Edexcel International A Level (IAL) Chemistry

Your notes

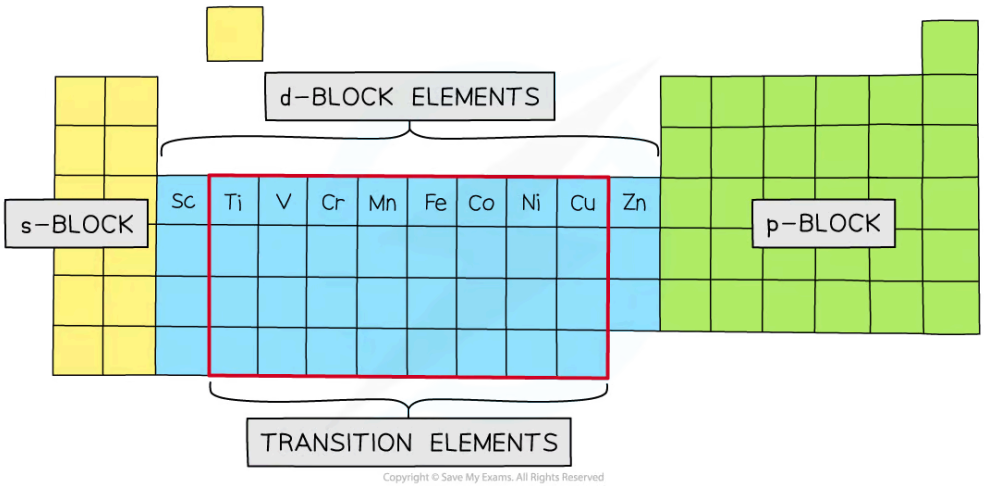
Transition Metals & Complexes

Contents

Your notes

Transition Metals – Electronic Configurations

- Transition metals are elements with an incomplete d-subshell that can form at least one stable ion with an incomplete d-subshell
- This definition distinguishes them from d-block elements, because scandium and zinc do not fit the definition
  - Scandium only forms the ion **Sc^{3+}**, configuration **[Ar] $3d^0$**
  - Zinc only forms the ion **Zn^{2+}**, configuration **[Ar] $3d^{10}$**
- The elements of the first transition series are therefore titanium to copper



The transition elements and the d-block elements

Electron Configuration

- The full electronic configuration of the first d-series transition metals is shown in the table below
- Following the **Aufbau Principle** electrons occupy the lowest energy subshells first
- The 4s overlaps with the 3d subshell so the 4s is filled first
- Remember that you can abbreviate the first five subshells, 1s-3p, as **[Ar]** representing the configuration of argon(known as the argon core)

Table showing the Electronic Configuration of the First d-series Transition Elements

Your notes

Element	Electronic Configuration
Ti	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
V	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$
Cr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
Mn	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
Fe	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
Co	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$
Ni	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
Cu	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

- From AS Chemistry you should recall two exceptions to the Aufbau Principle, chromium and copper
- In both cases an electron is promoted from the 4s to the 3d to achieve a half full and full d-subshell, respectively
- Chromium and copper have the following electron configurations, which are different to what you may expect:
  - Cr is [Ar] $3d^5\ 4s^1$ **not** [Ar] $3d^4\ 4s^2$
  - Cu is [Ar] $3d^{10}\ 4s^1$ **not** [Ar] $3d^9\ 4s^2$
- This is because the [Ar] $3d^5\ 4s^1$ and [Ar] $3d^{10}\ 4s^1$ configurations are **energetically more stable**

Worked Example

Writing electronic configuration of transition element ions

State the full electronic configuration of the manganese(III) ion

Answer

Step 1: Write out the electron configuration of the atom first:

Mn atomic number = 25

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

2 + 2 + 6 + 2 + 6 + 2 + 5 = 25 electrons

Step 2: Subtract the appropriate number of electrons starting from the 4s subshell

Mn(III) = 22 electrons

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$

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General properties

- Although the **transition elements** are metals, they have some properties unlike those of other metals on the periodic table, such as:
  - Variable **oxidation states**
  - Form **complex ions**
  - Form **coloured compounds**
  - Behave as **catalysts**

Oxidation Number

- Like other metals on the periodic table, the transition elements will lose electrons to form positively charged ions
- However, unlike other metals, transition elements can form more than one positive ion
  - They are said to have **variable oxidation states**
- Because of this, Roman numerals are used to indicate the oxidation state on the metal ion
- For example, the metal sodium (Na) will only form Na^+ ions (no Roman numerals are needed, as the ion formed by Na will always have an oxidation state of +1)
  - The transition metal iron (Fe) can form Fe^{2+} (Fe(II)) **and** Fe^{3+} (Fe(III)) ions
- When transition elements forms ions they lose electrons from the **4s** subshell first
- This is because when the orbitals are occupied, the repulsion between electrons pushes the **4s** into a higher energy state so that it now becomes slightly higher in energy than the **3d** subshell
  - The **4s** is now the outer shell and loses electrons first
- The loss of the **4s** electrons means that **+2** is a common oxidation state in transition metals
- The reason why the transition metals have variable oxidation states all comes down to energy

Table showing the Common Oxidation States of Transition Elements

Transition element	Common oxidation states
Ti	+2, +3, +4
V	+2, +3, +4, +5
Cr	+2, +3, +6
Mn	+2, +4, +6, +7
Fe	+2, +3
Co	+2, +3
Ni	+2, +3, +4
Cu	+1, +2

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Describing Complexes

- Transition element ions can form complexes which consist of a **central metal ion** and **ligands**
- A ligand is a molecule or ion that forms a dative covalent / co-ordinate bond with a transition metal by donating a pair of electrons to the bond
  - This is the definition of a Lewis base - electron pair donor
- This means ligands have a negative charge or a lone pair of electrons capable of being donated
  - This definition may seem familiar: a ligand is the same as a **nucleophile**
- Different **ligands** can form different numbers of dative covalent / co-ordinate bonds to the central metal ion in a complex
  - Some ligands can form **one** dative covalent / co-ordinate bond to the central metal ion
  - Other ligands can form **two** dative covalent / co-ordinate bonds, and some can form **multiple** dative covalent / co-ordinate bonds
- **Co-ordination number** is number of dative covalent / co-ordinate bonds to the central metal atom or ion

