

# OCR A Chemistry A-level

## Module 5.3: Transition Elements Detailed Notes

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## 5.3.1 Transition Elements

### Properties

The transition metals are elements in the **d-block** of the periodic table that form one or more **stable ions** with a **partially filled d-orbital**. Transition metals lose electrons to form positive ions, with the s-orbital electrons being removed first.

All transition metals have **similar physical properties** including similar atomic radius, high densities and high melting points. In addition, they all have **special chemical properties**:

- Form complexes
- Form coloured ions in solution
- Variable oxidation states
- Good catalysts

Transition metals have **variable oxidation states** because the 4s and 3d orbitals are very **close** in energy levels. This not only makes it possible for electrons to be lost from both orbitals relatively easily, but also means the remaining electrons can form **stable configurations**.

*Examples:*

**Scandium** - atomic number 21 -  $[\text{Ar}] 4s^2 3d^1$

**Nickel** - atomic number 28 -  $[\text{Ar}] 4s^2 3d^8$

**Iron** - atomic number 26 -  $[\text{Ar}] 4s^2 3d^6$

**Fe<sup>2+</sup>** - atomic number 26 (=24 electrons) -  $[\text{Ar}] 4s^0 3d^6$  or  $[\text{Ar}] 3d^6$

**Vanadium** - atomic number 23 -  $[\text{Ar}] 4s^2 3d^3$

**V<sup>2+</sup>** - atomic number 23 (=21 electrons) -  $[\text{Ar}] 4s^0 3d^3$  or  $[\text{Ar}] 3d^3$

### Exceptions

**Copper** and **chromium** are exceptions to the rule that the 4s subshell is filled before the 3d subshell.

- Chromium has 24 electrons. According to the above rule, its electron configuration should be  $[\text{Ar}] 4s^2 3d^4$ . However, it is more stable if one of the electrons from the 4s orbital is instead in the 3d orbital, **so that each 3d orbital contains one unpaired electron**. Therefore, the actual electron configuration of chromium is  $[\text{Ar}] 4s^1 3d^5$ .
- Similarly with copper, instead of the electron configuration  $[\text{Ar}] 4s^2 3d^9$ , it is more stable if the 3d subshell is **completely filled**. Therefore, one of the 4s electrons is moved to a 3d orbital to give the electron configuration  $[\text{Ar}] 4s^1 3d^{10}$ .





## Catalysts

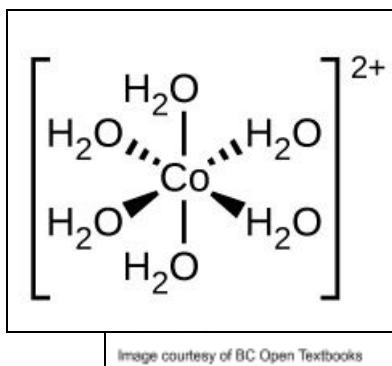
Some of the transition metal elements and compounds display **catalytic behaviour**. This can make transition metals and their compounds very useful in the industrial manufacture of chemicals.  $\text{Cu}^{2+}$  is used as a catalyst for the reaction of Zn with acids and  $\text{MnO}_2$  is used as a catalyst for decomposition of  $\text{H}_2\text{O}_2$ . It is beneficial to use catalysts in industry to reduce energy usage, however, there is also an increased risk from toxicity of many transition metals.

## Ligands and Complex Ions

### Complexes

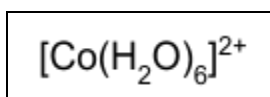
Transition metals form **complexes**, consisting of a **central metal ion** surrounded by **ligands**.

*Example:*



Complexes can also be represented by formulas using square brackets.

*Example:*



### Ligands

A ligand is a molecule or ion with a **lone electron pair** that is able to form a **dative (coordinate) bond** to the central metal ion by donation of this electron pair. Common ligands include:

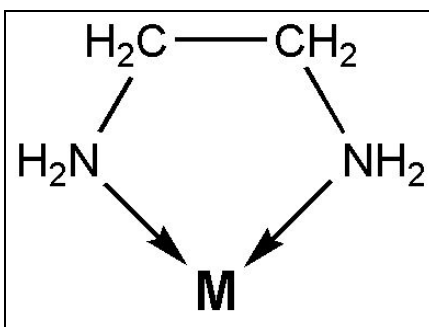
- $\text{Cl}^-$
- $\text{H}_2\text{O}$
- $\text{NH}_3$





**Monodentate** ligands each form **one** coordinate bond. Examples:  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$ ,  $\text{NH}_3$ .

