# The aqueous chemistry of cations

**Hydrolysis**

- when salts dissolve in water the ions are **stabilised by polar water molecules**
- **hydrolysis** can occur and the resulting solution can become acidic
- the acidity of the resulting solution depends on the cation present
- the greater the charge density of the cation, the more acidic the solution

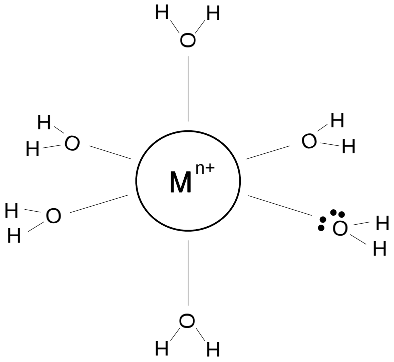
| *cation* | *charge* | *ionic radius* | *reaction with water and trend in pH of chloride* |
|---|---|---|---|
| **Na** | **1+** | **0.095 nm** | |
| **Mg** | **2+** | **0.065 nm** | |
| **Al** | **3+** | **0.050 nm** | |

**the greater charge density of the cation, the greater the polarising power and the more acidic the solution**

***Q.1*** *Predict what will happen when $SiCl_4$ is added to water.*

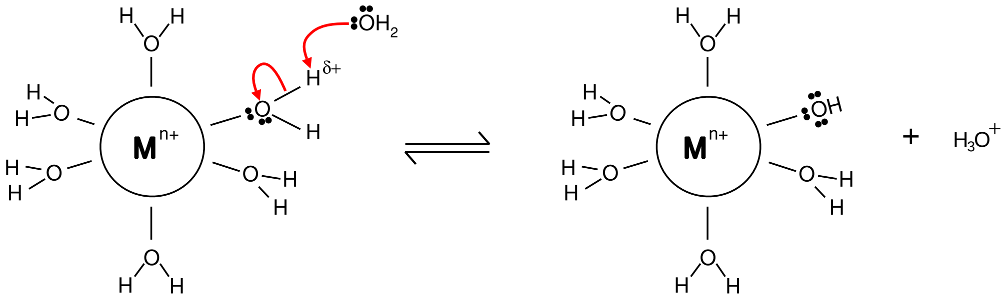
*Theory*

- aqueous metal ions attract water molecules
- many have **six water molecules** surrounding
- these are known as **hexaaqua ions**
- they are **octahedral** in shape
- water acts as a Lewis Base - lone pair donor
- water forms a co-ordinate bond to the metal ion
- metal ions accept the lone pair - Lewis Acids



*Acidity*

- as charge density increases, the cation exhibits a greater attraction for water
- the attraction extends to the shared pair of electrons in the O-H bonds of water
- the electron pair is pulled towards the O, making the bond more polar
- this makes the H more acidic (more δ+)
- it can then be removed by solvent water molecules to form $H_3O^+_{(aq)}$.



*Equations* *e.g.* $[M(H_2O)_6]^{2+}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons [M(H_2O)_5(OH)]^{+}{}_{(aq)} + H_3O^{+}{}_{(aq)}$

the equivalent reaction for $M^{3+}$ ions is

$$[M(H_2O)_6]^{3+}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons [M(H_2O)_5(OH)]^{2+}{}_{(aq)} + H_3O^{+}{}_{(aq)}$$

- the resulting solution will now be acidic as there are more protons in the water
- the greater the charge density of the cation, the more the equilibrium moves to the right
- this reaction is known as **hydrolysis -** the water causes the substance to split up

Stronger bases (e.g. $CO_3^{2-}$ , $NH_3$ and $OH^-$ ) can remove further protons ...

Lewis bases can attack the water molecules co-ordinated to metal ions. Theoretically, a proton can be removed from each water molecule turning the water from a neutral molecule to a negatively charged hydroxide ion. This will affect the overall charge on the complex ion.

$$[M(H_2O)_6]^{2+}{}_{(aq)} \rightleftharpoons [M(OH)(H_2O)_5]^{+}{}_{(aq)} \rightleftharpoons [M(OH)_2(H_2O)_4]_{(s)} \rightleftharpoons [M(OH)_3(H_2O)_3]^{-}{}_{(aq)}$$

$$\rightleftharpoons [M(OH)_4(H_2O)_2]^{2-}{}_{(aq)} \rightleftharpoons [M(OH)_5(H_2O)]^{3-}{}_{(aq)} \rightleftharpoons [M(OH)_6]^{4-}{}_{(aq)}$$

When sufficient protons have been removed the complex becomes neutral and precipitation of a hydroxide or carbonate occurs.

| | | | | |
|---|---|---|---|---|
| *e.g.* | $M^{2+}$ ions | $[M(H_2O)_4(OH)_2]_{(s)}$ | or | $M(OH)_2$ |
| | $M^{3+}$ ions | $[M(H_2O)_3(OH)_3]_{(s)}$ | or | $M(OH)_3$ |

In some cases, if the base is strong, further protons are removed and the precipitate dissolves as soluble anionic complexes are formed.

