

Cambridge (CIE) A Level Chemistry



Your notes

Colour of Complexes

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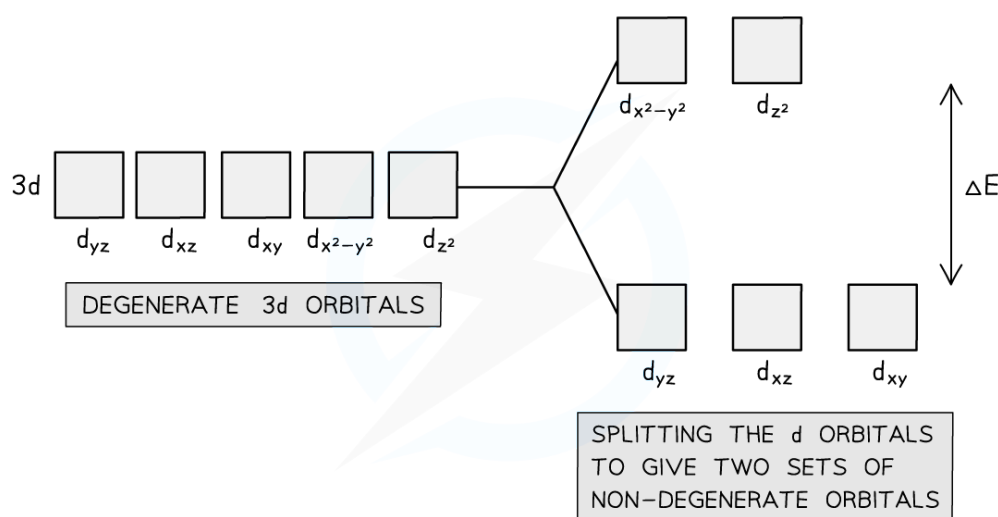
- * Degenerate & non-Degenerate d Orbitals
- * Coloured Complexes



