

CHAPTER 25: Transition Elements

25.1 Introduction to Transition Elements

25.2 Oxidation States of Transition Elements

25.3 Complex Ions

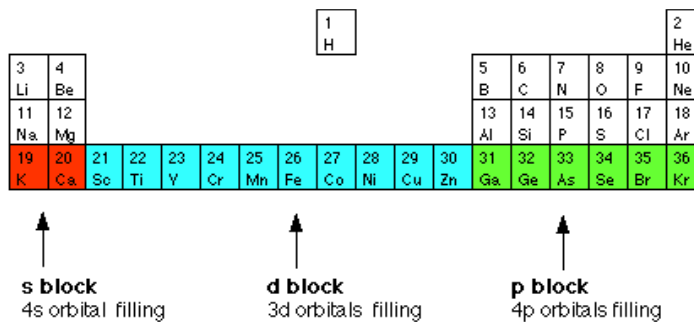
Learning outcomes:

- (a) explain what is meant by a transition element, in terms of *d*-block elements forming one or more stable ions with incomplete *d* orbitals.
- (b) state the electronic configuration of a first row transition element and of its ions.
- (c) contrast, qualitatively, the melting points and densities of the transition elements with those of calcium as a typical *s*-block element.
- (d) describe the tendency of transition elements to have variable oxidation states.
- (e) predict from a given electronic configuration, the likely oxidation states of a transition element.
- (f) describe and explain the use of $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{MnO}_4^-/\text{Mn}^{2+}$ and $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ as examples of redox systems.
- (g) predict, using *E* values, the likelihood of redox reactions.
- (h) explain the reactions of transition elements with ligands to form complexes, including the complexes of copper(II) ions with water, hydroxide, ammonia and chloride ions
- (i) (i) define the term ligand as a species that contains a lone pair of electrons that forms a dative bond to a central metal atom/ion.
(ii) define the term complex as a molecule or ion formed by a central metal atom/ion surrounded by one or more ligands.
(iii) describe transition metal complexes as linear, octahedral, tetrahedral or square planar.
- (j) explain qualitatively that ligand exchange may occur, including the complexes of copper(II) ions with water, hydroxide, ammonia and chloride ions.
- (k) describe the shape and symmetry of the *d* orbitals, and the splitting of degenerate *d* orbitals into two energy levels in octahedral complexes using the complexes of copper(II) ions with water and ammonia as examples.
- (l) explain the origin of colour in transition element complexes resulting from the absorption of light energy as an electron moves between two non-degenerate *d* orbitals.
- (m) describe, in qualitative terms, the effects of different ligands on absorption, and hence colour, using the complexes of copper(II) ions with water, hydroxide, ammonia and chloride ions as examples.
- (n) apply the above ideas of ligands and complexes to other metals, given information.

25.1 Introduction to Transition Elements

Transition and d-block elements

- 1) A *transition element* is one which forms one or more stable ions with incompletely filled orbitals.
- 2) A *d-block element* is one which has electrons filling the d-orbitals.



Element		Atomic no.	Electronic configuration						
Scandium	Sc	21	[Ar] <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td></td><td></td><td></td><td></td></tr></table> <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td></tr></table>	1					1
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Titanium	Ti	22	[Ar] <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td></td><td></td><td></td></tr></table> <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td></tr></table>	1	1				1
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Vanadium	V	23	[Ar] <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td>1</td><td></td><td></td></tr></table> <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td></tr></table>	1	1	1			1
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Chromium	Cr	24	[Ar] <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr></table> <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td></tr></table>	1	1	1	1	1	1
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Manganese	Mn	25	[Ar] <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr></table> <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td></tr></table>	1	1	1	1	1	1
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Iron	Fe	26	[Ar] <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr></table> <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td></tr></table>	1	1	1	1	1	1
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Cobalt	Co	27	[Ar] <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr></table> <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td></tr></table>	1	1	1	1	1	1
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Nickel	Ni	28	[Ar] <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr></table> <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td></tr></table>	1	1	1	1	1	1
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Copper	Cu	29	[Ar] <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr></table> <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td></tr></table>	1	1	1	1	1	1
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Zinc	Zn	30	[Ar] <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td><td>1</td><td>1</td><td>1</td><td>1</td></tr></table> <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td></tr></table>	1	1	1	1	1	1
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- 3) From the above definition, scandium and zinc are **not counted** as transition elements, although they are d-block elements. This is because:
 - i. scandium forms Sc^{3+} ion, which does not have any d-electrons.
 - ii. zinc forms Zn^{2+} ion, which has a completely-filled d-orbitals.