*e.g.* $[M(OH)_6]^{3-}{}_{(aq)}$ an octahedral, hexahydroxo ion

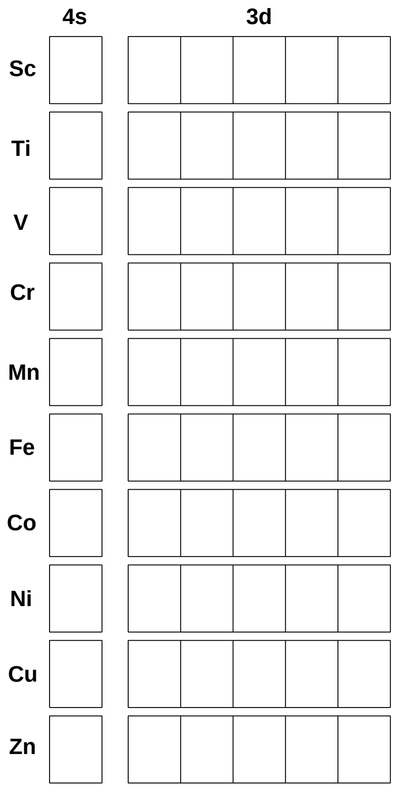
| | | | |
|---|---|---|---|
| *Summary* | Very weak bases | $H_2O$ | remove few protons |
| | Weak bases | $NH_3$, $CO_3^{2-}$ | remove protons until precipitation |
| | Strong bases | $OH^-$ | can remove all the protons |

# The First Row Transition Elements - an introduction

**Definition** D-block elements **forming one or more stable ions with partially filled (incomplete) d-sub shells.** The first row runs from scandium to zinc filling the 3d orbitals.

**Q.2** *Why, in terms of energy levels, are the 4s orbitals filled before the 3d orbitals ?*

**Electronic configs.** The filling proceeds according to the usual rules except that chromium and copper change slightly to achieve a more stable configuration.



**$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$**

The characteristic properties arise from an incomplete d sub-shell in atoms or ions

**Metallic properties**

- all the transition elements are metals
- **strong metallic bonds** result from **small size** and **close packing** of the atoms
- have **higher melting** and **boiling points** and **higher densities** than s-block metals

| | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | etc. |
|---|---|---|---|---|---|---|---|---|---|---|
| *m. pt / °C* | 63 | 850 | 1400 | 1677 | 1917 | 1903 | 1244 | 1539 | 1495 | |
| *density / g $cm^{-3}$* | 0.86 | 1.55 | 3 | 4.5 | 6.1 | 7.2 | 7.4 | 7.9 | 8.9 | |

**Variable oxidation state**

- arises from the similar energies required for removal of 4s and 3d electrons.
- maximum oxidation state rises across the group to manganese
- maximum falls as the energy required to remove more electrons becomes very high
- all (except scandium) have an $M^{2+}$ ion
- stability of the +2 oxidation state increases across the row - marked increase in 3rd I.E.

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| | | | | +7 | | | | | |
| | | | +6 | +6 | +6 | | | | |
| | | +5 | +5 | +5 | +5 | | | | |
| | +4 | +4 | +4 | +4 | +4 | +4 | | | |
| +3 | +3 | +3 | +3 | +3 | +3 | +3 | +3 | +3 | |
| | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +2 |
| | | | | | | | | +1 | |

**N.B.** **When electrons are removed they come from the 4s orbitals first**

*e.g.*

**Cu** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

**$Cu^+$** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

**$Cu^{2+}$** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

**Ti** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$

**$Ti^{2+}$** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$

**$Ti^{3+}$** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$

**$Ti^{4+}$** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

**Coloured ions**

- ions with a **$d^{10}$** (full) or **$d^0$** (empty) configuration are **colourless**
- ions with **partially filled d-orbitals** tend to be **coloured**
- caused by the ease of transition of electrons between energy levels
- energy is absorbed when an electron is promoted to a higher level
- the frequency of light is proportional to the energy difference

- colour depends on ... transition element
  oxidation state
  ligand
  coordination number

