

Structure 3.1 HL

Answers

IB CHEMISTRY HL

| | | | | | |
|---|------------------------------------|----------|------------------------------------|--------------------------------------|---|
| 25 Mn Manganese 54.938045 | 16 S Sulfur 32.065 | J | 6 C Carbon 12.0107 | 2 He Helium 4.002602 | 25 Mn Manganese 54.938045 |
|---|------------------------------------|----------|------------------------------------|--------------------------------------|---|

Structure 3.1.7

Understandings:

- Discontinuities occur in the trend of increasing first ionisation energy across a period.

Learning outcomes:

- Explain how these discontinuities provide evidence for the existence of energy sublevels.

Additional notes:

- Explanations should be based on the energy of the electron removed, rather than on the “special stability” of filled and half-filled sublevels.

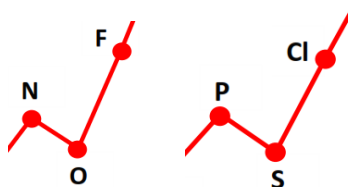
Discontinuities in first ionisation energy across a period

Be to B and Mg to Al

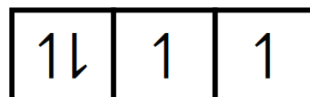
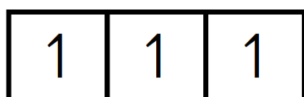


- Be has the electronic configuration $1s^2 2s^2$
- B has the electronic configuration $1s^2 2s^2 2p^1$
- Electrons in p orbitals are of higher energy and further from the nucleus than electrons in s orbitals, therefore they require less energy to remove.
- The same explanation can be applied for the drop in ionisation energy from Mg to Al, except that the electron configurations are $1s^2 2s^2 2p^6 3s^2$ and $1s^2 2s^2 2p^6 3s^2 3p^1$.

N to O and P to S



- N has the electronic configuration $1s^2 2s^2 2p^3$.
- O has the electronic configuration $1s^2 2s^2 2p^4$.
- For oxygen, the electron is removed from a doubly occupied p orbital. An electron in a doubly occupied orbital is repelled by the other electron and requires less energy to remove than an electron in a half-filled orbital.



Structure 3.1.8

Understandings:

- Transition elements have incomplete d-sublevels that give them characteristic properties.

Learning outcomes:

- Recognize properties, including: variable oxidation state, high melting points, magnetic properties, catalytic properties, formation of coloured compounds and formation of complex ions with ligands.

Additional notes:

- Knowledge of different types of magnetism will not be assessed.

Linking questions:

- Structure 2.3 What are the arguments for and against including scandium as a transition element?

Physical and chemical properties of the transition elements

| Physical properties | Chemical properties |
|--|---|
| High electrical and thermal conductivity | Have more than one oxidation state in compounds |
| High melting points | Form complex ions |
| Malleable and ductile | Form coloured compounds in solution |
| High tensile strength | Can act as catalysts |
| Show magnetic properties | |

Transition elements

- A transition element is an element whose atom has an incomplete d sub-level or can form positive ions with an incomplete d sub-level.
- The first-row d-block elements are shown below.

| | | | | | | | | | |
|--------------------------|--------------------------|-------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 21 Sc 44.96 | 22 Ti 47.87 | 23 V 50.94 | 24 Cr 52.00 | 25 Mn 54.94 | 26 Fe 55.85 | 27 Co 58.93 | 28 Ni 58.69 | 29 Cu 63.55 | 30 Zn 65.38 |
|--------------------------|--------------------------|-------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|

- Zinc is a d-block element but is not a transition element.
- Zn is not considered to be a transition element as it does not have an incomplete d sub-level as an atom or ion.