Physical properties of transition elements

- 1) i. Transition elements are all metals which are **hard and denser than s-block elements**.
 - ii. This is because the relative atomic masses of transition elements are higher and their radii are smaller compared to s-block elements. Hence, there are more mass per unit volume and the density is higher.
 - iii. For example, iron has a density of 7.9 g cm^{-3} while calcium has a density of 1.6 g cm^{-3} .
- 2) i. Transition elements have **higher melting points than s-block elements**.
 - ii. This is because the metallic bond of transition elements is stronger as both 3d and 4s electrons are involved in the bonding. In calcium, for example, only 3s electrons are involved.
 - iii. This is possible because 3d and 4s are very similar energy levels.
 - iv. For example, iron has a melting point of $1538 \text{ }^\circ\text{C}$ while calcium has a melting point of $839 \text{ }^\circ\text{C}$.

Characteristic properties of transition elements

- 1) The characteristic properties of transition elements are:
 - i. they have variable oxidation states.
 - ii. they form coloured ions.
 - iii. they form complex ions which are surrounded by ligands.
 - iv. they often act as catalysts.

25.2 Oxidation States of Transition Elements

Variable oxidation states

- 1) i. One characteristic property of transition elements is that **they have variable oxidation states**.
 - ii. For example, iron can exist in 0, +2 or +3 oxidation state.
- 2) This is because the 4s and 3d electrons have very similar energy levels, therefore the transition element can easily lose or gain electrons to form ions/compounds of roughly the same stability.

- 3) All the possible oxidation states of the transition elements are shown below, the most common ones are bolded.

<i>Element</i>	<i>Electronic configuration</i>	<i>Known oxidation states</i>
Ti	[Ar] 3d ² 4s ²	+1, +2, +3 , +4
V	[Ar] 3d ³ 4s ²	+1, +2, +3 , +4 , +5
Cr	[Ar] 3d ⁵ 4s ¹	+1, +2 , +3 , +4, +5, +6
Mn	[Ar] 3d ⁵ 4s ²	+1, +2, +3, +4 , +5, +6 , +7
Fe	[Ar] 3d ⁶ 4s ²	+1, +2, +3 , +4, +5, +6
Co	[Ar] 3d ⁷ 4s ²	+1, +2, +3 , +4, +5
Ni	[Ar] 3d ⁸ 4s ²	+1, +2, +3, +4
Cu	[Ar] 3d ¹⁰ 4s ¹	+1 , +2 , +3

- 4) An oxidation state of +2 implies that two electrons have been lost from the neutral element. The same goes for other oxidation states.
- 5) The maximum oxidation state of a compound can be obtained by **counting the number of 4s electrons and the number of unpaired 3d electrons**. Only copper breaks this pattern.
- 6) i. For small oxidation states, the transition element normally exists as simple M^{a+} ions.
- ii. For large oxidation states, the transition element normally exists in oxo-compounds. This is because the ions formed would have a very high charge density and it will polarise adjacent molecules (water, oxygen) to form the oxo-compounds.
- iii. For example, Cr⁶⁺ does not exist, chromium with oxidation state +6 exists as CrO₄²⁻.

Redox reactions of transition elements.