Common Ligands

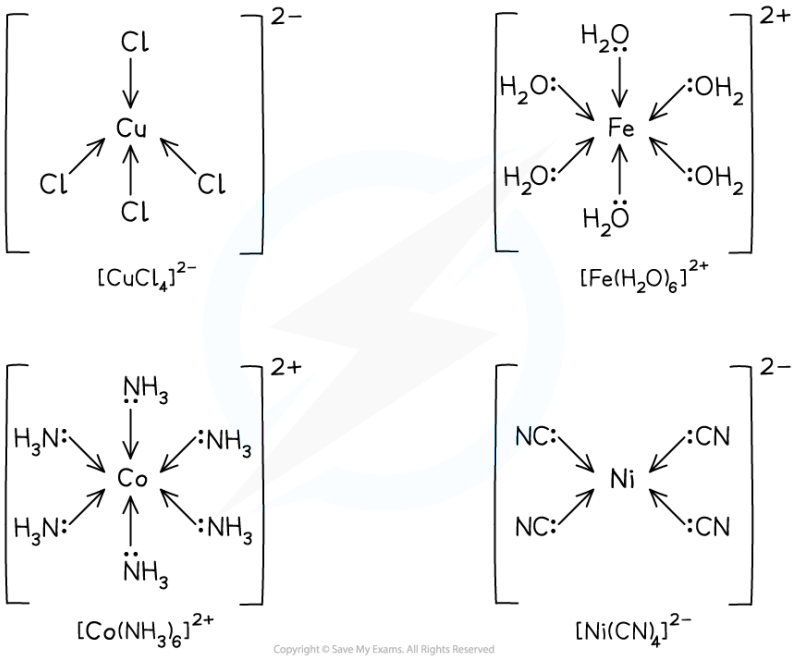
- Water molecules frequently act as ligands. Each water molecule makes a single bond with the metal ion using one of the lone pairs on the oxygen atom
- The lone pair is donated to the partially filled d-subshell of the transition metal ion

Table Showing Examples of Common Monodentate Ligands

Name of Ligand	Formula of Ligand
Water	H_2O
Ammonia	NH_3
Chloride	Cl^-
Cyanide	CN^-
Hydroxide	OH^-

Representing complex ions

- Square brackets are used to group together the ligands and metal ion in a representation of the geometrical arrangement
- The overall charge on the complex ion is the sum of the oxidation states of all the species present
- If the ligands are neutral then the overall charge will be the same as the oxidation state of the metal ion



Examples of complexes with monodentate ligands

Naming complexes

- Complexes are named in the following way
- If the overall ion is a cation then the nomenclature is:

Prefix for number of ligands/ligand name/element/oxidation number

- The prefixes are the same ones used in organic chemistry: di, tetra, hexa for 2, 4 & 6 respectively (3 & 5 are rarely encountered except in mixed ligand complexes)
- If the overall ion is an anion, the name of element is modified to have the name ending 'ate' and sometimes Latin word stems are used
  - **tetrachlorcuprate(II)**
  - **hexaaquairon(II)**
  - **hexaamminecobalt(II)**
  - **tetracyanonickelate(II)**
- Using the examples in the illustration above, the names are:

Your notes

- Notice in these examples that
  - cuprate(Latin - cuprum) and nickelate are used in place of copper and nickel as they are anions
  - Ammonia takes the prefix ammine as a ligand, which is spelt with a double 'm' unlike the functional group amine

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Colour in Aqueous ions

Perception of colour

- Most transition metal compounds appear coloured. This is because they absorb energy corresponding to certain parts of the visible **electromagnetic spectrum**
- The colour that is seen is made up of the parts of the visible spectrum that aren't absorbed
- For example, a green compound will absorb all frequencies of the spectrum apart from green light, which is transmitted
- The colours absorbed are **complementary** to the colour observed

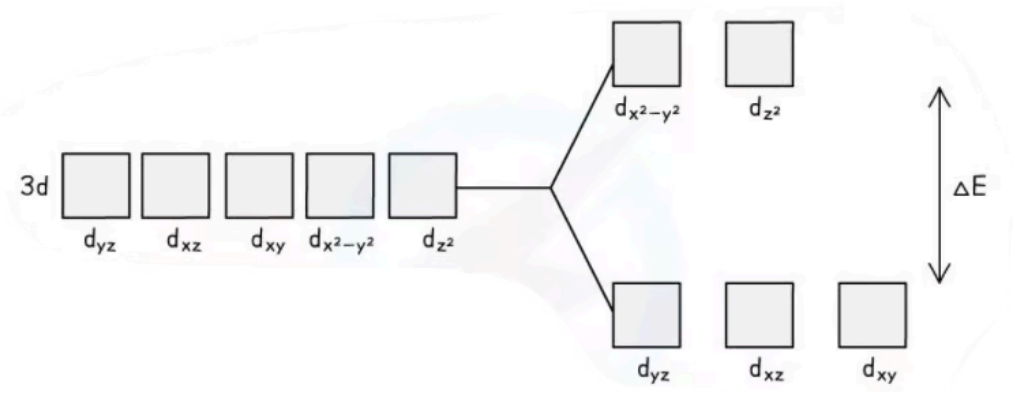
The colour wheel showing complementary colours in the visible light region of the electromagnetic spectrum

- Complementary colours are any two colours which are directly opposite each other in the colour wheel
  - For example, the complementary colour of red is green and the complementary colours of red-violet are yellow-green

Splitting of 3d energy levels

- In a transition metal atom, the five orbitals that make up the d-subshell all have the same energy.
- Ions that have completely filled 3d energy levels (such as Zn^{2+}) and ions that have no electrons in their 3d subshells (such as Sc^{3+}) are not coloured

- Transition metals have a partially filled 3d energy level
- When ligands attach to the central metal ion the energy level splits into two levels with slightly different energies
  - If one of the electrons in the lower energy level absorbs energy from the visible spectrum it can move to the higher energy level
  - This process is known as **promotion / excitation**
- The amount of energy absorbed depends on the difference between the energy levels
  - A larger energy difference means the electron absorbs more energy
- The amount of energy gained by the electron is directly proportional to the frequency of the absorbed light and inversely proportional to the wavelength



Upon bonding to ligands, the d orbitals of the transition element ion split into sets of orbitals with different energies

