

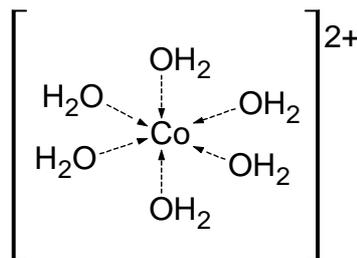
Reactions of Aqueous Ions

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Chemrevise.org

Metal-aqua ions

Metal aqua ions are formed
in aqueous solution

Most transition metals form
either +2 or +3 metal aqua ions



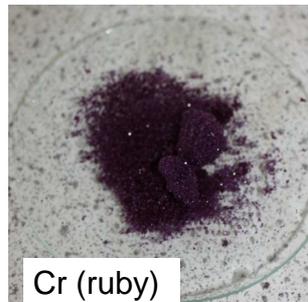
$[\text{M}(\text{H}_2\text{O})_6]^{2+}$, are formed by $\text{M} = \text{Fe}, \text{Co}$ and Cu ;
 $[\text{M}(\text{H}_2\text{O})_6]^{3+}$, are formed by $\text{M} = \text{Al}, \text{V}, \text{Cr}$ and Fe .

Aqua ions can also be present in the solid state (e.g.
 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$).

Colour of aqueous ions

$[\text{M}(\text{H}_2\text{O})_6]^{2+}$, limited to M = Fe (green) , Co(pink) and Cu (blue);
 $[\text{M}(\text{H}_2\text{O})_6]^{3+}$, 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



Cr (ruby)



Fe (violet)

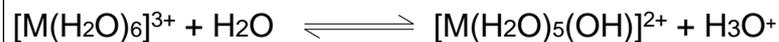
Acidity/hydrolysis reactions of metal aqua ions

Metal aqua ions form acidic solutions

One of the water molecules acting as the ligand is split so that H^+ ions come off leaving the OH^- on the complex.



and



For example,



The M^{3+} ions form acidic solutions and the M^{2+} ions form very weakly acidic solutions.

The acidity of $[M(H_2O)_6]^{3+}$ is greater than that of $[M(H_2O)_6]^{2+}$ because the polarising power (charge/size ratio) of the metal ion is greater on the 3+ 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 of Metal aqua ions with bases

Metal aqua ions can also do acidity type reactions with the bases (sodium hydroxide) OH^- , (ammonia) NH_3 and (sodium carbonate) CO_3^{2-} .

Reaction with hydroxides

Aqueous complex ions react with sodium hydroxide to form coloured precipitates.

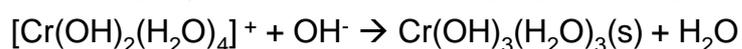
$$Cu(H_2O)_6^{2+} (aq) + 2OH^- (aq) \rightarrow Cu(H_2O)_4(OH)_2 (s) + H_2O (l)$$

Examples

$Cu(H_2O)_4(OH)_2 (s)$ blue ppt	$Al(H_2O)_3(OH)_3 (s)$ white ppt
$Co(H_2O)_4(OH)_2 (s)$ blue green ppt	$Cr(OH)_3(H_2O)_3 (s)$ green ppt.
$Fe(H_2O)_4(OH)_2 (s)$ green ppt	$Fe(H_2O)_3(OH)_3 (s)$ brown ppt

The reaction between the metal ions and sodium hydroxide occurs stepwise.

One proton is removed at each step until the hydroxide precipitate is formed.



$\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3(\text{s})$ is a green ppt.



If we continue adding sodium hydroxide then further deprotonation takes place, the hydroxide precipitate dissolves and $[\text{Cr}(\text{OH})_6]^{3-}$ is formed.

Only Cr and Al dissolve in excess NaOH. Al forms $[\text{Al}(\text{OH})_4]^-$

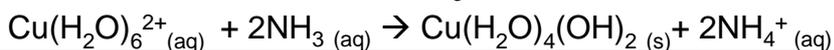
Reaction with limited amount of Ammonia

If a few drops of ammonia is added to metal aqua ions the same acidity reactions occur as with sodium hydroxide and the same coloured precipitates form.

