COBALT

- aqueous solutions contain the pink, octahedral hexaaquacobalt(II) ion.
- hexaaqua ions can also be present in solid samples of the hydrated salts.
- as it is a 2+ ion, the solutions are weakly acidic but protons can be removed by bases...

\[
\text{OH}^- \quad \text{[Co(H}_2\text{O)}_6]^{2+}_{\text{aq}} + 2\text{OH}^-_{\text{aq}} \quad \longrightarrow \quad \text{[Co(OH)}_2\text{(H}_2\text{O)}_4\text{]}_{\text{s}} + 2\text{H}_2\text{O(l)}
\]

**pink, octahedral**  **blue / pink ppt. soluble in XS NaOH**

ALL hexaaqua ions precipitate a hydroxide with OH\(^-\)\(_{\text{aq}}\). Some redissolve in excess NaOH.

\[
\text{NH}_3 \quad \text{[Co(H}_2\text{O)}_6]^{2+}_{\text{aq}} + 2\text{NH}_3_{\text{aq}} \quad \longrightarrow \quad \text{[Co(OH)}_2\text{(H}_2\text{O)}_4\text{]}_{\text{s}} + 2\text{NH}_4^+_{\text{aq}}
\]

**ALL hexaaqua ions precipitate a hydroxide with NH}_3_{\text{aq}}.** It removes protons.

Some hydroxides redissolve in excess NH}_3_{\text{aq} as ammonia substitutes as a ligand.

\[
\text{[Co(OH)}_2\text{(H}_2\text{O)}_4\text{]}_{\text{s}} + 6\text{NH}_3_{\text{aq}} \quad \longrightarrow \quad \text{[Co(NH}_3)_6]^{2+}_{\text{aq}} + 4\text{H}_2\text{O(l)} + 2\text{OH}^-_{\text{aq}}
\]

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

\[
\text{[Co(NH}_3)_6]^{2+}_{\text{aq}} \quad \longrightarrow \quad \text{[Co(NH}_3)_6]^{3+}_{\text{aq}} + \text{e}^-
\]

**yellow / brown octahedral**  **red / brown octahedral**

\[
\text{CO}_3^{2-} \quad \text{[Co(H}_2\text{O)}_6]^{2+}_{\text{aq}} + \text{CO}_3^{2-}_{\text{aq}} \quad \longrightarrow \quad \text{CoCO}_3_{\text{s}} + 6\text{H}_2\text{O(l)}
\]

**mauve ppt.**

ALL hexaaqua ions of metals with charge 2+ precipitate a carbonate but 3+ ones don’t.

\[
\text{Cl}^- \quad \text{[Co(H}_2\text{O)}_6]^{2+}_{\text{aq}} + 4\text{Cl}^-_{\text{aq}} \quad \longrightarrow \quad \text{[CoCl}_4]^{2-}_{\text{aq}} + 6\text{H}_2\text{O(l)}
\]

**blue, tetrahedral**

- Cl\(^-\) ligands are larger than H\(_2\)O and are charged
- the complex is more stable if the shape changes to tetrahedral - less repulsion between ligands
- adding excess water reverses the reaction
COPPER

Copper (II) Aqueous solutions of copper(II) contain the blue, octahedral hexaaquacopper(II) ion. Most substitution reactions are similar to cobalt(II).

\[ \text{OH}^- \quad [\text{Cu(H}_2\text{O)}_6]^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow [\text{Cu(OH)}_2(\text{H}_2\text{O})_4]_{(s)} + 2\text{H}_2\text{O}_{(l)} \]

\text{blue, octahedral}

\text{pale blue ppt.}

\text{insoluble in XS NaOH}

\[ \text{CO}_3^{2-} \quad [\text{Cu(H}_2\text{O)}_6]^{2+}_{(aq)} + \text{CO}_3^{2-}_{(aq)} \rightarrow \text{CuCO}_3_{(s)} + 6\text{H}_2\text{O}_{(l)} \]

\text{blue ppt.}

\[ \text{NH}_3 \quad [\text{Cu(H}_2\text{O)}_6]^{2+}_{(aq)} + 2\text{NH}_3_{(aq)} \rightarrow [\text{Cu(OH)}_2(\text{H}_2\text{O})_4]_{(s)} + 2\text{NH}_4^+_{(aq)} \]