Electron configurations of first row d-block elements and their ions

| First row d-block element | Electron configuration of atom | Ion formed | Electron configuration of ion |
|---------------------------|---------------------------------------|------------------|--------------------------------------|
| Sc | [Ar] 4s ² 3d ¹ | Sc ³⁺ | [Ne] 3s ² 3p ⁶ |
| Ti | [Ar] 4s ² 3d ² | Ti ²⁺ | [Ar] 3d ² |
| V | [Ar] 4s ² 3d ³ | V ²⁺ | [Ar] 3d ³ |
| Cr | [Ar] 4s ¹ 3d ⁵ | Cr ³⁺ | [Ar] 3d ³ |
| Mn | [Ar] 4s ² 3d ⁵ | Mn ⁴⁺ | [Ar] 3d ³ |
| Fe | [Ar] 4s ² 3d ⁶ | Fe ³⁺ | [Ar] 3d ⁵ |
| Co | [Ar] 4s ² 3d ⁷ | Co ²⁺ | [Ar] 3d ⁷ |
| Ni | [Ar] 4s ² 3d ⁸ | Ni ²⁺ | [Ar] 3d ⁸ |
| Cu | [Ar] 4s ¹ 3d ¹⁰ | Cu ²⁺ | [Ar] 3d ⁹ |
| Zn | [Ar] 4s ² 3d ¹⁰ | Zn ²⁺ | [Ar] 3d ¹⁰ |

- As can be seen from the above table, Sc to Cu all have either an atom with an incomplete d sub-level or a positive ion (cation) with an incomplete d sub-level.
- Zn does not have an incomplete d sub-level in either its atom or ion, therefore it is not considered to be a transition element.

Exercises:

1. Outline what is meant by the term 'transition element'

A transition element is an element whose atom has an incomplete d sub-level or can form a positive ion with an incomplete d sub-level.

2. Explain why even though the Cu atom has a full d sub-level, it is still considered a transition element.

Cu forms a Cu^{2+} ion with the electron configuration $[\text{Ar}] 3d^9$ – it forms an ion with an incomplete d sub-level, therefore, it is classified as a transition element.

3. Explain why Zn is not considered to be a transition element.

Zn is not considered to be a transition element because its atom and ion (Zn^{2+}) both have a full d sub-level.

Electron configuration of Zn atom $[\text{Ar}] 4s^2 3d^{10}$

Electron configuration of Zn^{2+} ion $[\text{Ar}] 3d^{10}$

Magnetism in the transition elements

- Magnetism in the transition elements is due to presence of unpaired electrons in the d sub-level.
- Substances that have unpaired electrons have magnetic properties.
- Substances that have no unpaired electrons do not.
- The table below shows the effect in a magnetic field and the number of unpaired electrons in the Zn^{2+} , Cu^{2+} , Ni^{2+} and Mn^{4+} ions.

| Ion | Effect in external magnetic field | Unpaired 3d electrons |
|------------------|-----------------------------------|--|
| Zn^{2+} | No effect* | $\overset{3d}{\begin{array}{ c c c c c } \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \\ \hline \end{array}}$ |
| Cu^{2+} | Weak effect | $\overset{3d}{\begin{array}{ c c c c c } \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow \\ \hline \end{array}}$ |
| Ni^{2+} | Stronger effect | $\overset{3d}{\begin{array}{ c c c c c } \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow & \uparrow \\ \hline \end{array}}$ |
| Mn^{4+} | Strongest effect | $\overset{3d}{\begin{array}{ c c c c c } \hline \uparrow & \uparrow & \uparrow & & \\ \hline \end{array}}$ |

- Zn^{2+} shows no effect in a magnetic field as it has no unpaired d electrons.
- The remaining ions have magnetic properties because of the presence of unpaired electrons.

Exercises: Which of the following compounds have magnetic properties?

MnSO_4

ScCl_3

ZnSO_4

FeSO_4

CoCl_2

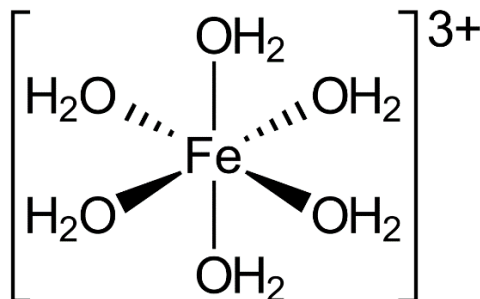
All have unpaired electrons in the d sub-level except Zn^{2+} in ZnSO_4 .

Complex ions

- Transition elements form complex ions in solution.
- A complex ion consists of a central metal ion bonded to ligands by coordinate covalent bonds.

