

15. Transition Metals

General properties of transition metals

Transition metal characteristics of elements Sc → Cu arise from an **incomplete d sub-level** in ions

these characteristics include

- **complex formation,**
- **formation of coloured ions,**
- **variable oxidation state**
- **catalytic activity.**

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

When forming ions lose 4s before 3d

Sc $3+ [Ar] 4s^0 3d^0$
 Ti $3+ [Ar] 4s^0 3d^1$
 V $3+ [Ar] 4s^0 3d^2$
 Cr $3+ [Ar] 4s^0 3d^3$
 Mn $2+ [Ar] 4s^0 3d^5$
 Fe $3+ [Ar] 4s^0 3d^5$
 Co $2+ [Ar] 4s^0 3d^7$
 Ni $2+ [Ar] 4s^0 3d^8$
 Cu $2+ [Ar] 4s^0 3d^9$
 Zn $2+ [Ar] 4s^0 3d^{10}$

Why is Zn not a transition metal?

Zn can only form a +2 ion. In this ion the Zn^{2+} has a **complete** d orbital and so does not meet the criteria of having an incomplete d orbital in one of its compounds.

Why is Sc not a transition metal?

Sc can only form a +3 ion. In this ion the Sc^{3+} has an empty d orbital and so does not meet the criteria of having an incomplete d orbital in one of its ions.

The successive ionization energies for the elements Sc to Zn show a gradual increase in ionisation energy until all the 4s and 3d electrons have been removed. There is then a big jump as electrons start to be removed from the inner core electrons

Complex formation

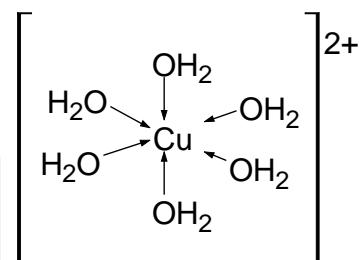
complex: is a central metal ion surrounded by ligands.

ligand: An atom, ion or molecule which can donate a **lone electron pair**

Co-ordinate bonding is involved in complex formation.

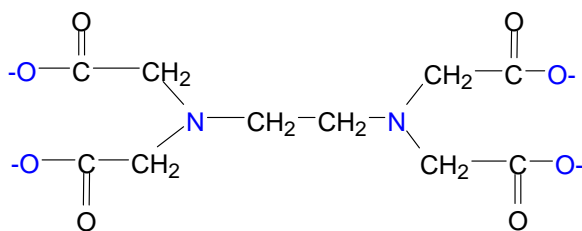
Co-ordinate bonding is when **the shared pair of electrons** in the covalent bond come from **only one of the bonding atoms**.

Co-ordination number: The number of co-ordinate bonds formed to a central metal ion

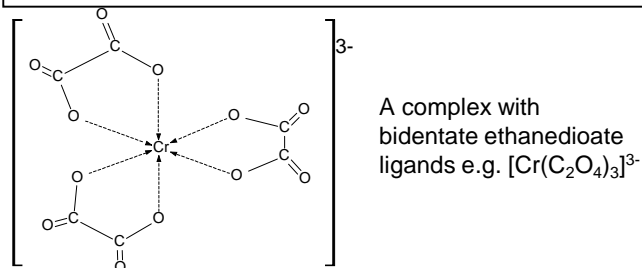
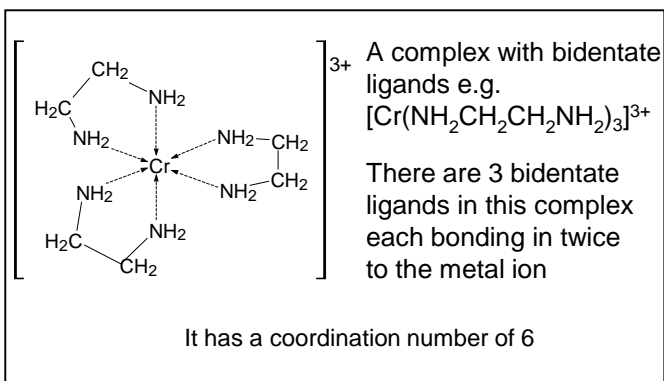


Ligands can be **monodentate** (e.g. H_2O , NH_3 and Cl^-) which can form one coordinate bond per ligand or **bidentate** (e.g. $NH_2CH_2CH_2NH_2$ and ethanedioate ion $C_2O_4^{2-}$) which have two atoms with lone pairs and can form two coordinate bonds per ligand or **multidentate** (e.g. $EDTA^{4-}$ which can form six coordinate bonds per ligand).

The $EDTA^{4-}$ anion has the formula

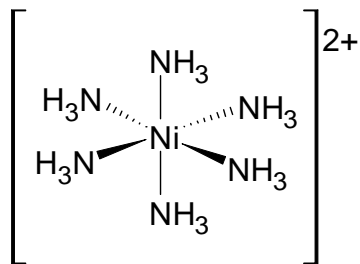


with six donor sites (4O and 2N) and forms a 1:1 complex with metal(II) ions

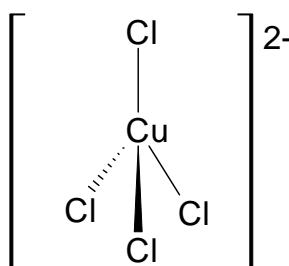


Shapes of complex ions

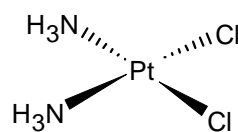
transition metal ions commonly form **octahedral** complexes with small ligands (e.g. H_2O and NH_3).



