

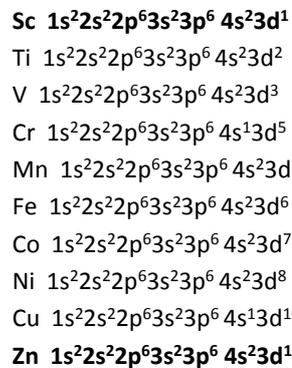
Transition Metals

General properties of transition metals

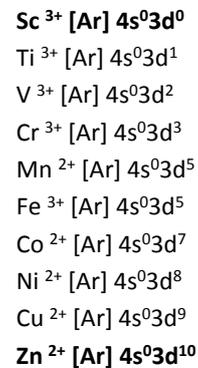
transition metal characteristics of elements Ti → Cu arise from an **incomplete d sub-level** in atoms or ions

these characteristics include

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



→
When forming ions lose 4s before 3d



Why are Zn and Sc not transition metals?

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 a incomplete d orbital in one of its compounds.

Sc only forms a +3 ion with the electronic structure

The Sc^{3+} ion had an **empty** d orbital and so also does not meet the criteria

Complex formation

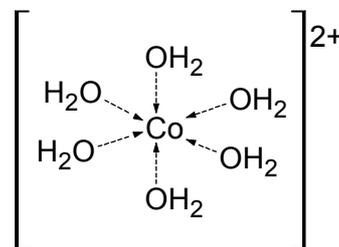
complex : is a central metal ion surrounded by ligands.

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

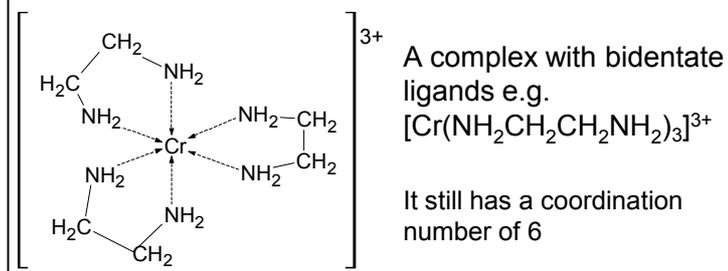
Co-ordinate bonding is involved in complex formation.

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

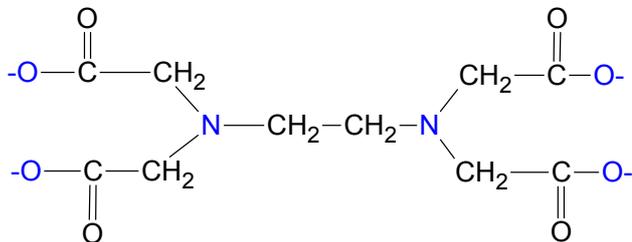
Co-ordination number: The number of co-ordinate bonds formed to a central metal ion



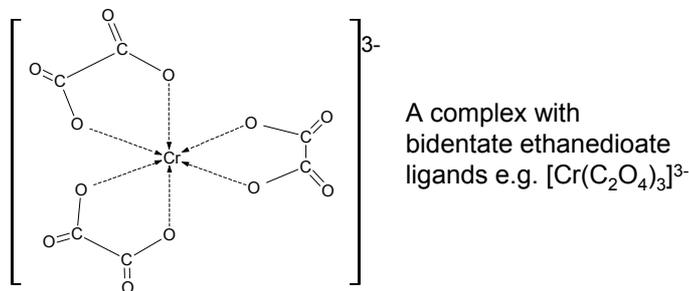
ligands can be **unidentate** (e.g. H_2O , NH_3 and Cl^-) which can form one coordinate bond per ligand or **bidentate** (e.g. $NH_2CH_2CH_2NH_2$ and ethanedioate ion $C_2O_4^{2-}$) which have two atoms with lone pairs and can form two coordinate bonds per ligand or **multidentate** (e.g. $EDTA^{4-}$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



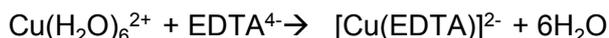
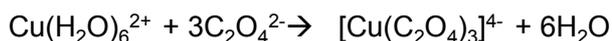
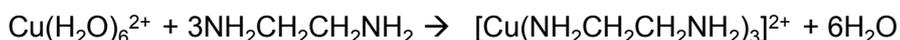
The $EDTA^{4-}$ anion has the formula



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



Equations to show formation of bidentate and multidentate complexes



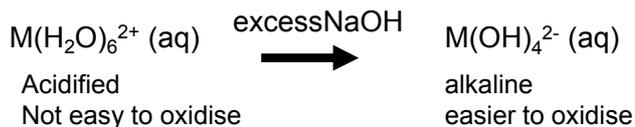
Learn the two bidentate ligands mentioned above but it is not necessary to remember the structure of EDTA

haem is an iron(II) complex with a multidentate ligand.