$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ - hexaaquairon(III) ion

Complex ions consist of a central metal ion – in this example, the Fe^{3+} ion.



The water molecules are known as ligands – they use their lone pairs of electrons to form a coordinate covalent bond to the central metal ion.

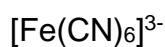
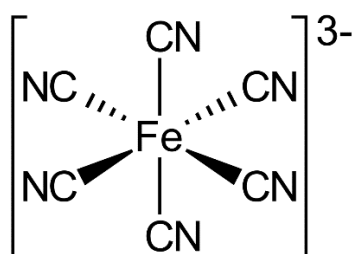
- The coordination number of a complex ion is the number of coordinate covalent bonds between the ligands and the central metal ion.
- The above complex ion has a coordination number of six as there are six coordinate covalent bonds between the ligands and the central metal ion.

Exercises:

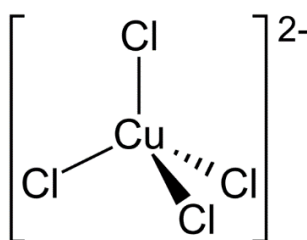
1. Describe the structure of a complex ion.

A complex ion consists of a central metal ion bonded to ligands by coordinate covalent bonds.

2. Determine the coordination number and geometry of the following complex ions:



6 – octahedral



4 – tetrahedral

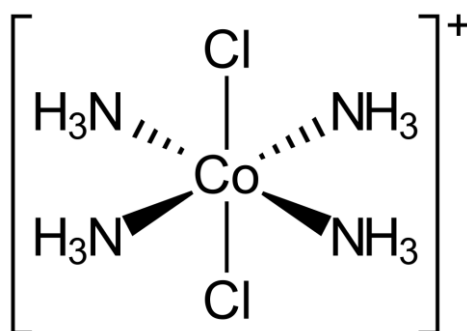


2 – linear

3. A complex ion has a coordination number of 6 – how many coordinate covalent bonds are formed with the central metal ion?

The coordination number is the number of coordinate covalent bonds formed by the ligands to the central metal ion. A coordination number of 6 means that there are 6 coordinate covalent bonds between the ligands and the central metal ion.

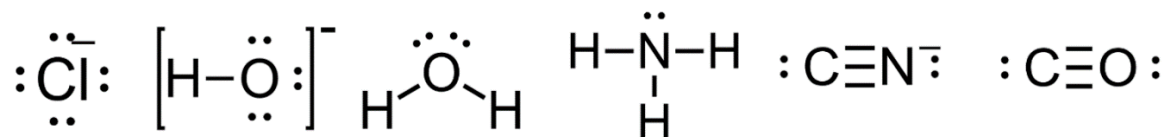
4. Deduce the geometry of the complex ion below.



Octahedral

Ligands

- Ligands are species with lone pairs of electrons that form coordinate covalent bonds with a central metal ion.
- Some examples of ligands are shown below.



- Ligands use their lone pairs of electrons to form coordinate covalent bonds (both the bonding electrons in the bond come from the same atom).
- Ligands are also Lewis bases (they are electron pair donors).

Exercises:

1. Define the term *ligand*.

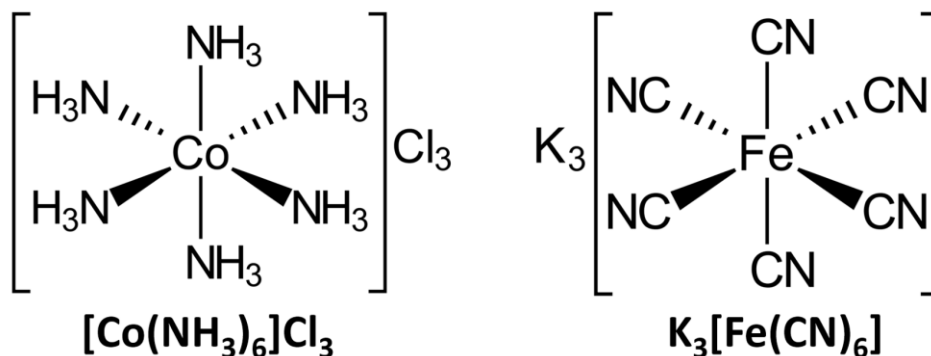
A ligand is a species with a lone pair of electrons that forms a coordinate covalent bond to a central metal ion. Ligands can be negative ions (CN⁻) or neutral molecules (NH₃).

