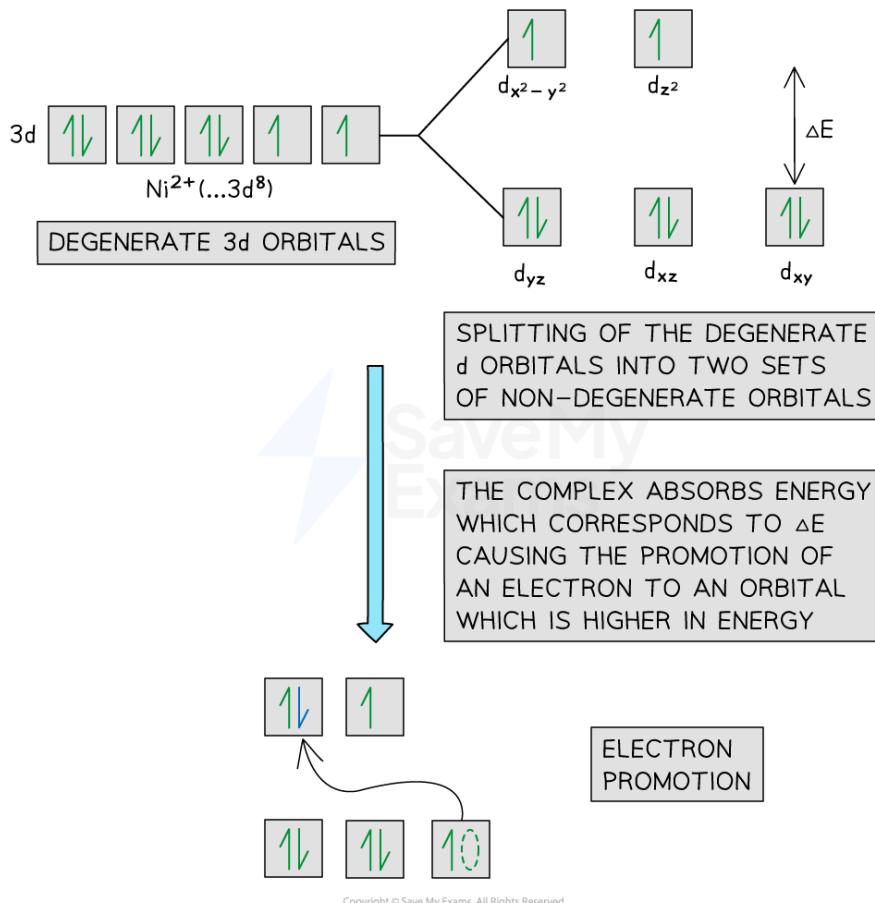
$$\Delta E = h \times v$$

- Where:

- $\hbar = \text{Planck's constant } (6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1})$
- $\nu = \text{frequency (Hertz, Hz or s}^{-1}\text{)}$
- The electron uses the energy from the light to jump into a higher, non-degenerate energy level
 - This is also called **electron promotion**
- The other frequencies of light which are **not absorbed** combine to make the **complementary colour**
- The diagram below shows an example of electron promotion in an octahedral complex of a nickel(II) Ni^{2+} ion



Electron promotion in a Ni(II) complex when light shines on the solution



An electron gains enough energy to be promoted from a lower energy non-degenerate orbital to a higher energy non-degenerate orbital

Effects of Ligands on Complementary Colour

- Transition element complexes absorb the frequency of light which corresponds to the exact energy difference (ΔE) between their **non-degenerate** d orbitals
- The frequencies of light which are not absorbed combine to make the **complementary colour** of the complex
- It is the complementary colour which is seen
- However, the exact energy difference (ΔE) is affected by the different ligands which surround the transition element ion
- Different ligands will split the d orbital by a different amount of energy
- This depends on the **repulsion** that the d orbital experiences from these ligands
- Therefore, the **size** of ΔE and thus the **frequency** of light absorbed by the electrons will be slightly different
- As a result, a different colour of light is absorbed by the complex solution and a different **complementary colour** is observed
- This means that complexes with **similar transition elements ions**, but **different ligands**, can have different colours
 - For example, in copper complexes:
 - $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex has a **light blue** colour
 - $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ has a **dark blue** colour
 - Despite the copper ion having an oxidation state of +2 in both complexes
 - This is evidence that the ligands surrounding the **complex ion** affect the colour of the complex

Ligand Exchange in Copper(II) & Cobalt(II) Complexes

- Different ligands may affect the complementary colour of a transition ion complex solution
- This is shown by ligand exchange reactions in copper(II) and cobalt(II) complexes, as this causes a change in colour of the complexes