- Note: 1) There is no point learning this here, you should already have a decent knowledge on the Fe³⁺/Fe²⁺, MnO₄⁻/Mn²⁺ and Cr₂O₇²⁻/Cr³⁺ systems up to this point of the syllabus.
- 2) You need to know how to:
- construct redox equations.
 - calculate oxidation states.
 - calculate the amount of substance (mass/volume) from a titration that involves oxidation and reduction.
 - select suitable oxidising and reducing agents.
 - calculate cell potentials.

25.3 Complex Ions

Ligand and complex

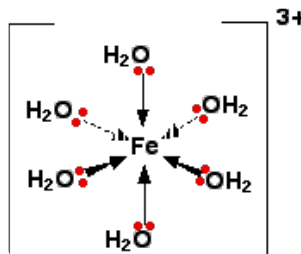
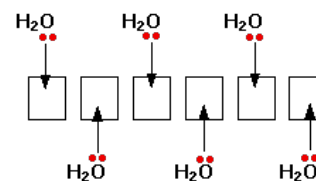
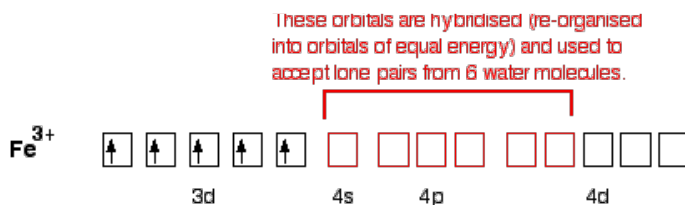
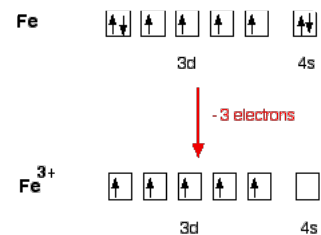
- 1) A *ligand* is a molecule or ion with a lone pair of electrons, capable of forming a co-ordinate bond to a metal atom or ion. Some examples of ligands are water, ammonia and chloride ion.
- 2) A *complex* is a molecule or ion containing a central metal ion surrounded by one or more ligands. Some examples are $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

Formation of a complex

- 1) A complex is formed when ligands bond with the central metal ion via **co-ordinate bonding**.

- 2) Take $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ as an example:

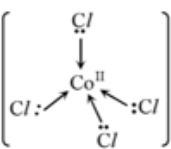
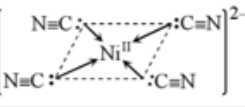
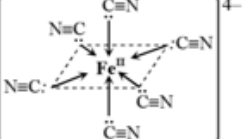
- i. Fe ion has an electronic structure of $[\text{Ar}]3d^64s^2$. When it loses electrons to become Fe^{3+} , the electronic structure becomes $[\text{Ar}]3d^5$.
- ii. The ion then uses 6 orbitals from the 4s, 4p and 4d levels to accept lone pairs from the water molecules.



- 3) Note: i. **For small ligands** such as water and ammonia, **six** is the maximum number of ligands it can bond to the central metal ion.
- ii. **For larger ligands** such as chloride ions, it can only form **four** co-ordinate bonds with the central metal ion.

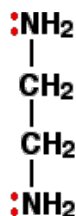
4) The co-ordination number of a complex is the **total number of co-ordinate bond the ligands formed with the central metal ion**. For example, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ has a co-ordination number of 6.

5) Some other co-ordination numbers and the geometry of the complex:

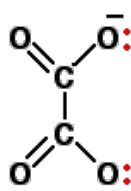
Co-ordination no.	Shape	Examples
2	linear	$[\text{CuCl}_2]^-$ $[\text{H}_3\text{N}:\rightarrow\text{Ag}\leftarrow:\text{NH}_3]^+$ $[\text{Ag}(\text{NH}_3)_2]^+$
4	tetrahedral	$\text{Ni}(\text{CO})_4$ $[\text{CoCl}_4]^{2-}$ $[\text{Cu}(\text{CN})_4]^{3-}$ $[\text{Zn}(\text{NH}_3)_4]^{2+}$ 
	square planar	$[\text{CuCl}_4]^{2-}$ $[\text{Ni}(\text{CN})_4]^{2-}$ $[\text{Cu}(\text{NH}_3)_4]^{2+}$ 
6	octahedral	$[\text{Fe}(\text{CN})_6]^{3-}$ $[\text{Fe}(\text{CN})_6]^{4-}$ $[\text{Ni}(\text{NH}_3)_6]^{2+}$ $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ 

6) A ligand is said to be **unidentate** if it forms **one co-ordinate bond** with the central metal ion only. Water, ammonia and chloride are unidentate ligands.