2. Explain how ligands are also able to act as Lewis bases.

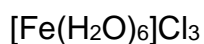
Ligands have lone pairs of electrons that they donate to the central metal ion, therefore, they can act as Lewis bases. The central metal ion is the Lewis acid.

Coordination compounds

- Coordination compounds are made up of a complex ion and counter ions which balance the charge of the complex ion.
- Coordination compounds are neutral because of the counter ions.



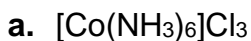
Example:



The complex ion is $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

The counter ions are Cl⁻ ions

Exercise: Determine the complex ion and counter ions in the following coordination compounds.



The complex ion is $[\text{Co}(\text{NH}_3)_6]^{3+}$

The counter ions are 3Cl⁻



The complex ion is $[\text{Fe}(\text{CN})_6]^{3-}$

The counter ions are 3K⁺



The complex ion is $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$

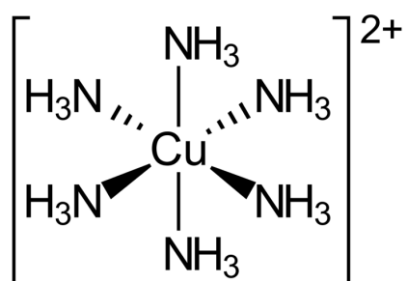
The counter ions are 2Cl⁻

Deduce the charge on a central metal ion

- Below is a table of the common ions formed by the transition elements.

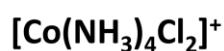
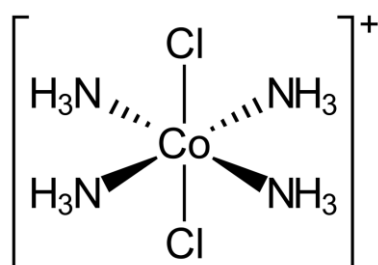
| Transition element | Common ions formed | Oxidation state |
|--------------------|---|-----------------|
| Chromium | Chromium(II) Cr^{2+} Chromium(III) Cr^{3+} | +2 +3 |
| Cobalt | Cobalt(II) Co^{2+} Cobalt(III) Co^{3+} | +2 +3 |
| Copper | Copper(I) Cu^+ Copper(II) Cu^{2+} | +1 +2 |
| Iron | Iron(II) Fe^{2+} Iron(III) Fe^{3+} | +2 +3 |
| Nickel | Nickel(II) Ni^{2+} | +2 |

Example 1:



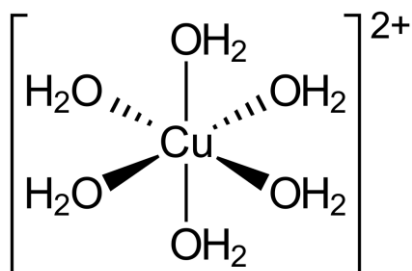
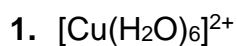
If the ligands are neutral, the charge on the complex ion is the same as the charge on the central metal ion.
The central metal ion is the Cu^{2+} ion (oxidation state +2).

Example 2:

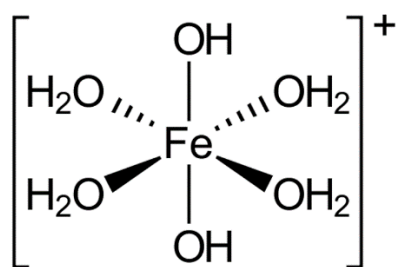
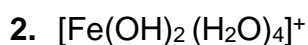


If the ligands are negatively charged, subtract the total charge of the ligands from the charge on the complex ion.
The central metal ion is the Co^{3+} (oxidation state +3).