Reaction of copper ion with NaOH.



Reaction of copper ion with NH_3 .



If excess ammonia is added some of the precipitates dissolve in a different type of reaction

Cu²⁺ copper(II)

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+} (\text{aq})$
 blue solution

$\xrightarrow{\text{NaOH (aq) or NH}_3 (\text{aq})}$

$\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2 (\text{s})$
 blue precipitate




$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow [\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4](\text{s}) + 2\text{H}_2\text{O}(\text{l})$
 $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} (\text{aq}) + 2\text{NH}_3(\text{aq}) \rightarrow [\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4](\text{s}) + 2\text{NH}_4^+(\text{aq})$

Co²⁺ cobalt(II)

$[\text{Co}(\text{H}_2\text{O})_6]^{2+} (\text{aq})$
 pink solution

$\xrightarrow{\text{NaOH (aq) or NH}_3 (\text{aq})}$

$\text{Co}(\text{H}_2\text{O})_4(\text{OH})_2 (\text{s})$
 blue precipitate




$[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow [\text{Co}(\text{OH})_2(\text{H}_2\text{O})_4](\text{s}) + 2\text{H}_2\text{O}(\text{l})$
 $[\text{Co}(\text{H}_2\text{O})_6]^{2+} (\text{aq}) + 2\text{NH}_3(\text{aq}) \rightarrow [\text{Co}(\text{OH})_2(\text{H}_2\text{O})_4](\text{s}) + 2\text{NH}_4^+(\text{aq})$

Cr³⁺ chromium(III)

$[\text{Cr}(\text{H}_2\text{O})_6]^{3+} (\text{aq}) \xrightarrow{\text{NaOH} (\text{aq}) \text{ or } \text{NH}_3 (\text{aq})} \text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3 (\text{s}) \xrightarrow{\text{excess NaOH} (\text{aq})} [\text{Cr}(\text{OH})_6]^{3-} (\text{aq})$

red-blue solution appears green because of hydrolysis green precipitate excess NaOH (aq) green solution

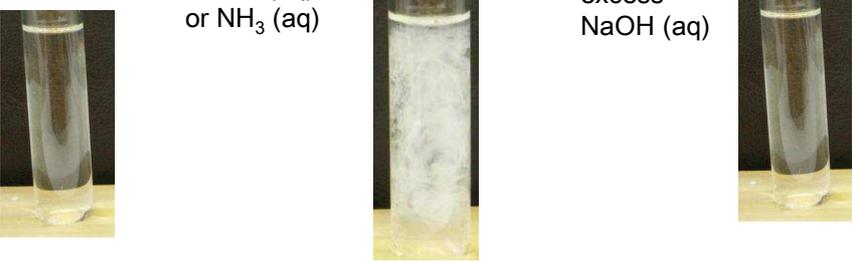


$[\text{Cr}(\text{H}_2\text{O})_6]^{3+} (\text{aq}) + 3\text{OH}^- (\text{aq}) \rightarrow [\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3] (\text{s}) + 3\text{H}_2\text{O} (\text{l})$
 $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} (\text{aq}) + 3\text{NH}_3 (\text{aq}) \rightarrow [\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3] (\text{s}) + 3\text{NH}_4^+ (\text{aq})$
 $[\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3] (\text{s}) + 3\text{OH}^- (\text{aq}) \rightarrow [\text{Cr}(\text{OH})_6]^{3-} (\text{aq}) + 3\text{H}_2\text{O} (\text{l})$

Al³⁺ Aluminium(III)

$[\text{Al}(\text{H}_2\text{O})_6]^{3+} (\text{aq}) \xrightarrow{\text{NaOH} (\text{aq}) \text{ or } \text{NH}_3 (\text{aq})} \text{Al}(\text{H}_2\text{O})_3(\text{OH})_3 (\text{s}) \xrightarrow{\text{excess NaOH} (\text{aq})} [\text{Al}(\text{OH})_4]^- (\text{aq})$