Oxidation in alkaline solution

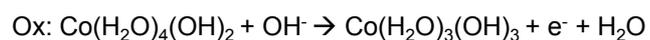
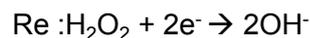
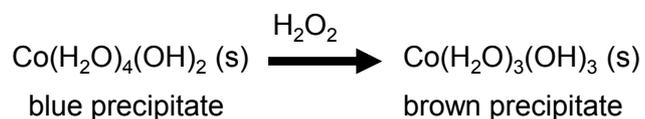
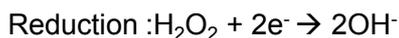
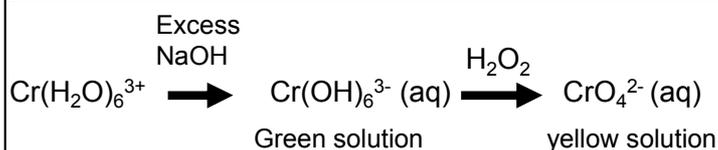
When transition metals in low oxidation states are in alkaline solution they are more easily oxidised than when in acidic solution

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 and sometimes by standing in air

Chromium and cobalt compounds can be oxidised by using the **oxidising agent** hydrogen peroxide



Half equations in alkaline conditions:

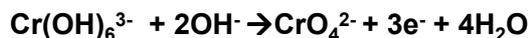
These are more difficult to do than half equations under acidic conditions. The easiest way of doing it is to balance as if under acidic conditions then add OH⁻ ions to both sides to convert to alkaline

For change $\text{Cr(OH)}_6^{3-} \rightarrow \text{CrO}_4^{2-}$

Add H₂O to balance O: $\text{Cr(OH)}_6^{3-} \rightarrow \text{CrO}_4^{2-} + 2\text{H}_2\text{O} + 3\text{e}^-$

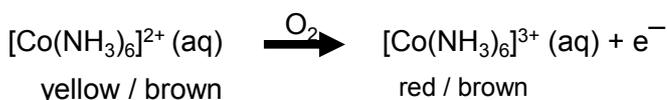
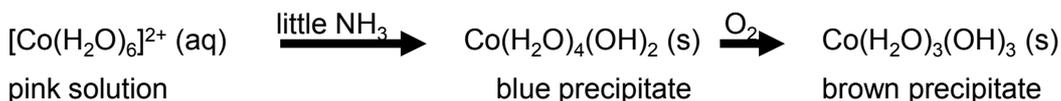
Add H⁺ to balance H: $\text{Cr(OH)}_6^{3-} \rightarrow \text{CrO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+ + 3\text{e}^-$

Add OH⁻ to both sides to cancel out H⁺: $\text{Cr(OH)}_6^{3-} + 2\text{OH}^- \rightarrow \text{CrO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+ + 2\text{OH}^- + 3\text{e}^-$



Ammonical oxidation of Cobalt

Ammonia ligands make the Co(II) state unstable. Air oxidises Co(II) to Co(III).



H₂O₂ could also bring about the oxidation

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

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).

Examples 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 $2V_2O_4 + O_2 \rightarrow 2V_2O_5$

Cr_2O_3 catalyst is used in the manufacture of methanol from carbon monoxide and hydrogen
 $CO + 2H_2 \rightarrow CH_3OH$

Poisoning Catalysts

catalysts can become poisoned by impurities and consequently have reduced efficiency

It is important to ensure the purity of the reactants if poisoning can occur

Homogeneous catalysis

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

Adsorption of reactants at active sites on the surface may lead to catalytic action. In this case the reactants tend to adsorb (chemically bond) 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

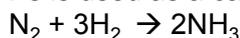
Transition Metals can use the 3d and 4s e- of atoms on the metal surface to form weak bonds to the reactants.