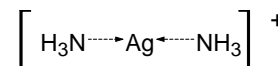
transition metal ions commonly form **tetrahedral** complexes with larger ligands (e.g. Cl^-).



square planar complexes are also formed, e.g. cisplatin



Ag^+ commonly forms **linear** complexes e.g. $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ and $[\text{Ag}(\text{CN})_2]^-$ (all colourless).



Cisplatin

The Pt(II) complex cisplatin is used as an anticancer drug.

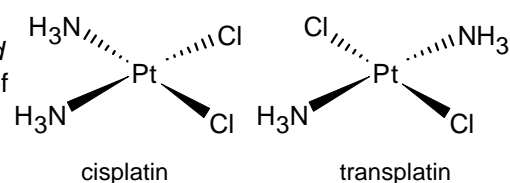
The cisplatin version only works as two chloride ions are displaced and the molecule joins on to the DNA. In doing this it stops the replication of cancerous cells.

In the body one Cl ligand is substituted by a water molecule



Be able to apply your knowledge of bonding to given information in the question to explain how it bonds to DNA molecule- generally a combination of dative covalent bonding and hydrogen bonding

Platin binds to DNA of cancer cells and stops cancer cells dividing



It can also prevent the replication of healthy cells by bonding on to healthy DNA which may lead to unwanted side effects like hair loss

Fe(II) in haemoglobin enables oxygen to be transported in the blood. Haem is an iron(II) complex with a multidentate ligand.

CO is toxic to humans as CO can form a strong coordinate bond with haemoglobin and replaces oxygen in a ligand exchange reaction. This is a stronger bond than that made with oxygen and so it prevents the oxygen attaching to the haemoglobin.

Variable oxidation states

Transition elements show variable oxidation states

When transition metals form ions they lose the 4s electrons before the 3d

Transition metals form various oxidation states. They are able to donate and receive electrons and are able to oxidize and reduce. This is because the ions contain partially filled sub-shells of d electrons that can easily lose or gain electrons. The energy differences between the oxidation states are small.

General trends

- Relative stability of +2 state with respect to +3 state increases across the period
- Compounds with high oxidation states tend to be oxidising agents e.g MnO_4^-
- Compounds with low oxidation states are often reducing agents e.g V^{2+} & Fe^{2+}

Vanadium

Vanadium has four main oxidation states

VO_2^+ Oxidation state +5 (a yellow solution)

VO^{2+} Oxidation state + 4 (a blue solution)

V^{3+} Oxidation state + 3 (a green solution)

V^{2+} Oxidation state + 2 (a violet solution)

The ion with the V at oxidation state +5 exists as a solid compound in the form of a VO_3^- ion, usually as NH_4VO_3 (ammonium vanadate (V)). It is a reasonably strong oxidising agent. Addition of acid to the solid will turn into the yellow solution containing the VO_2^+ ion.

Addition of **zinc** to the vanadium (V) in acidic solution will reduce the vanadium down through each successive oxidation state, and the colour would successively change from yellow to blue to green to violet

Redox Equation	E° Values
$\text{VO}_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}$	+1.00 V
$\text{VO}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}$	+0.34 V
$\text{V}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{V}^{2+}(\text{aq})$	- 0.26 V



As zinc has a more negative electrode potential than all the vanadium half equations, zinc will reduce down to V^{2+}

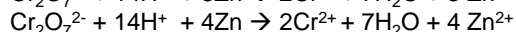
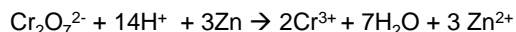


Tin metal will only reduce the vanadium to the +3 state

Chromium Reactions

Reducing Chromium

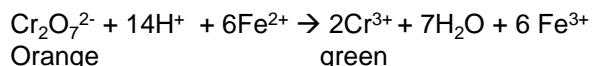
Cr³⁺ (green) and then **Cr²⁺ (blue)** are formed by reduction of Cr₂O₇²⁻ (orange) by the strong reducing agent **zinc** in (HCl) acid solution. **Fe²⁺** is a less strong reducing agent and will **only** reduce the dichromate to **Cr³⁺**



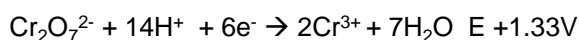
Keeping the zinc/dichromate under a hydrogen atmosphere is needed to reduce it to Cr²⁺, because O₂ in air will oxidise Cr²⁺ up to Cr³⁺

The Cr²⁺ state can be stabilised by forming a stable complex ion with a ligand such as the ethanoate ion. If the blue Cr²⁺ ions are bubbled through sodium ethanoate, a stable red precipitate of chromium(II) ethanoate is formed.