Colour Changes in Aqueous ions

The size of the splitting energy ΔE in the d-orbitals is influenced by the following four factors:

- **The size and type of ligands**
- **The nuclear charge and identity of the metal ion**
- **The oxidation state of the metal**
- **The shape of the complex**

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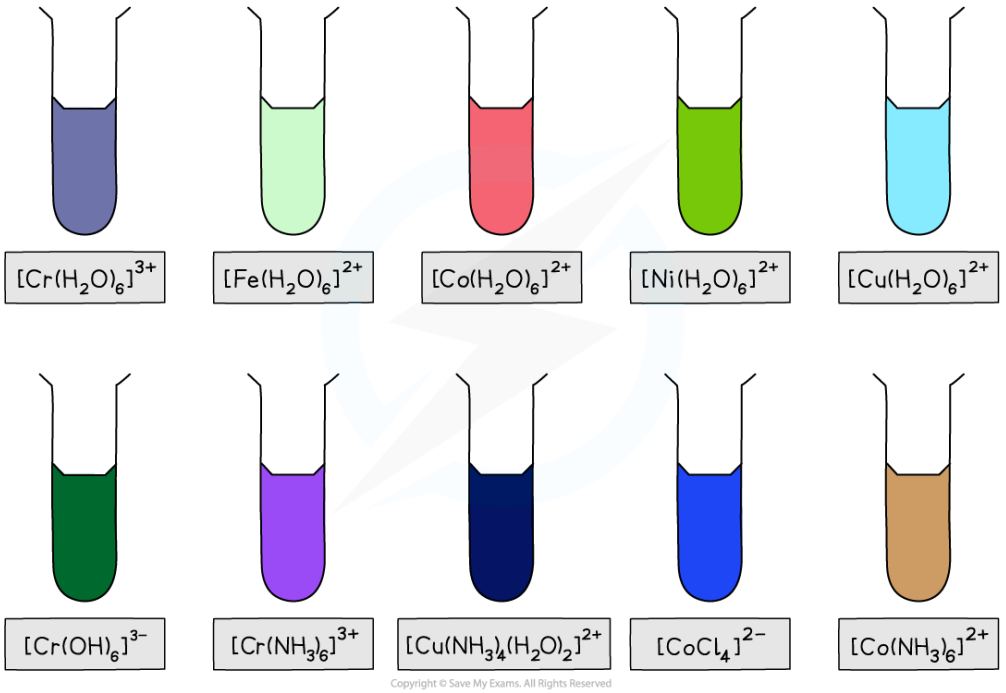

The large variety of coloured compounds is a defining characteristic of transition metals

Size and type of ligand

- The nature of the ligand influences the strength of the interaction between ligand and central metal ion
- Ligands vary in their charge density
- The greater the charge density; the more strongly the ligand interacts with the metal ion causing greater splitting of the d-orbitals
- The further it is then shifted towards the region of the spectrum where it absorbs higher energy
- As a result, a different colour of light is absorbed by the complex solution and a different **complementary colour** is observed
- This means that complexes with the same **transition elements ions,** but **different ligands,** can have different colours
  - For example, the $[Cu(H_2O)_6]^{2+}$ complex has a **light blue** colour
  - Whereas the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ has a **dark blue** colour despite the copper(II) ion having an oxidation state of +2 in both complexes

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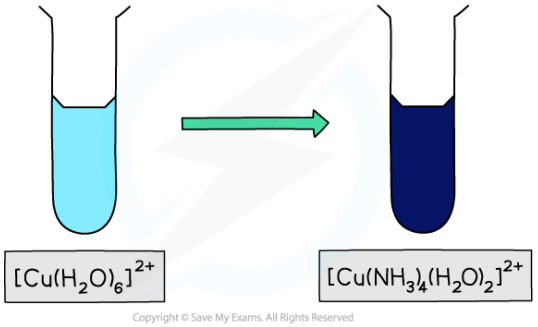

Ligand exchange of the water ligands by ammonia ligands causes a change in colour of the copper(II) complex solution

Oxidation number

- When the same metal has a higher oxidation number that will also create a stronger interaction with the ligands
- If you compare iron(II) and iron (III):
  - $[Fe(H_2O)_6]^{2+}$ absorbs in the red region and appears green
  - But, $[Fe(H_2O)_6]^{3+}$ absorbs in blue region and appears orange

Coordination number

- The change of colour in a complex is also partly due to the change in coordination number and geometry of the complex ion
- The splitting energy, ΔE, of the d-orbitals is affected by the relative orientation of the ligand as well as the d-orbitals
- Changing the coordination number generally involves changing the ligand as well, so it is a combination of these factors that alters the strength of the interactions
  - For example, the $[Cu(H_2O)_6]^{2+}$ complex has a **light blue** colour
  - Whereas the $[CuCl_4]^{2-}$ has a **yellow** colour due to the change in the ligand and the change in the coordination number from 6 to 4
    - In practice, there would be a change from light blue to green (due to a mixture of both ions) to yellow
  - Since the reaction is reversible, it can also go from yellow, $[CuCl_4]^{2-}$, to green to light blue, $[Cu(H_2O)_6]^{2+}$

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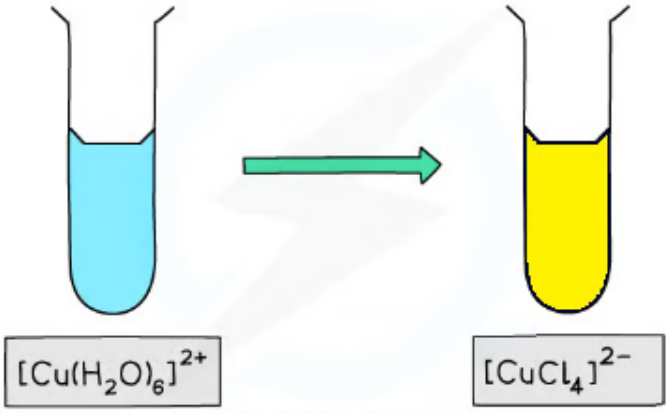