Steps in Heterogeneous Catalysis

1. Reactants 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. This in turn weakens bonds between product and catalyst and product leaves (desorbs)

Learn the equations for this mechanism. 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

Fe is used as a catalyst in the Haber Process



Poisoning has a cost implication e.g. poisoning by sulphur in the Haber Process and by lead in catalytic converters in cars means that catalysts lose their efficiency and may need to be replaced

Leaded petrol cannot be used in cars fitted with a catalytic converter since lead strongly adsorbs onto the surface of the catalyst

The intermediate will often 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

Examples of homogenous catalysts

Learn these 2 examples and equations carefully

Reaction between iodide and persulphate ions

The reaction between I^- and $S_2O_8^{2-}$ catalysed by Fe^{2+}
overall $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

Catalysed alternative route

stage 1 $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$

stage 2 $2I^- + 2Fe^{3+} \rightarrow 2Fe^{2+} + I_2$

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**

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

Autocatalytic reaction between Ethanedioate and Manganate ions

The autocatalysis by Mn^{2+} in titrations of $C_2O_4^{2-}$ with MnO_4^-

overall $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Catalysed alternative route

Step 1 $4Mn^{2+} + MnO_4^- + 8H^+ \rightarrow 5Mn^{3+} + 4H_2O$

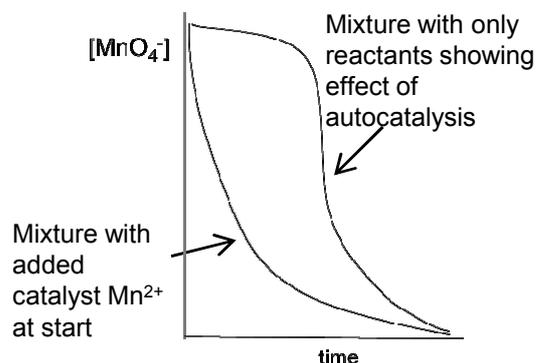
Step 2 $2Mn^{3+} + C_2O_4^{2-} \rightarrow 2Mn^{2+} + 2CO_2$

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

As the Mn^{2+} ions are produced act as an **autocatalyst** and the reaction starts to speed up as 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**

Other applications of transition metal complexes

Fe(II) in haemoglobin enables oxygen to be transported in the blood,

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

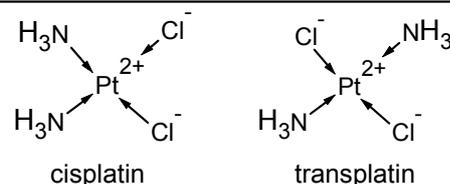
The Pt(II) complex cisplatin is used as an anticancer drug.

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



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

$[Ag(NH_3)_2]^+$ is used in Tollen's reagent to distinguish between aldehydes and ketones

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 as it donating a pair of electrons in the dative covalent bond and the metal ion is the Lewis acid

Metal-aqua ions

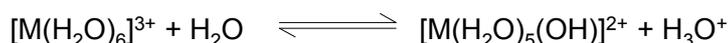
Metal aqua ions are formed in aqueous solution

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



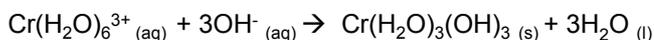
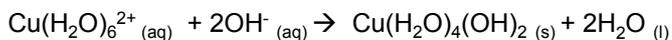
The equilibria lead to generation of acidic solutions with M^{3+} ions, and very weakly acidic solutions with M^{2+} ions.