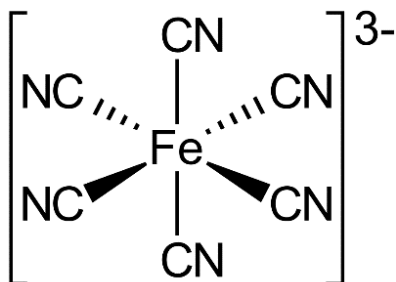
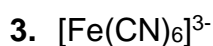
Exercise: For each of the complex ions, deduce the charge and oxidation state on the central metal ion.



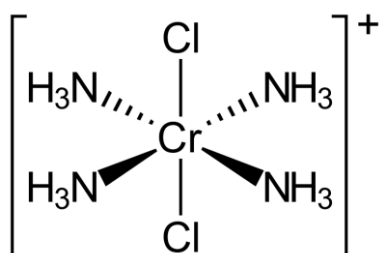
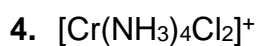
H_2O is neutral; the charge on the Cu ion is 2+ (Cu^{2+})
oxidation state +2



OH^- has a 1- charge and H_2O is neutral; the charge on the Fe ion is 3+ (Fe^{3+})
oxidation state +3



CN^- has a 1- charge; the charge on the Fe ion is 3+ (Fe^{3+})
oxidation state +3



CN^- has a 1- charge; the charge on the Fe ion is 3+ (Fe^{3+})
oxidation state +3

Structure 3.1.9

Understandings:

- The formation of variable oxidation states in transition elements can be explained by the fact that their successive ionisation energies are close in value.

Learning outcomes:

- Deduce the electron configurations of ions of the first-row transition elements.

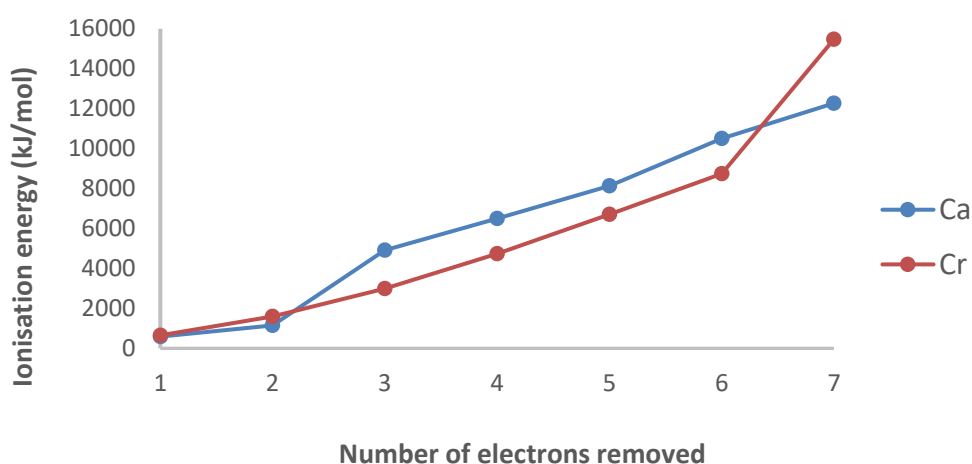
Variable oxidation states of the transition elements

- Transition metals have variable oxidation states.

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | +1 | |
| | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +2 |
| +3 | +3 | +3 | +3 | +3 | +3 | +3 | | | |
| | +4 | +4 | | +4 | | | | | |
| | | +5 | | | | | | | |
| | | | +6 | +6 | | | | | |
| | | | | +7 | | | | | |

- All transition elements (except Sc) can have an oxidation state of +2.
- This is because the 4s electrons are lost first when transition elements form ions.

Comparison of successive ionisation energies in calcium and chromium



- Ca has a large increase in ionisation energy when the 3rd electron is removed, whereas Cr shows a large increase when the 7th electron is removed.
- In transition elements, the 3d and 4s orbitals are close in energy which results in a gradual increase in successive ionisation energies.
- Therefore, chromium has variable oxidation states.

Catalytic properties of the transition elements

- A catalyst is a substance that provides an alternative reaction pathway with a lower activation energy.
- Catalysts can be either homogeneous (same state) or heterogeneous (different state).
- Transition elements can act as heterogeneous and homogeneous catalysts.

