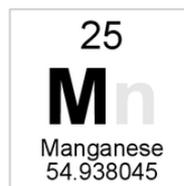
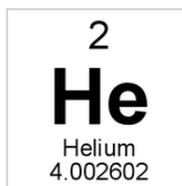
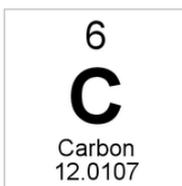
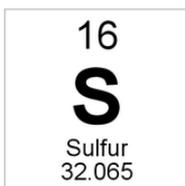
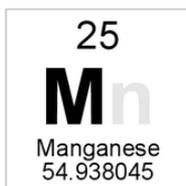


# Periodicity HL

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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.

## Syllabus checklist

<b>Objective</b>	<b>I am confident with this</b>	<b>I need to review this</b>	<b>I need help with this</b>
Outline the requirements for an element to be considered as a transition element in terms of incomplete d sub-level			
Describe the structure and bonding in a complex ion			
State the coordination number and geometry of a complex ion			
Determine the charge on a central metal ion based on the number of ligands and their charges			
Explain why transition elements have variable oxidation states			
Outline the meaning of the terms diamagnetic and paramagnetic			
Explain the magnetic properties of the transition elements in terms of half-filled d orbitals			
State examples of transition elements as catalysts			

## 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 <b>Sc</b> 44.96	22 <b>Ti</b> 47.87	23 <b>V</b> 50.94	24 <b>Cr</b> 52.00	25 <b>Mn</b> 54.94	26 <b>Fe</b> 55.85	27 <b>Co</b> 58.93	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.55	30 <b>Zn</b> 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 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 <sup>2</sup> 3d <sup>1</sup>	Sc <sup>3+</sup>	[Ne] 3s <sup>2</sup> 3p <sup>6</sup>
Ti	[Ar] 4s <sup>2</sup> 3d <sup>2</sup>	Ti <sup>2+</sup>	[Ar] 3d <sup>2</sup>
V	[Ar] 4s <sup>2</sup> 3d <sup>3</sup>	V <sup>2+</sup>	[Ar] 3d <sup>3</sup>
Cr	[Ar] 4s <sup>1</sup> 3d <sup>5</sup>	Cr <sup>3+</sup>	[Ar] 3d <sup>3</sup>
Mn	[Ar] 4s <sup>2</sup> 3d <sup>5</sup>	Mn <sup>4+</sup>	[Ar] 3d <sup>3</sup>
Fe	[Ar] 4s <sup>2</sup> 3d <sup>6</sup>	Fe <sup>3+</sup>	[Ar] 3d <sup>5</sup>
Co	[Ar] 4s <sup>2</sup> 3d <sup>7</sup>	Co <sup>2+</sup>	[Ar] 3d <sup>7</sup>
Ni	[Ar] 4s <sup>2</sup> 3d <sup>8</sup>	Ni <sup>2+</sup>	[Ar] 3d <sup>8</sup>
Cu	[Ar] 4s <sup>1</sup> 3d <sup>10</sup>	Cu <sup>2+</sup>	[Ar] 3d <sup>9</sup>
Zn	[Ar] 4s <sup>2</sup> 3d <sup>10</sup>	Zn <sup>2+</sup>	[Ar] 3d <sup>10</sup>

- 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.

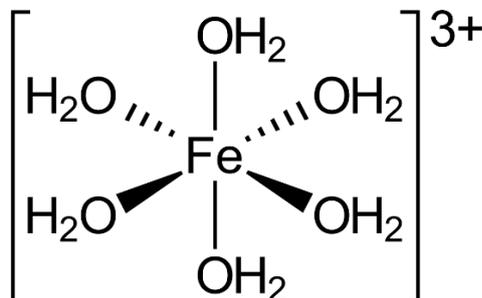


## Complex ions

- 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  $\text{Fe}^{3+}$  ion.

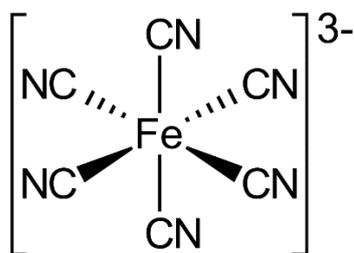


The water molecules are known as ligands – they use their lone pairs of electrons to form a coordinate covalent bond to the central metal ion.