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



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

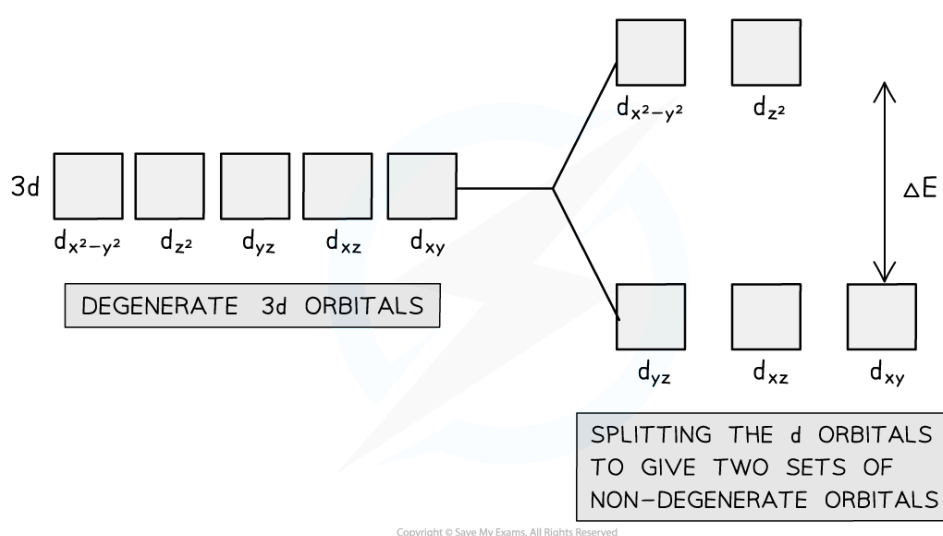
Splitting in octahedral complexes

- 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

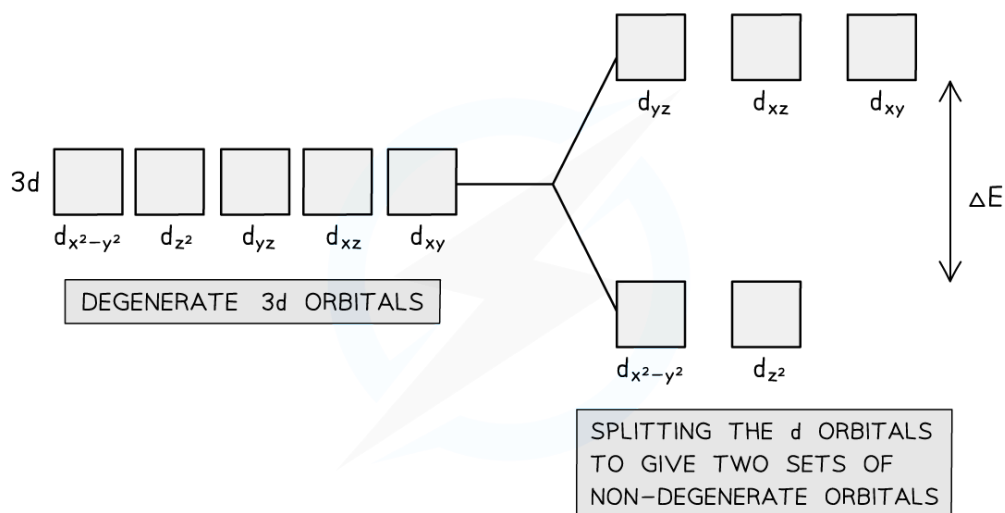
Splitting in tetrahedral complexes

- 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



Your notes



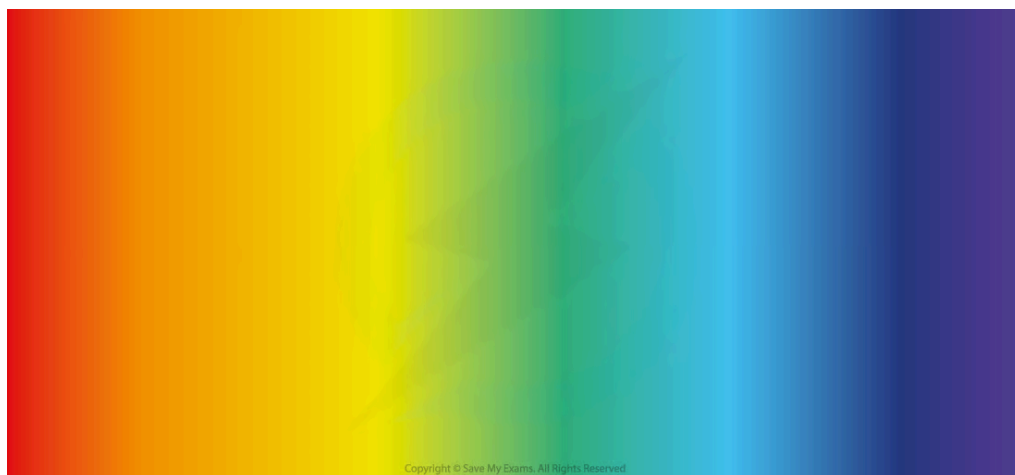
The $3d_{yz}$, $3d_{xz}$ and $3d_{xy}$ non-degenerate orbitals are slightly higher in energy than the $3d_{x^2-y^2}$ and $3d_{z^2}$ non-degenerate orbitals



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

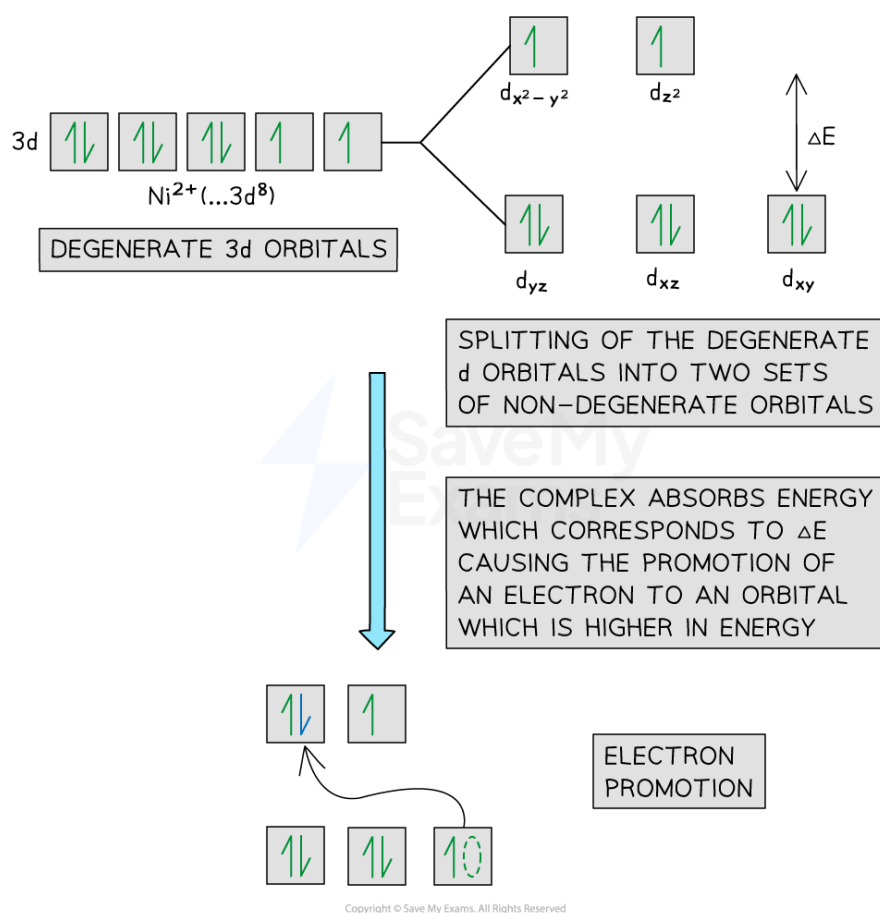
- In an **isolated transition element ion** (which is not bonded to any ligands), all of the 3d orbitals are **degenerate**
- However, when ligands are attached to the central metal ion through dative covalent bonds, these orbitals are split into two sets of **non-degenerate orbitals**
- The difference 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:

$$\Delta E = h \times \nu$$



- Where:
 - h = Planck's constant ($6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$)
 - ν = frequency (Hertz, Hz or s^{-1})
- 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



Your notes

- 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

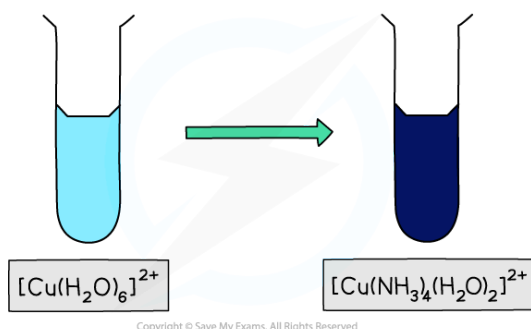
Copper(II) & cobalt(II) ions

- 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



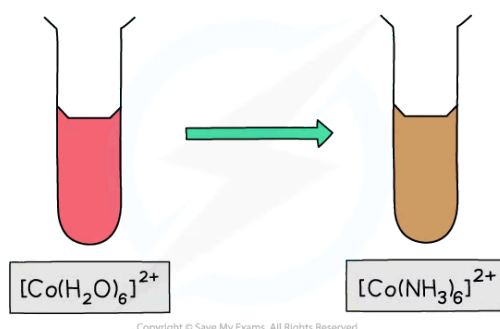
- $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is a **pink** solution whereas $[\text{Co}(\text{NH}_3)_6]^{2+}$ is a **brown** solution
- The colour change results from the ammonia ligands, which cause the d orbitals to split by a different amount of energy (ΔE)
- Therefore, the size of ΔE and the frequency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



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

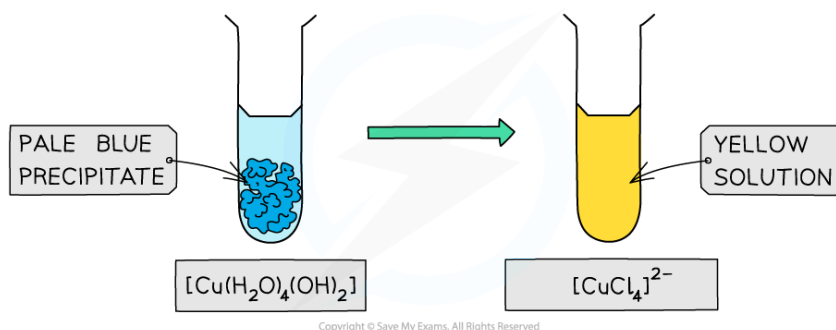


Ligand exchange of the water ligands by ammonia ligand causes a change in the colour of the cobalt(II) complex solution from pink to brown

- 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)

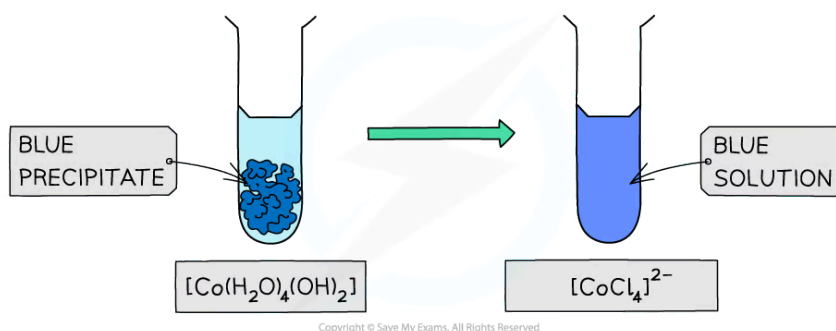
- Therefore, the size of ΔE and the frequency of light absorbed by the electrons will be slightly different
- As a result, a different colour of light is absorbed and thus a different **complementary colour** is observed

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