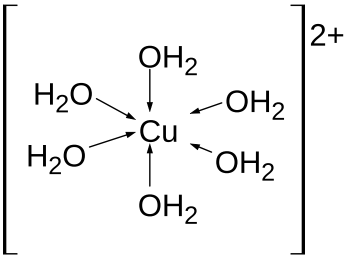
Reactions of Inorganic Compounds in Aqueous Solution

Metal-aqua ions

Metal aqua ions are formed in aqueous solution. Each complex has six water ligands arranged in a octahedral shape. The complex has the same charge as the metal ion as water is a neutral ligand



$[Cu(H_2O)_6]^{2+}$
blue

$[Co(H_2O)_6]^{2+}$
pink

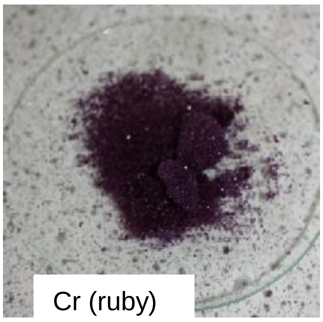
$[Fe(H_2O)_6]^{2+}$
green

$[Fe(H_2O)_6]^{3+}$
Violet
(appears
Yellow)

$[Cr(H_2O)_6]^{3+}$
Ruby
(appears
green)

$[Al(H_2O)_6]^{3+}$
colourless

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)

$[Zn(H_2O)_6]^{2+}$
colourless

$[Mn(H_2O)_6]^{2+}$
Very pale pink

$[Ni(H_2O)_6]^{2+}$
green

Acidity or hydrolysis reactions

The following equilibria happen in aqueous solutions of metal ions.

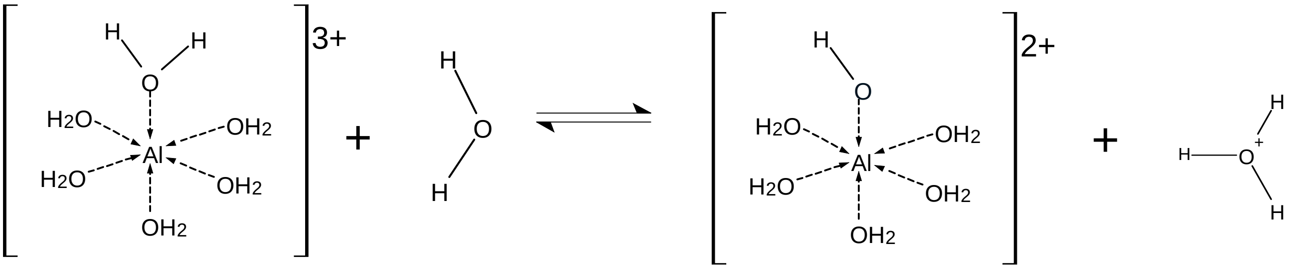
$$[M(H_2O)_6]^{2+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{+} + H_3O^{+}$$

$$[M(H_2O)_6]^{3+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{2+} + H_3O^{+}$$

For example,

$$[Cu(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Cu(H_2O)_5(OH)]^{+} + H_3O^{+}$$

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 $[M(H_2O)_6]^{2+}$ 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.

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

Reaction with limited OH^- and limited NH_3

Aqueous complex ions react with limited amounts of sodium hydroxide and ammonia to form coloured precipitates. The colours of the precipitates formed can be used to identify the metal ion

Examples

$Cu(H_2O)_4(OH)_{2\,(s)}$

blue ppt

$Co(H_2O)_4(OH)_{2\,(s)}$

blue green ppt

$Fe(H_2O)_4(OH)_{2\,(s)}$

green ppt

$Ni(H_2O)_4(OH)_{2\,(s)}$

Green ppt

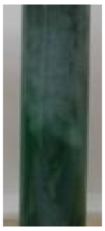
$Mn(H_2O)_4(OH)_{2\,(s)}$

pale brown ppt

$Zn(H_2O)_4(OH)_{2\,(s)}$

White ppt


$Al(H_2O)_3(OH)_{3\,(s)}$ white ppt


$Cr(OH)_3(H_2O)_{3\,(s)}$ green ppt.