***Q.3*** *Find out the colours of the following ions in aqueous solution*

$Sc^{3+}$ $V^{2+}$ $Fe^{2+}$

$Fe^{3+}$ $Co^{2+}$ $Zn^{2+}$

$Cr^{3+}$ $Mn^{2+}$ $Cu^{2+}$

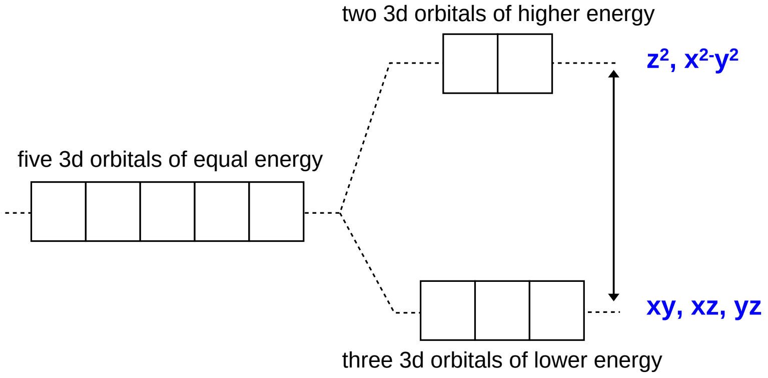
## Splitting of d orbitals

Placing ligands around a central metal ion changes the energies of the d orbitals
Some of the d orbitals gain energy and some lose energy

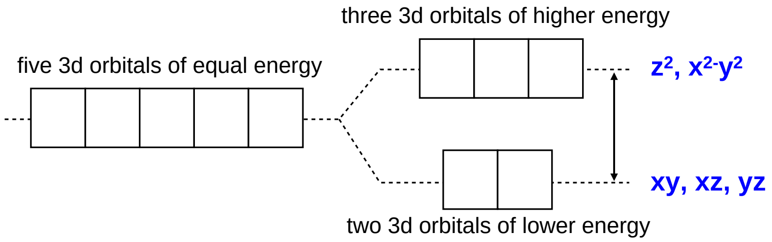
The amount of splitting depends on the
- central ion
- ligand

The difference in energy between the new levels affects how much energy will be absorbed when an electron is promoted to a higher level.

The amount of energy will govern the colour of light which will be absorbed.



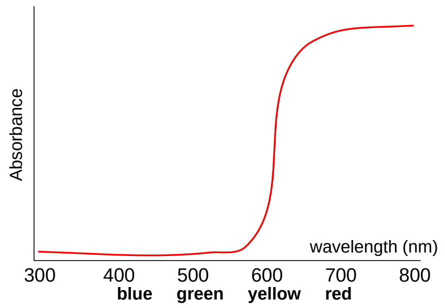
**OCTAHEDRAL COMPLEX**



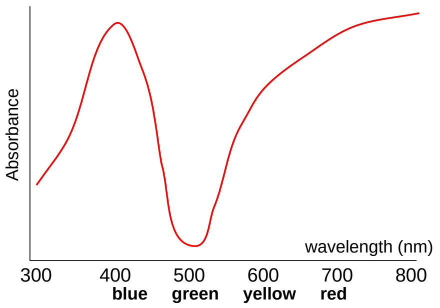
**TETRAHEDRAL COMPLEX**

| Absorbed colour | λ nm | Observed colour | λ nm |
|---|---|---|---|
| VIOLET | 400 | GREEN-YELLOW | 560 |
| BLUE | 450 | YELLOW | 600 |
| BLUE-GREEN | 490 | RED | 620 |
| YELLOW-GREEN | 570 | VIOLET | 410 |
| YELLOW | 580 | DARK BLUE | 430 |
| ORANGE | 600 | BLUE | 450 |
| RED | 650 | GREEN | 520 |

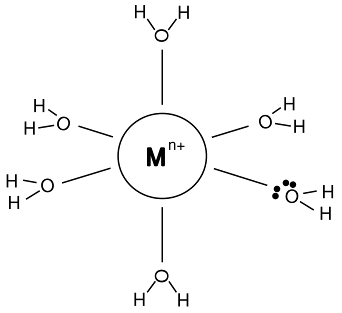
*a solution of copper(II)sulphate is blue because red and yellow wavelengths are absorbed*



*What colour is this hexaaqua complex?*



**COMPLEX IONS** Formed when species called **ligands** form **co-ordinate bonds** to a central species such as a transition metal ion.



