A-LEVEL CHEMISTRY • EXERCISE SHEET

28.3 Colour of complexes

Name: _____ Class: _____ Date: _____ **Total: 28 marks**

KEY WORDS degenerate 简并 • non-degenerate 非简并 • complementary colour 互补色 • colour of complexes 配合物的颜色 • complex 配合物

Objective

Build the skills to answer exam questions on the **colour of complexes** 配合物的颜色 — **d-orbital splitting** d 轨道分裂 and why transition complexes are coloured.

You must be able to:

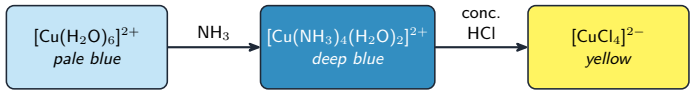
- define degenerate and non-degenerate d orbitals
- describe the splitting in octahedral and tetrahedral complexes
- explain colour in terms of the frequency of light absorbed (ΔE)

1 Worked examples

d-orbital splitting and colour

the complex absorbs light of energy ΔE, so we see the **complementary colour**

*Ligands split the five **degenerate** d orbitals into two **non-degenerate** sets separated by a gap ΔE*



Ligand exchange changes the complex colour

- **octahedral:** three lower + two higher.
- **tetrahedral:** two lower + three higher.

A complex absorbs light whose energy equals ΔE, promoting a d electron to the higher set. We **see** the **complementary colour** of the light absorbed. Different ligands give a different ΔE → different colour (why ligand exchange changes colour).

Why a complex is coloured, and what changes the colour

In a free gaseous ion the five 3d orbitals are **degenerate** — equal in energy. When **ligands** approach, their lone pairs repel the d electrons unequally: the orbitals pointing towards the ligands rise in energy and the others fall, so the set **splits** into two levels separated by ΔE.

The colour, in the order the marks are awarded:

1. The complex absorbs a photon whose energy equals ΔE.
2. That promotes an electron from the lower set to the higher — a **d–d transition**.
3. The frequency absorbed follows $\Delta E = h\nu$, so a larger ΔE means a higher frequency and a shorter wavelength absorbed.
4. The colour **seen** is the **complement** of the light absorbed: a complex absorbing red looks green; absorbing green, it looks red.

Why some ions are colourless. A d–d transition needs a **partially filled** d subshell. Sc^{3+} ($3d^0$), Cu^+ and Zn^{2+} ($3d^{10}$) have no vacancy to promote an electron into, absorb no visible light, and are colourless.

Three things change ΔE, and therefore the colour:

Change	Effect
the ligand	ligands have a fixed order of splitting power (the spectrochemical series): $I^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^-$ — a stronger-field ligand gives a larger ΔE
the oxidation state	a higher charge pulls the ligands closer, increasing the repulsion and so ΔE
the coordination number / shape	octahedral and tetrahedral fields split the orbitals differently, so a change of geometry changes the colour

Worked example. Adding concentrated ammonia to pale blue $[Cu(H_2O)_6]^{2+}$ gives a deep blue solution. Explain. Ammonia replaces four of the water ligands by ligand exchange. Ammonia is higher in the spectrochemical series than water, so the splitting ΔE increases. A larger ΔE means light of a different (higher) frequency is absorbed, so the complementary colour transmitted changes, and the solution deepens to blue.

2 Practice

2.1 Define **degenerate** d orbitals. [1]

2.2 State how the five d orbitals split in an **octahedral** complex. [1]

2.3 Explain why Zn^{2+} complexes are colourless. [2]

2.4 State the relationship between the energy gap ΔE and the frequency of light absorbed. [1]

2.5 Name three factors that change the size of ΔE. [3]

3 Exam-style questions

3.1 A transition-metal complex is coloured because an electron is promoted: [1]

- **A** out of the atom
- **B** between two non-degenerate d orbitals
- **C** into the nucleus
- **D** between s orbitals

3.2 The colour we see is: [1]

- **A** the colour of light absorbed
- **B** the complementary colour of the light absorbed
- **C** always green
- **D** white

3.3 Explain, in terms of d orbitals, why $[Cu(H_2O)_6]^{2+}$ is coloured. [3]

3.4 Explain why changing the ligand around a transition-metal ion changes the colour of the complex. [2]

3.5 Aqueous cobalt(II) chloride is pink because of the complex $[Co(H_2O)_6]^{2+}$.

(a) Explain, in terms of d orbitals, why this complex is coloured. [4]

(b) The pink solution absorbs green light. State the relationship between the colour absorbed and the colour seen. [1]

(c) Concentrated hydrochloric acid is added and the solution turns blue, forming $[CoCl_4]^{2-}$. Explain the colour change, referring to both the ligand and the shape. [4]

(d) A solution of $[Sc(H_2O)_6]^{3+}$ is colourless. Explain why. [2]

(e) Predict, with a reason, whether $[Co(CN)_6]^{4-}$ would absorb light of a higher or lower frequency than $[Co(H_2O)_6]^{2+}$. [2]

Solutions

2.1 d orbitals that have the same energy.

2.2 into a lower set of three and a higher set of two orbitals.

2.3 Zn^{2+} has a full $3d^{10}$ sub-shell; there is no vacancy to promote an electron into, so no d–d transition occurs and no visible light is absorbed.

2.4 $\Delta E = h\nu$, so a larger gap corresponds to a higher frequency absorbed.

2.5 The identity of the ligand; the oxidation state of the metal ion; the coordination number or the shape of the complex.

3.1 B. An electron is promoted between two non-degenerate d orbitals.

3.2 B. We see the complementary colour of the light absorbed.

3.3 the ligands split the d orbitals into two sets separated by ΔE; the complex absorbs light of energy equal to ΔE, promoting a d electron to the higher set; the colour seen is the complementary colour of the light absorbed.

3.4 a different ligand gives a different splitting energy ΔE; so a different frequency of light is absorbed, and a different complementary colour is seen.

3.5 (a) The ligands split the five degenerate 3d orbitals into two levels separated by ΔE; Co^{2+} has a partially filled d sub-shell, so an electron can be promoted; it absorbs a photon whose energy equals ΔE, a d–d transition; the light not absorbed is transmitted, and the complementary colour is what is seen.
(b) The colour seen is the complement of the colour absorbed.
(c) Chloride ligands replace the water by ligand exchange; chloride is lower in the spectrochemical series than water, so ΔE decreases; the coordination number also falls from 6 to 4 and the shape changes from octahedral to tetrahedral, which splits the orbitals differently; a different frequency is therefore absorbed and the complementary colour seen changes from pink to blue.
(d) Sc^{3+} has an empty $3d^0$ sub-shell; with no d electrons there can be no d–d transition, so no visible light is absorbed.
(e) A higher frequency; cyanide is higher in the spectrochemical series than water, so it produces a larger ΔE, and $\Delta E = h\nu$.