**Bidentate** ligands each form **two** coordinate bonds. Example:  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ .



**Hexadentate** ligands each form six coordinate bonds. Example:  $\text{EDTA}^{4-}$ .

'**Polydentate**' and '**multidentate**' ligands are general terms for any ligands that form **more than one** coordinate bond.

### Coordination Number

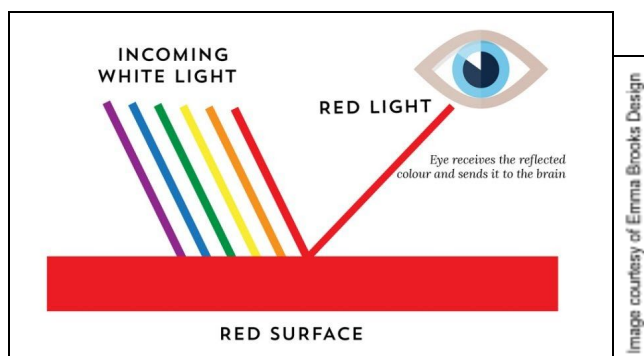
The **coordination number** of a transition metal complex is the total number of **coordinate bonds** formed with the central metal ion. Silver complexes have a coordination number of 2 and platinum complexes commonly have a coordination number of 4. The coordination number determines the **shape** of the complex ion.

### Coloured Ions

Transition metal ions can be identified by their **colour**, which changes depending on the **coordination number** of the complex, the type of **ligand** bonded to the ion and the **oxidation state**. Aqueous solutions of transition metal ions tend to be coloured.

Colour arises because of how substances **absorb and reflect** light. When white light shines on a substance, some of the wavelengths of light are absorbed, but the remaining wavelengths are **reflected and transmitted** to the human eye.

*Example:*



In transition metal complexes, ligands cause the d-orbital to split, meaning some electrons exist in a slightly higher energy level (in an **'excited state'**).

The change in energy ( $\Delta E$ ) between these states corresponds to a specific **wavelength and frequency** of light. If this wavelength of light is within the visible region of the electromagnetic spectrum then a coloured compound will be seen.

### Colourless Ions

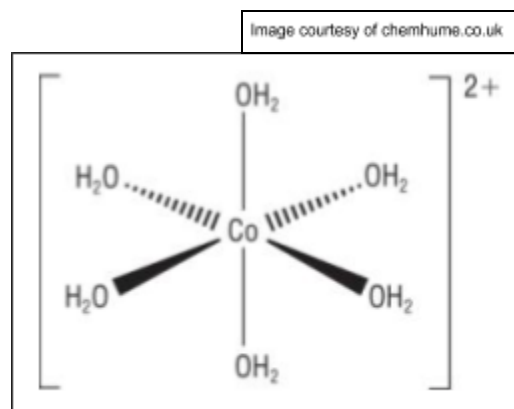
Some metal ions and complexes are colourless. Colour arises when some wavelengths of light are absorbed while others are reflected. This involves the **excitation of electrons**. Ions and complexes where there are **no available electrons to excite** cannot absorb light and are therefore **colourless**.

For example, zinc is in the d-block of the periodic table and has completely filled d-orbitals. Therefore, there are **no unfilled or partially filled d orbitals** into which an electron can be promoted. Therefore, zinc is colourless.

### Shapes of Complex Ions

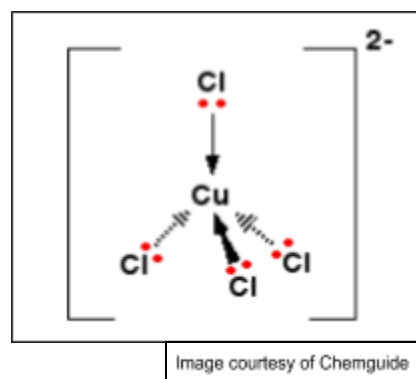
#### Octahedral Complexes

Transition metal complexes with  $H_2O$  and  $NH_3$  ligands commonly form **octahedral** complexes with a **bond angle of  $90^\circ$** . Octahedral complexes are formed when there is six-fold coordination.



