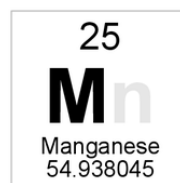
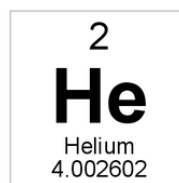
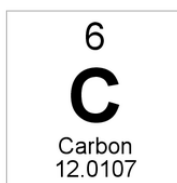
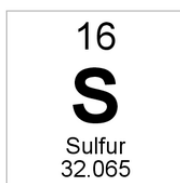
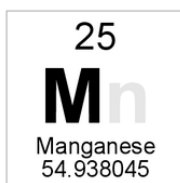


Periodicity HL (answers)

IB CHEMISTRY HL



13.1 First row d-block elements

Understandings:

- Transition elements have variable oxidation states, form complex ions with ligands, have coloured compounds, and display catalytic and magnetic properties.
- Zn is not considered to be a transition element as it does not form ions with incomplete d-orbitals.
- Transition elements show an oxidation state of +2 when the s-electrons are removed.

Applications and skills:

- Explanation of the ability of transition metals to form variable oxidation states from successive ionization energies.
- Explanation of the nature of the coordinate bond within a complex ion.
- Deduction of the total charge given the formula of the ion and ligands present.
- Explanation of the magnetic properties in transition metals in terms of unpaired electrons.

Guidance:

- Common oxidation numbers of the transition metal ions are listed in the data booklet in sections 9 and 14.

Definition of a transition element:

- 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
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- 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 transition elements and their ions

Transition element	Electronic configuration	Ion of transition element	Electronic configuration
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] 4s² 3d¹⁰	Zn²⁺	[Ar] 3d¹⁰

- 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 with an incomplete d sub-level.
- Zn is included to show that it 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. Define the term 'transition element'

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.

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 electronic 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.

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

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

Physical and chemical properties of the transition elements

Physical properties:

- High electrical and thermal conductivity
- High melting point
- Malleable – can be beaten into shape
- High tensile strength
- Ductile – can be drawn into wires
- Fe, Co and Ni are ferromagnetic

Chemical properties:

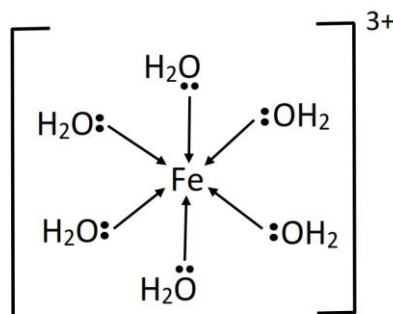
- Form compounds with more than one oxidation number
- Form positive ions
- Form coloured compounds
- Can act as catalysts

Complex ions

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



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

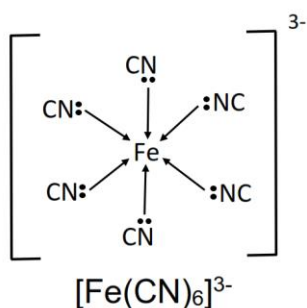


The water molecules are known as ligands – they use their lone pairs of electrons to form a coordinate covalent bond to the central metal ion.

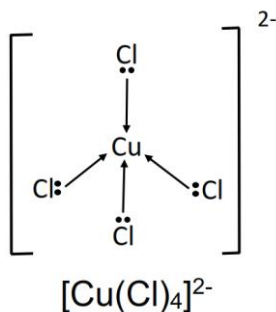
- The coordination number of a complex ion is the number of coordinate covalent bonds between the ligands and the central metal ion.
- The above complex ion has a coordination of six as there are six coordinate covalent bonds between the ligand and the central metal ion.