$Fe(H_2O)_3(OH)_{3\,(s)}$ brown ppt

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

$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Cu(H_2O)_4(OH)_{2\,(s)} + 2H_2O_{\,(l)}$

$[Ni(H_2O)_6]^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Ni(H_2O)_4(OH)_{2\,(s)} + 2H_2O_{\,(l)}$

$[Co(H_2O)_6]^{2+}{}_{(aq)} + 2NH_{3\,(aq)} \rightarrow Co(H_2O)_4(OH)_{2\,(s)} + 2NH_4^+{}_{(aq)}$

$[Zn(H_2O)_6]^{2+}{}_{(aq)} + 2NH_{3\,(aq)} \rightarrow Zn(H_2O)_4(OH)_{2\,(s)} + 2NH_4^+{}_{(aq)}$

$[Cr(H_2O)_6]^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Cr(H_2O)_3(OH)_{3\,(s)} + 3H_2O_{\,(l)}$

$[Fe(H_2O)_6]^{3+}{}_{(aq)} + 3NH_{3\,(aq)} \rightarrow Fe(H_2O)_3(OH)_{3\,(s)} + 3NH_4^+{}_{(aq)}$

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

This process can happen step wise removing one proton at a time.
One proton is removed at each step until the hydroxide precipitate is formed.

e.g. $[Cr(H_2O)_6]^{3+}{}_{(aq)} + OH^-{}_{(aq)} \rightarrow [Cr(H_2O)_5(OH)]^{2+}{}_{(aq)} + H_2O_{\,(l)}$

$[Cr(H_2O)_5(OH)]^{2+}{}_{(aq)} + OH^-{}_{(aq)} \rightarrow [Cr(H_2O)_4(OH)_2]^+{}_{(aq)} + H_2O_{\,(l)}$

$[Cr(H_2O)_4(OH)_2]^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow Cr(H_2O)_3(OH)_{3\,(s)} + H_2O_{\,(l)}$

In some cases if sodium hydroxide is continued to be added until in excess then further deprotonation takes place, and the hydroxide precipitate dissolves.

Reaction with excess OH^-

With excess NaOH, the Cr, Zn and Al hydroxides dissolve.
Cr becomes $[Cr(OH)_6]^{3-}$ (aq) green solution.
Al becomes $[Al(OH)_4]^-$ (aq) colourless solution.
Zn becomes $[Zn(OH)_4]^{2-}{}_{(aq)}$ colourless solution

$Cr(H_2O)_3(OH)_{3\,(s)} + 3OH^-{}_{(aq)} \rightarrow [Cr(OH)_6]^{3-}{}_{(aq)} + 3H_2O_{(l)}$

$Al(H_2O)_3(OH)_{3\,(s)} + OH^-{}_{(aq)} \rightarrow [Al(OH)_4]^-{}_{(aq)} + 3H_2O_{\,(l)}$

$Zn(H_2O)_4(OH)_{2\,(s)} + 2OH^-{}_{(aq)} \rightarrow [Zn(OH)_4]^{2-}{}_{(aq)} + 4H_2O_{\,(l)}$

The hydroxides are classed as **amphoteric** because they react and dissolve in both acids and bases.

$$\underset{\text{acidic}}{[Al(H_2O)_6]^{3+}} \xleftarrow{\quad H^+ \quad} \underset{\text{neutral}}{[Al(OH)_3(H_2O)_3](s)} \xrightarrow{\quad OH^- \quad} \underset{\text{alkaline}}{[Al(OH)_4]^-}$$

$Cr(H_2O)_3(OH)_{3\,(s)} + 3H^+{}_{(aq)} \rightarrow [Cr(H_2O)_6]^{3+}{}_{(aq)}$
$Al(H_2O)_3(OH)_{3\,(s)} + 3H^+{}_{(aq)} \rightarrow [Al(H_2O)_6]^{3+}{}_{(aq)}$

Reaction with excess NH_3

With **excess NH_3 ligand substitution** reactions occur with some of the hydroxides and their precipitates dissolve
Cu, Co, Zn, Ni and Cr hydroxides all dissolve in excess ammonia

Cr becomes $[Cr(NH_3)_6]^{3+}$ purple solution
Zn becomes $[Zn(NH_3)_4]^{2+}$ colourless solution
Ni becomes $[Ni(NH_3)_6]^{2+}$ blue solution
Co becomes $[Co(NH_3)_6]^{2+}$ pale yellow solution
Cu becomes $[Cu(NH_3)_4(H_2O)_2]^{2+}$ deep blue solution