\text{then blue ppt. soluble in excess NH}_3

\[ [\text{Cu(OH)}_2(\text{H}_2\text{O})_4]_{(s)} + 4\text{NH}_3_{(aq)} \rightarrow [\text{Cu(NH}_3)_4(\text{H}_2\text{O})_2]^{2+}_{(aq)} + 2\text{H}_2\text{O}_{(l)} + 2\text{OH}^-_{(aq)} \]

\text{royal blue solution}

\text{NOTE THE FORMULA}

\[ \text{Cl}^- \quad [\text{Cu(H}_2\text{O)}_6]^{2+}_{(aq)} + 4\text{Cl}^-_{(aq)} \rightarrow [\text{CuCl}_4]^{2-}_{(aq)} + 6\text{H}_2\text{O}_{(l)} \]

\text{yellow, tetrahedral}

\text{Cl}^- \text{ ligands are larger than H}_2\text{O and are charged}

\text{the complex is more stable if the shape changes to tetrahedral}

\text{adding excess water reverses the reaction}

\[ \text{I}^- \quad 2\text{Cu}^{2+}_{(aq)} + 4\text{I}^-_{(aq)} \rightarrow 2\text{CuI}_{(s)} + \text{I}_2_{(aq)} \]

\text{off white ppt.}

\text{a redox reaction}

\text{used in the volumetric analysis of copper using sodium thiosulphate}

Copper(I) The aqueous chemistry of copper(I) is unstable with respect to copper(0) and copper (II).

\[ \text{Cu}^+_{(aq)} + \text{e}^- \rightarrow \text{Cu}_{(s)} \quad \text{E}^o = +0.52 \text{ V} \]

\[ \text{Cu}^{2+}_{(aq)} + \text{e}^- \rightarrow \text{Cu}^+_{(aq)} \quad \text{E}^o = +0.15 \text{ V} \]

\text{subtracting}

\[ 2\text{Cu}^+_{(aq)} \rightarrow \text{Cu}_{(s)} + \text{Cu}^{2+}_{(aq)} \quad \text{E}^o = +0.37 \text{ V} \]

\text{DISPROPORTIONATION:- a species is simultaneously oxidised and reduced to more stable forms. This explains why the aqueous chemistry of copper(I) is very limited.}

\text{Stabilisation} Copper(I) can be stabilised by forming complexes \[ [\text{Cu(NH}_3)_2]^+ \quad [\text{Cu(CN)}_2]^- \]

\text{USES} Copper is used in alloys such as brass and bronze
Chromium(III) ions are typical of M$^{3+}$ ions in this block. Aqueous solutions contain the violet, octahedral hexaaquachromium(III) ion.

\[
\text{OH}^- \quad [\text{Cr(H}_2\text{O)}_6]^{3+} \text{(aq)} + 3\text{OH}^- \text{(aq)} \rightarrow [\text{Cr(OH)}_3(\text{H}_2\text{O)}_3]_\text{(s)} + 3\text{H}_2\text{O(l)}
\]

As with all hydroxides the precipitate reacts with acid

\[
[\text{Cr(OH)}_3(\text{H}_2\text{O)}_3]_\text{(s)} + 3\text{H}^+ \text{(aq)} \rightarrow [\text{Cr(H}_2\text{O)}_6]^{3+} \text{(aq)}
\]

being a 3+ hydroxide it is AMPHOTERIC as it dissolves in excess alkali

\[
[\text{Cr(OH)}_3(\text{H}_2\text{O)}_3]_\text{(s)} + 3\text{OH}^- \text{(aq)} \rightarrow [\text{Cr(OH)}_6]^{3-} \text{(aq)} + 3\text{H}_2\text{O(l)}
\]

The carbonate is not precipitated but the hydroxide is. The high charge density of M$^{3+}$ ions makes the solutions too acidic to form the carbonate. CARBON DIOXIDE IS EVOLVED.

\[
\text{CO}_3^{2-} \quad 2[\text{Cr(H}_2\text{O)}_6]^{3+} \text{(aq)} + 3\text{CO}_3^{2-} \text{(aq)} \rightarrow 2[\text{Cr(OH)}_3(\text{H}_2\text{O)}_3]_\text{(s)} + 3\text{H}_2\text{O(l)} + 3\text{CO}_2(g)
\]

In the presence of alkali, Cr(III) is unstable and can be oxidised to Cr(VI) with peroxide.

