

13.2 Coloured complexes

Understandings:

- The d sub-level splits into two sets of orbitals of different energy in a complex ion.
- Complexes of d-block elements are coloured, as light is absorbed when an electron is excited between the d orbitals.
- The colour absorbed is complementary to the colour observed.

Guidance

The relation between the colour observed and absorbed is illustrated by the colour wheel in the IB Data booklet in section 17.

Applications and skills:

- Explanation of the effect of the identity of the metal ion, the oxidation number of the metal, and the identity of the ligand on the colour of transition metal ion complexes.

Guidance

Students are not expected to recall the colour of specific complex ions.

- Explanation of the effect of different ligands on the splitting of the d orbitals in transition metal complexes and colour observed using the spectrochemical series.

Guidance

The spectrochemical series is given in the IB data booklet in section 15. A list of polydentate ligands is given in the data booklet in section 16. Students are not expected to know the different splitting patterns and their relation to the coordination number. Only the splitting of the 3-d orbitals in an octahedral crystal field is required.

Complementary colours



CuSO₄ absorbs orange light. What colour does it appear to us?

Blue

Ion	Electron configuration	Colour
Sc ³⁺	[Ar]	colourless
Ti ³⁺	[Ar] 3d ¹	violet
V ³⁺	[Ar] 3d ²	green
Cr ³⁺	[Ar] 3d ³	violet
Mn ²⁺	[Ar] 3d ⁵	pink
Ni ²⁺	[Ar] 3d ⁸	yellow
Fe ²⁺	[Ar] 3d ⁶	green
Co ²⁺	[Ar] 3d ⁷	pink
Ni ³⁺	[Ar] 3d ⁷	blue
Zn ²⁺	[Ar] 3d ¹⁰	colourless

What colour light does Fe²⁺ absorb?

Purple

Why do transition metals absorb light?
In an isolated metal atom, all the d-orbitals are of equal energy.

However, in an octahedral complex (where ligands form coordinate bonds along the x, y and z axes) such as [Ti(H₂O)₆]³⁺ the ligands interact more strongly with the pair of d-orbitals that are orientated along the axes. This increases the energy of these orbitals.

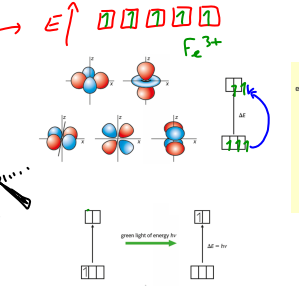
d-orbitals split into 2 sub levels

(In a tetrahedral complex, the ligands form coordinate bonds in between the axes and therefore the splitting pattern is reversed.)

The more interaction between the d-orbitals and the ligands = greater splitting between the sub-levels

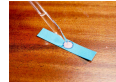
The energy separation between the orbitals is ΔE and hence the colour of the complex depends on the following factors:

- the nuclear charge and the identity of the central metal ion;
- the charge density of the ligand;
- the geometry of the complex ion (the electric field created by the ligand's lone pair of electrons depends on the geometry of the complex ion);
- the number of d electrons present and hence the oxidation number of the central ion.

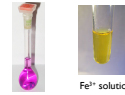


Exercises

51 Explain why the two cobalt complex ions [Co(H₂O)₆]²⁺ and [CoCl₄]²⁻ are different colours.



The colour depends on the nuclear charge and identity of the central metal ion



Mn²⁺ solution

Both in octahedral
How does the charge on the central ion relates to the colour? (use the info above)

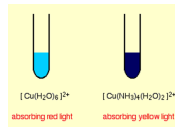
A higher charge attracts ligands more strongly → more ligand-metal interaction → larger splitting of d-orbitals
Charge density of the ligand

Why is the charge density of ammonia greater than that of water?



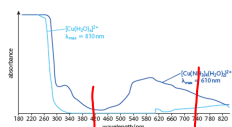
More as it (NH₃) will be pulled more strongly towards

[Cu(H₂O)₆]²⁺ absorbs (green/blue) colour. If we add NH₃ to this solution we replace 4 of the water molecules to form a complex ion - [Cu(NH₃)₄(H₂O)₂]²⁺



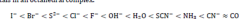
[Cu(H₂O)₆]²⁺ absorbing red light

[Cu(NH₃)₄(H₂O)₂]²⁺ absorbing yellow light



15. Spectrochemical series

Ligands can be arranged in a spectrochemical series according to the energy difference they produce between the two sets of d-orbitals in an octahedral complex.



