

28.3 COLOUR OF COMPLEXES

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Learning outcomes

Candidates should be able to:

1. Define and use the terms degenerate and non-degenerate d orbitals
2. Describe the splitting of degenerate d orbitals into two non-degenerate sets of d orbitals of higher energy, and the use of ΔE in:
 - (a) octahedral complexes, two higher and three lower d orbitals
 - (b) tetrahedral complexes, three higher and two lower d orbitals
3. Explain why transition elements form coloured compounds in terms of the frequency of light absorbed as an electron is promoted between two non-degenerate d orbitals
4. Describe, in qualitative terms, the effects of different ligands on ΔE , frequency of light absorbed, and hence the complementary colour that is observed
5. Use the complexes of copper(II) ions and cobalt(II) ions with water and ammonia molecules and hydroxide and chloride ions as examples of ligand exchange affecting the colour observed

Introduction

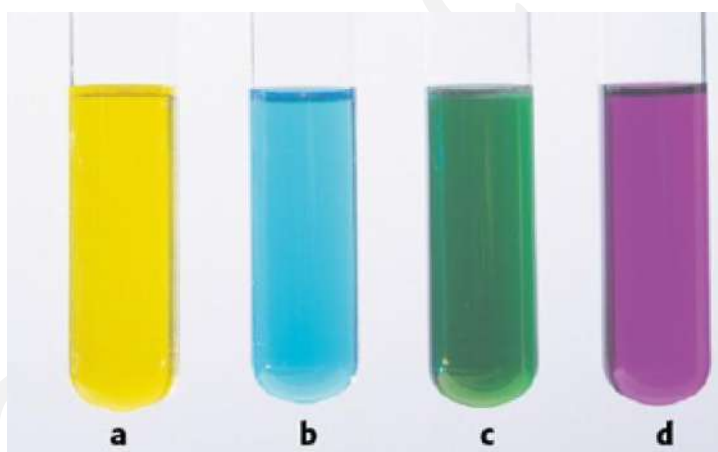


Figure: Vanadium and its oxidation states: **a** a solution containing VO_2^+ ions, **b** a solution containing VO^{2+} ions, **c** a solution containing V^{3+} ions, **d** a solution containing V^{2+} ions.

Why are transition-metal complexes coloured? 🎨

White light contains a range of visible wavelengths. When visible light passes through a transition-metal complex, some wavelengths may be absorbed.

In a transition-metal complex, the five d orbitals split into two groups with different energies. An electron can absorb visible light and move from the lower-energy d orbitals to the higher-energy d orbitals.

The colour observed is the **complementary colour** to the colour absorbed.

White light is made up of all the colours of the visible spectrum. When a solution containing a transition metal ion in a complex appears coloured, part of the visible spectrum is absorbed by the solution.

The colour we see is called the complementary colour, made up of light with frequencies not absorbed. For example, copper(II) ions absorb light from the red end of the spectrum, so the complementary colour seen is a pale blue (called cyan). Here is a list of complementary pairs of colours:

red	cyan
yellow	blue
green	magenta

To explain why part of the spectrum is absorbed by transition metal ions, we must look in more detail at the d orbitals in the ions.

Degenerate and non-degenerate orbitals

The five d orbitals in an isolated transition metal atom or ion are degenerate, meaning they are all at the same energy level.

In the presence of ligands, a transition metal ion is not isolated. The dative (or co-ordinate) bonding from the ligands causes the five d orbitals in the transition metal ion to split into two sets. The two sets of orbitals are described as **non-degenerate orbitals** as they are at slightly different energy levels.