Exercises:

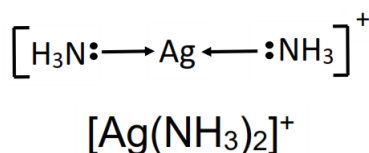
1. Describe the structure of a complex ion.
A complex ion consists of a central metal ion bonded to ligands by coordinate covalent bonds.
2. Determine the coordination number and shape of the following complex ions:



6 – octahedral



4 – tetrahedral

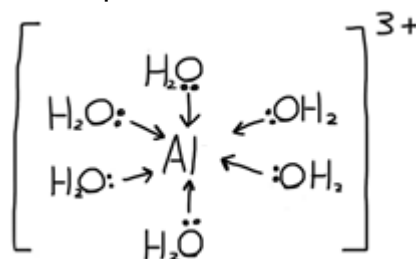


2 – linear

3. A complex ion has a coordination number of 6 – how many coordinate covalent bonds are formed to 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 shape of the complex ion below:



Octahedral

5. How does a coordinate covalent bond differ from a 'normal' covalent bond?

In a coordinate covalent bond, both electrons in the bond come from one atom. In a conventional covalent bond, each atom supplies one electron in the bond.

Ligands

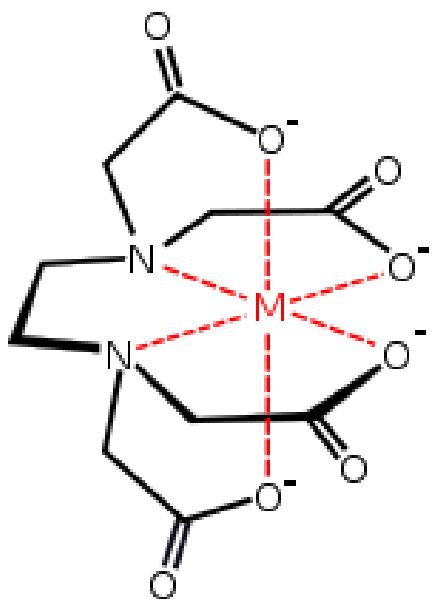
- Ligands are species with lone pairs of electrons that form coordinate covalent bonds with a central metal ion.
- Common examples include:



- 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).

Polydentate ligands

- A polydentate ligand is a species that has more than one lone pair of electrons to form a coordinate covalent bond to a metal ion.
- EDTA⁴⁻ is an example of a polydentate ligand that has 6 lone pairs of electrons (hexadentate ligand).



EDTA⁴⁻ occupies all the octahedral sites of the central metal ion (coordination number = 6).

It grips the central metal ion in a 6 pronged claw called a chelate.

EDTA⁴⁻ acts as a food additive by removing metal ions from solution, therefore inhibiting enzyme catalysed reactions.

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.

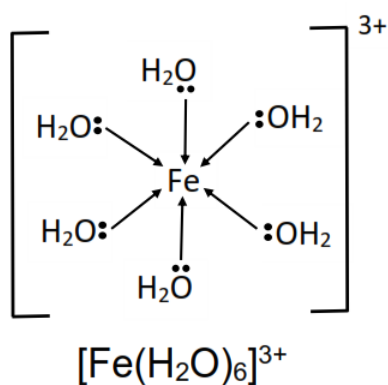
Ligands have lone pairs of electrons, therefore, they can act as Lewis bases. The central metal ion is the Lewis acid.

- 3) Explain why EDTA⁴⁻ is classified as a hexadentate ligand.

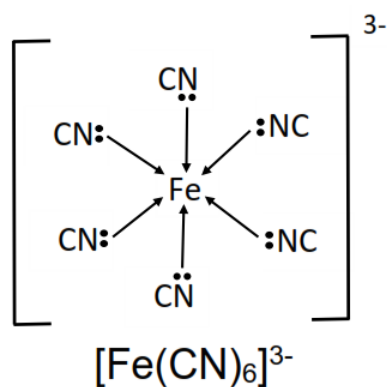
EDTA⁴⁻ has 6 lone pairs of electrons, therefore it can form 6 coordinate covalent bonds with the central metal ion.

Deduce the charge on the central metal ion

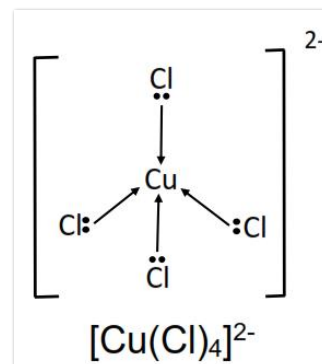
For each of the following, deduce the charge on the central metal ion:



H_2O is a neutral molecule, therefore charge on Fe ion is 3+



CN^- has a 1- charge therefore charge on Fe ion is 3+



Cl^- has a 1- charge therefore charge on Cu ion is 2+

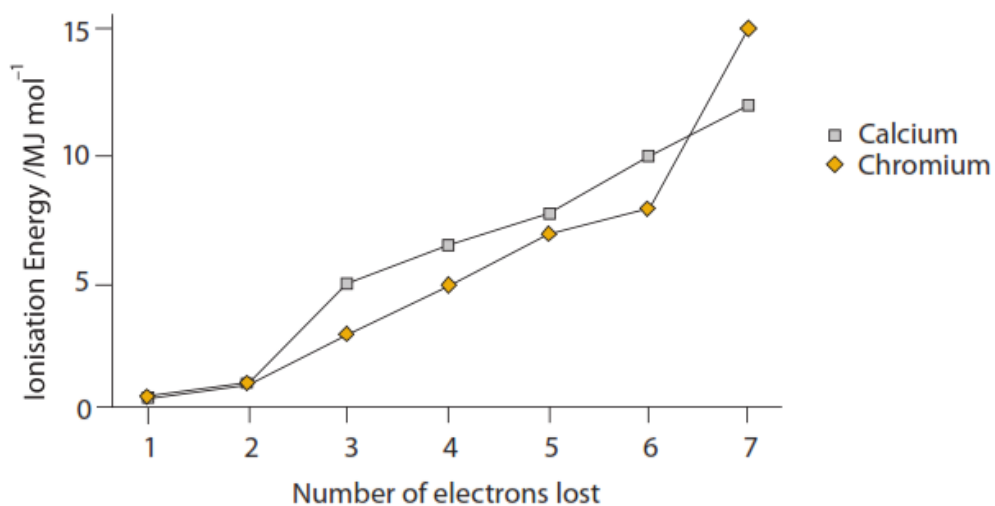
Variable oxidation states of the transition elements

- 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 6th electron is removed.
- This is due to the closeness in energy of the 4s and 3d sub-levels.
- Therefore, chromium has variable oxidation states (as do all transition elements).

Magnetism in the transition elements

- Magnetism in the transition elements is due to presence of unpaired 3d electrons.
- Substances that have unpaired electrons are known as being paramagnetic.
- Substances that have no unpaired electrons are known as being diamagnetic.
- The table below shows the effect in a magnetic field and the number of unpaired 3d electrons in the Zn^{2+} , Cu^{2+} , Ni^{2+} and Mn^{4+} ions.

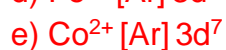
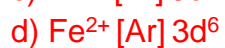
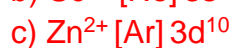
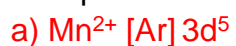
Ion	Effect in external magnetic field	Unpaired 3d electrons
Zn^{2+}	No effect*	$\overset{3d}{\begin{array}{ c c c c c } \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \\ \hline \end{array}}$
Cu^{2+}	Weak effect	$\overset{3d}{\begin{array}{ c c c c c } \hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow \\ \hline \end{array}}$
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 (it is diamagnetic).
- The remaining ions, with their increasing number of unpaired electrons, show an increasing paramagnetic effect.
- The Mn^{4+} ion shows the strongest paramagnetic effect, and the Cu^{2+} ion shows the weakest paramagnetic effect.

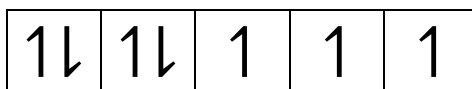
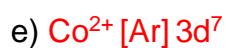
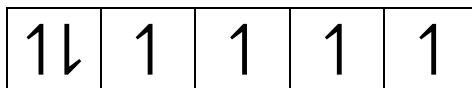
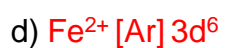
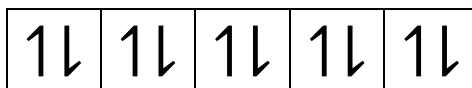
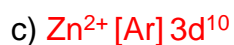
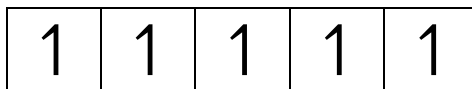
Exercises: The following compounds are placed in an external magnetic field:



1. Write abbreviated electron configurations for the metal ions in the above compounds.



2. a) Mn²⁺ [Ar] 3d⁵



3. Draw orbital diagrams showing only the d sub-level for the above metal ions.
See above
4. Classify the ions as diamagnetic or paramagnetic, and explain your choice for each ion.
- a) **Mn²⁺ is paramagnetic - it has unpaired d electrons**
 - b) **Sc³⁺ is diamagnetic - it has no unpaired electrons**
 - c) **Zn²⁺ is diamagnetic - it has no unpaired d electrons**
 - d) **Fe²⁺ is paramagnetic - it has unpaired d electrons**
 - e) **Co²⁺ is paramagnetic - it has unpaired d electrons**
5. Which compound would you expect to show the strongest paramagnetic effect? Explain your answer.

MnSO₄ - the Mn²⁺ has 5 unpaired d electrons; the greater number of unpaired electrons, the greater the paramagnetic effect.

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 homogenous 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
- MnO₂ in the decomposition of H₂O₂
- V₂O₅ in the Contact process

Transition elements as homogenous catalysts:

- Fe in haemoglobin (transports oxygen around the body)
- Co in vitamin B₁₂ (important for production of red blood cells and a healthy nervous system)

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.

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.
- 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.

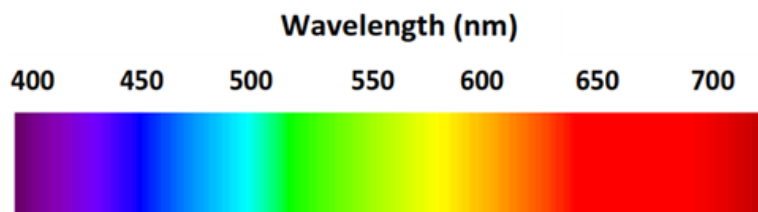
Guidance:

- The spectrochemical series is given in the data booklet in section 15. A list of polydentate ligands is given in the data booklet in section 16.
- Students are not expected to recall the colour of specific complex ions
- The relation between the colour observed and absorbed is illustrated by the colour wheel in the data booklet in section 17.
- 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.

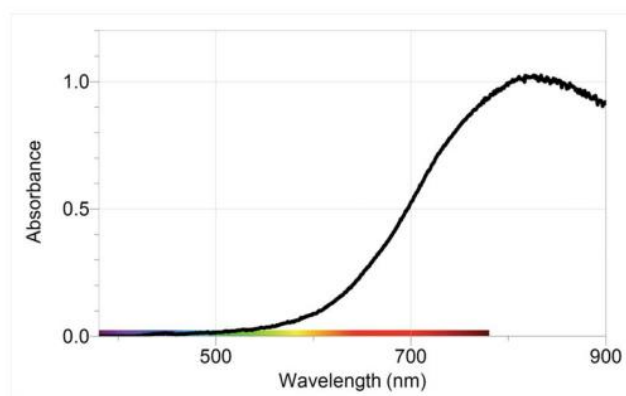
Coloured complexes

Why do complex ions form coloured compounds?

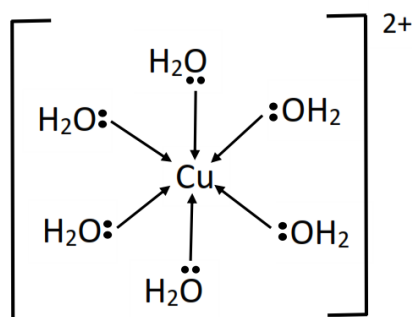
- White light is composed of all the wavelengths of the visible spectrum (shown below).



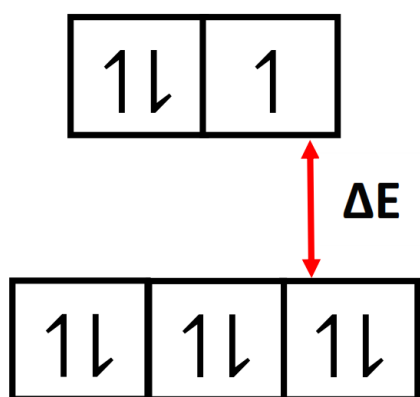
- When light passes through a solution of Cu^{2+} ions, certain wavelengths of light are absorbed and certain wavelengths of light are transmitted.
- The $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ion appears blue in solution.
- The absorption spectrum of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$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