$[Cu(NH_3)_4(H_2O)_2]^{2+}$

$[Co(NH_3)_6]^{2+}$

$[Ni(NH_3)_6]^{2+}$

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, Ni and Cr.

$$Cr(OH)_3(H_2O)_{3(s)} + 6NH_{3\,(aq)} \rightarrow [Cr(NH_3)_6]^{3+}{}_{(aq)} + 3H_2O_{(l)} + 3OH^-{}_{(aq)}$$

$$Co(OH)_2(H_2O)_{4(s)} + 6NH_{3\,(aq)} \rightarrow [Co(NH_3)_6]^{2+}{}_{(aq)} + 4H_2O_{\,(l)} + 2OH^-{}_{(aq)}$$

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

$$Cu(OH)_2(H_2O)_{4(s)} + 4NH_{3\,(aq)} \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}{}_{(aq)} + 2H_2O_{\,(l)} + 2OH^-{}_{(aq)}$$

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

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 H_2O and NH_3 ligands so therefore ligand exchange can involve a change of co-ordination number.

Addition of conc HCl to aqueous ions of Cu, Co and Ni lead to a change in coordination number from 6 to 4.
$[CuCl_4]^{2-}$ yellow/green solution
$[CoCl_4]^{2-}$ blue solution
$[NiCl_4]^{2-}$

These are tetrahedral in shape

$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$

$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$

Reactions with Carbonate solution

The 2+ ions react differently to the 3+ ions with carbonate solutions.

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

$$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$$
$$H^+ + HCO_3^- \rightleftharpoons H_2O + CO_2$$

The metal aqua 2+ ions are acidic but not sufficiently acidic to bring about the changes mentioned above as the following equilibrium does not produce enough H^+ ions

$$[M(H_2O)_6]^{2+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^+ + H_3O^+$$

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

The **2+** ions with **carbonate** solution results in **MCO_3 ppt** being formed
Cu = blue/green ppt , Co = pink ppt , Fe(II)= green ppt, Zn = white ppt, Mn= pink ppt, Ni= green ppt

$Mn^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow MnCO_{3\,(s)}$

$Cu^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CuCO_{3\,(s)}$

$Fe^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow FeCO_{3\,(s)}$

$Co^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CoCO_{3\,(s)}$

$[Cu(H_2O)_6]^{2+} + CO_3^{2-} \rightarrow CuCO_3 + 6H_2O$

$[Fe(H_2O)_6]^{2+} + CO_3^{2-} \rightarrow FeCO_3 + 6H_2O$

$[Co(H_2O)_6]^{2+} + CO_3^{2-} \rightarrow CoCO_3 + 6H_2O$

These are **precipitation** reactions


$CoCO_3$


$CuCO_3$

The **3+** ions with **carbonate** solution form **a $M(OH)_3$ ppt and CO_2** gas is evolved.

MCO_3 is formed with 2+ ions but $M_2(CO_3)_3$ is not formed with 3+ ions.
The difference is explained by the greater polarising power of the 3+ ion due to its higher charge density. The greater the polarising power, the more strongly it attracts the water molecule. This weakens the O-H bond so it breaks more easily, producing a high concentration of H^+ ions.
The metal aqua ion reacts releasing H^+ ions and forms the hydroxide precipitate $M(OH)_3(H_2O)_3$