The Fe²⁺ and Cr₂O₇²⁻ in acid solution reaction can be used as a quantitative redox titration. This does not need an indicator



Redox Potentials



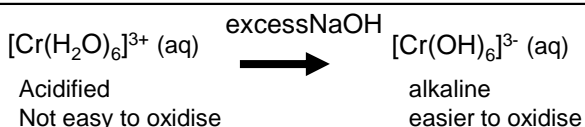
The electrode potential of Iron(II) is in between the two chromium half equations, so Fe²⁺ will reduce chromium down to Cr³⁺

As zinc has a more negative electrode potential than all the chromium half equations, zinc will reduce chromium down to Cr²⁺

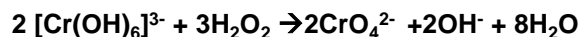
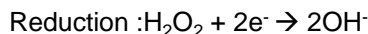
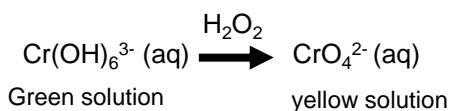
Oxidising Chromium

When transition metals in low oxidation states are in alkaline solution they are more easily oxidised than when in acidic solution

It is easier to remove an electron from a negatively charged ion



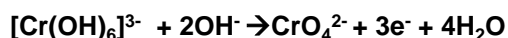
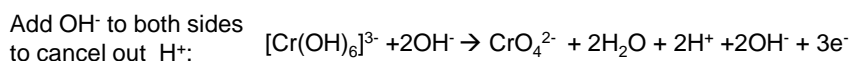
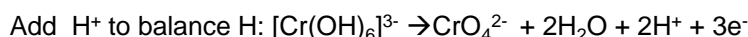
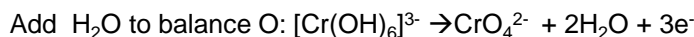
The metal ions can be oxidised by using oxidising agents such as hydrogen peroxide



Half equations in alkaline conditions:

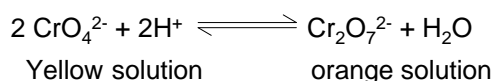
These are more difficult to do than half equations under acidic conditions. The easiest way of doing it is to balance as if under acidic conditions then add OH⁻ ions to both sides to convert to alkaline.

For change Cr(OH)₆³⁻ → CrO₄²⁻



Chromate/ dichromate equilibrium

The chromate CrO_4^{2-} and dichromate $\text{Cr}_2\text{O}_7^{2-}$ ions can be converted from one to the other by the following equilibrium reaction.