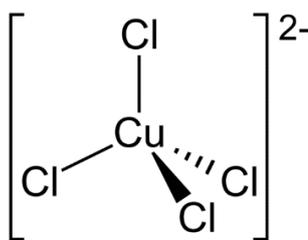
- The coordination number of a complex ion is the number of coordinate covalent bonds between the ligands and the central metal ion.
- The above complex ion has a coordination number of six as there are six coordinate covalent bonds between the ligands and the central metal ion.

## Exercises:

1. Describe the structure of a complex ion.
2. Determine the coordination number and shape (geometry) of the following complex ions:



$[\text{Fe}(\text{CN})_6]^{3-}$



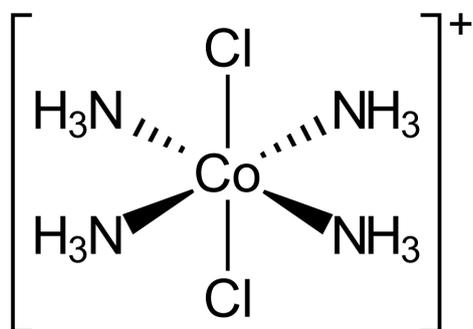
$[\text{CuCl}_4]^{2-}$



$[\text{CuCl}_2]^-$

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

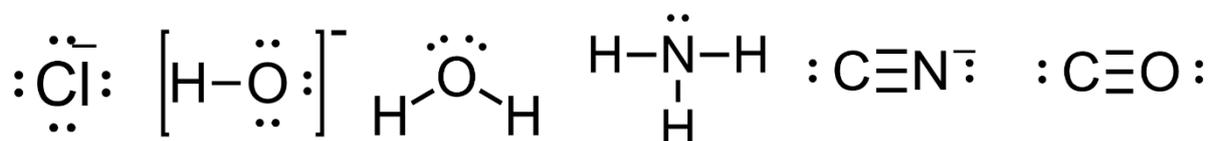
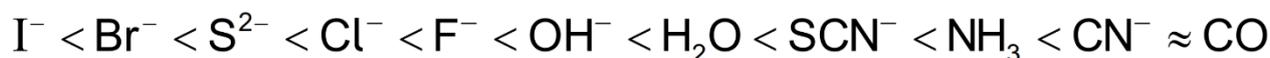
4. Deduce the shape of the complex ion below:



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

## Ligands

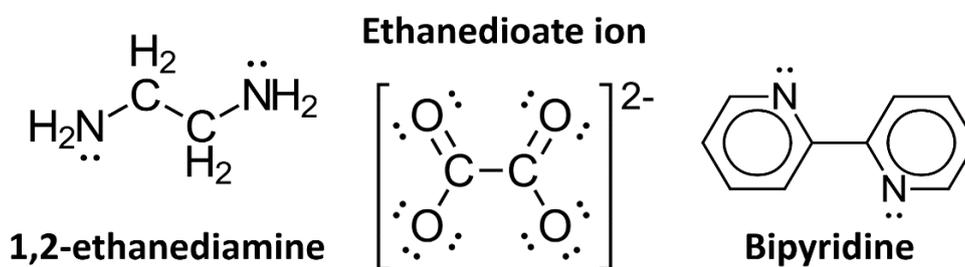
- Ligands are species with lone pairs of electrons that form coordinate covalent bonds with a central metal ion.
- Monodentate ligands use only one lone pair of electrons to bond to a central metal ion.



- 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).

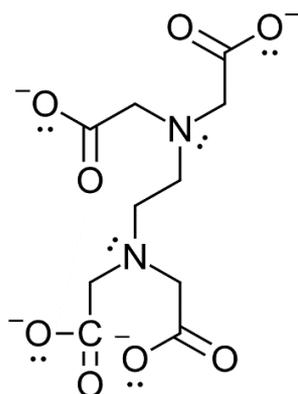
## Bidentate ligands

- Bidentate ligands use two lone pairs of electrons to bond to a central metal ion.



## Polydentate ligands

- Polydentate ligands use multiple lone pairs of electrons to bond to a central metal ion.
- EDTA<sup>4-</sup> is an example of a polydentate ligand that has 6 lone pairs of electrons (hexadentate ligand).



EDTA<sup>4-</sup> has six lone pairs of electrons to bond with the central metal ion – it occupies all the octahedral sites of the central metal ion (coordination number = 6).