\[
2\text{Cr}^{3+} \text{(aq)} + 3\text{H}_2\text{O}_2(l) + 10\text{OH}^- \text{(aq)} \rightarrow 2\text{CrO}_4^{2-} \text{(aq)} + 8\text{H}_2\text{O(l)}
\]

Acidification of the yellow chromate will produce the orange dichromate(VI) ion

Chromium(III) can be reduced to the less stable chromium(II) by zinc in acidic solution.

\[
2[\text{Cr(H}_2\text{O)}_6]^{3+} \text{(aq)} + \text{Zn(s)} \rightarrow 2[\text{Cr(H}_2\text{O)}_6]^{2+} \text{(aq)} + \text{Zn}^{2+} \text{(aq)}
\]
Chromium (VI) Occurs as dichromate (VI) $\text{Cr}_2\text{O}_7^{2-}$ orange

and chromate (VI) $\text{CrO}_4^{2-}$ yellow

**Interconversion**

Dichromate is stable in acid solution; chromate is stable in alkaline solution.

- In alkali: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightleftharpoons 2\text{CrO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(l)$

- In acid: $2\text{CrO}_4^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}(l)$

Oxidising power Being in the highest oxidation state (+6), they will be oxidising agents.

In acidic solution, dichromate is widely used in both organic (oxidation of alcohols) and inorganic chemistry. It can also be used as a volumetric reagent but with special indicators as its colour change (orange to green) makes the end point hard to observe.

$$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(l) \quad [E^\circ = +1.33 \text{ V}]$$

- Its $E^\circ$ value is lower than that of $\text{Cl}_2$ (1.36V) so can be used in the presence of $\text{Cl}^-$ ions.
- $\text{MnO}_4^-(E^\circ = 1.52V)$ oxidises chloride in HCl so must be acidified with sulphuric acid.
- Chromium(VI) can be reduced back to chromium(III) using zinc in acid solution.

MANGANESE

Mn (VII)

- Manganese is in its highest oxidation state therefore Mn(VII) will be an oxidising agent
- Occurs in the purple, tetraoxomanganate(VII) (permanganate) ion $\text{MnO}_4^{-}$.
- It acts as an oxidising agent in acidic or alkaline solution.

- **Acidic** $\text{MnO}_4^{-}(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(l) \quad E^\circ = + 1.52 \text{ V}$

- **Alkaline** $\text{MnO}_4^{-}(\text{aq}) + 2\text{H}_2\text{O}(l) + 3\text{e}^- \rightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq}) \quad E^\circ = + 0.59 \text{ V}$

**N.B.** Acidify with dilute $\text{H}_2\text{SO}_4$ NOT dilute $\text{HCl}$

In volumetric analysis it must be acidified with dilute sulphuric acid as $\text{MnO}_4^{-}$ is powerful enough to oxidise the chloride ions in hydrochloric acid.

It is used to estimate iron(II), hydrogen peroxide, ethanedioic (oxalic) acid and ethanedioate (oxalate) ions. The last two titrations are carried out above 60°C due to the slow rate of reaction.

No indicator is required; the end point being the first sign of a permanent pale pink colour.
Iron (II)  When iron reacts with acids it gives rise to iron(II) (ferrous) salts. Aqueous solutions of such salts contain the pale green, octahedral hexaaquairon(II) ion.

\[
\text{OH}^- + [\text{Fe(H}_2\text{O)}_6]^{2+} \rightarrow [\text{Fe(OH)}_2(\text{H}_2\text{O})_4]^{2+} + 2\text{H}_2\text{O} \quad \text{pale green} \rightarrow \text{dirty green ppt.}
\]

It only re-dissolves in very conc. OH\(^-\) but on standing in air it slowly turns a rusty brown colour due to oxidation to iron(III). Increasing the pH renders iron(II) unstable.

\[
\text{Fe(OH)}_2 \rightarrow \text{Fe(OH)}_3 \quad \text{dirty green} \rightarrow \text{rusty brown}
\]

CO\(_3^{2-}\)  Off-white coloured iron(II) carbonate, FeCO\(_3\), precipitated.

NH\(_3\)  Iron(II) hydroxide precipitated, insoluble in excess ammonia.