Transition elements as heterogeneous catalysts:

- Fe in the Haber process
- Ni in the hydrogenation of margarine
- Palladium (Pd) and Platinum (Pt) in catalytic converters
- MnO_2 in the decomposition of H_2O_2
- V_2O_5 in the Contact process

Transition elements as homogeneous catalysts:

- Fe in haemoglobin (transports oxygen around the body)
- Co in vitamin B_{12} (important for production of red blood cells and a healthy nervous system)

Structure 3.1.10

Understandings:

- Transition element complexes are coloured due to the absorption of light when an electron is promoted between the orbitals in the split d-sublevels. The colour absorbed is complementary to the colour observed.

Learning outcomes:

- Apply the colour wheel to deduce the wavelengths and frequencies of light absorbed and/or observed.
- The colour wheel and the equation $c = \lambda f$ are given in the data booklet.

Additional notes:

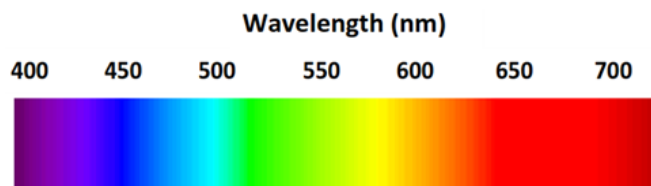
- Students are not expected to know the different splitting patterns and their relation to the coordination number.

Linking questions:

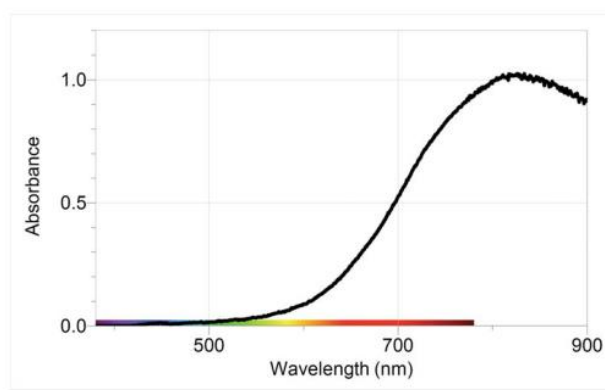
- Reactivity 3.4 What is the nature of the reaction between transition element ions and ligands in forming complex ions?

Coloured complexes - why do complex ions from coloured compounds?

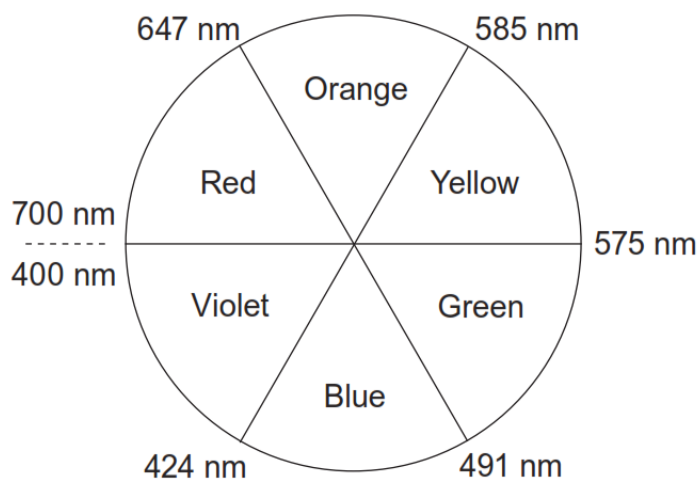
- White light is composed of all the wavelengths of the visible spectrum (shown below).



- When light passes through a solution of Cu^{2+} ions, certain wavelengths of light are absorbed, and certain wavelengths of light are transmitted.
- The $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ion appears blue in solution.
- The absorption spectrum of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is shown below.