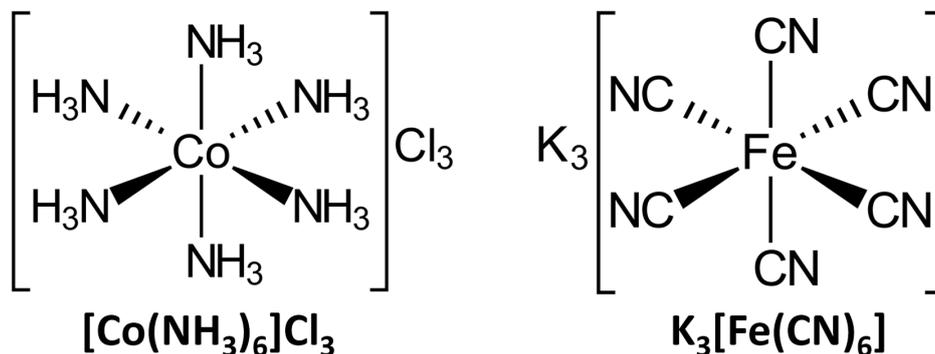
EDTA<sup>4-</sup> acts as a food additive by removing metal ions from solution, therefore inhibiting enzyme catalysed reactions.

**Exercises:**

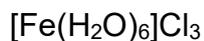
1. Outline what is meant by the term *ligand*.
2. Explain how ligands are also able to act as Lewis bases.
3. Explain why EDTA<sup>4-</sup> is classified as a hexadentate ligand.

## 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<sup>-</sup> ions

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

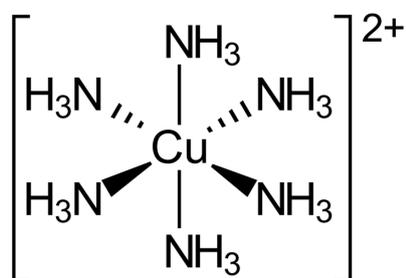
- a.  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- b.  $\text{K}_3[\text{Fe}(\text{CN})_6]$
- c.  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

## Deduce the charge on a central metal ion

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

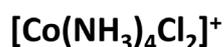
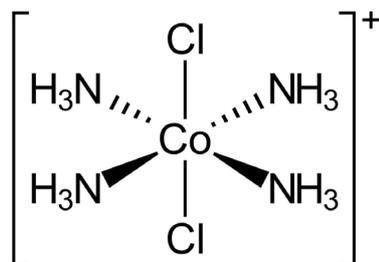
Transition element	Common ions formed	Oxidation state
Chromium	Chromium(II) $\text{Cr}^{2+}$ Chromium(III) $\text{Cr}^{3+}$	+2 +3
Cobalt	Cobalt(II) $\text{Co}^{2+}$ Cobalt(III) $\text{Co}^{3+}$	+2 +3
Copper	Copper(I) $\text{Cu}^+$ Copper(II) $\text{Cu}^{2+}$	+1 +2
Iron	Iron(II) $\text{Fe}^{2+}$ Iron(III)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

### Example 1:



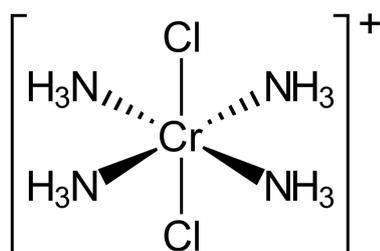
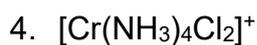
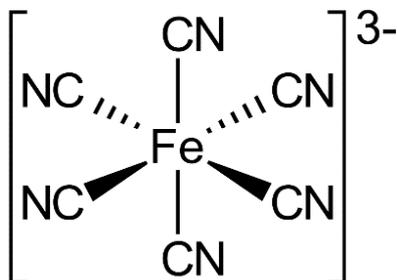
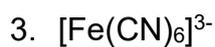
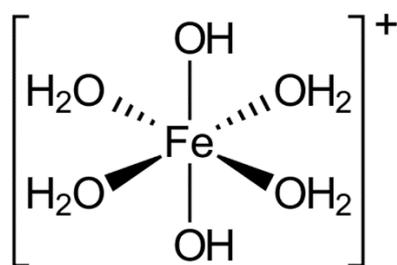
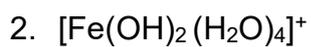
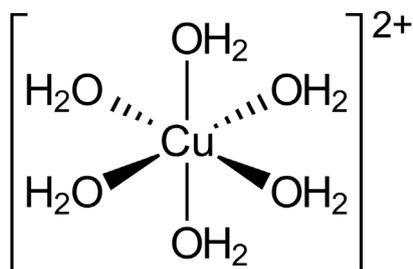
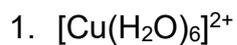
If the ligands are neutral, the charge on the complex ion is the same as the charge on the central metal ion.  
The central metal ion is the  $\text{Cu}^{2+}$  ion (oxidation state +2).