Volumetric  Iron(II) can be analysed by titration with potassium manganate(VII) in acidic (H\(_2\)SO\(_4\)) solution. No indicator is required.

\[
\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \quad \text{this means that} \quad \frac{\text{moles of Fe}^{2+}}{\text{moles of MnO}_4^-} = \frac{5}{1}
\]

Iron(III)  Aqueous solutions contain the yellow-green, octahedral hexaaquairon(III) ion. It behaves as a typical M\(^{3+}\) ion.

\[
\text{OH}^- + [\text{Fe(H}_2\text{O)}_6]^{3+} \rightarrow [\text{Fe(OH)}_3(\text{H}_2\text{O})_3]^{2+} + 3\text{H}_2\text{O} \quad \text{yellow} \rightarrow \text{rusty-brown ppt. insoluble in XS}
\]

CO\(_3^{2-}\)  2 [Fe(H\(_2\)O\(_6\)]^{3+} + 3CO\(_3^{2-}\) \rightarrow 2 [Fe(OH\(_3\)(H\(_2\)O\(_3\))]^{2+} + 3\text{H}_2\text{O} + 3\text{CO}_2(g) \quad \text{rusty-brown ppt.}

The carbonate is not precipitated but the hydroxide is. High charge density of M\(^{3+}\) ions makes the solutions too acidic to form the carbonate. CARBON DIOXIDE EVOLVED.

NH\(_3\)  [Fe(H\(_2\)O\(_6\)]^{3+} + 3NH\(_3\) \rightarrow [Fe(OH\(_3\)(H\(_2\)O\(_3\))]^{2+} + 3\text{NH}_4^+ \quad \text{rusty-brown ppt. insoluble in XS}

SCN\(^-\)  [Fe(H\(_2\)O\(_6\)]^{3+} + SCN\(^-\) \rightarrow [Fe(SCN)(H\(_2\)O\(_5\))]^{2+} + \text{H}_2\text{O} \quad \text{blood-red colour}

Very sensitive. A blood red colour confirms Fe(III). No reaction with Fe(II)
Silver (I)

Occurrence  The diammine silver(I) ion is formed when ammonia dissolves silver halides

\[
\text{e.g. } \text{AgCl}_\text{(s)} + 2\text{NH}_3\text{(aq)} \rightarrow [\text{Ag(NH}_3\text{)}_2]^+\text{(aq)} + \text{Cl}^-\text{(aq)}
\]

*see notes on identification of halide ions in solution*

Complexes  Silver(I) complexes are **colourless in aqueous solution** and tend to be **linear**.

\([\text{Ag(SO}_3\text{)}_2]^{3-}\)  Formed when silver salts are dissolved in sodium thiosulphate "hypo" solution. The reaction is important in photographic fixing; silver bromide which has not been exposed to light is dissolved away leaving the black image of silver as the negative.

\[
\text{AgBr} + 2\text{S}_2\text{O}_3^{2-} \rightarrow [\text{Ag(S}_2\text{O}_3\text{)}_2]^{3-} + \text{Br}^-
\]

\([\text{Ag(CN)}_2]^-\)  Formed when silver salts are dissolved in sodium or potassium cyanide and the solution used for silver electroplating.

\([\text{Ag(NH}_3\text{)}_2]^+\)  • Used in Tollen’s reagent (SILVER MIRROR TEST)

* Tollen’s reagent is used to differentiate between aldehydes and ketones. Aldehydes produce a silver mirror on the inside of the test tube.

• Formed when silver halides dissolve in ammonia - TEST FOR HALIDES

OTHER IMPORTANT COMPOUNDS INVOLVING COMPLEXES

**Haemoglobin**  A complex containing iron(II) which is responsible for the red colour in blood and for the transport of oxygen by red blood cells.

Co-ordination of CO molecules interferes with the process

**Cis-platin**  An important anti-cancer drug. It is a square planar, 4 co-ordinate complex of platinum.
VANADIUM  Reduction using zinc in acidic solution shows the various oxidation states of vanadium.

\[
\begin{align*}
\text{Vanadium(V)} & \quad \text{VO}_2^{+}(\text{aq}) + 2\text{H}^{+}(\text{aq}) + e^- \rightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(l) & E^o & = +1.00 \text{ V} \\
\text{yellow} & \quad \text{blue} \\
\text{Vanadium(IV)} & \quad \text{VO}^{2+}(\text{aq}) + 2\text{H}^{+}(\text{aq}) + e^- \rightarrow \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(l) & E^o & = +0.34 \text{ V} \\
\text{blue} & \quad \text{blue/green} \\
\text{Vanadium(III)} & \quad \text{V}^{3+}(\text{aq}) + e^- \rightarrow \text{V}^{2+}(\text{aq}) & E^o & = -0.26 \text{ V} \\
\text{blue/green} & \quad \text{lavender}
\end{align*}
\]

Uses  \( \text{V}_2\text{O}_5 \)  Vanadium(V) oxide is used as a catalyst in the CONTACT PROCESS. It has the ability to change its oxidation state.