Number of d electrons and oxidation state of the central metal ion

The strength of the interaction between the ligand and the central metal ion and the amount of electron repulsion between the ligand and the d electrons depends on the number of d electrons and hence the oxidation state of the metal. For example, [Fe(H₂O)₆]²⁺ absorbs violet light and so appears green/yellow, whereas [Fe(H₂O)₆]³⁺ absorbs blue light and appears orange/brown.



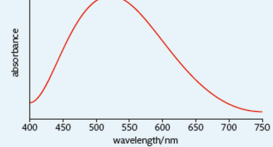
Exercises

52 The colour of transition metal complexes depends on several factors.

- Suggest why the colour of [Cr(H₂O)₆]³⁺ is different from the colour of [Fe(H₂O)₆]²⁺.
- Suggest why the colour of [Fe(H₂O)₆]²⁺ is different from the colour of [Fe(H₂O)₆]³⁺.
- Suggest why the colour of [Fe(H₂O)₆]²⁺ is different from the colour of [Fe(CN)₆]²⁻.

53 Explain why Fe²⁺(aq) is coloured and can behave as a reducing agent, whereas Zn²⁺(aq) is not and does not behave as a reducing agent.

54 The absorption spectrum of [Ti(H₂O)₆]³⁺ is shown below. Use the colour wheel to suggest a colour for the complex.



55 (a) Draw a diagram to show how the electrons are arranged in Fe²⁺ when it is present in the [Fe(H₂O)₆]²⁺ ion.

(b) Predict whether the splitting of the d orbitals in [Fe(CN)₆]⁴⁻ would be less than or greater splitting in [Fe(H₂O)₆]²⁺.

56 (a) Explain why [Fe(H₂O)₆]²⁺ and [Cr(H₂O)₆]³⁺ have different colours.

(b) Explain why [Fe(H₂O)₆]³⁺ and [Fe(H₂O)₆]²⁺ have different colours.

52 (a) difference in nuclear charge of metal (ion)

(b) difference in oxidation number

(c) difference in ligand

53 Fe²⁺ has configuration [Ar]3d⁶ and Zn²⁺ is [Ar]3d¹⁰. Colour in transition metal complexes is due to the splitting of the d orbitals into two sets of orbitals with different energy levels; the absorption of visible light results in electrons being excited from the lower energy set to the higher energy set and the colour observed is complementary to the colour (wavelength) of light absorbed. Light can only be absorbed if the d orbitals are partially filled and the higher energy set has an empty or partially filled orbital that can accept an electron from the lower energy set. Fe²⁺ has partially filled d orbitals so electronic transitions can occur from the lower energy set to the higher energy set and the absorption of visible light and it appears coloured in solution. In Zn²⁺ all the d orbitals are fully occupied so an electronic transition cannot occur from the lower energy set to its higher energy set so it is unable to absorb visible light and Zn²⁺ is not coloured in solution.

Fe³⁺ not in its highest oxidation state and so be oxidized by removal of d electrons. Zn²⁺ in highest oxidation state and so can't be oxidized (and so can't act as reducing agent).

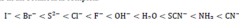
54 λ_{max} = 555 nm. The colour absorbed is green; colour transmitted is red.

55 (a) [Ar]3d⁶

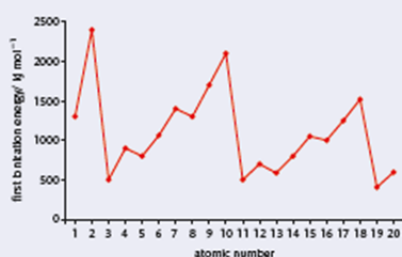
(b) The splitting would be greater for [FeCN]₆⁴⁻

15. Spectrochemical series

Ligands can be arranged in a spectrochemical series according to the energy difference they produce between the two sets of d-orbitals in an octahedral complex.



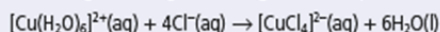
19 The graph below of the first ionization energy plotted against atomic number for the first 20 elements shows periodicity.