### 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  $\text{Co}^{3+}$  ion (oxidation state +3).

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



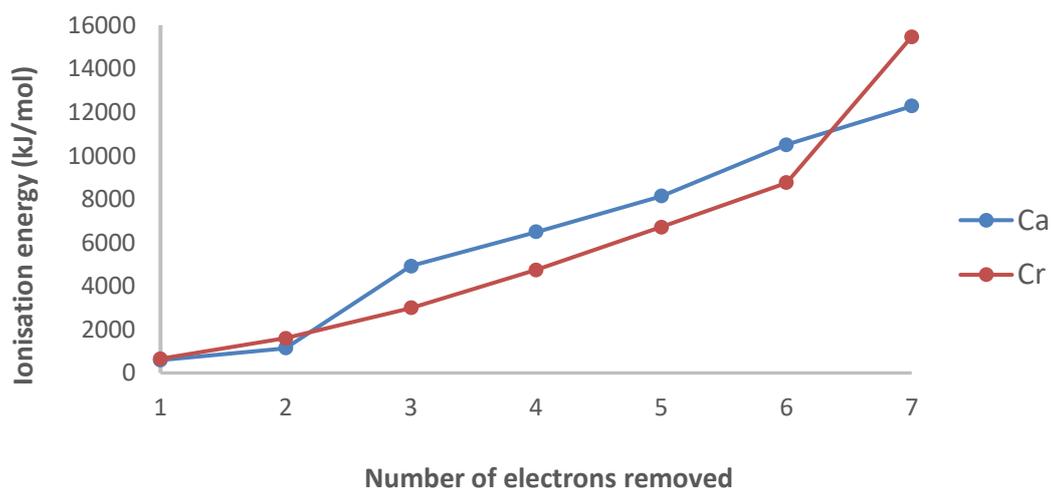
## Variable oxidation states of the transition elements

- 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 3<sup>rd</sup> electron is removed, whereas Cr shows a large increase when the 6<sup>th</sup> 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 (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  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mn}^{4+}$  ions.

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

- $\text{Zn}^{2+}$  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  $\text{Mn}^{4+}$  ion shows the strongest paramagnetic effect, and the  $\text{Cu}^{2+}$  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. Draw orbital diagrams showing only the d sub-level for the above metal ions.
3. Classify the ions as diamagnetic or paramagnetic and explain your choice for each ion.
4. Which compound would you expect to show the strongest paramagnetic effect? Explain your answer.

### **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
- $\text{MnO}_2$  in the decomposition of  $\text{H}_2\text{O}_2$
- $\text{V}_2\text{O}_5$  in the Contact process

### **Transition elements as homogeneous catalysts:**

- Fe in haemoglobin (transports oxygen around the body)
- Co in vitamin  $\text{B}_{12}$  (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.

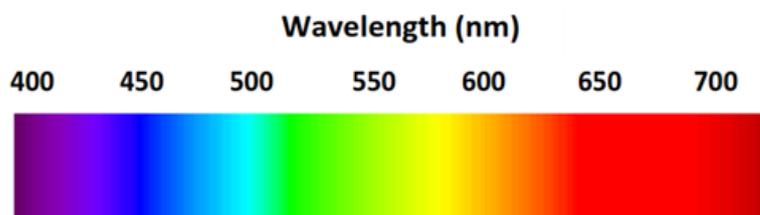
### Syllabus checklist

Objective	I am confident with this	I need to review this	I need help with this
Explain why complex ions form coloured compounds			
Explain the factors that affect the colour of complex ions in solution based on the wavelengths of light absorbed and transmitted			
Explain the effect of different ligands on the splitting of the two sets of d orbitals using the spectrochemical series			