7) i. A ligand is said to be **bidentate** if it forms **two co-ordinate bonds** with the central metal ion. 1,2-diaminoethane and ethanedioate ion are bidentate ligands.



1,2-diaminoethane

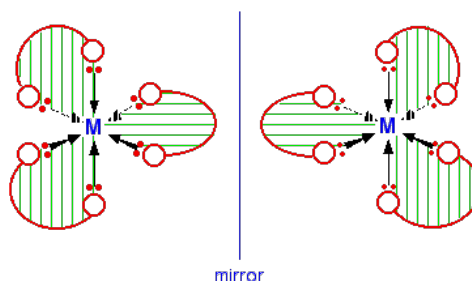


ethanedioate ion

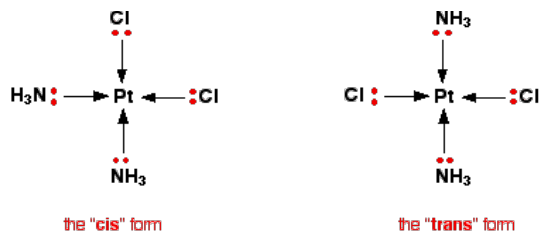


These can both be used to form co-ordinate bonds with the same metal ion.

ii. A complex ion which has bidentate ligands attached to it **exhibits optical isomerism**.



iii. In addition, a complex ion which has the ligands arranged in a square planar structure **exhibits geometrical isomerism**.



Naming complexes

- 1) Naming complexes is very similar in naming organic compounds.
- 2) Each ligand is given a code:

ligand	name
water	aqua
ammonia	ammine
carbon monoxide	carbonyl
cyanide ion	cyano
chloride ion	chloro
hydroxide ion	hydroxy
oxygen molecule	oxo
nitrogen monoxide	nitroso

- 3) Some examples:
 - i. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is **hexaaquairon(III)** ion
 - **hexa** shows there are six ligands.
 - **aqua** shows the ligands are water molecules.
 - **iron** shows the name of the central metal ion.
 - **(III)** shows the the oxidation number of the central metal ion.
- 4) If there are more than one type of ligands, the ligands are named according to alphabetical order, ignoring the prefixes. For example, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ is called tetraamminediaquacopper(II) ion.
- 5) i. For cationic complex, the name of the central metal ion is the same as its original name.
 - ii. For anionic complex, the name of the central metal ion follows this coding:

Element	part of a negative ion
vanadium	vanadate
titanium	titanate
chromium	chromate
manganese	manganate
iron	ferrate
cobalt	cobaltate
nickel	nickelate
copper	cuprate

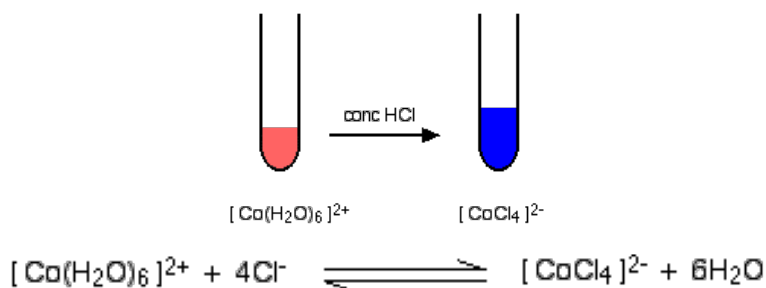
iii. For example, $[\text{CuCl}_4]^{2-}$ is called tetrachlorocuprate(II) ion. (It is yellow colour)