Splitting of degenerate orbitals

In a complex with six ligands, the ligands are arranged in an octahedral shape around the central metal ion. The lone pairs donated by the ligands to the transition metal ion repel electrons in the two $d_{x^2-y^2}$ and d_{z^2} orbitals more than those in the other three d orbitals. This happens because these two d orbitals line up with the dative (co-ordinate) bonds in the complex's octahedral shape. Because the electrons in the $d_{x^2-y^2}$ and d_{z^2} orbitals are closer to the bonding electrons in the octahedral arrangement, electron-electron repulsion increases. Therefore, the d orbitals are split, with these two d orbitals at a slightly higher energy level than the d_{yz} , d_{xz} and d_{xy} orbitals.

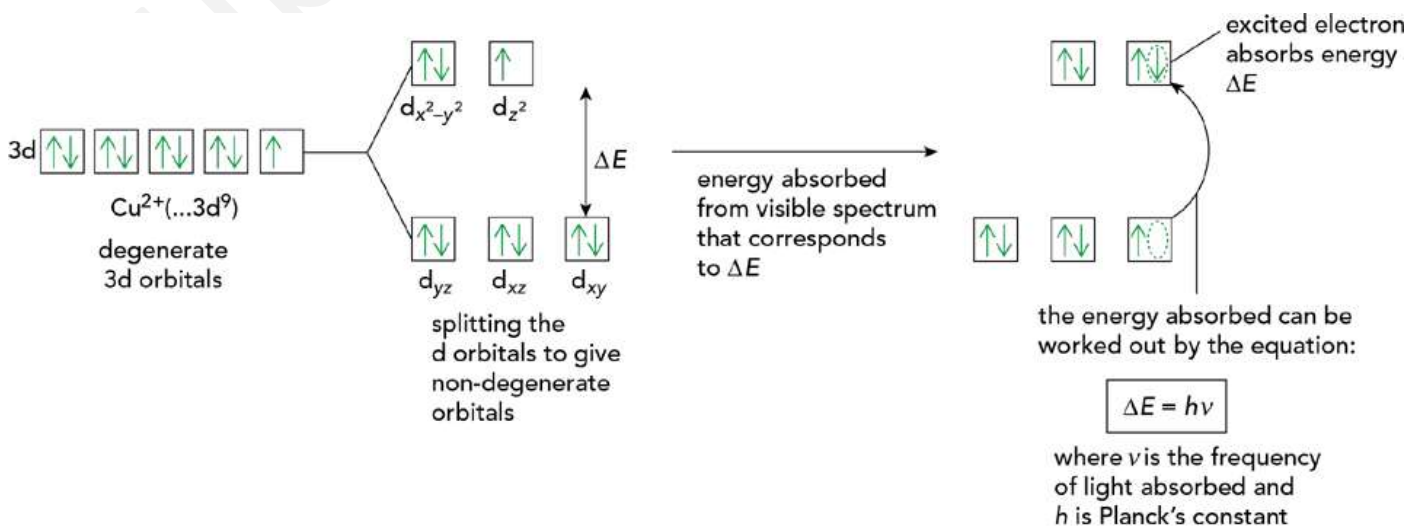


Fig: The splitting of the 3d orbitals in the octahedral $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ion.

A Cu^{2+} ion has an electronic configuration of $[\text{Ar}] 3d^9$. The above figure shows how the nine d electrons are distributed between the non-degenerate orbitals formed in a complex with ligands. The difference in energy between the non-degenerate d orbitals is labelled ΔE .

ΔE corresponds to part of the visible spectrum of light. So, when light shines on the solution containing the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex, an electron absorbs this amount of energy. It uses this energy to jump into the higher of the two non-degenerate energy levels. In copper complexes, the rest of the visible spectrum that passes through the solution makes it appear blue in colour.

In tetrahedral complexes, such as $[\text{CoCl}_4]^{2-}$, the splitting of the d orbitals is different. The bonding pairs of electrons from four ligands line up with the d_{yz} , d_{xz} and d_{xy} orbitals of the transition metal ion.