- Wavelengths of light that correspond to red 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

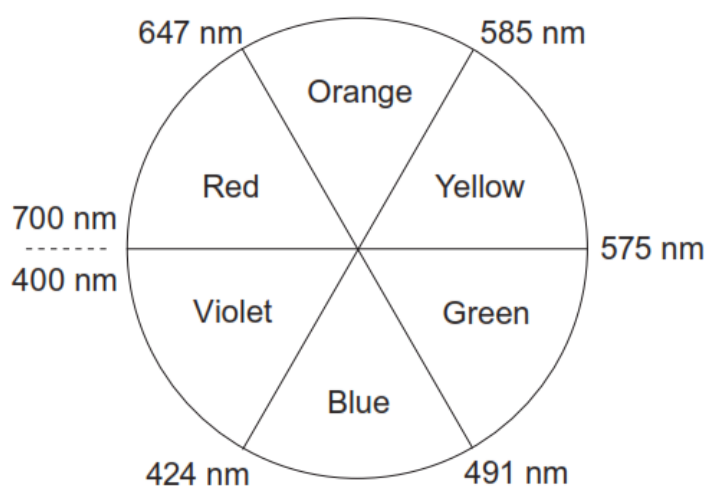


When ligands bond to the central metal ion, there is repulsion between the ligands and the d orbitals of the metal ion.

This repulsion causes the five d orbitals to split into two different sets; two with higher energy and three with lower energy.

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

- Electrons can transition from the lower set to the higher set of d orbitals.
- 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 – 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 wavelength 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 (from the colour wheel).

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.

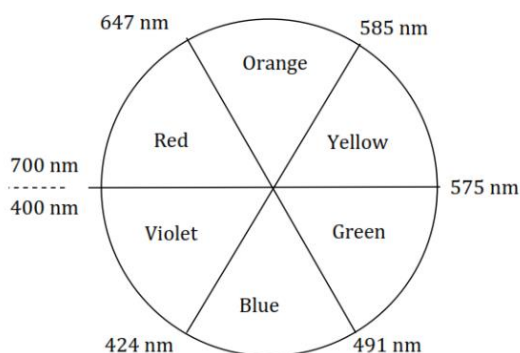
The Cu^{2+} ion has an incomplete d sub-level (or incomplete d orbitals).

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

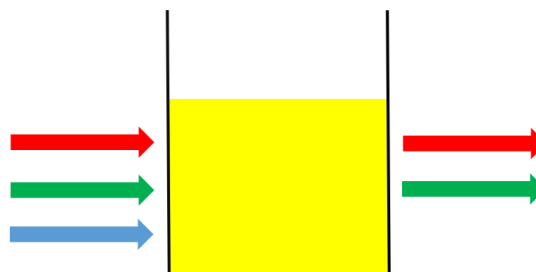
The Zn^{2+} ion has a full d sub-level therefore electron transitions between d orbitals are not possible, and it is colourless.

2. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (hexaaquairon(III) ion) forms a yellow solution. Use the colour wheel to explain why the hexaaquairon(III) ion is coloured.

- The Fe^{3+} ion has an incomplete d sub-level (or incomplete d orbitals).
- When the ligands (H_2O) form coordinate bonds with the Fe^{3+} ion, repulsion between the electrons of the ligand and the electrons of the central metal ion cause the d orbitals of the ion to be split into 2 sets (2 orbitals of higher energy, 3 orbitals of lower energy).
- The energy difference between the 2 sets of d orbitals corresponds to the wavelengths of visible light.
- Electrons absorb wavelengths of visible light when they transition from the lower set of d orbitals to the higher set.
- In the case of the hexaaquairon (III) ion, the wavelength of light absorbed corresponds to the wavelength of blue light.
- The complementary colour (yellow) is transmitted, therefore the solution appears yellow.