Ligand exchange

1) A ligand exchange reaction is a reaction in which **one ligand in a complex ion is replaced by a different one.**

2) **Example 1: Replacing water with chloride ions.**

i. When concentrated hydrochloric acid is added to a solution containing hexaaquacobalt(II) ions, the solution turns from pink to dark rich blue. The six water molecules are replaced by four chloride ions.



ii. Only four chloride ions are attached because chloride ions are larger, therefore six chloride ions cannot fit in around the central metal ion.

iii. The co-ordination number of the complex changes from 6 to 4. The geometry of ligands around changes from octahedral to tetrahedral.

iv. By Le Chatelier's principle, the process can be reversed by adding water to it.

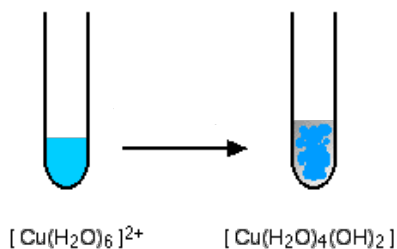
3) **Example 2: Replacing water with ammonia.**

i. The ammonia can **act as a base and also a ligand.** This is because **hexaaqua- ions are acidic.**

ii. The acidity of hexaaqua- ions is due to the electron pair in the water molecule being pulled towards the central positive charge, making the hydrogen more positive, and easily lost.

Stage 1: Ammonia as a base (Acid-base reaction)

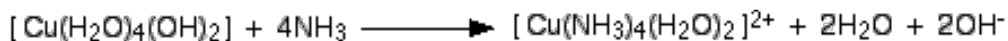
iii. When small amount of ammonia is added, hydrogen ions from the water are pulled out, leaving hydroxide ions.



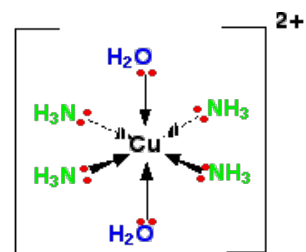
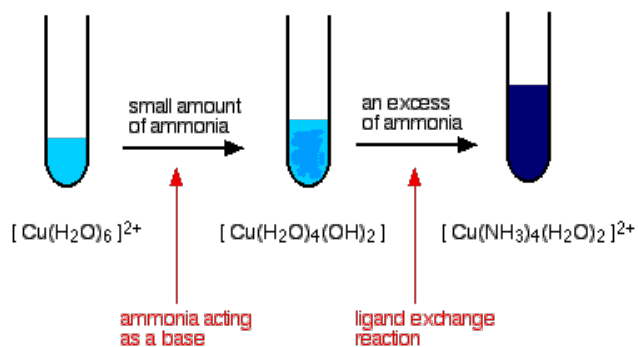
iv. **A precipitate will be formed** when two hydrogen ions have been removed. This is because a **neutral complex** is produced and it is unattractive to water molecules. Hence, it is no longer soluble in water.

Stage 2: Ammonia as a ligand (ligand exchange reaction)

v. When excess ammonia is added, **the precipitate dissolves**. The ammonia replaces water as a ligand to give tetraammineaquaacopper(II) ions. Notice that only 4 of the 6 water molecules are replaced.



Overall reaction:



the tetraammineaquaacopper(II) ion

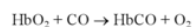
4) Certain ligands are stronger than other and **central metal ions generally prefer to be bonded to stronger ligands**. Therefore a ligand exchange reaction may not happen if the new ligand is weaker than the original ligand.

A red colour is observed when $\text{KSCN}(\text{aq})$, is added to a solution of the complex $[\text{FeCl}_4]^-$, but no such red colour is formed when $\text{KSCN}(\text{aq})$ is added to a solution of the complex $[\text{Fe}(\text{CN})_6]^{3-}$.