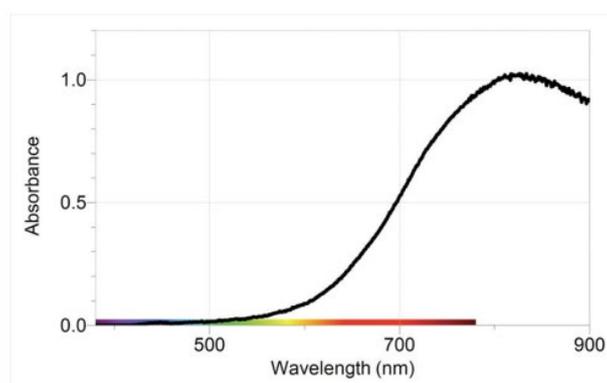
## Coloured complexes

Why do complex ions form coloured compounds?

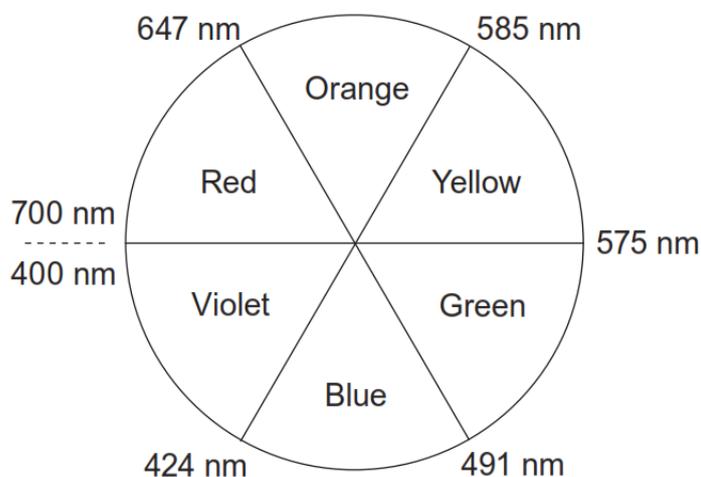
- White light is composed of all the wavelengths of the visible spectrum (shown below).



- When light passes through a solution of  $\text{Cu}^{2+}$  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.

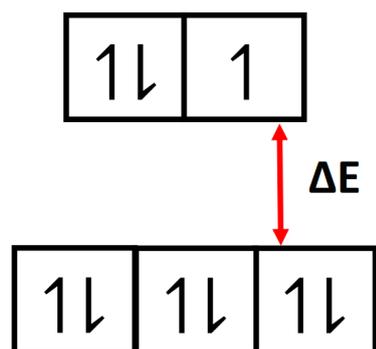
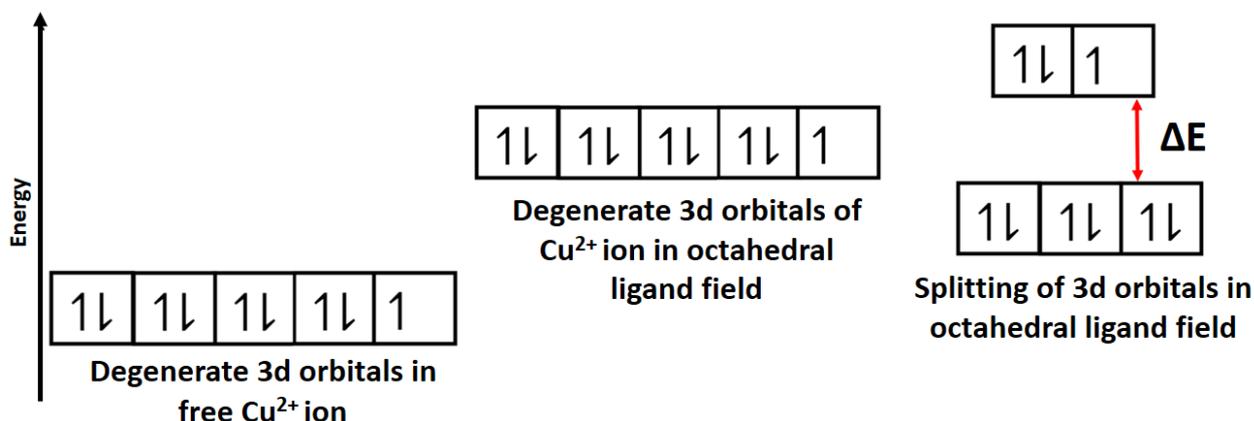


- Wavelengths of light that correspond to orange light are being absorbed and wavelengths that correspond to blue light are being transmitted.
- Blue light is transmitted, therefore, the solution appears blue.