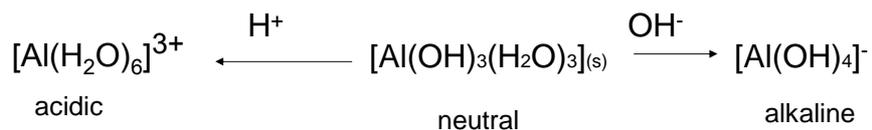
colourless solution white precipitate excess NaOH (aq) colourless solution



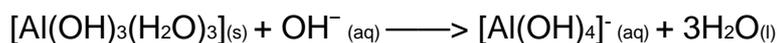
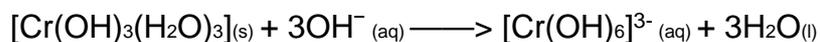
$[\text{Al}(\text{H}_2\text{O})_6]^{3+} (\text{aq}) + 3\text{OH}^- (\text{aq}) \rightarrow [\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3] (\text{s}) + 3\text{H}_2\text{O} (\text{l})$
 $[\text{Al}(\text{H}_2\text{O})_6]^{3+} (\text{aq}) + 3\text{NH}_3 (\text{aq}) \rightarrow [\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3]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

Amphoteric Character of some hydroxides

Some metal hydroxides show **amphoteric** character by dissolving in both acids and bases (e.g. hydroxides of Al^{3+} and Cr^{3+}).



The amphoteric hydroxides dissolve in excess sodium hydroxide



Reactions of chromium (VI) with acid and alkali

The equilibrium reaction between chromate and dichromate is also caused by the addition of acid or alkali



Yellow
solution

chromate

Orange
solution

dichromate



Note this is not a redox reaction because the Cr does not change oxidation number.

Reaction with carbonate ions

If H^+ ions are added in sufficient concentrations to carbonate ions the following equilibria are pushed to towards products and CO_2 is produced

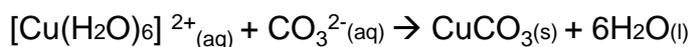


The metal aqua $2+$ ions are acidic but not sufficiently acidic to bring about the changes mentioned above

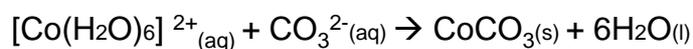


So when $2+$ metal aqua ions are added to carbonate ions they form coloured carbonate precipitates

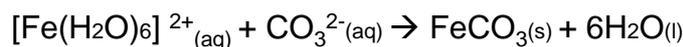
So when $2+$ metal aqua ions are added to carbonate ions they form coloured carbonate precipitates



blue precipitate



pink precipitate



green precipitate

These are **Precipitation** reactions



Reaction of 3+ metal ions with carbonate ions

The acidity of $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ is greater than that of $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ because the polarising power (charge/size ratio) of the metal ion is greater on the 3+ ion.

This acidity decomposes the CO_3^{2-} ions



The metal aqua reacts releasing H^+ ions and forms the hydroxide precipitate $\text{M}(\text{OH})_3(\text{H}_2\text{O})_3$

The distinctive coloured hydroxide precipitate is formed in addition to the fizzing of the CO_2 evolved.

It is not possible to form solid +3 carbonates $\text{M}_2(\text{CO}_3)_3$ whereas +2 carbonate form easily MCO_3

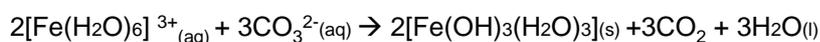
Reaction of 3+ metal ions with carbonate ions

Chromium



green precipitate *and*
colourless bubbles of CO_2 (g)

Iron III



brown precipitate *and*
colourless bubbles of CO_2 (g)

Aluminium



white precipitate *and*
colourless bubbles of CO_2 (g)

These are classed as acidity reactions

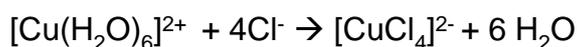
Substitution Reactions of complex ions

The metal aqua ions can also react by substituting one ligand for another



light blue

deep blue



light blue

green

Different ligands form complex ions of varying stability. One ligand can displace another in a complex ion if it can form a more stable complex.