- Relative stability of complexes: $[\text{Fe}(\text{CN})_6]^{3-} > [\text{Fe}(\text{SCN})_6]^{3-} > [\text{FeCl}_4]^-$.
- When $\text{KSCN}(\text{aq})$ is added to a solution of $[\text{FeCl}_4]^-$, Cl^- ligands are replaced by the stronger SCN^- ligands and so, a red colour is observed due to the formation of the *more stable* $[\text{Fe}(\text{SCN})_6]^{3-}$ complex.
- When $\text{KSCN}(\text{aq})$ is added to a solution of $[\text{Fe}(\text{CN})_6]^{3-}$, no such red colour is formed because CN^- ligands are stronger than SCN^- ligands and so, are not replaced; i.e. $[\text{Fe}(\text{SCN})_6]^{3-}$ complex is not produced.

Ligand exchange (CO/O_2) in haemoglobin

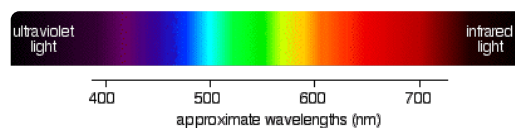
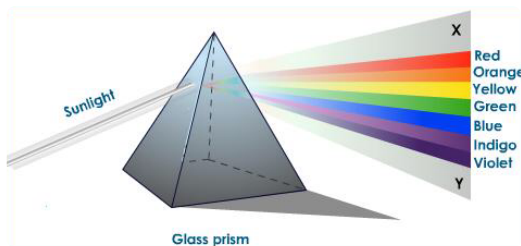
Ligands such as *carbon monoxide* (CO) forms dative bond with iron atom in haemoglobin more readily than O_2 molecule (since iron-CO bond is *stronger* than iron- O_2 bond); i.e. CO *displaces the oxygen* in oxyhaemoglobin (HbO_2) to form carboxyhaemoglobin (HbCO).



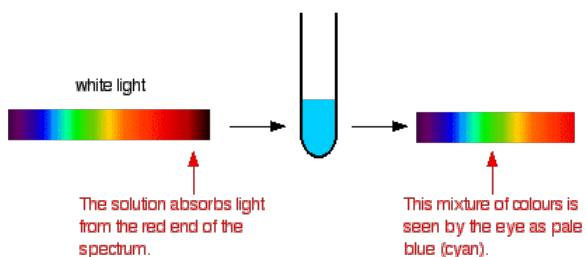
- This consequently cuts down the supply of oxygen to the body and so, accounts for the toxic nature of carbon monoxide.
- A patient suffering from carbon monoxide poisoning can be treated by being given pure oxygen to breathe. This treatment is effective because pure oxygen displaces carbon monoxide by a *mass action effect*.

Colour of complexes

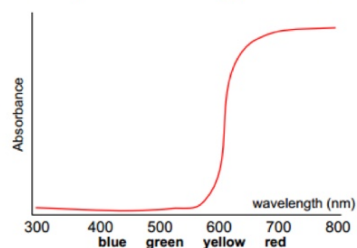
- 1) Visible light is the visible part of the electromagnetic spectrum which has wavelengths between 400 nm to 700 nm.
- 2) White light is composed of **all the wavelengths** in the visible part of the electromagnetic spectrum. When white light is passed through a prism, it splits into its constituent colours. This phenomenon is known as dispersion of light.



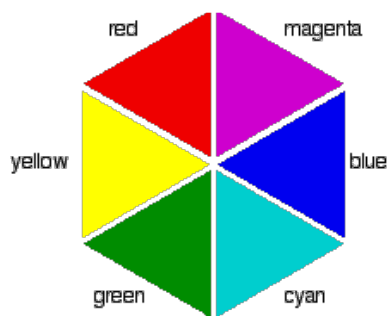
- 3) When white light passes through copper(II) sulfate, CuSO_4 solution, visible light with wavelengths in the red and yellow region is absorbed. The unabsorbed ones combine to give a pale blue(cyan) colour.



a solution of copper(II)sulphate is blue because red and yellow wavelengths are absorbed