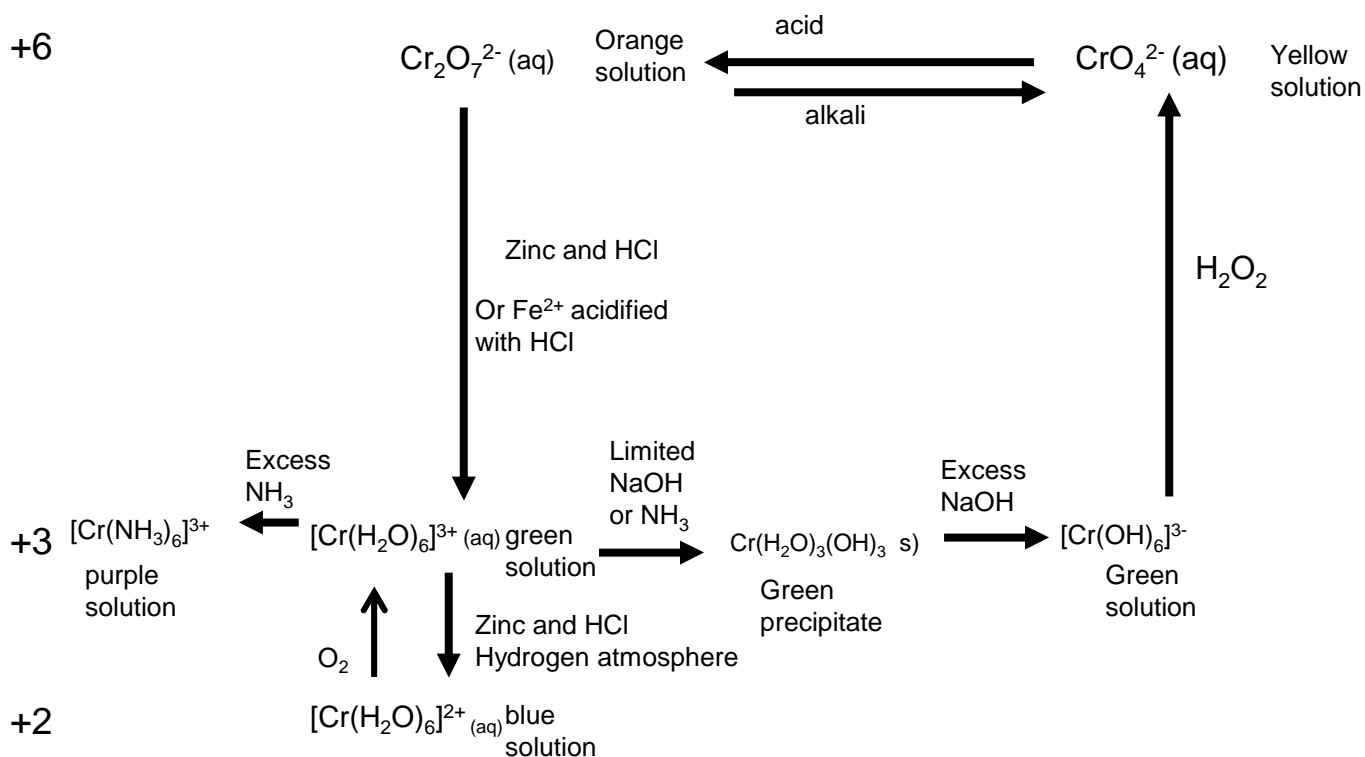


This is not a redox reaction as both the chromate and dichromate ions have an oxidation number of +6. This is an acid base reaction.

Addition of acid will by application of le Chatelier push the equilibrium to the dichromate.

Addition of alkali will remove the H^+ ions and, by application of le Chatelier, push the equilibrium to the chromate.

Chromium Summary



Reactions of Inorganic Compounds in Aqueous Solution

Lewis acids and bases

Definitions: **Lewis acid**: electron pair acceptor
Lewis base: electron pair donator

In the formation of complex ions the ligand is the Lewis base because it is donating a pair of electrons in the dative covalent bond and the metal ion is the Lewis acid.

Metal-aqua ions

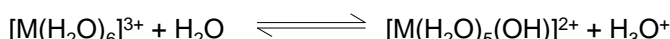
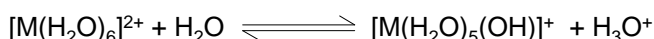
Metal aqua ions are formed in aqueous solution.

$[M(H_2O)_6]^{2+}$, limited to M = Fe (green), Co (pink) and Cu (blue);
 $[M(H_2O)_6]^{3+}$, limited to M = Cr (ruby) and Fe (violet)

In solution Cr(III) often appears green and Fe(III) appears yellow/brown due to hydrolysis reactions. The ruby and violet colour is only really seen in solid hydrated salts that contain these complexes.

Acidity or hydrolysis reactions

The following equilibria happen in aqueous solutions of metal ions.



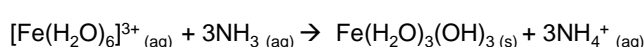
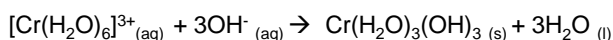
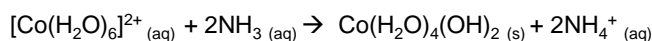
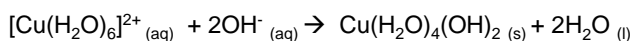
The equilibria lead to generation of acidic solutions with M^{3+} ions, and very weakly acidic solutions with M^{2+} ions. The 3^+ ions are noticeably more acidic.

The acidity of $[M(H_2O)_6]^{3+}$ is greater than that of $[M(H_2O)_6]^{2+}$ because the $3+$ metal ions have **higher charge density** (charge/size ratio) and have greater polarising power. The greater the polarising power, the more strongly it attracts the water molecule. This **weakens the O-H bond** so it breaks more easily **releasing H^+ ions**.

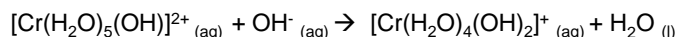
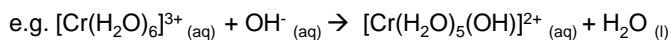
Reaction with limited OH^- and limited NH_3

The bases OH^- and ammonia when in limited amounts form the same hydroxide precipitates. They form in **deprotonation acid base reactions**

$M(OH)_2(H_2O)_4(s)$: Cu blue ppt, Co blue ppt, Fe (II) green ppt
 $M(OH)_3(H_2O)_3(s)$: Cr (III) green ppt, Fe(III) brown ppt,



This process can happen step wise removing one proton at a time. Be able to write equations for this too.

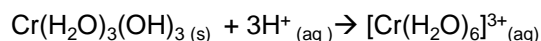
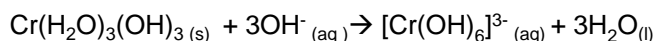


Here the NH_3 and OH^- ions are acting as **Bronsted-Lowry bases** accepting a proton

Reaction with excess OH^-

With excess NaOH, the Cr hydroxide dissolves. Cr becomes $[Cr(OH)_6]^{3-}(aq)$ green solution.

This hydroxide is classed as **amphoteric** because they react and dissolve in both acids and bases.



Reaction with excess NH_3

With **excess NH_3 ligand substitution** reactions occur with Cu, Co and Cr and their precipitates dissolve.

The ligands NH_3 and H_2O are similar in size and are uncharged. Ligand exchange occurs without a change of co-ordination number for Co and Cr.

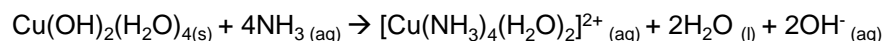
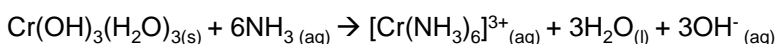
Cr becomes $[Cr(NH_3)_6]^{3+}$ purple solution

Co becomes $[Co(NH_3)_6]^{2+}$ pale yellow solution

Remember this Co complex is oxidised to +3 on standing in air.