Oxidation and reduction of transition metal ions - Summary

Oxidation  
- hexaaqua metal ions  
- are stable in acid solution  
- tend to be less stable in alkaline solution  
- in alkaline conditions they form neutral hydroxides and/or anionic complexes  
- it is easier to remove electrons from species which are neutral or negatively charged  
- conditions involve addition of sodium hydroxide followed by hydrogen peroxide.

\[
\begin{align*}
\text{e.g.} & \quad \text{Fe(OH)}_2(s) + \text{OH}^- (\text{aq}) \rightarrow \text{Fe(OH)}_3(s) + e^- \\
\text{Co(OH)}_2(s) + \text{OH}^- (\text{aq}) & \rightarrow \text{Co(OH)}_3(s) + e^- \\
2\text{Cr}^{3+}(\text{aq}) + 3\text{H}_2\text{O}_2(l) + 10\text{OH}^- (\text{aq}) & \rightarrow 2\text{CrO}_4^{2-}(\text{aq}) + 8\text{H}_2\text{O}(l)
\end{align*}
\]

- Solutions of cobalt(II) can be oxidised by air under ammoniacal conditions
  \[
  [\text{Co(NH}_3)_6]^{2+}(\text{aq}) \rightarrow [\text{Co(NH}_3)_6]^{3+}(\text{aq}) + e^- 
  \]

Reduction  
- zinc metal is used to reduce transition metal ions to lower oxidation states  
- acts in acid solution as follows . . .  \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \)

\[
\begin{align*}
\text{e.g.} & \quad \text{it reduces iron(III)} \rightarrow \text{iron(II)} \\
& \quad \text{vanadium(V)} \rightarrow \text{vanadium (IV)} \\
& \quad \text{vanadium(IV)} \rightarrow \text{vanadium(III)}
\end{align*}
\]
ALUMINIUM

Properties
- aluminium is not a transition metal as it doesn’t make use of d orbitals... however
- due to their high charge density, aluminium(III) ions behave as typical M$^{3+}$ ions
- aqueous solutions contain the colourless, octahedral hexaaquaaluminium(III) ion

\[
\text{OH}^- + [\text{Al(H}_2\text{O)}_6]^{3+}_{(aq)} + 3\text{OH}^-_{(aq)} \rightarrow [\text{Al(OH)}_3(\text{H}_2\text{O})_3]_{(s)} + 3\text{H}_2\text{O}_{(l)}
\]

colourless, octahedral \hspace{1cm} white ppt. soluble in XS NaOH

As with all hydroxides the precipitate reacts with acid

\[
[\text{Al(OH)}_3(\text{H}_2\text{O})_3]_{(s)} + 3\text{H}^+_{(aq)} \rightarrow [\text{Al(H}_2\text{O)}_6]^{3+}_{(aq)}
\]

being a 3$^+$ hydroxide it is AMPHOTERIC and dissolves in excess alkali

\[
[\text{Al(OH)}_3(\text{H}_2\text{O})_3]_{(s)} + 3\text{OH}^-_{(aq)} \rightarrow [\text{Al(OH)}_6]^{3-}_{(aq)} + 3\text{H}_2\text{O}_{(l)}
\]

colourless, octahedral

\[
2[\text{Al(H}_2\text{O)}_6]^{3+}_{(aq)} + 3\text{CO}_3^{2-}_{(aq)} \rightarrow 2[\text{Al(OH)}_3(\text{H}_2\text{O})_3]_{(s)} + 3\text{H}_2\text{O}_{(l)} + 3\text{CO}_2(g)
\]

The carbonate is not precipitated but the hydroxide is. The high charge density of M$^{3+}$ ions makes the solutions too acidic to form the carbonate. CARBON DIOXIDE IS EVOLVED.

\[
\text{NH}_3 + [\text{Al(H}_2\text{O)}_6]^{3+}_{(aq)} + 3\text{NH}_3_{(aq)} \rightarrow [\text{Al(OH)}_3(\text{H}_2\text{O})_3]_{(s)} + 3\text{NH}_4^+_{(aq)}
\]

white ppt. insoluble in XS NH$_3$