#### Tetrahedral Complexes

When complexes form with **larger ligands** such as  $Cl^-$ , they form **tetrahedral** complexes with a **bond angle of  $109.5^\circ$**  and 4 ligands coordinated. Tetrahedral complexes can show optical isomerism.





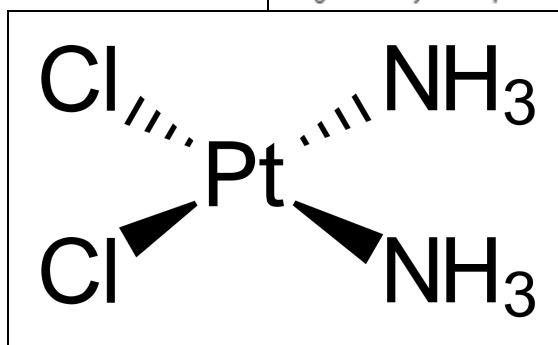
## Square Planar Complexes

**Platinum and nickel** complexes form in a **square planar** shape. This consists of four coordinate bonds with a **bond angle of  $90^\circ$** .

### Cisplatin

This is the **cis isomer** of a square planar complex of **platinum**. It has both chlorine atoms on the **same side**. It is commonly used as a **cancer therapy drug**. Drugs like cisplatin target components of cells that are **chiral**, so only one isomer of the drug will be the correct orientation to 'fit' the cells. Therefore, only this **single isomer will work** and cure the disease.

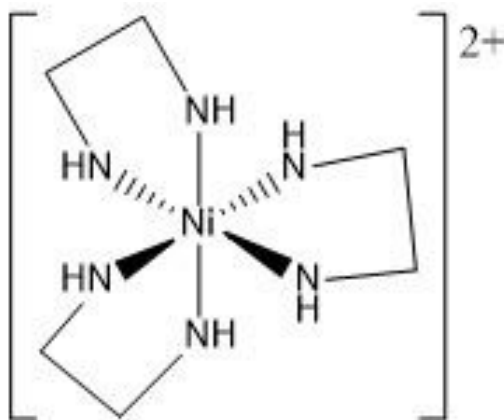
Image courtesy of Wikipedia



Cisplatin can cause serious **side effects** such as hair loss, meaning it has to be administered in **small amounts** to try and reduce these effects whilst still targeting the cancerous cells.

### Optical Isomerism

Optical isomerism is seen in some octahedral complexes with **bidentate** ligands. These complexes have **non-superimposable** mirror images.

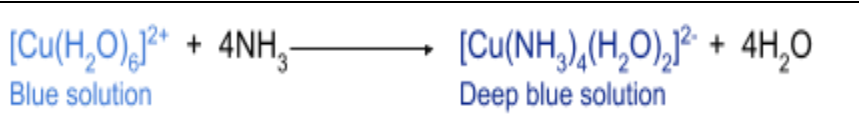
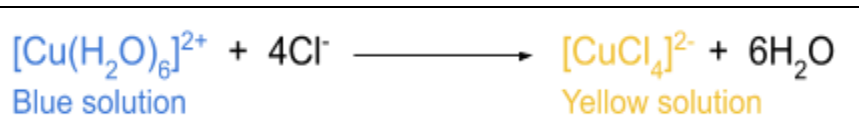


## Ligand Substitution

Ligands in a transition metal complex can be **exchanged** for other ligands.

Copper and cobalt aqua ions can undergo substitution with chloride ions.

The  $\text{Cl}^-$  ligand is much **larger** than the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  ligands meaning substitution with this ligand results in a **change in coordination number** for that complex.

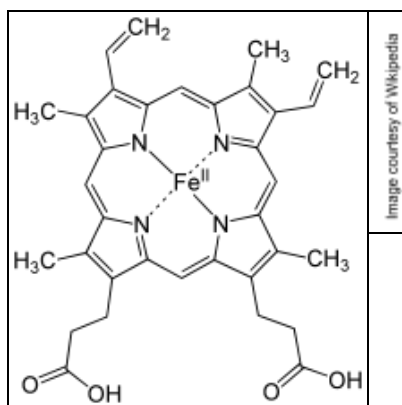


Complexes with just  $\text{Cl}^-$  ligands always have a coordination number of **four**, producing a **tetrahedral** shaped complex.