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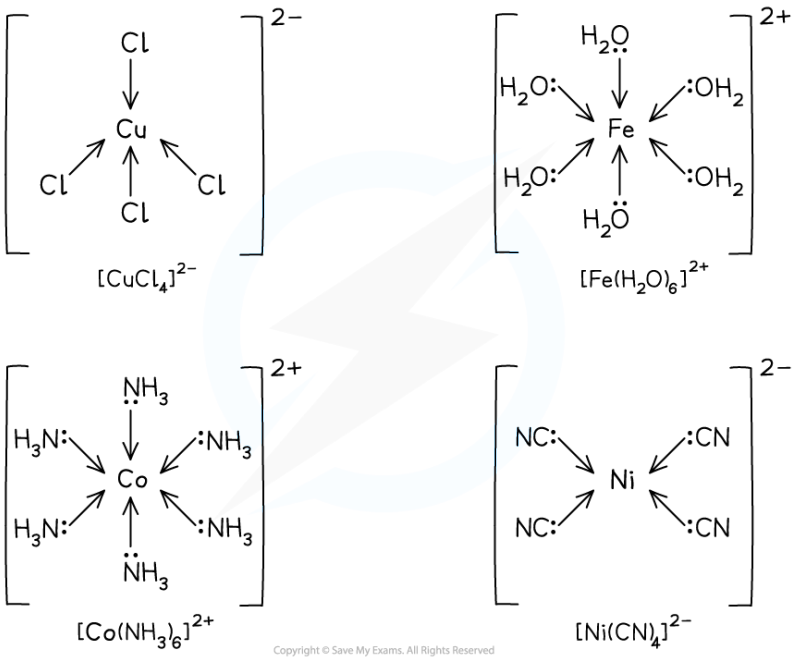
Monodentate ligands

- **Monodentate** ligands can form only **one** dative bond to the central metal ion
- This is because they have a single lone pair of electrons to form a dative bond with the metal ion
- Examples of monodentate ligands are:
  - Water (H_2O) molecules
  - Ammonia (NH_3) molecules
  - Chloride (Cl^-) ions
  - Cyanide (CN^-) ions



Examples of complexes with monodentate ligands

Bidentate & Multidentate Ligands

Bidentate Ligands

- **Bidentate** ligands can each form **two** dative bonds to the central metal ion
- This is because each ligand contains **two** atoms with lone pairs of electrons
- Examples of bidentate ligands are:
  - 1,2–diaminoethane ($H_2NCH_2CH_2NH_2$) which is also written as '**en**'

- Ethanedioate ion ($C_2O_4^{2-}$) which is sometimes written as **'ox'**

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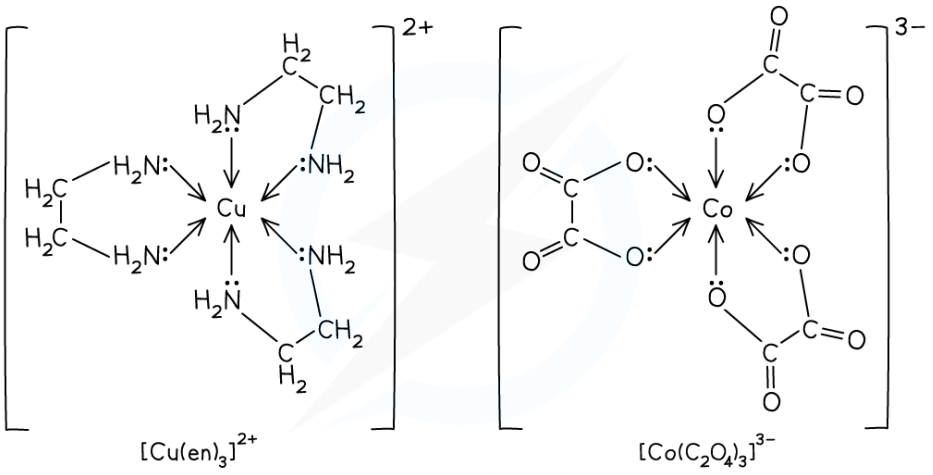
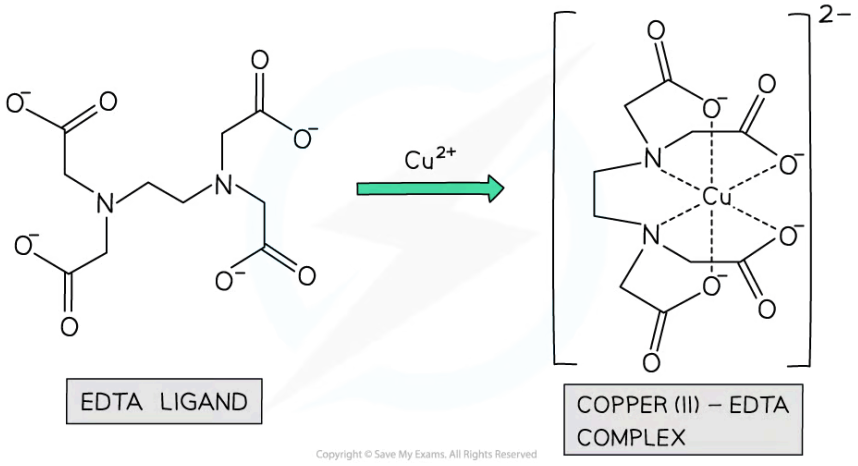


Examples of complexes with bidentate ligands

Multidentate Ligands

- Some ligands contain more than two atoms with lone pairs of electrons
- These ligands can form more than two dative bonds to the and are said to be **multidentate** ligands
- An example of a multidentate ligand is $EDTA^{4-}$, which is a **hexadentate** ligand as it forms 6 dative covalent bonds to the central metal ion



Example of a polydentate ligand complex

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Exchanging Ligands

- **Ligand exchange** (or **ligand substitution**) is when one **ligand** in a complex is replaced by another
- Ligand exchange forms a new complex that is **more stable** than the original one
- The ligands in the original complex can be **partially** or **entirely** substituted by others
- The complex ion can change its charge or remain the same depending on the ligand involved
- There are no changes in coordination number, or the geometry of the complex, if the ligands are of a **similar size**
- But, if the ligands are of a **different size**, for example water ligands and chloride ligands, then a change in coordination number and the geometry of the complex will occur
- Addition of a high concentration of chloride ions (from conc HCl or saturated NaCl) to an aqueous ion leads to a ligand substitution reaction.
- The Cl^- ligand is **larger** than the uncharged H_2O and NH_3 ligands so therefore ligand exchange can involve a change of co-ordination number
- For example when concentrated hydrochloric acid is added slowly and continuously to a copper(II) sulfate solution the colour changes from blue to green then finally yellow
- The equation for this reaction is