This substitution may, however, be incomplete as in the case with Cu.

Cu becomes $[Cu(NH_3)_4(H_2O)_2]^{2+}$ deep blue solution



In these reactions NH_3 is acting as a **Lewis base** donating an electron pair.

Ligand exchange reactions with chloride ions

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 H₂O and NH₃ ligands so therefore ligand exchange can involve a change of co-ordination number.

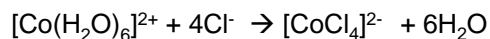
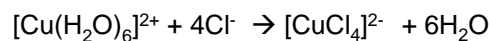
Be careful: If solid copper chloride (or any other metal) is **dissolved in water** it forms the **aqueous [Cu(H₂O)₆]²⁺** complex and **not** the chloride [CuCl₄]²⁻ complex

Addition of conc HCl to aqueous ions of Cu and Co lead to a change in coordination number from 6 to 4

[CuCl₄]²⁻ yellow/green solution

[CoCl₄]²⁻ blue solution

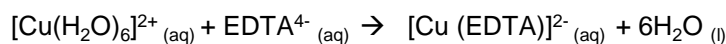
These are tetrahedral in shape



Stability of complexes

The substitution of monodentate ligand with a bidentate or a multidentate ligand leads to a more stable complex.

This chelate effect can be explained in terms of a positive entropy change in these reactions as more molecules of products than reactants

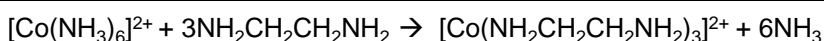
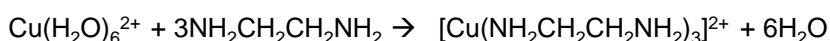


The copper complex ion has changed from having monodentate ligands to a multidentate ligand. In this reaction there is **an increase** in the **entropy of the system** because there are **more moles of products** than reactants (from 2 to 7), creating more disorder.

The stability of the EDTA complexes has many applications. It can be added to rivers to remove poisonous heavy metal ions as the EDTA complexes are not toxic. It is in many shampoos to remove calcium ions present in hard water, so helping lathering.

Ethane-1-2-diamine

Ethane-1-2-diamine is a common bidentate ligand.

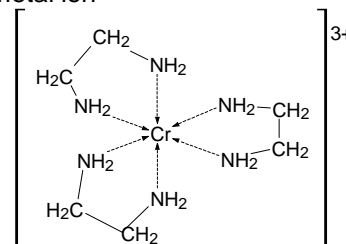


This reaction has an increase in entropy because of the increase in moles from 4 to 7 in the reaction. **S_{system} is positive.**

Its enthalpy change **H (and S_{surroundings})** is close to zero as **the number** of dative covalent and **type** (N to metal coordinate bond) **are the same** so the energy required to break and make bonds will be the same.

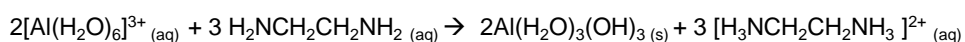
Therefore **S_{Total}** will be positive and the complex formed is stable

There are 3 bidentate ligands in this complex each bonding in twice to the metal ion



It has a coordination number of 6
Octahedral shape
Bond angle around Cr 90°

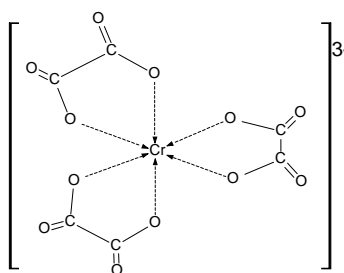
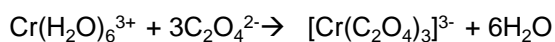
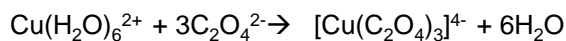
Ethane-1-2-diamine, as a base, can also carry out the deprotonation reactions (similar to those of ammonia) forming hydroxide precipitates.



Note small molecules such as NH₂NH₂ cannot act as bidentate ligands because even though they have two lone pairs they are too close together and would not be able to fit around the metal ion

More on some common ligands

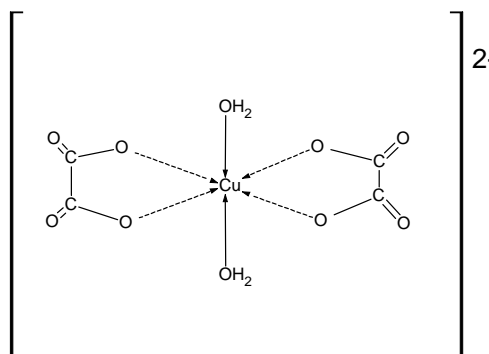
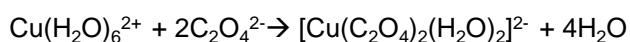
Ethanedioate $\text{C}_2\text{O}_4^{2-}$



A 6 coordination number complex with bidentate ethanedioate ligands e.g. $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

Octahedral shape with 90° bond angles

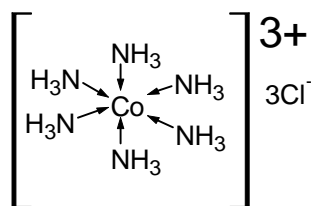
Partial substitution of ethanedioate ions may occur when a dilute aqueous solution containing ethanedioate ions is added to a solution containing aqueous copper(II) ions. In this reaction four water molecules are replaced and a new complex is formed.