## Haem

**Haem**, a component of haemoglobin, is another common example involving multidentate ligands. It consists of a central  $\text{Fe}^{2+}$  ion and a tetradentate porphyrin ring. The central  $\text{Fe}^{2+}$  ion can also form coordinate bonds with one or two additional axial ligands. This gives haemoglobin an overall **octahedral** structure. The shape and structure allow it to **transport oxygen** around the body.

*Example:*



A **ligand substitution reaction** occurs when the oxygen usually bound to haem is replaced with **carbon monoxide**. The carbon monoxide binds more strongly than oxygen so can not be removed. Therefore, carbon monoxide is **toxic** to humans as it prevents oxygen from being transported around the body.





## The Chelate Effect

In ligand substitution reactions, a **positive entropy change is favourable** as it means a more stable complex is being formed. Therefore, it is favourable to have more moles on the right of the reaction than on the left. This is achieved by substituting monodentate ligands with bidentate or polydentate ligands. This is known as the **chelate effect**.

The greater the entropy change, the **more negative** the free energy change ( $\Delta G$ ) will be, meaning the reaction is **more favourable**.

## Enthalpy Change

The enthalpy change ( $\Delta H$ ) for ligand substitution reactions is **very small** as the bonds being formed are very similar to the bonds that were broken. Therefore, overall enthalpy change is **near to zero**.

## Precipitation Reactions

### Reactions of Transition Metal Ions with Sodium Hydroxide and Ammonia

Metal ions become **hydrated** in water when **H<sub>2</sub>O ligands** form around the central metal ion. The reactions of five major metal aqua ions have to be known for this A-level specification:

**chromium(III), iron(II), iron(III), manganese(II) and copper(II)**. These metal aqua ions react with sodium hydroxide and ammonia to form **coloured precipitates**.

Solutions of metal aqua ions react as **acids** with aqueous sodium hydroxide. Some react further with **excess sodium hydroxide**.

### Reactions with NaOH:

Transition Metal Ion	Metal-aqua ion	With OH <sup>-</sup>	With excess OH <sup>-</sup>
Cr <sup>3+</sup>	Violet solution [Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	Green precipitate Cr(OH) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub>	Green solution [Cr(OH) <sub>6</sub> ] <sup>3-</sup>
Fe <sup>2+</sup>	Green solution [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	Green precipitate Fe(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	No change
Fe <sup>3+</sup>	Yellow solution [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	Brown precipitate Fe(OH) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub>	No change
Mn <sup>2+</sup>	Pale pink solution [Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	Pale brown precipitate Mn(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	No change
Cu <sup>2+</sup>	Blue solution [Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	Blue precipitate Cu(OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	No change

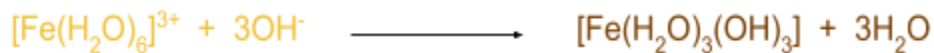
*It is easiest to remember the formulas of the precipitates by remembering that the number of OH<sup>-</sup> substituted is the same as the value of the charge on the initial ion.*







Example equations:



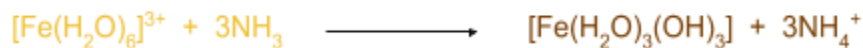
Solutions of metal aqua ions react as **acids** with aqueous ammonia. Some react further with **excess ammonia**. Initially, ammonia acts as a **base** to remove one  $\text{H}^+$  ion per ammonia molecule used. With excess ammonia, some metal ions undergo **ligand substitution** with  $\text{NH}_3$ .

Reactions with  $\text{NH}_3$ :

Transition Metal Ion	Metal-aqua ion	With $\text{NH}_3$	With excess $\text{NH}_3$
$\text{Cr}^{3+}$	Violet solution $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	Green precipitate $\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$	Purple solution $[\text{Cr}(\text{NH}_3)_6]^{3+}$
$\text{Fe}^{2+}$	Green solution $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	Green precipitate $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4$	No change
$\text{Fe}^{3+}$	Yellow solution $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	Brown precipitate $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3$	No change
$\text{Mn}^{2+}$	Pale pink solution $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	Pale brown precipitate $\text{Mn}(\text{OH})_2(\text{H}_2\text{O})_4$	No change
$\text{Cu}^{2+}$	Blue solution $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	Blue precipitate $\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4$	Dark blue solution $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$

***It is easiest to remember the formulas of the precipitates by remembering that the number of OH- substituted is the same as the value of the charge on the initial ion.***

Example equations:





## Redox Reactions

One of the key chemical properties of transition metals is their **variable oxidation states**. Redox reactions are used to change the oxidation state of a transition metal. These changes are often accompanied by a **colour change**.