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

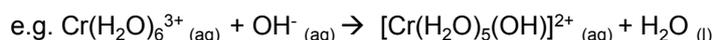
Reaction with limited OH^- and limited NH_3

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, Al white ppt



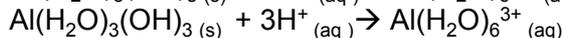
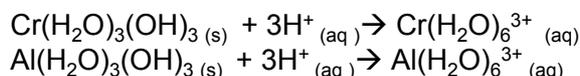
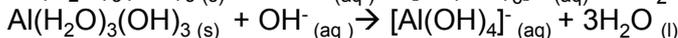
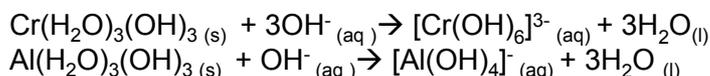
This process can happen step wise removing one proton at a time. Be able to write equations for this too



Reaction with excess OH^-

With excess NaOH, the Cr and Al hydroxides dissolve.
Cr becomes $[Cr(OH)_6]^{3-}(aq)$ green solution
Al becomes $[Al(OH)_4]^{-}(aq)$ colourless solution

These hydroxides are classed as **amphoteric** as they dissolve in both acids and bases



Reaction with excess NH_3

With **excess NH_3** 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 change of co-ordination number for Co and Cr

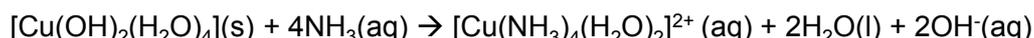
Cr becomes $[Cr(NH_3)_6]^{3+}$ purple solution

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

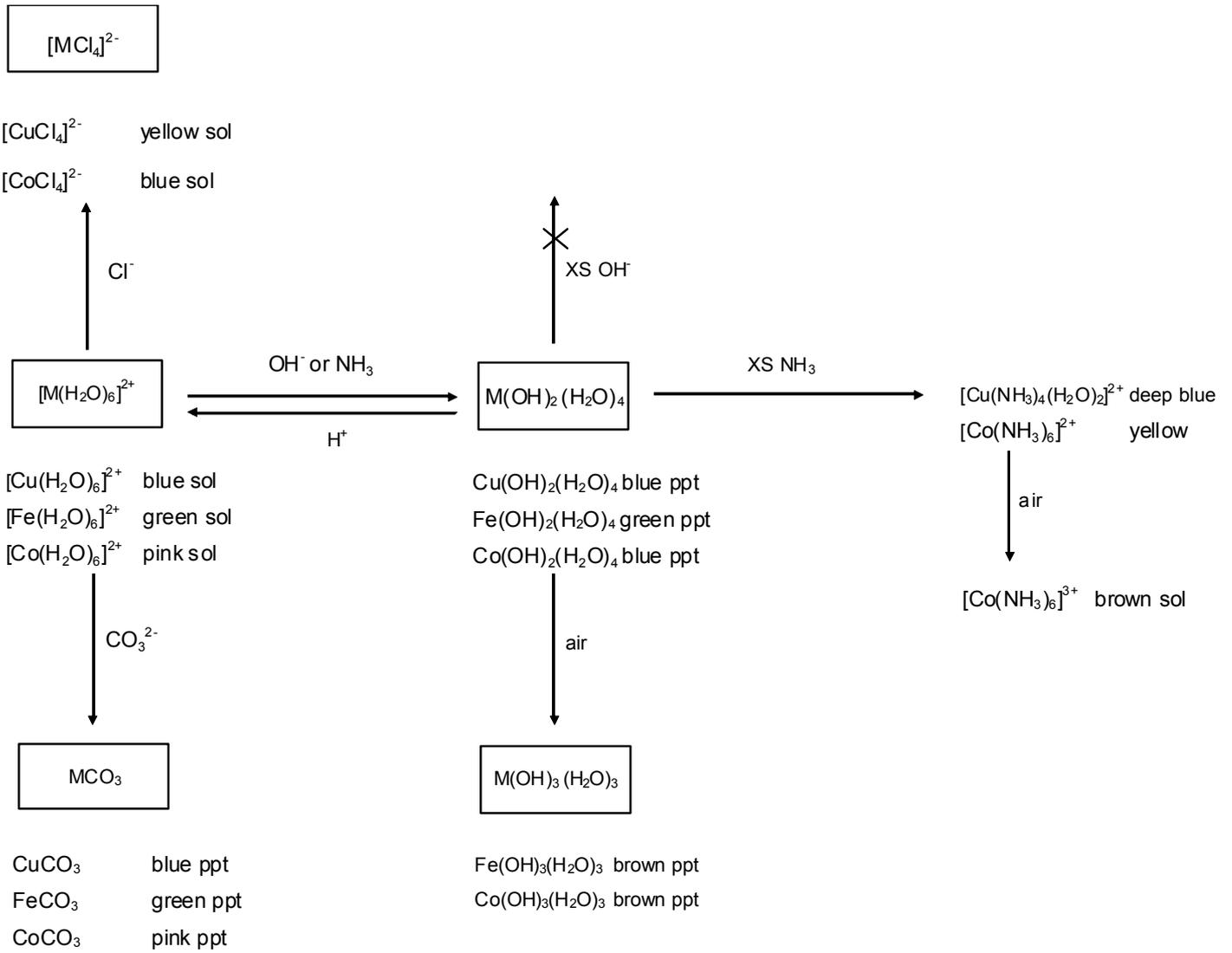
Remember this Co complex is oxidised to +3 on standing in air