Copper(II) & cobalt(II) ions

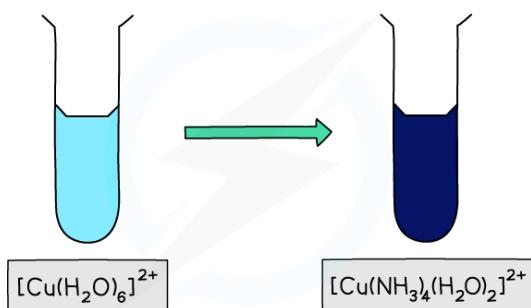
- The ligand exchange of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ by NH_3 ligands causes a change in the colour of the solutions
 - $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is **light blue** in colour whereas $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ is **deep blue** in colour



Your notes

- $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is a **pink** solution whereas $[\text{Co}(\text{NH}_3)_6]^{2+}$ is a **brown** solution
- The colour change results from the ammonia ligands, which cause the d orbitals to split by a different amount of energy (ΔE)
- Therefore, the size of ΔE and the frequency of light absorbed by the electrons will be slightly different
- As a result, a different colour of light is absorbed and thus a different **complementary colour** is observed

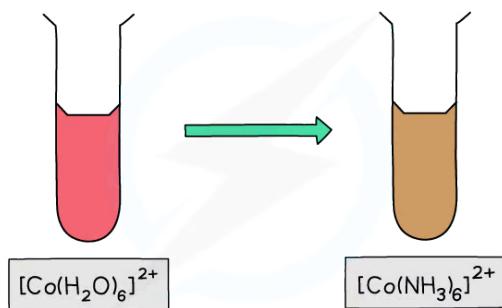
Ligand exchange of hexaaqua copper(II) by ammonia



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Ligand exchange of the water ligands by ammonia ligands causes a change in the colour of the copper(II) complex solution from blue to dark blue

Ligand exchange of hexaaqua cobalt(II) by ammonia



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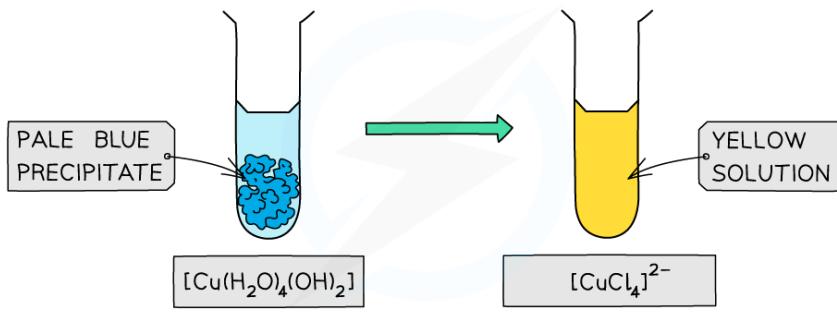
Ligand exchange of the water ligands by ammonia ligand causes a change in the colour of the cobalt(II) complex solution from pink to brown

- Similarly, full ligand exchange by chloride ions in copper(II) and cobalt(II) complexes results in a change in complementary colour
 - $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2]$ is a **pale blue precipitate** whereas $[\text{CuCl}_4]^{2-}$ is a **yellow solution**
 - $[\text{Co}(\text{H}_2\text{O})_4(\text{OH})_2]$ is a **blue precipitate** whereas $[\text{CoCl}_4]^{2-}$ is a **blue solution**
- The colour change results from the chloride ligands, which cause the d orbitals to split by a different amount of energy (ΔE)

- Therefore, the size of ΔE and the frequency of light absorbed by the electrons will be slightly different
- As a result, a different colour of light is absorbed and thus a different **complementary colour** is observed

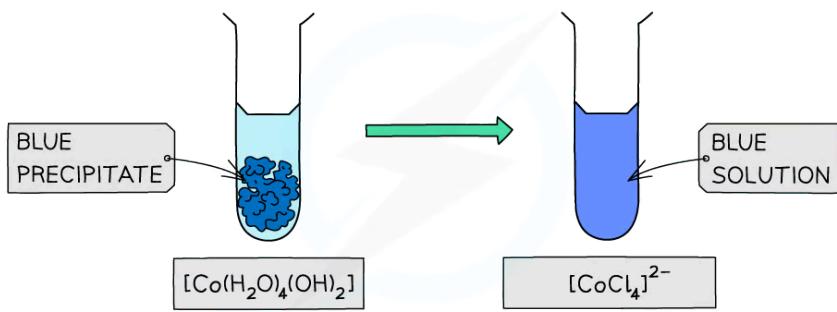


Ligand exchange of $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2]$ by chloride ions



Ligand exchange by chloride ligands causes a colour and state change in the colour of the copper(II) complex from a pale blue precipitate to a yellow solution

Ligand exchange of $[\text{Co}(\text{H}_2\text{O})_4(\text{OH})_2]$ by chloride ions



Ligand exchange by chloride ligands causes a colour and state change in the colour of the cobalt(II) complex from a blue precipitate to a blue solution

- As before, this suggests that different ligands will split the d orbitals differently