Reaction of excess ammonia with metal aqua ions

When ammonia is added to some metal aqua ions the hydroxide precipitate first forms which then dissolves on addition of more ammonia. This second step is a ligand substitution reaction

The ligands NH_3 and H_2O are similar in size and are uncharged, and so ligand exchange occurs without change of co-ordination number (e.g. Co^{2+} and Cr^{3+}).

When excess ammonia is added to Chromium hydroxide a purple solution forms



Reaction of excess ammonia with cobalt

Similarly when excess ammonia is added to Cobalt hydroxide a pale brown solution forms



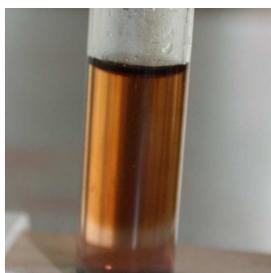
but ... ammonia ligands make the Co(II) state unstable.

Air oxidises Co(II) to Co(III).



yellow / brown

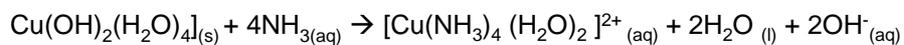
red / brown



So it is important to keep air away from this mixture

Reaction of excess ammonia with copper

However, with copper(II) the reaction with excess ammonia gives incomplete substitution

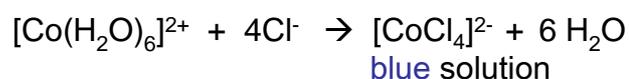
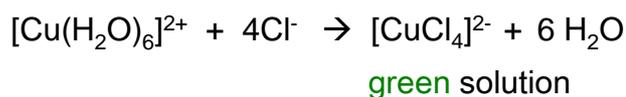


royal blue solution



Substitution with Cl⁻ ligand

The Cl⁻ ligand is larger than the uncharged water and ammonia ligands. Therefore ligand exchange with Cl⁻ ions can involve a change of co-ordination number



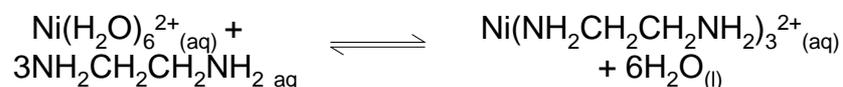
There is therefore a change from octahedral to tetrahedral shape.

Explaining the trends in stability using entropy

In general the order of stability for a complex ion goes

unidentate- bidentate – tetradentate- hexadentate

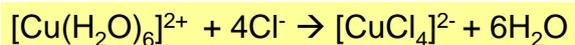
—————→
increasing stability



The Ni complex ion has changed from having unidentate ligands to bidentate ligands

In this reaction there is an increase in the entropy of the system because there are more moles of products than reactants (from 4 to 7), creating more disorder.

Stability constants



If this reaction is considered as equilibria then equilibrium expressions can be written

$$K = \frac{[\text{CuCl}_4^{2-} \text{ aq}]}{[\text{Cu}(\text{H}_2\text{O})_6^{2+} \text{ aq}] [\text{Cl}^- \text{ aq}]^4}$$

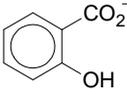
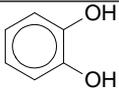
H_2O is not included in the expression because its concentration is assumed to be constant.

The value of K is called the stability constant for complex ions. The larger the stability constant the more stable the complex ion.

extra

A complex ion with a small stability constant will not displace the ligand from a more stable complex ion with a large stability constant.

eg adding ammonia to a complex ion of copper and edta will not result in a colour change

Ligand		Lg K
Cl^-	Chloride	5.62
NH_3	Ammonia	13.1
	2-hydroxybenzoate	16.9
	1,2-dihydroxybenzene	25.0
Edta^{4-}	Ethylenediaminetetraacetate	18.8

extra