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

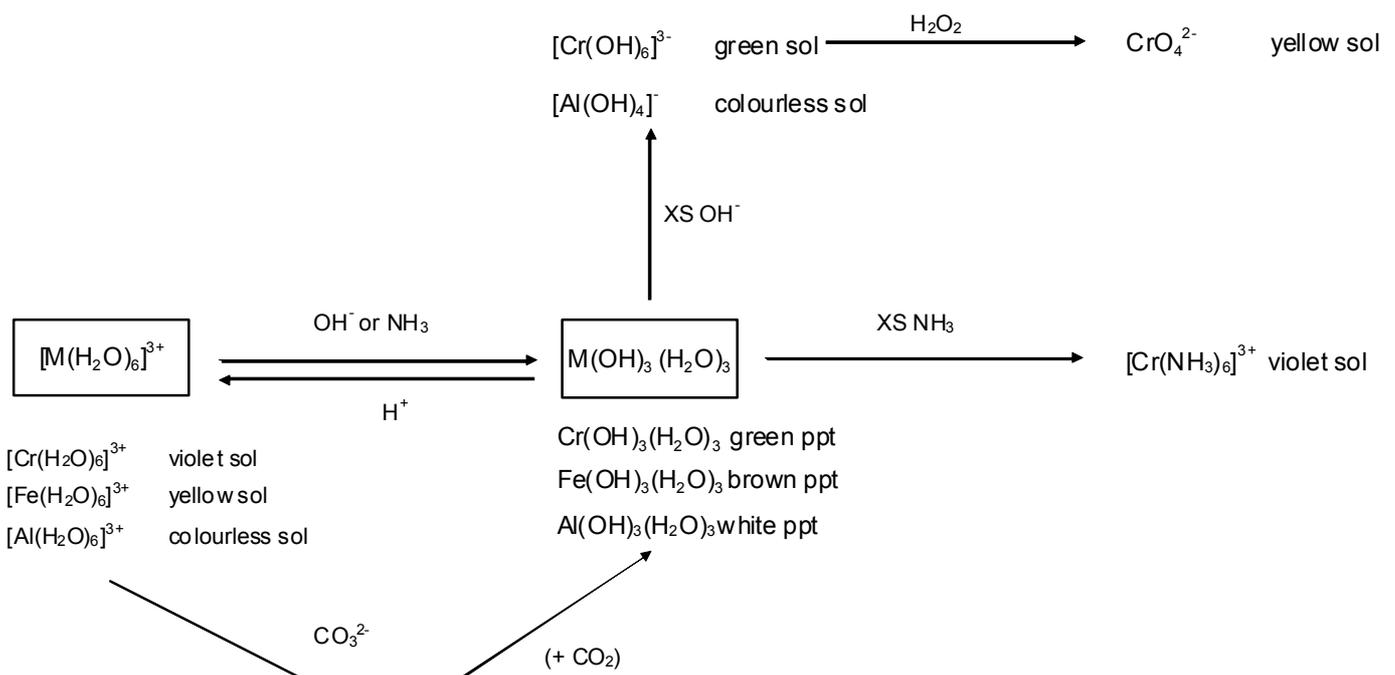
This substitution may, however, be incomplete as in the case with Cu