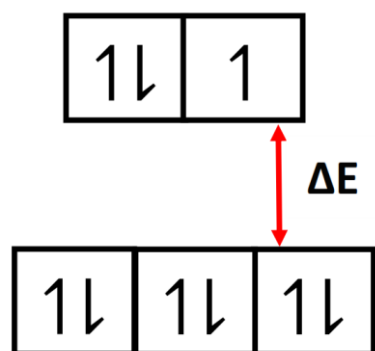
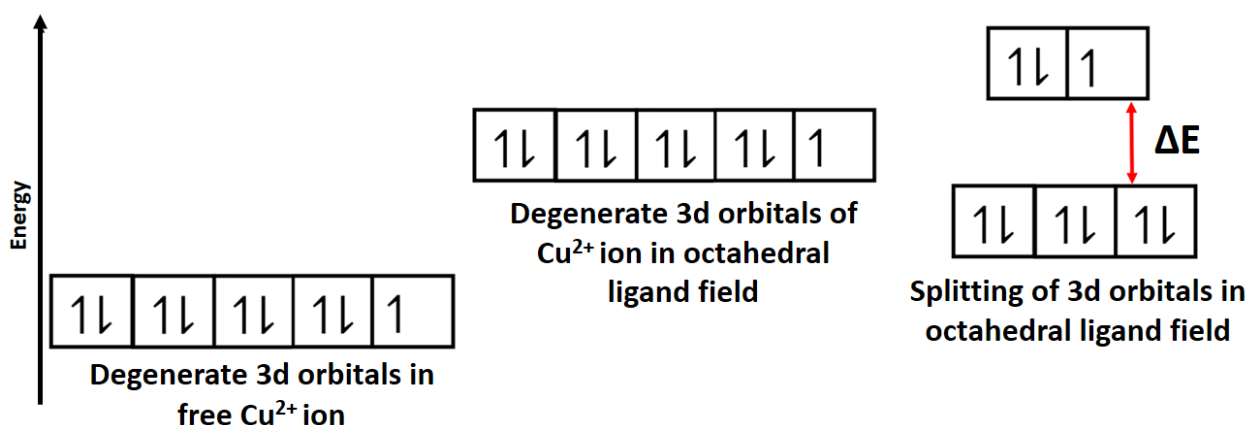


- Wavelengths of light that correspond to orange light are being absorbed and wavelengths that correspond to blue light are being transmitted.
- Blue light is transmitted, therefore, the solution appears blue.



Splitting of d orbitals

- Crystal field theory states that the properties of complex ions are caused by the splitting of the d orbitals into two sets of different energies.
- The splitting occurs when ligands approach the central metal ion; this causes repulsion between the lone pairs of electrons on the ligands and the electrons in the five d orbitals of the central metal ion.
- The d electrons are repelled unequally which causes splitting, with two d orbitals of higher energy and three d orbitals of lower energy.



Electrons can transition between the two sets of d orbitals by absorbing energy (d-d transitions).

The energy difference between the two sets of d orbitals corresponds to the wavelengths of visible light.

In $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, the energy (ΔE) required to promote an electron to the higher set of d orbitals corresponds to a wavelength of 650 to 700 nm.

This corresponds to orange/red light being absorbed. The complementary colour (blue) is transmitted.

Summary

- Transition elements have an incomplete d sub-level.
- The d orbitals are split into 2 sets of higher and lower energy when the ligands bond to the central metal ion.
- The energy difference between the two sets of d orbitals corresponds to the wavelengths of visible light.
- Electrons can transition from the lower to higher set of d orbitals by absorbing certain wavelengths of visible light.
- The complementary colour of the colour that is absorbed is transmitted.

Exercises:

1. Explain why copper(II) sulfate ($\text{CuSO}_4(\text{aq})$) forms a blue solution but a solution of zinc sulfate ($\text{ZnSO}_4(\text{aq})$) is colourless.

The Cu^{2+} ion has an incomplete d sub-level.

Colour in transition elements is caused by electron transitions between d orbitals.

The Zn^{2+} ion has a fully occupied d sub-level, therefore, electron transitions between d orbitals are not possible, and it is colourless.

2. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (hexaaquairon(III) ion) forms a yellow solution. Use the colour wheel to determine the wavelength of light absorbed by the solution.

The wavelength of light absorbed is between 400 nm and 424 nm.

3. $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is green and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is blue. Compare the wavelengths of light absorbed by the solutions.

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ absorbs wavelengths of light between 647 nm and 700 nm.

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ absorbs wavelengths of light between 585 nm and 647 nm.