- (a) Define the term *first ionization energy* and state what is meant by the term *periodicity*. (2)
- (b) State the electron configuration of argon and explain why the noble gases, helium, neon, and argon, show the highest first ionization energies for their respective periods. (3)
- (c) A graph of atomic radius plotted against atomic number shows that the atomic radius decreases across a period. Explain why chlorine has a smaller atomic radius than sodium. (1)
- (d) Explain why a sulfide ion, S^{2-} , is larger than a chloride ion, Cl^- . (1)
- (e) Explain why the melting points of the Group 1 metals (Li to Cs) decrease down the group whereas the melting points of the Group 17 elements (F to I) increase down the group. (3)

(Total 10 marks)

20 When concentrated hydrochloric acid is added to a solution containing hydrated copper(II) ions, the colour of the solution changes from light blue to green. The equation for the reaction is:



- (a) Explain what the square brackets around the copper containing species represent. (1)
- (b) Explain why the $[Cu(H_2O)_6]^{2+}$ ion is coloured and why the $[CuCl_4]^{2-}$ ion has a different colour. (2)

(Total 3 marks)

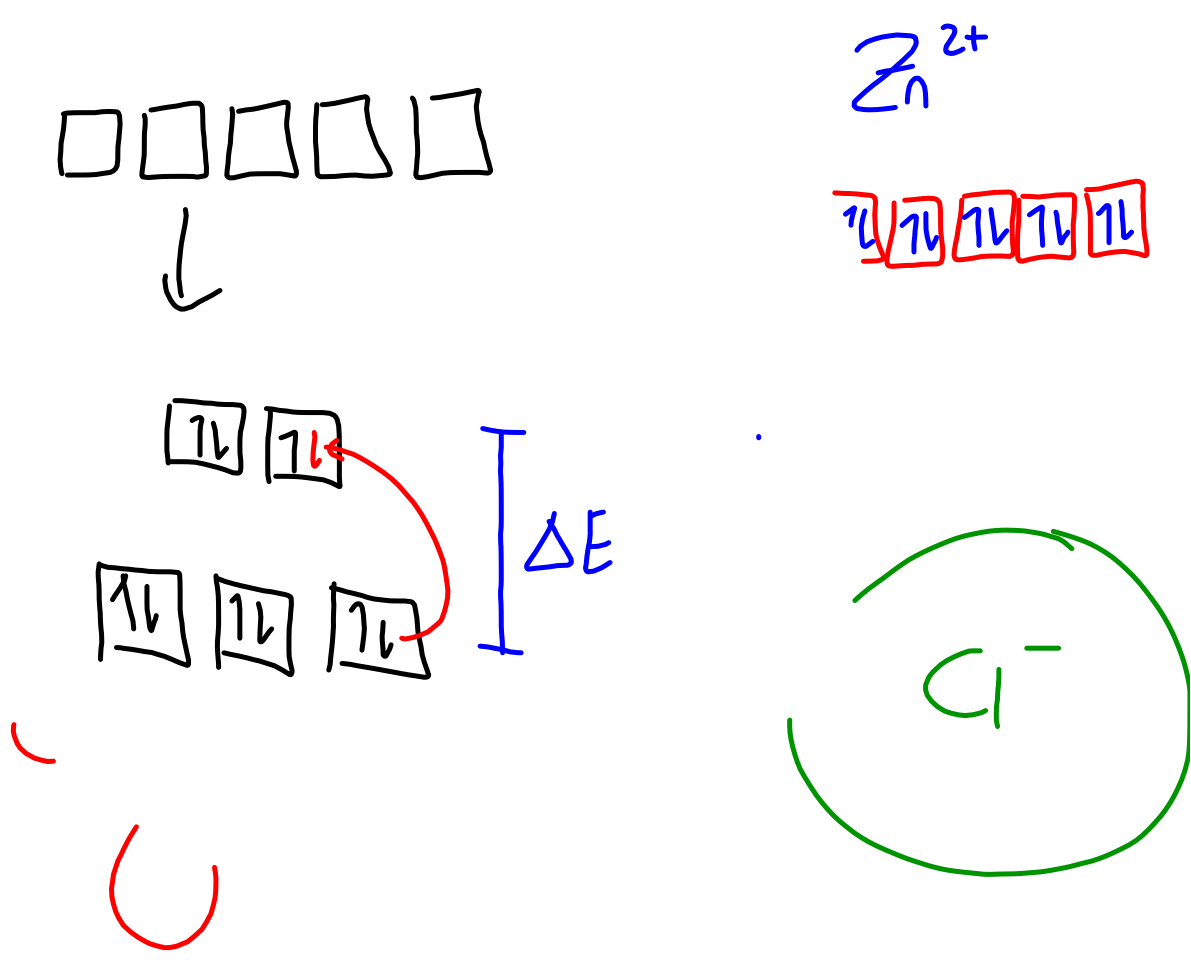
(c)

(d)

(e)

20 (a)

(b)



Homework for Friday
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