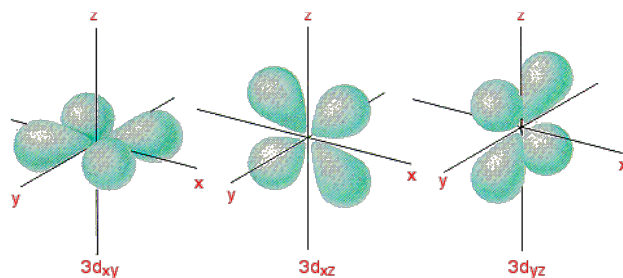


- 4) The colour we see is the **complementary colour of the wavelength(colour) of the light absorbed by the substances**. The complementary colour wheel can be used to **estimate** the colour of a substance. Colours on opposite sites are complementary colours.

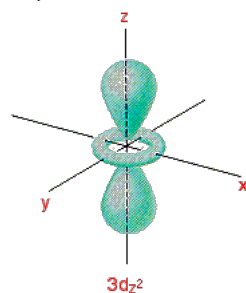


Shapes of d-orbitals

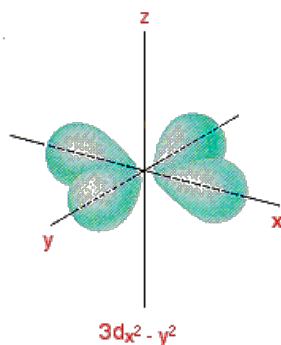
- 1) There are five types of d-orbitals, named **d_{xy} , d_{xz} , d_{yz} , d_{z^2} and $d_{x^2-y^2}$** .
- 2) i. d_{xy} , d_{xz} and d_{yz} have the 'lobes' in the x-y, x-z and y-z planes respectively. Note that the 'lobes' does not touch the axes, they are located between the axes.



- ii. d_{z^2} has the 'lobes' along the z-axis, with a 'collar'.



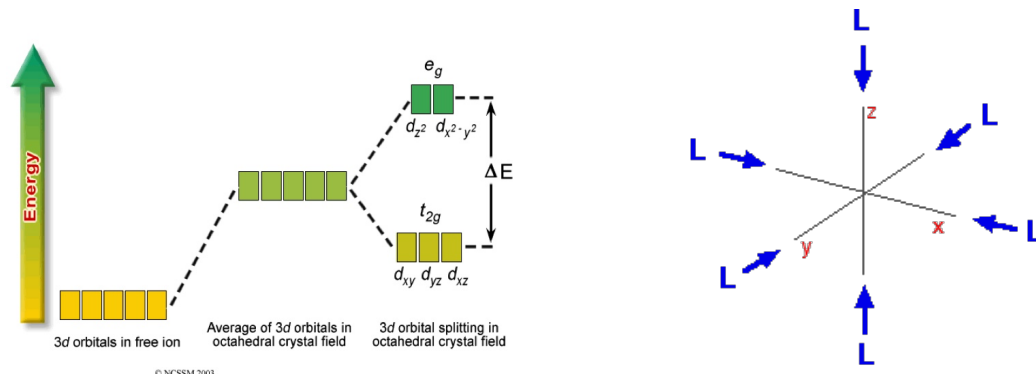
- iii. $d_{x^2-y^2}$ has the 'lobes' along the x- and y-axes.



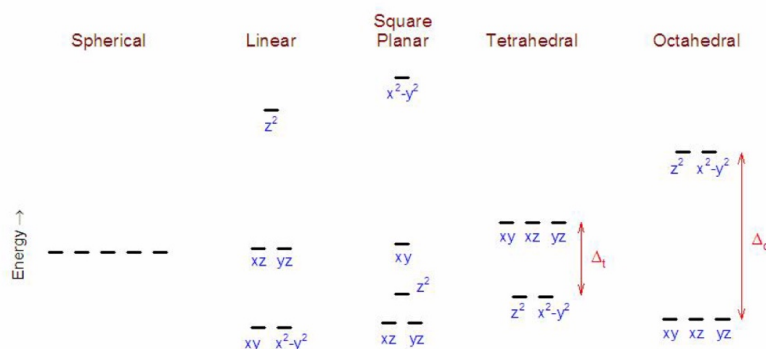
Factors affecting the colour of complexes

- 1) The colour of a complex ion depends on the wavelength(or frequency) of the visible light absorbed. This in turn depends on the **energy gap, ΔE between the two groups of d-orbitals**(see below).