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$$

- We can see that all six water ligands have been replaced by four chloride ions
- This reaction involves a change in coordination number from 6 to 4
- Note that despite the charge on the complex changing from +2 to -2, there has been no change in oxidation number of the copper
- We can also see that this reaction is reversible, which helps to explain the observed colour change
  - The hexaaquacopper(II) ion is blue
  - The tetrachlorocuprate(II) ion is yellow
  - The green colour is due to a mixture of the blue and yellow complex ions
- A similar reaction also takes place with cobalt resulting in a blue solution and a change in coordination number from 6 to 4

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

Examiner Tips and Tricks

Be careful: If solid copper chloride (or any other metal) is dissolved in water it forms the aqueous $[Cu(H_2O)_6]^{2+}$ complex and not the chloride $[CuCl_4]^{2-}$ complex

Your notes

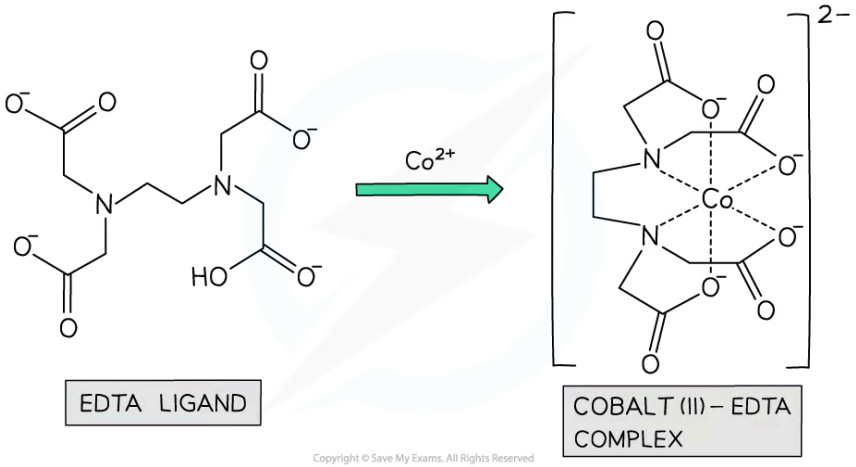
Entropy & Stability

- The replacement of monodentate ligands with bidentate and multidentate ligands in complex ions is called the **chelate effect**
- It is an energetically favourable reaction, meaning that $\Delta G^{\ominus}$ is negative
- The driving force behind the reaction is entropy
- The Gibbs equation reminds us of the link between enthalpy and entropy:

$$\Delta G^{\ominus} = \Delta H_{reaction}^{\ominus} - T\Delta S_{system}^{\ominus}$$

- Reactions in solution between aqueous ions usually come with relatively small enthalpy changes
- However, the entropy changes are always positive in chelation because the reactions produce a net increase in the number of particles
- A small enthalpy change and relative large positive entropy change generally ensures that the overall free energy change is negative
- For example, when EDTA chelates with aqueous cobalt(II) two reactants becomes seven product species

$$[Co(H_2O)_6]^{2+}(aq) + EDTA^{4-}(aq) \rightarrow [CoEDTA]^{2-}(aq) + 6H_2O(l)$$



The ligand EDTA readily chelates with aqueous transition metal ions in an energetically favourable reaction

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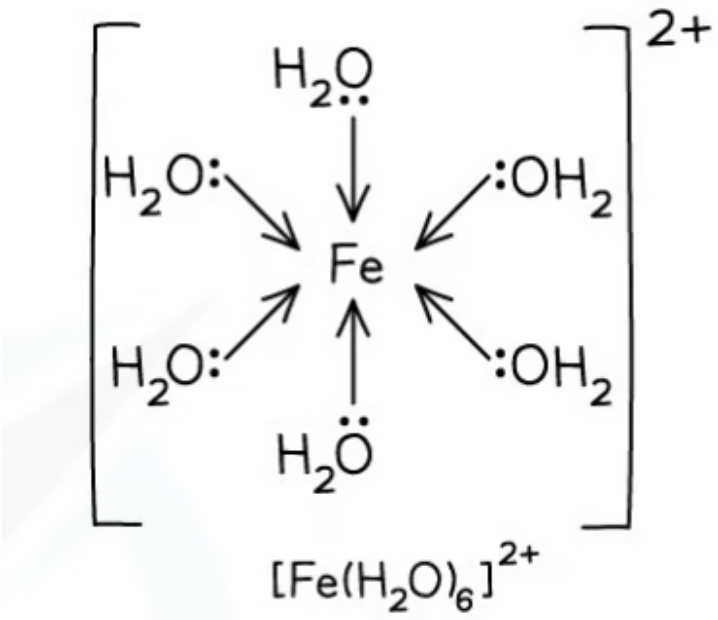
Octahedral & Tetrahedral Complexes

- **Octahedral** complexes are formed when a central metal atom or ion forms **six coordinate bonds**
- This could be six coordinate bonds with **six** small, **monodentate** ligands
  - Examples of such ligands are **water** and **ammonia** molecules and **hydroxide** and **thiocyanate** ions
  - As there are six ligands, these complexes are sometimes described as having **six-fold coordination**

Table Showing Examples of Common Monodentate Ligands

Name of Ligand	Formula of Ligand
Water	H_2O
Ammonia	NH_3
Chloride	Cl^-
Cyanide	CN^-
Hydroxide	OH^-