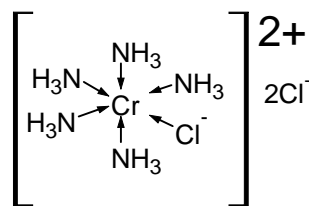
Using silver nitrate to work out formulae of chloride containing complexes

Sometimes a compound containing a complex may have Cl^- ions acting as ligands inside the complex and Cl^- ions outside the complex attracted ionically to it. If silver nitrate is added to such a compound it will only form the silver chloride precipitate with the free chloride ions outside of the complex.

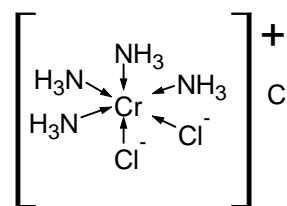
e.g. $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ reacts on a 1:3 mole ratio with silver nitrate as there are three free Cl^- ions. So all 3 Cls are outside the complex



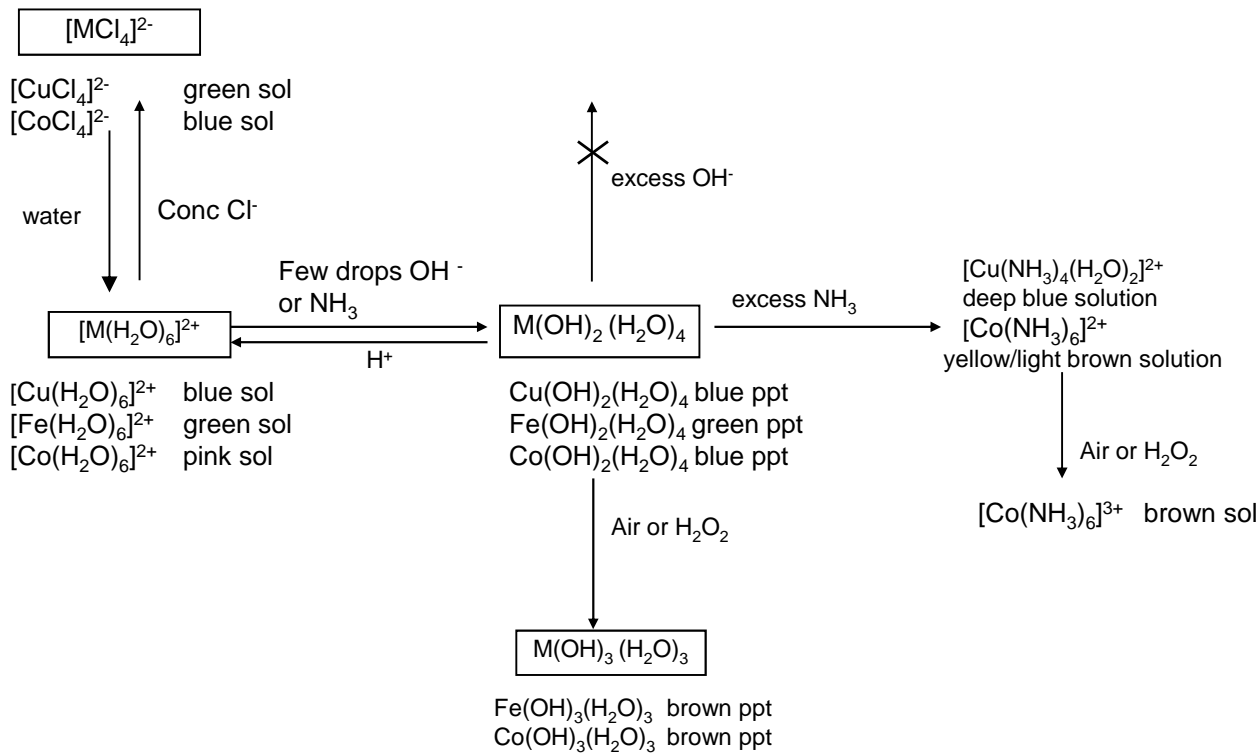
e.g. $\text{Cr}(\text{NH}_3)_5\text{Cl}_3$ reacts on a 1:2 mole ratio with silver nitrate as there are two free Cl^- ions. So 1 Cl is a ligand and 2 are outside the complex