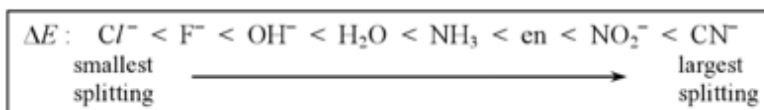
- 2) For an octahedral complex:
- The central metal ion has five degenerate d-orbitals. They **split into two groups**, **two with higher energy and the other three with lower** when ligands are attached to it.
 - This is because as the lone pairs on the ligands approach the central metal ion, the **d-electrons in the central metal ion are repelled**.
 - Due to the shape of the octahedral complex, the d-electrons repelled are the ones in the **d_{z^2} and $d_{x^2-y^2}$ orbitals**, and these orbitals will have higher energy.



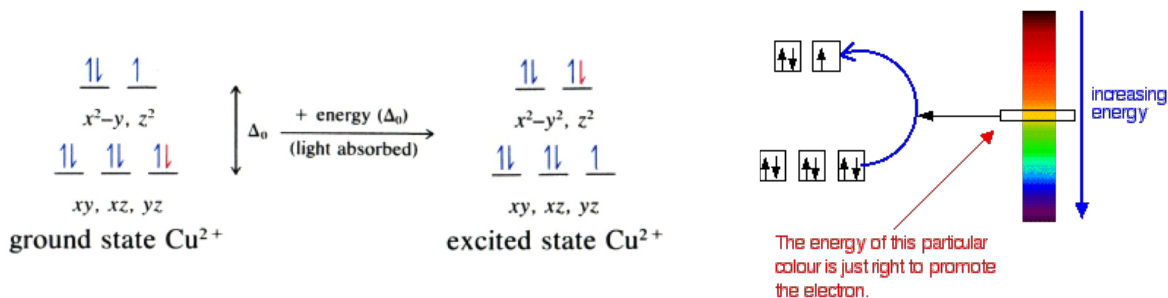
3) Other shapes have the splitting as below(not required in A-levels).



- 4) The size of the energy gap, ΔE depends on:
- the oxidation number of the central metal ion.**
 - In general, the higher the oxidation state of the central metal ion, the larger the size of ΔE .
 - the nature of ligands.**
 - In general, the splitting, ΔE is larger if the lone pair comes from a less electronegative atom.



- 5) The origin of colour of complexes:
- As the electromagnetic radiation (photons) with frequencies within the visible region of the electromagnetic spectrum passes through the complex, some of the photons are absorbed.
 - The photon absorbed **must have energy equal to the energy gap of the two groups of d-orbitals**, which is given by $\Delta E = hf$.
 - The absorbed energy is used **to promote an electron from a lower energy d-orbital to a higher energy one**. This is called **d-d transition**.



- The colour of the complex is the result of the unabsorbed frequencies of light combining. It can then be estimated using the complementary colour wheel.
- 6) The reason why different complexes have different colours is because **they all have different energy gap size, ΔE** . The incoming photon must have frequency exactly equal to $\Delta E/h$ to be absorbed and be used to promote an electron. Different colours and wavelengths of light have different frequencies, which is why they have different colours.
- 7) Non-transition metal complexes are often not coloured because **they do not have partly-filled d-electrons**. Hence no photon is absorbed and no electron is promoted.
- 8) Note: for non-physics students:
- The higher the frequency, f of light (photon), the higher its energy, which is given by $\Delta E = hf$, where h is the Planck's constant.
 - There is an inverse relationship between frequency, f and wavelength, λ , which is given by $c = f\lambda$, where c is the speed of light.
 - In the visible spectrum, red light has the lowest energy and violet the highest.