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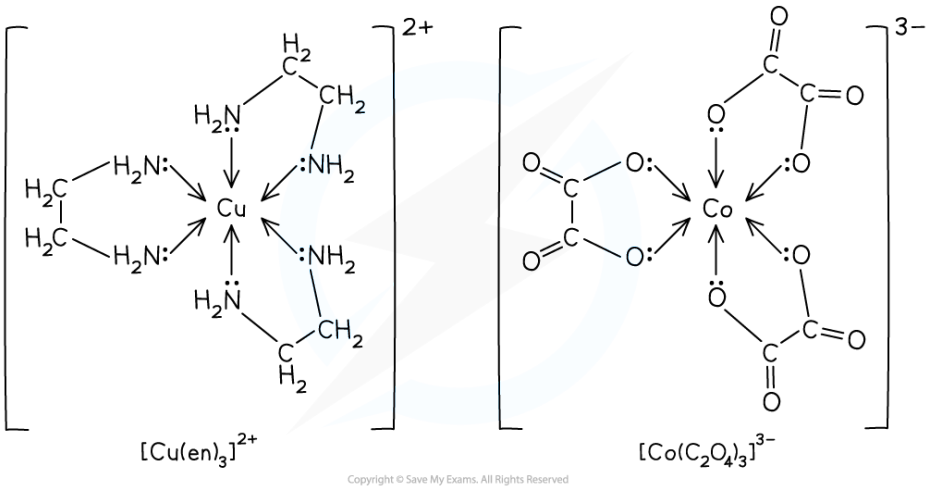
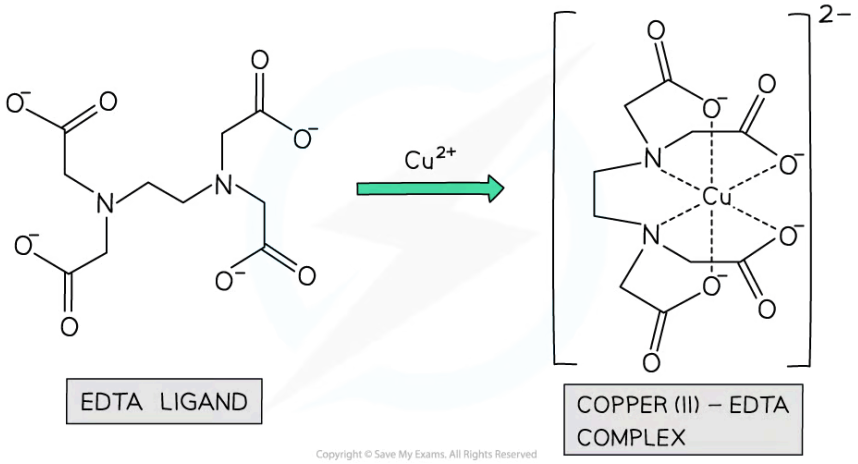
Example of an octahedral complex with monodentate ligands

- It could be six-coordinate bonds with **three bidentate** ligands
  - Each bidentate ligand will form two coordinate bonds, meaning six-coordinate bonds in total
  - Examples of these ligands are **1,2-diaminoethane** and the **ethanedioate ion**



Example of an octahedral complex with bidentate ligands

- It could be six-coordinate bonds with **one multidentate** ligand
  - The multidentate ligand, for example, $EDTA^{4-}$, forms all six-coordinate bonds



Example of an octahedral complex with a polydentate ligand

- The bond angles in an octahedral complex are 90°
- The **coordination number** of a complex is the number of dative bonds formed between the central metal ion and the ligands
  - Since there are 6 dative bonds, the coordination number for the complex is 6

Your notes

Examiner Tips and Tricks

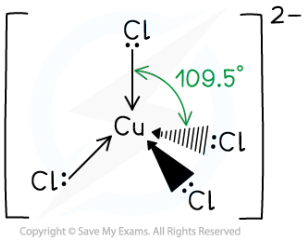
Electron pair repulsion theory can be extended to predict and explain the shape of transition metal complexes. The only difference is you should ignore the 3d elctrons in the transition metal ion and overall charge on the complex - just count the number of electron pairs donated by the ligands.

Changes to the central metal ion

- The main example of the central metal ion changing oxidation state is when Fe^{2+} is oxidised to form Fe^{3+}
  - $Fe^{2+} \rightarrow Fe^{3+} + e^-$
- Hexaaquairon(II) is a pale green solution, which slowly oxidises on standing in air to give a yellow solution of hexaaquairon(III) ions.
  - $[Fe(H_2O)_6]^{2+} \rightarrow [Fe(H_2O)_6]^{3+}$
- The same oxidation reaction can be achieved with different iron(II) complex ions
  - These are often performed by bubbling oxidising agents, such as chlorine gas, through a solution of the iron(II) complex ion
  - For example, bubbling chlorine gas through a yellow solution of potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$, results in the formation of a red solution of potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$
  - $2K_4[Fe(CN)_6] + Cl_2 \rightarrow 2K_3[Fe(CN)_6] + 2K^+ + 2Cl^-$

Tetrahedral complexes

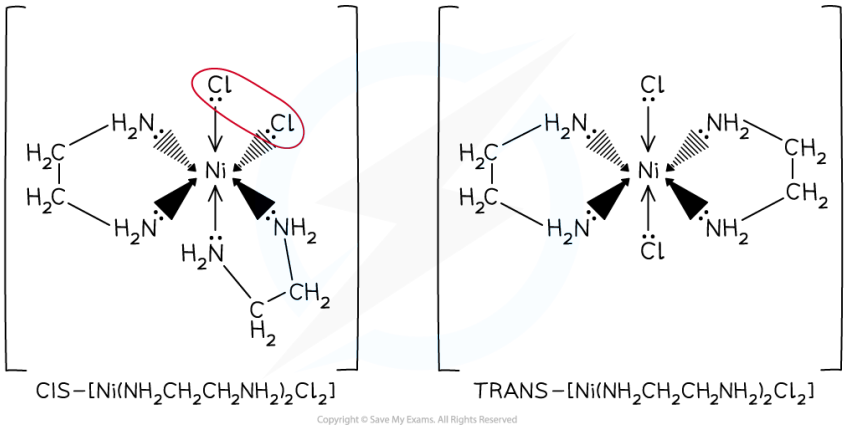
- When there are **four coordinate bonds** the complexes often have a **tetrahedral** shape
  - Complexes with four **chloride ions** most commonly adopt this geometry
  - Chloride ligands are large, so only four will fit around the central metal ion
- The bond angles in tetrahedral complexes are 109.5°