### Iron

The most stable oxidation states of iron are **Fe<sup>2+</sup> and Fe<sup>3+</sup>**.

Compounds containing Fe<sup>2+</sup> ions are **pale green** in colour. Fe<sup>2+</sup> can be oxidised with MnO<sub>4</sub><sup>-</sup> in acidic conditions.

Compounds containing Fe<sup>3+</sup> ions are **orange/brown** in colour. Fe<sup>3+</sup> can be reduced with I<sup>-</sup>.

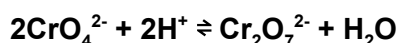
### Chromium

The most stable oxidation states of chromium are +6, +3, and +2, found in the species **Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, Cr<sup>3+</sup>, and Cr<sup>2+</sup>** respectively. These can be interconverted by oxidation and reduction reactions.

Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> can be reduced to Cr<sup>3+</sup> and Cr<sup>2+</sup> ions by **reduction** with **zinc** in **acidic conditions**.

Cr<sup>3+</sup> can be **oxidised** to Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> by **hydrogen peroxide** in **alkaline conditions**. The reaction first forms CrO<sub>4</sub><sup>2-</sup> which is then converted to Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> by **acidification**.

This occurs because there is an **equilibrium** between the two chromium(VI)-containing species:



**Acidification** of a solution containing CrO<sub>4</sub><sup>2-</sup> will, therefore, cause the equilibrium to **shift** to the right (to use up the additional H<sup>+</sup> ions), so the concentration of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> will **increase**.

### Copper

The most stable oxidation states of copper are **Cu<sup>+</sup> and Cu<sup>2+</sup>**.

Cu<sup>2+</sup> can be reduced to Cu by zinc.

Cu<sup>+</sup> readily **disproportionates** to Cu and Cu<sup>2+</sup>.





## 5.3.2 Qualitative Analysis

### Tests for Ions

Qualitative analysis can be performed to **identify ions** in an unknown compound.

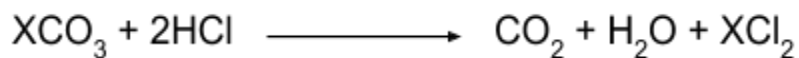
### Tests for Anions

The following tests can be used to determine if any of these **anions** are present. They should be performed in the order carbonate, sulfate, then halide, if a mixture of ions is present.

#### Carbonate ( $\text{CO}_3^{2-}$ ) and Hydrogencarbonate ( $\text{HCO}_3^-$ )

When an acid such as HCl is added, the substance containing the carbonate ions will **fizz and  $\text{CO}_2$  gas is given off**. This gas can be collected and bubbled through **limewater** which will turn **cloudy**, confirming its identity as carbon dioxide.

Example:



#### Sulfate ( $\text{SO}_4^{2-}$ )

Sulfate ions are tested for using **acidified  $\text{BaCl}_2$**  which reacts to form a **white precipitate** of barium sulfate.

Example:



#### Halide ions ( $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ )

When combined with acidified silver nitrate, halide ions react to form different **coloured precipitates** depending on the ion present. The precipitates can then be tested further with ammonia.

Halide Ion	$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$
+ $\text{AgNO}_3$	White precipitate (AgCl)	Cream precipitate (AgBr)	Yellow Precipitate (AgI)
+ dilute $\text{NH}_3$	Precipitate dissolves	No Change	No Change
+ conc. $\text{NH}_3$	Precipitate dissolves	Precipitate dissolves	No Change





## Tests for Cations

The following tests can be used to determine if any of these **cations** are present.

### Ammonium ( $\text{NH}_4^+$ )

If ammonium ions are present, adding NaOH and gently warming results in the formation of **ammonia gas**, which is **basic**. Therefore, the presence of ammonium ions can be tested by holding **damp red litmus paper** over a petri dish of the substance being tested. It will **turn blue** if ammonium ions are present.

### Transition Metal Ions

Transition metals form coloured compounds. This property can be used to determine which transition metal ions are present in a compound. The previous section explores the colours of **chromium(III), iron(II), iron(III), manganese(II) and copper(II)** metal-aqua ions and their precipitation reactions with sodium hydroxide and ammonia.