## 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 ( $\Delta E$ ) 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.



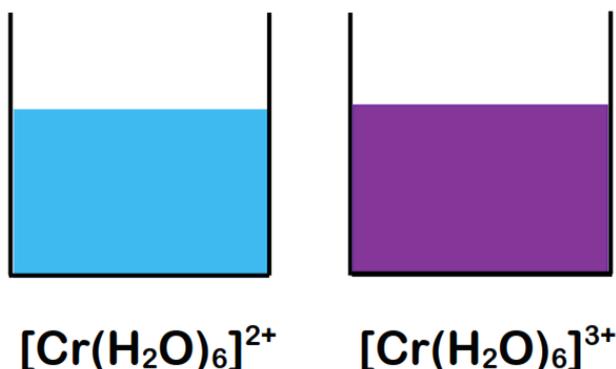
## Factors that affect the colour of complex ions

- 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 ( $\Delta E$ ) 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



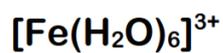
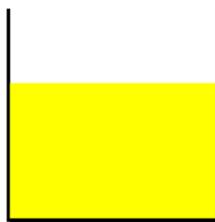
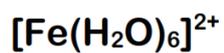
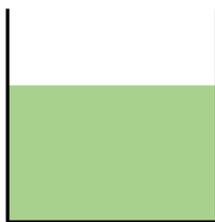
**Example:** Deduce the oxidation state of the metal ion in each of the complex ions and explain why they are different colours.

- 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.

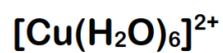
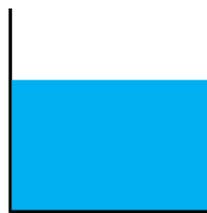
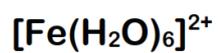
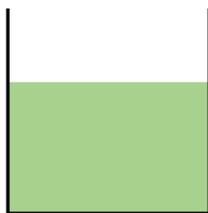
**Exercises:**

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.

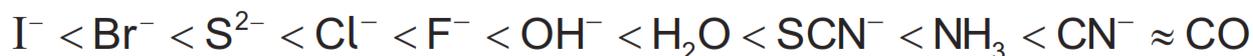


## Spectrochemical series

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

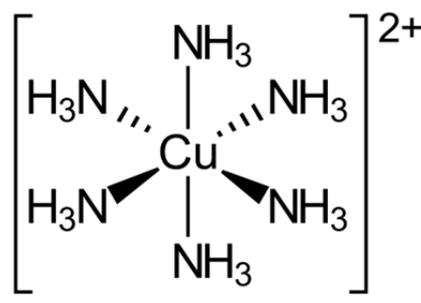
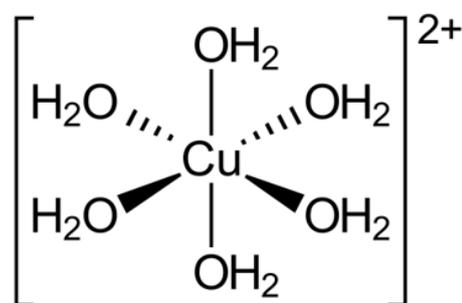
Weaker field ligands

Stronger field ligands



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

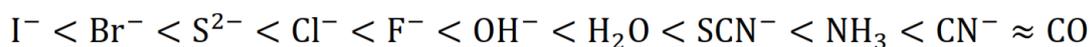
**Example:** Use the spectrochemical series to explain why the two complex ions below are different colours.



- NH<sub>3</sub> 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 ( $\text{OH}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{S}^{2-}$ ,  $\text{CN}^-$ ,  $\text{I}^-$ ) in order of d orbital splitting from greatest to least.



2. Arrange the ligands ( $\text{OH}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{S}^{2-}$ ,  $\text{CN}^-$ ,  $\text{I}^-$ ) in order of the wavelength of light absorbed from shortest wavelength to longest wavelength.

3. Consider the two complex ions below:



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