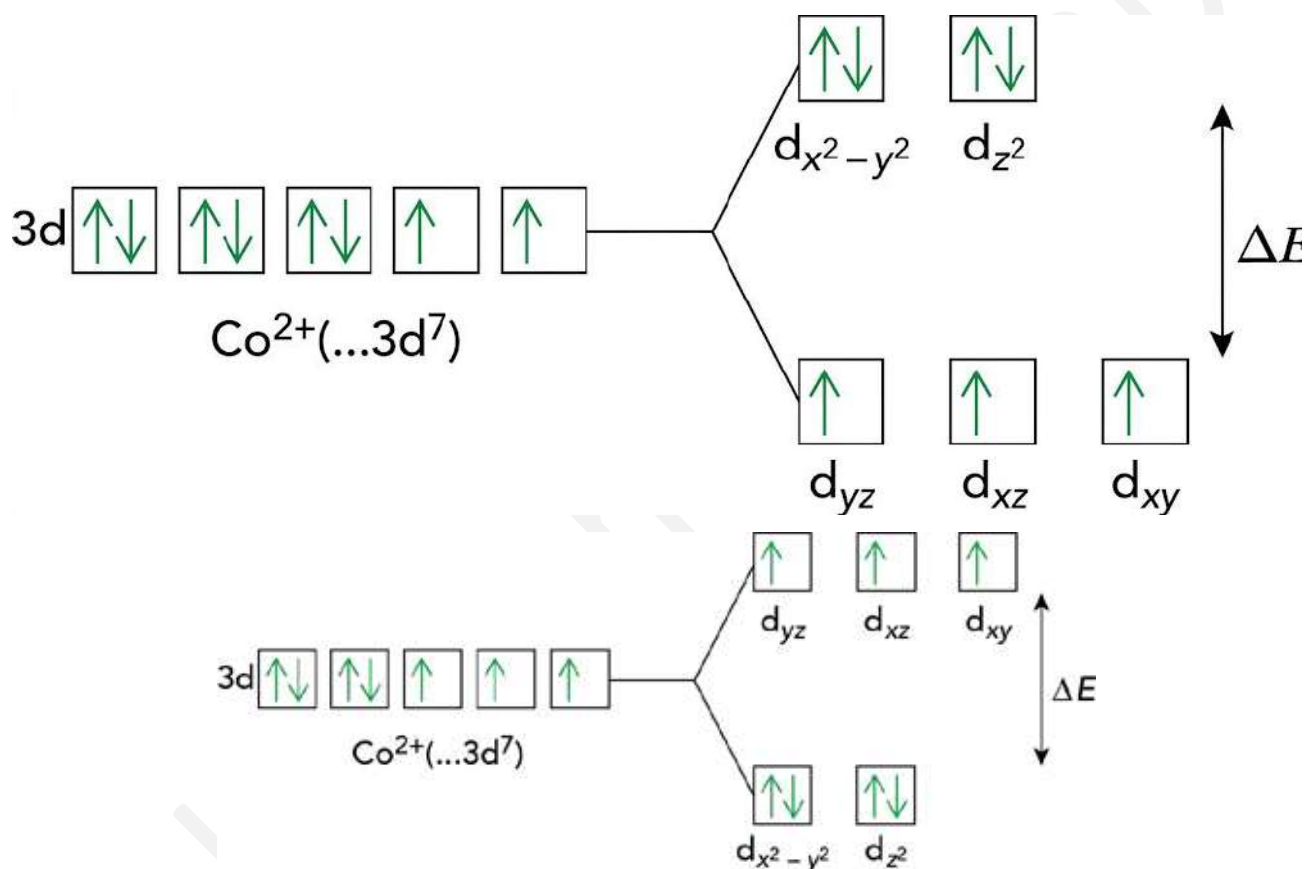


Fig: The splitting of the 3d orbitals in the tetrahedral $[\text{CoCl}_4]^{2-}$ complex ion.