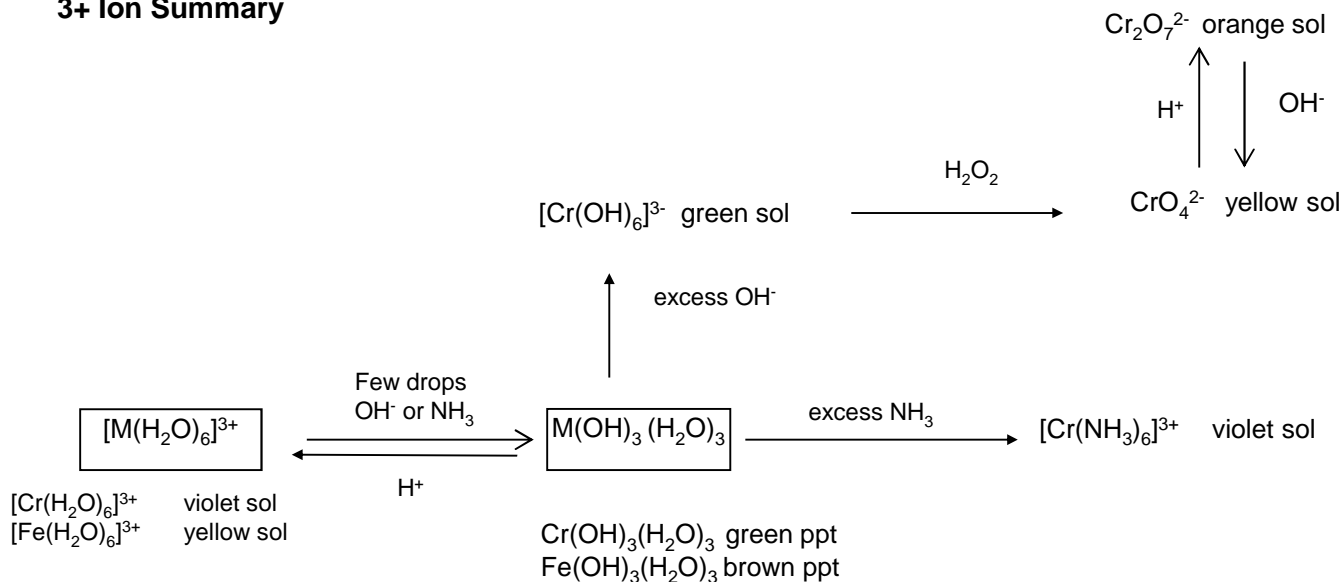
e.g. $\text{Cr}(\text{NH}_3)_4\text{Cl}_3$ reacts on a 1:1 mole ratio with silver nitrate as there is one free Cl^- ion. So 2 Cl's are ligands and 1 is outside the complex



2+ Ion Summary



3+ Ion Summary



Catalysis

Catalysts increase reaction rates without getting used up. They do this by **providing an alternative route** with a **lower activation energy**

Transition metals and their compounds can act as heterogeneous and homogeneous catalysts.

A **heterogeneous catalyst** is in a different phase from the reactants

A **homogeneous catalyst** is in the same phase as the reactants

Heterogeneous catalysis

Heterogeneous catalysts are usually solids whereas the reactants are gaseous or in solution. The reaction occurs at the surface of the catalyst.

Strength of adsorption

The strength of adsorption helps to determine the effectiveness of the catalytic activity

Some metals e.g. **W** have **too strong** adsorption and so the products cannot be released

Some metals e.g. **Ag** have **too weak** adsorption, and the reactants do not adsorb in high enough concentration
Ni and Pt have about the right strength and are most useful as catalysts

Adsorption of reactants at active sites on the surface may lead to catalytic action. The **active site** is the place where the **reactants adsorb** on to the **surface of the catalyst**. This can result in the bonds within the reactant molecules becoming weaker, or the molecules being held in a more reactive configuration. There will also be a higher concentration of reactants at the solid surface so leading to a higher collision frequency

Transition Metals can use the 3d and 4s e- of atoms on the metal surface to form weak bonds to the reactants.

Advantages of heterogeneous catalysts

Heterogeneous catalysts can be filtered off and are easy to separate from any liquid or gaseous products. They are also suited to continuous processes rather than batch processes

Surface area:

Increasing the surface area of a solid catalyst will improve its effectiveness. A support medium is often used to maximise the surface area and minimise the cost (e.g. Rh on a ceramic support in catalytic converters).

Example of heterogeneous catalysts

V_2O_5 is used as a catalyst in the Contact Process.

Overall equation : $2SO_2 + O_2 \rightarrow 2SO_3$

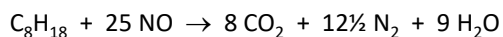
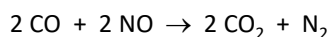
step 1 $SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$

step 2 $2V_2O_4 + O_2 \rightarrow 2V_2O_5$

Note the oxidation number of the vanadium changes and then changes back. It is still classed as a catalyst as it returns to its original form

Catalytic converters

These remove CO , NO_x and unburned hydrocarbons (e.g. octane, C_8H_{18}) from the exhaust gases, turning them into 'harmless' CO_2 , N_2 and H_2O .



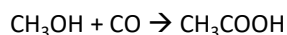
Converters have a ceramic honeycomb coated with a thin layer of catalyst metals **Platinum, Palladium, Rhodium** – to give a large surface area.