Blue light is absorbed, red and green light are transmitted (yellow is seen)



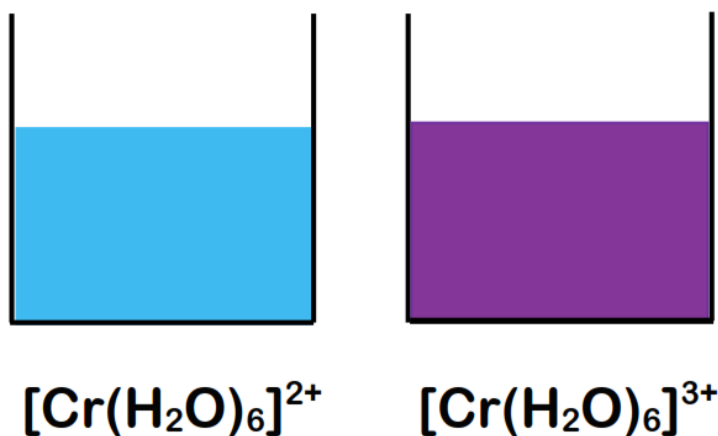
Factors that affect the colour of complex ions

- When ligands bond to a central metal ion, repulsion between electrons in the ligand and in the central metal ion cause the d orbitals to split into two sets, one set of higher and one set of lower energy.
- Any factor that changes the difference in energy (ΔE) between the two sets of d orbitals will change the wavelength of light that is absorbed when electrons transition from the lower to higher set, and therefore the colour of the complex ion.

The factors that affect the colour of complex ions are:

- Identity of the central metal ion
- Oxidation state of the central metal ion
- Identity of the ligands
- Geometry of the complex ion (octahedral, tetrahedral or linear)

Oxidation state of metal ion



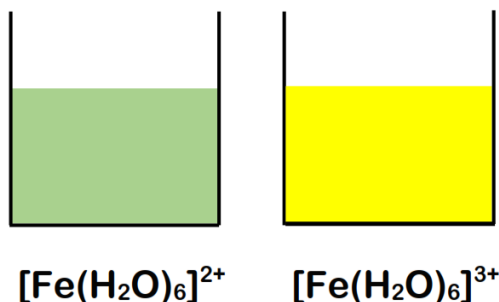
Example: Deduce the oxidation state of the metal ion in each of the complex ions and explain why they are different colours.

- As the oxidation state of the metal ion increases, the amount of splitting of the d orbitals also increases.
- A change in the oxidation state of the Cr ion (from +2 to +3) increases the difference in energy between the two sets of d orbitals.
- As the energy difference between the d orbitals increases, the wavelength of light absorbed decreases.

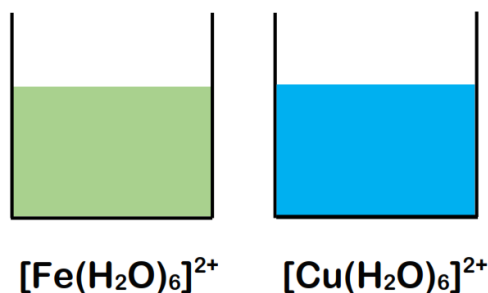
Exercises:

1) Describe and explain the colour changes of the following complex ions:

(i) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is pale green, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is yellow.



(ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is pale green, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is blue.

**Answers:**

1) (i)

- In the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ complex ion, the oxidation number of the iron is +2.
- In the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ complex ion, the oxidation number of the iron is +3.
- The higher oxidation number increases the splitting of the d orbitals, therefore increases the energy difference between the two sets of d orbitals.
- The bigger the difference in energy between the 2 sets of d orbitals, the more energy is absorbed by the electron as it transitions from the lower to upper set of d orbitals.
- Higher energy = shorter wavelength of light absorbed.
- The complementary colour is transmitted, therefore the colour changes from pale green to yellow.

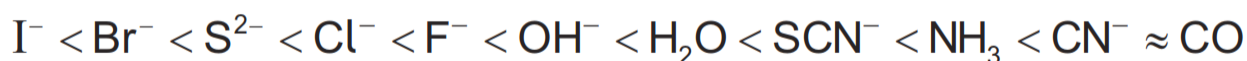
(ii)

- The identity of the central metal ion changes from Fe^{2+} to Cu^{2+}
- The ligand (H_2O), the oxidation state of the central metal ion (+2) and the shape (octahedral) are the same for each complex ion.
- The change from Fe^{2+} to Cu^{2+} changes the wavelength of light that is absorbed.
- $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ absorbs red light (longer wavelength) and transmits pale green light.
 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ absorbs orange light (shorter wavelength) and transmits blue light.