Unlike the octahedral arrangement, the $d_{x^2-y^2}$ and d_{z^2} orbitals in a tetrahedral complex lie between the metal-ligand bonds. So, there is less repulsion between electrons in $d_{x^2-y^2}$ and d_{z^2} orbitals and the lone pairs of bonding electrons donated by the ligands. Therefore, when the d orbitals split in this case, the $d_{x^2-y^2}$ and d_{z^2} are at a lower, more stable energy level than the d_{yz} , d_{xz} and d_{xy} orbitals.

■ Octahedral: 2 up, 3 down

▲ Tetrahedral: 3 up, 2 down

The exact energy difference (ΔE) between the non-degenerate d orbitals in a transition metal ion is affected by many factors. One of these factors is the identity of the ligands that surround the transition metal ion. As you have seen, a solution containing $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is a light blue, whereas a

solution containing $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ is a very deep shade of blue. The colour change arises because the presence of the ammonia ligands causes the d orbitals to split by a different amount of energy. This means ΔE changes, so electrons absorb a slightly different amount of energy when they jump to the higher orbitals. Therefore, a different colour is absorbed from visible light, so a different colour is seen.

$$\Delta E = h\nu$$

Larger $\Delta E \rightarrow$ higher frequency light absorbed

Smaller $\Delta E \rightarrow$ lower frequency light absorbed

ligand field $\rightarrow$ d-orbital splitting $\rightarrow$ d-d transition $\rightarrow$ absorption of visible light $\rightarrow$ complementary colour

1. Explain why chromium complexes are coloured. (9701 s 21 qp23) [4]

{MS:

M1: (complexes have two sets of) d orbital(s) of different energy / d-d splitting occurs

OR d orbital(s) / d (sub)-shell splits

OR (inferred from a movement of an electron) from a lower d to higher d orbital

M2: electron(s) promoted / excited

OR electron(s) moves to higher (d-)orbital

OR electron(s) jumps up (to d-orbital) / jumps to higher (d-orbital)

M3: wavelength / frequency / light / photon / $h\nu$ absorbed

OR radiation / energy from visible (region) absorbed

M4: colour seen is complementary (to colour absorbed)

OR wavelength / frequency / colour / light not absorbed is transmitted / reflected / seen}

2. Explain why compounds of transition elements are usually coloured. (9071 w 16 qp 42) [3]

{MS: d orbitals split into lower and upper orbitals [1]

light / photon absorbed [1]

electron(s) promoted / excited / jumps up to (higher) (d-) orbital or

electron(s) moves / jumps (from lower (d-)) to higher (d-) orbital [1]}

3. The Ni^{2+} ion forms many different complexes. A solution containing the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex ion is green. When an excess of 1,2-diaminoethane, *en*, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, is added, the colour of the solution changes to blue. This is due to the formation of the $[\text{Ni}(\text{en})_3]^{2+}$ complex ion.

Explain why the two solutions are coloured, and why the colours are different. [4]

{MS:

- **d orbital(s)** of different energy / **d-d** splitting occurs [1]

- **electron(s)** promoted / excited [1]

- wavelength of visible light absorbed

AND complementary colour seen [1]

- different energy gap / different ΔE

OR different frequency/wavelength of light is absorbed [1]}

Ligand exchange

Metal ion / ligand	Complex formed	Observation
$\text{Cu}^{2+} + \text{H}_2\text{O}$	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	pale blue solution
$\text{Cu}^{2+} + \text{NH}_3$	$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	deep blue solution
$\text{Cu}^{2+} + \text{OH}^-$	$\text{Cu}(\text{OH})_2$	pale blue precipitate
$\text{Co}^{2+} + \text{H}_2\text{O}$	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	pink solution
$\text{Co}^{2+} + \text{Cl}^-$	$[\text{CoCl}_4]^{2-}$	blue solution
$\text{Co}^{2+} + \text{NH}_3$	ammine complex	colour change
$\text{Co}^{2+} + \text{OH}^-$	$\text{Co}(\text{OH})_2$	blue precipitate

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