Steps in Heterogeneous Catalysis in catalytic converter

1. CO and NO molecules form bonds with atoms at **active sites** on the surface of the catalyst - **adsorbed** onto the surface
2. As a result bonds in the reactants are weakened and break
3. New bonds form between the reactants held close together on catalyst surface
4. Desorption of CO_2 and N_2 product molecules from the surface of the catalyst

Developing New Catalysts

Making ethanoic acid from methanol and carbon monoxide is a preferable industrial production method because it has a high atom economy.



A iridium/iodine based catalyst is currently used.

Over the years the catalyst used for this reaction has been developed using different transition metal catalysts. This has led to greater selectivity of the catalysts, cheaper catalysts, milder conditions being used and improved separation processes.

The scientific community reports and validates new discoveries by publishing new discoveries in scientific journals that are peer reviewed.

Homogeneous catalysis

When catalysts and reactants are in the same phase, the reaction proceeds through an intermediate species

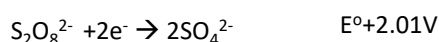
The intermediate will have a different oxidation state to the original transition metal. At the end of the reaction the original oxidation state will reoccur. This illustrates importance of variable oxidation states of transition metals in catalysis

Transition metals can act as homogeneous catalysts because they can form various oxidation states. They are able to donate and receive electrons and are able to oxidize and reduce. This is because the ions contain partially filled sub-shells of d electrons that can easily lose or gain electrons.

Example of homogeneous catalysts

Reaction between iodide and persulfate ions

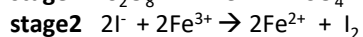
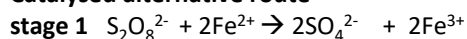
The reaction between I^- and $\text{S}_2\text{O}_8^{2-}$ catalysed by Fe^{2+}
overall $\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_2$



The uncatalysed reaction is very slow because the reaction needs a collision between **two negative ions**. **Repulsion** between the ions is going to hinder this – meaning **high activation energy**

For a substance to act as a homogenous catalyst its electrode potential must lie in between the electrode potentials of the two reactants, so it can first reduce the reactant with the more positive electrode potential and then in the second step oxidize the reactant with the more negative electrode potential

Catalysed alternative route



Both of the individual stages in the catalysed mechanism involve collision between positive and negative ions and will have lower activation energies.

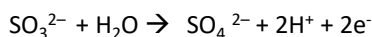
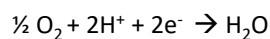
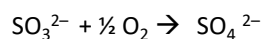
Using E values to find a catalyst only shows that catalysis is possible. It does not guarantee that the rate of reaction will be increased

Fe^{3+} ions can also act as the catalyst because the two steps in the catalysed mechanism can occur in any order

Constructing a catalysed mechanism for a reaction Example

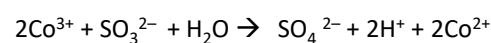
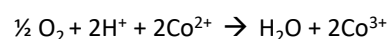
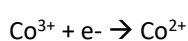
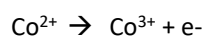
The following reaction is catalysed by Co^{2+} ions in an acidic solution. $\text{SO}_3^{2-} + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_4^{2-}$.
Write a mechanism for the catalysed reaction by writing two equations involving Co^{2+} and Co^{3+} ions

Split full equation into its two half equations



Add in cobalt to make two new redox equations.

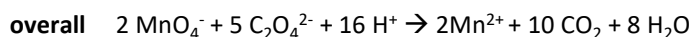
Making sure the oxidised cobalt equation is combined with the original reduced half equation and vice versa



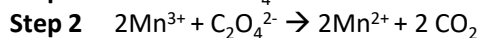
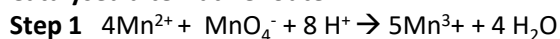
Check your two mechanism equations add up to the original full non catalysed equation

Autocatalytic Reaction between Ethanedioate and Manganate ions

The autocatalysis by Mn^{2+} in titrations of $\text{C}_2\text{O}_4^{2-}$ with MnO_4^-



Catalysed alternative route

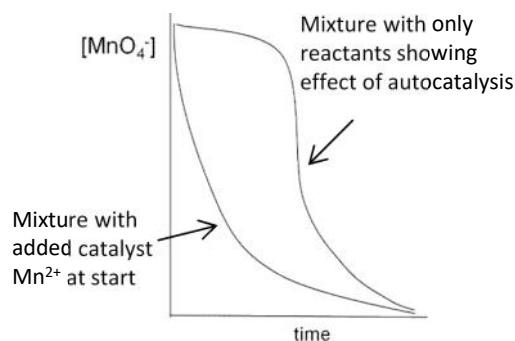


The initial uncatalysed reaction is **slow** because the reaction is a collision between **two negative ions** which **repel each other** leading to a **high activation energy**.

The Mn^{2+} ions produced act as an **autocatalyst** and therefore the reaction starts to speed up because they bring about the alternative reaction route with lower activation energy.

The reaction eventually slows as the **MnO_4^- concentration drops**.

This is an example of **autocatalysis** where one of the products of the reaction can catalyse the reaction.



Following the reaction rate

This can be done by removing samples at set times and titrating to work out the concentration of MnO_4^- .

It could also be done by use of a spectrometer measuring the intensity of the purple colour. This method has the advantage that it **does not disrupt the reaction mixture**, using up the reactants and it leads to a much **quicker determination of concentration**.