- Therefore, the Cu^{2+} ions produce the biggest splitting of the d orbitals.
- The bigger the difference in energy between the 2 sets of d orbitals, the more energy is absorbed by the electron as it transitions from the lower to upper set of d orbitals.
- Higher energy = shorter wavelength of light absorbed
- The complementary colour is transmitted, therefore the colour changes from pale green to blue.

Spectrochemical series

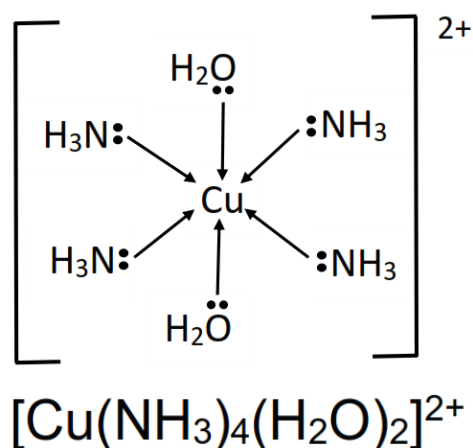
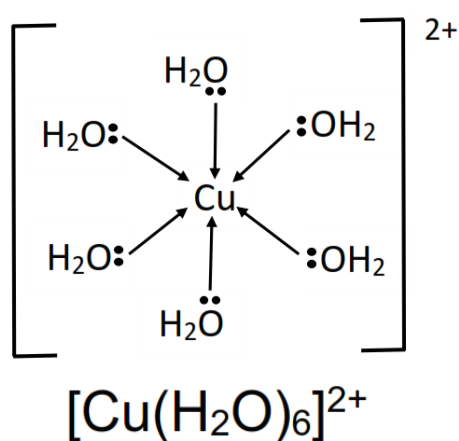
- The spectrochemical series below arranges ligands in order of their ability to split d orbitals in an octahedral complex ion.



- The higher up in the series, the greater the splitting of the d orbitals (therefore the greatest energy difference).
- Higher energy corresponds to a shorter wavelength and vice-versa.
- CO produces the greatest splitting of the d orbitals, and produces the greatest energy difference.

Example:

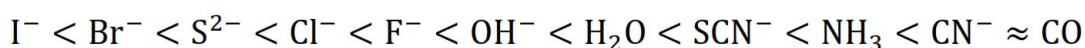
Use the spectrochemical series to explain why the two complex ions below are different colours.



- NH_3 produces the greatest splitting of the d orbitals, therefore the greatest difference in energy between the two sets of d orbitals.
- More energy is absorbed by the electron transitions from the lower to upper d orbitals, therefore the wavelength of light absorbed decreases (as energy increases, wavelength decreases).
- Red/orange light is absorbed by $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and blue/green light is transmitted.
- Yellow light is absorbed by $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ and blue/violet light is transmitted.

Exercises:

1) Use the spectrochemical series below to arrange the following ligands (OH^- , H_2O , S^{2-} , CN^- , I^-) in order of d orbital splitting from greatest to least.



Decreasing d orbital splitting

The higher the ligand is in the electrochemical series, the greater the splitting of the d orbitals. Therefore CN^- would produce the greatest splitting of the d orbitals, and I^- the least.

2) Arrange the same ligands (OH^- , H_2O , S^{2-} , CN^- , I^-) in order of the wavelength of light absorbed from shortest wavelength to longest wavelength.



Decreasing wavelength of light absorbed

- The higher up in the electrochemical series, the greater the splitting of the d orbitals and the greater energy difference between the two sets of d orbitals.
- As energy increases, wavelength decreases, therefore a complex ion with CN^- ligands would absorb the shortest wavelength (greatest energy) of light and I^- the longest wavelength (lowest energy).

3) Consider the two complex ions below:



Use the spectrochemical series to describe and explain how the wavelength of light absorbed changes as the ligand changes.

- As the ligand changes from H_2O to NH_3 , the wavelength of light absorbed decreases.
- NH_3 is higher up in the spectrochemical series, therefore it produces the greatest splitting of the d orbitals, and the greatest energy difference between the 2 sets of d orbitals.
- The energy that the electrons absorb to transition between the two sets of d orbitals increases from H_2O to NH_3 , therefore the wavelength of light absorbed decreases.