Example of a tetrahedral complex

Isomerism in transition element complexes

- Transition element complexes can exhibit **stereoisomerism**
- Even though transition element complexes do not have a **double bond**, they can still have **geometrical isomers**
- **Square planar** and **octahedral** complexes with **two pairs of different** ligands exhibit *cis-trans* isomerism
- Examples of octahedral complexes that exhibit geometrical isomerism are the $[Co(NH_3)_4(H_2O)_2]^{2+}$ and $[Ni(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+}$ complexes
  - $[Ni(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+}$ can also be written as $[Ni(en)_2(H_2O)_2]^{2+}$
- Like in the square planar complexes such as cis-platin and trans-platin, if the two 'different' ligands are next to each other then that is the 'cis' isomer, and if the two 'different' ligands are opposite each other then this is the 'trans' isomer
  - In $[Co(NH_3)_4(H_2O)_2]^{2+}$, the two water ligands are next door to each other in the cis isomer and are opposite each other in the trans isomer



Octahedral transition metal complexes exhibiting geometrical isomerism

Optical isomerism

- **Octahedral** complexes with **bidentate ligands** also have **optical isomers**
- This means that the two forms are **non-superimposable mirror images** of each other
  - They have no plane of symmetry, and one image cannot be placed directly on top of the other
- The optical isomers only differ in their ability to rotate the plane of polarised light in opposite directions
- Examples of octahedral complexes that have optical isomers are the $[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}$and $[Ni(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+}$ complexes
  - The ligand $H_2NCH_2CH_2NH_2$ can also be written as 'en' instead

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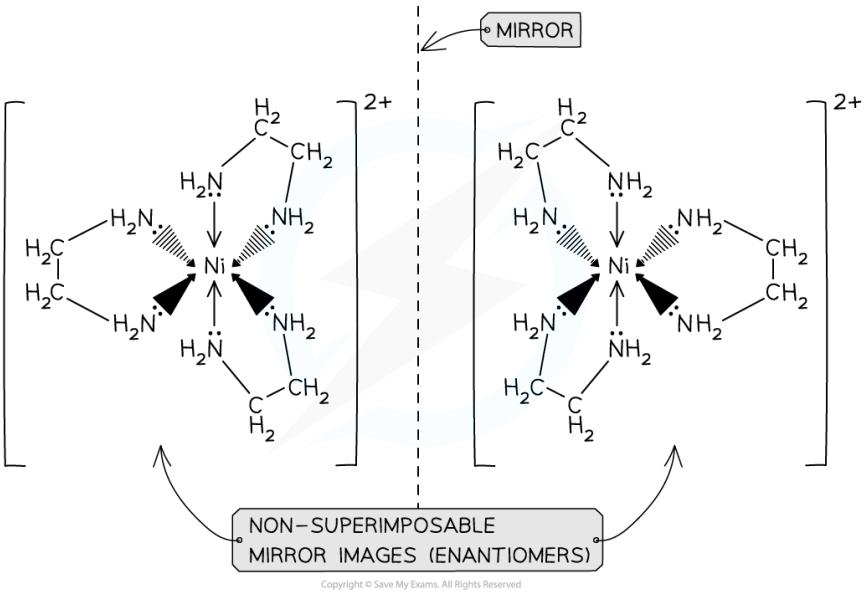

Octahedral transition metal complexes exhibiting optical isomerism

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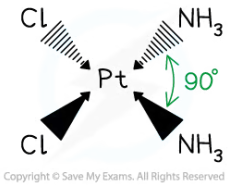
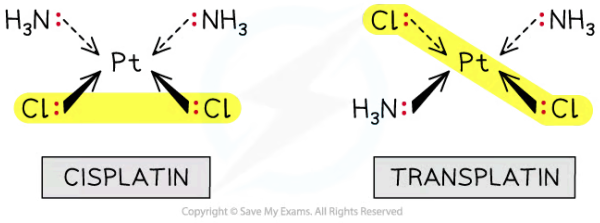
Square Planar Complexes

- Sometimes, complexes with **four coordinate bonds** may adopt a **square planar** geometry instead of a tetrahedral one
  - Cyanide ions (CN^-) are the most common ligands to adopt this geometry
  - An example of a square planar complex is **cisplatin**
- The bond angles in a square planar complex are 90°



Cisplatin is an example of a square planar complex

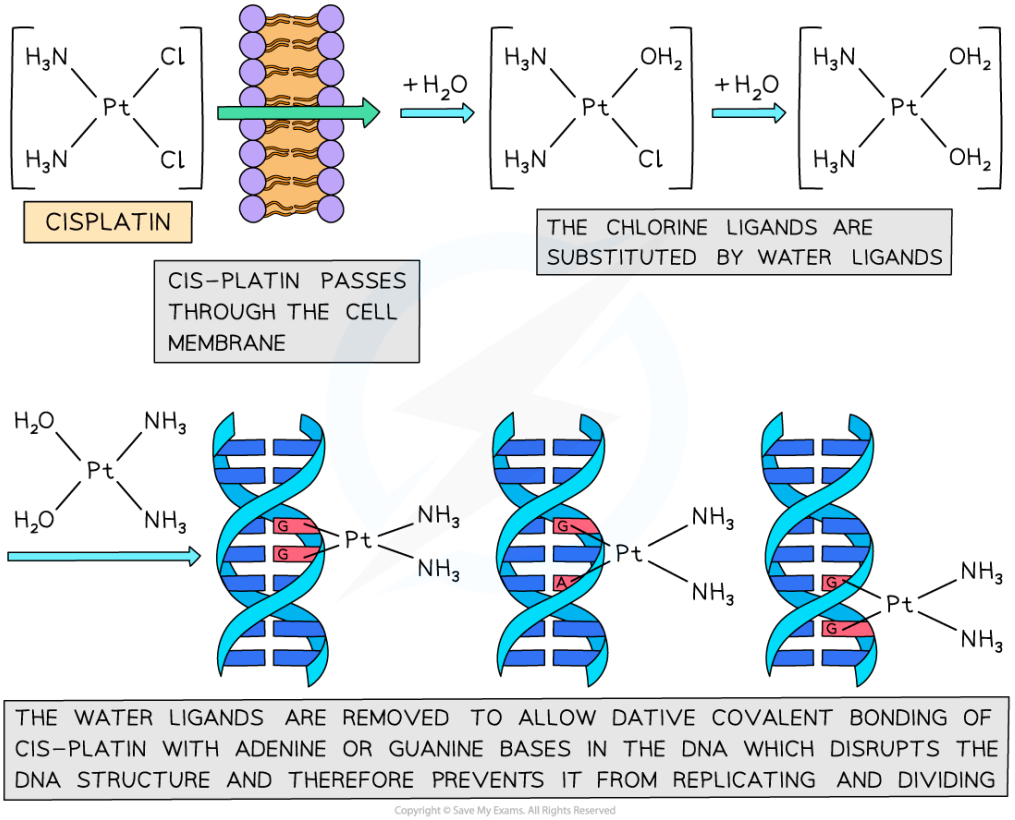
- In the 1960s the drug cis-platin was discovered, which has been extremely effective in treating a number of different types cancer such as testicular, ovarian, cervical, breast, lung and brain cancer
- Cancer cells grow and replicate much faster than normal cells
- Cis-platin is a square planar molecule that has a geometric isomer with the side groups in different positions
- Cis-platin has beneficial medical effects by binding to DNA in cancer cells, *trans*-platin cannot be used in cancer treatment