This acidity decomposes the CO_3^{2-} ions

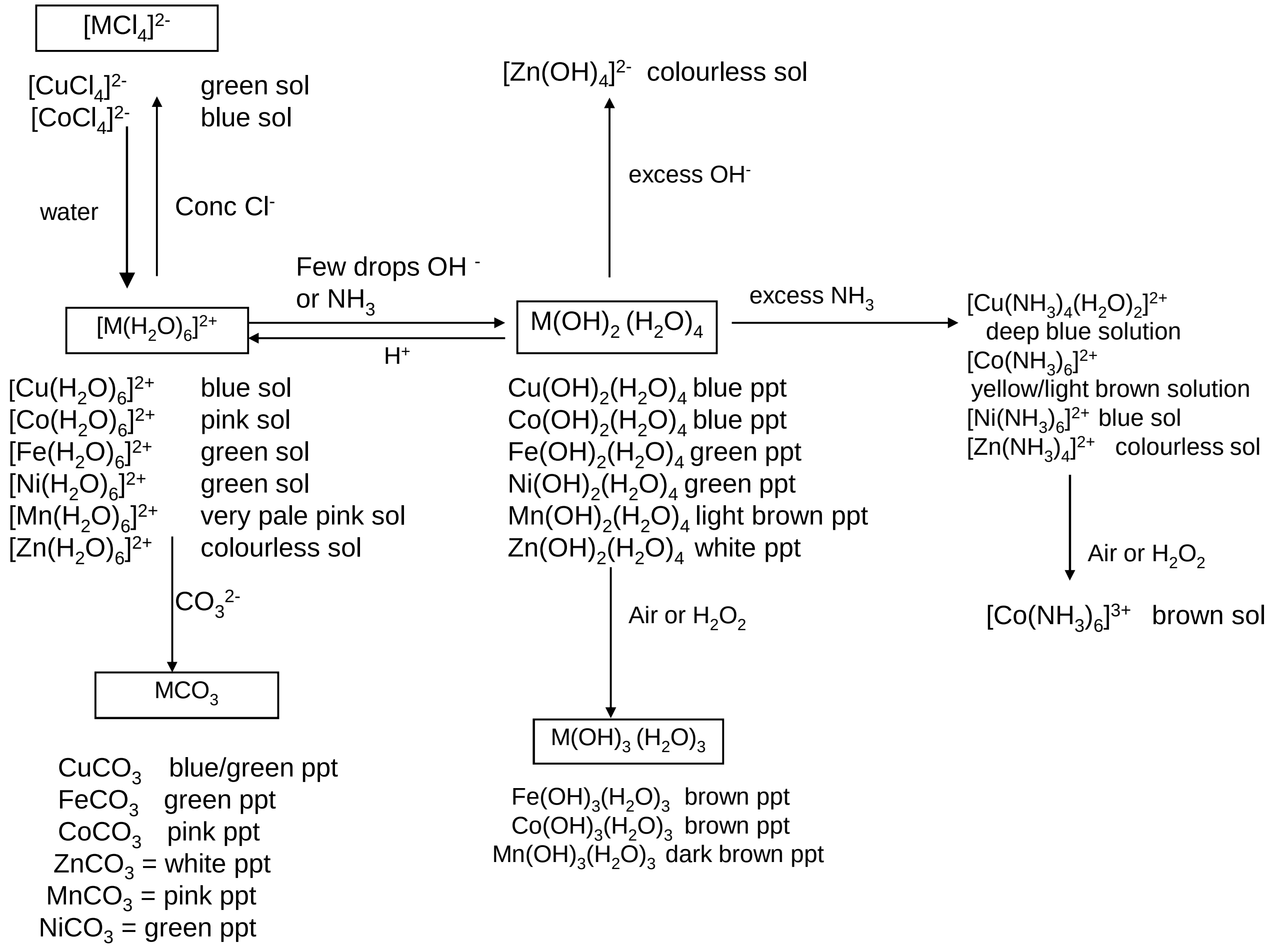
$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$$

Al forms white ppt of $Al(OH)_3\,(H_2O)_3 + CO_2$
Cr (III) forms green ppt of $Cr(OH)_3(H_2O)_3 + CO_2$
Fe(III) forms brown ppt of $Fe(OH)_3\,(H_2O)_3 + CO_2$

$$2[Cr(H_2O)_6]^{3+}{}_{(aq)} + 3CO_3^{2-}{}_{(aq)} \rightarrow 2Cr(OH)_3(H_2O)_{3(s)} + 3CO_2 + 3H_2O_{(l)}$$
$$2[Fe(H_2O)_6]^{3+}{}_{(aq)} + 3CO_3^{2-}{}_{(aq)} \rightarrow 2Fe(OH)_3(H_2O)_{3(s)} + 3CO_2 + 3H_2O_{(l)}$$
$$2[Al\,(H_2O)_6]^{3+}{}_{(aq)} + 3CO_3^{2-}{}_{(aq)} \rightarrow 2Al(OH)_3(H_2O)_{3(s)} + 3CO_2 + 3H_2O_{(l)}$$

These are classed as **acidity reactions.**

2+ Ion Summary



3+ Ion Summary