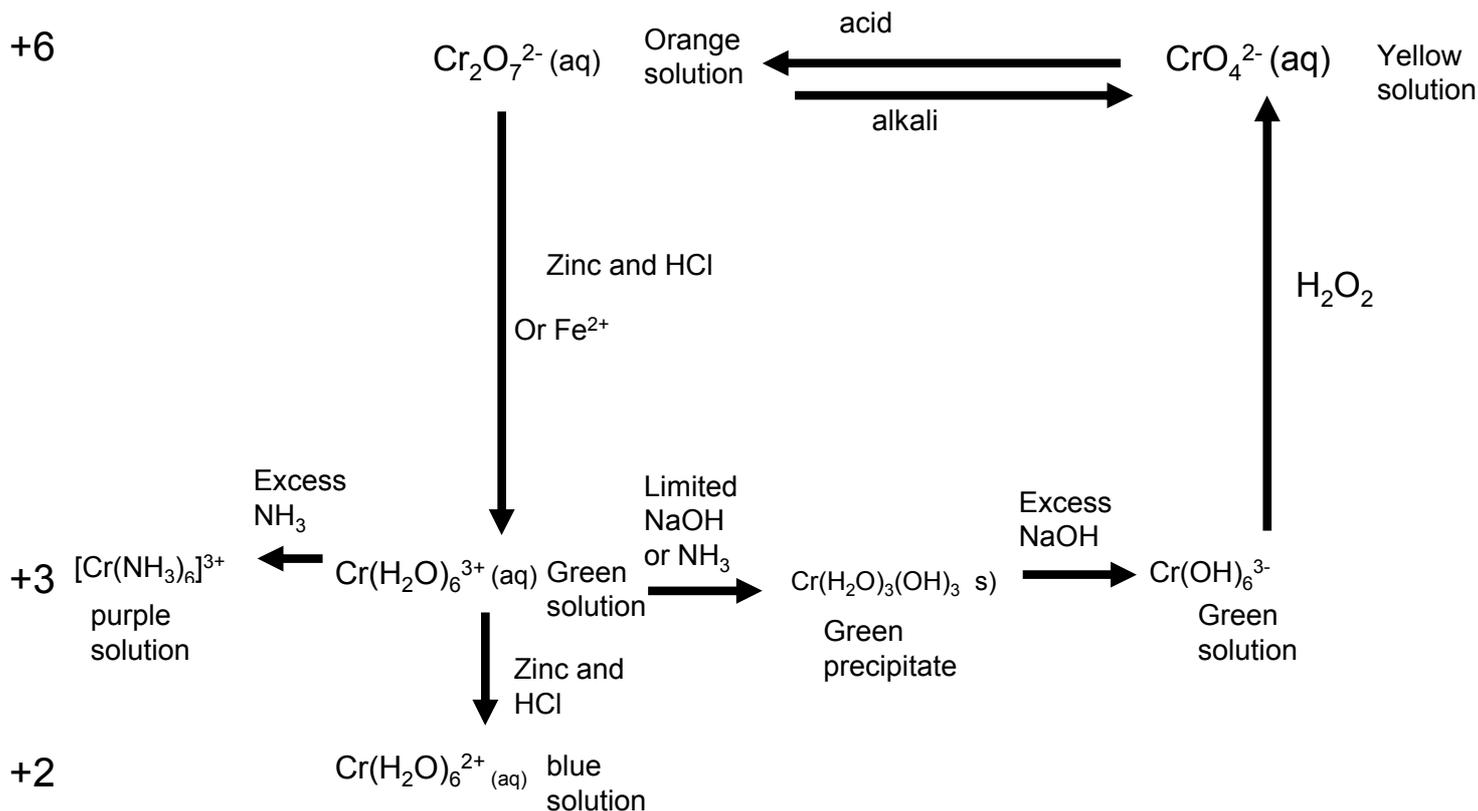
2+ ion summary



3+ ion summary



Chromium summary



Silver Chemistry

Reactions of halides with Silver nitrate

Fluorides produce no precipitate
 Chlorides produce a white precipitate
 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
 Bromides produce a cream precipitate
 $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$
 Iodides produce a pale yellow precipitate
 $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$

The silver halide precipitates can be treated with ammonia solution to help differentiate between them if the colours look similar:

Silver chloride dissolves in **dilute ammonia** to form a complex ion



Silver bromide dissolves in **concentrated ammonia** to form a complex ion



Silver iodide does not react with ammonia – it is too insoluble.

A2 questions often link module 2 halide silver nitrate chemistry to transition metals