Cis-platin is an example of a square planar transition element complex that exhibits geometrical isomerism

- The cis-platin works by binding to the nitrogen atoms on the bases in DNA
- The cis-platin passes through the cell membrane and undergoes ligand exchange where the chlorines are replaced by water molecules
- The nitrogen is a better ligand than water and forms dative covalent bonds with the cis-platin

- The cis-platin distorts the shape of the DNA and prevents the DNA from replicating



The process by which cis-platin binds to DNA and prevents replication

Adverse Effects

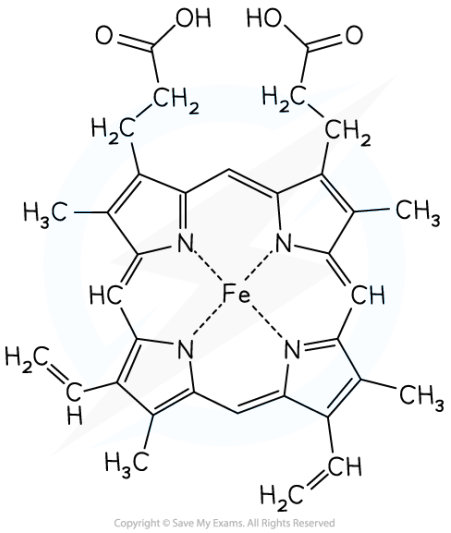
- Cis-platin binds to healthy cells as well as cancerous cells, but affects cancer cells more as they are replicating faster
- Unfortunately, this means that other healthy cells which replicate quickly, such as hair follicles, are also affected by cis-platin
- This is why hair loss is a side-effect of people undergoing cancer treatment
- Despite this drawback, cisplatin is a highly effective drug and society needs to find a balance between the adverse effects of drugs and their therapeutic value
- New therapeutic pathways are constantly under development that aim to deliver drugs that target cancer cells while leaving healthy cells untouched

Your notes

Your notes

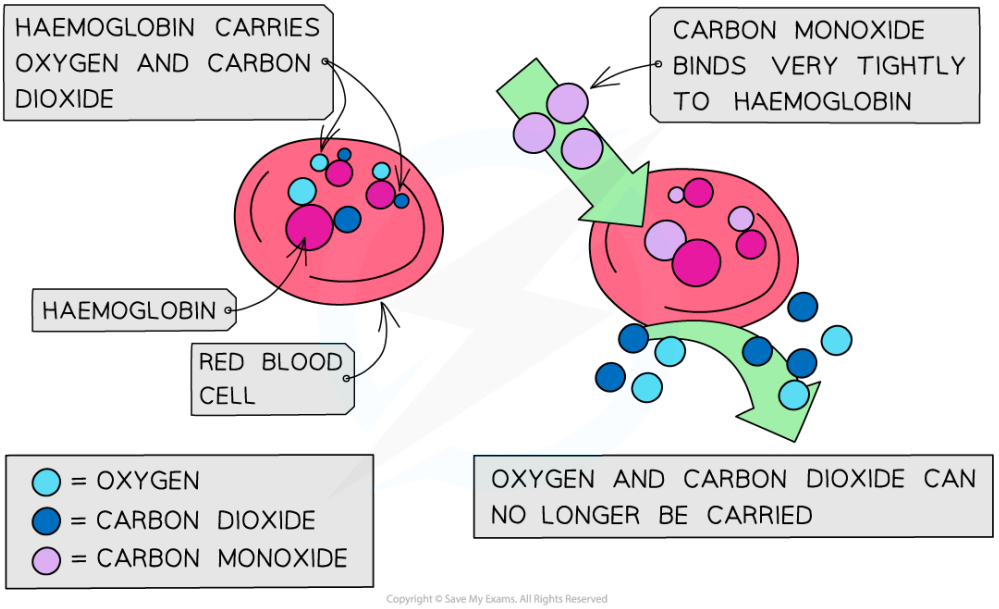
Haemoglobin & Ligand Exchange

- Haemoglobin is one of nature's complexes using a transition metal ion
- The haem molecule is a complex with iron(II) at its centre
- The haemoglobin complex contains a multidentate ligand made up of four haem groups
  - These consist of mostly carbon and hydrogen atoms
  - Each haem group has a nitrogen atom forming a dative covalent bond to the Fe^{2+} ion in a square planar complex
- There is a fifth dative bond from the protein (globin) to the Fe^{2+} ion
- Oxygen atoms form a dative covalent bond with the iron(II) which enables oxygen molecules to be transported around the body in the blood



The haem molecule with iron(II) at its centre

- Oxygen molecules are not very good ligands and bond weakly to the iron(II)
- The weak bonds allows them to break off easily and be transported into cells



Your notes

Examiner Tips and Tricks

You do not need to be familiar with the structure of the haem group

- Carbon monoxide is toxic because it is a better ligand than oxygen and binds strongly to the iron(II) preventing oxygen from being carried to the cells
  - The reason for the strength of the carbon monoxide binding more strongly to haemoglobin is that it forms stronger dative covalent bonds, although it can be displaced from heamoglobin
- If oxygen attached to the haemoglobin (oxyhaemoglobin) is replaced by carbon monoxide (carboxyhaemoglobin), a darker red colour is produced in the haem complex
  - This is a sign of carbon monoxide poisoning
- The condition anaemia occurs when a person does not have enough haemoglobin in their blood due to a loss of blood or deficiency in iron
  - Deficiency in iron can be restored by taking iron sulfate tables in the diet