**Ligands**

- atoms, or ions, which possess **lone pairs** of electrons
- form **co-ordinate bonds** to the central ion
- donate a lone pair of electrons into vacant orbitals on the central species

| *Ligand* | *Formula* | *Name of ligand* |
|---|---|---|
| chloride | $Cl^-$ | chloro |
| cyanide | $NC^-$ | cyano |
| hydroxide | $HO^-$ | hydroxo |
| oxide | $O^{2-}$ | oxo |
| water | $H_2O$ | aqua |
| ammonia | $NH_3$ | ammine |

- some ligands attach themselves using two or more lone pairs
- classified by the **number of lone pairs they use**, not the number they have
- multidentate and bidentate ligands lead to more stable complexes

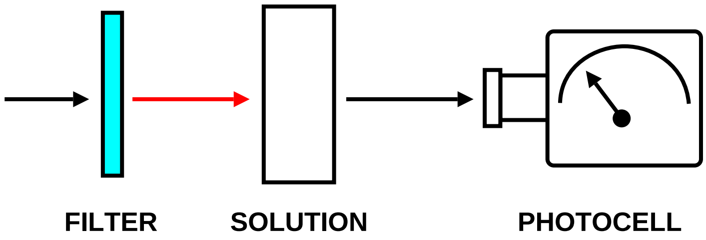
| | | |
|---|---|---|
| **Unidentate** | form one co-ordinate bond | $H_2O$ , $NH_3$ , $Cl^-$ and $OH^-$ |
| **Bidentate** | form two co-ordinate bonds | $H_2NCH_2CH_2NH_2$ , $C_2O_4^{2-}$ |
| **Multidentate** | form several co-ordinate bonds | EDTA , Haem |

**Q.4** *Draw structures for some bidentate and multidentate ligands*

# FINDING COMPLEX ION FORMULAE USING COLORIMETRY

**Colorimetry**

- a change of ligand can change the colour of a complex
- this property can be used to find the formula of a complex ion
- light of a certain wavelength is passed through a solution
- the greater the colour intensity, the greater the absorbance
- the concentration of each species in the complex is altered
- the mixture which gives the greatest absorbance identifies ratio of ligands and ions



**Examples**

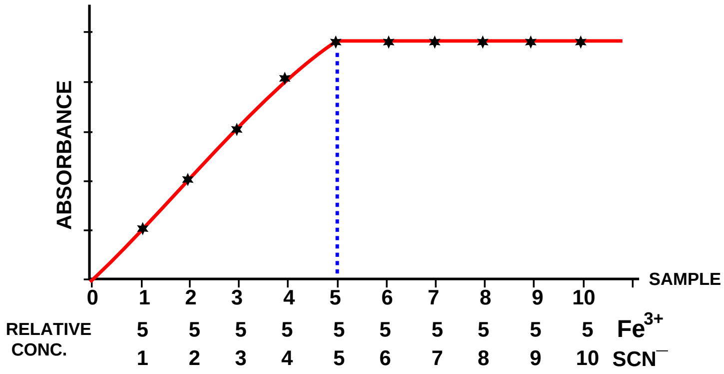
- finding the formula of the iron(III) complex **$Fe[(H_2O)_5SCN]^{2+}$**
  the complex formed between nickel(II) and edta

**Fe(III)**

White light is passed through a **blue filter**. The resulting **red light** is passed through various mixtures of an aqueous solution of iron(III) and potassium thiocyanate solution.

The **maximum absorbance occurs first** when the ratio of $Fe^{3+}$ and $SCN^{-}$ is 1:1.

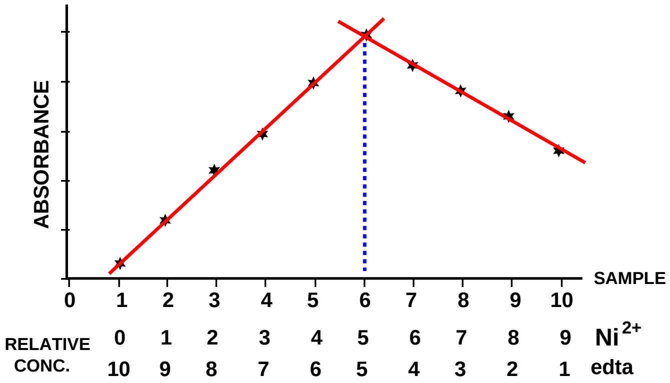
This shows the complex has the formula **$[Fe(H_2O)_5SCN]^{2+}$**



**Ni(II)**

Filtered light is passed through various mixtures of an aqueous solution of nickel(II) sulphate and edta solution.

The **maximum absorbance** occurs when the ratio of $Ni^{2+}$ and edta is 1:1.



# Naming Complexes

*Rules*

- Ligands are named before the central ion.
- Anionic ligands are named before neutral ones (alphabetical order within each type)
- If a ligand appears more than once it is given a prefix... di, tri, tetra, penta, hexa
- Anionic (negatively charged) ligands end in **o** (see table).
- The oxidation number of the central ion is given roman numerals in brackets following the name of the metal.
- If the complex has an overall negative charge then the metal name ends in **ate**. Some change their name (they tend to be those with latin derivations for their name).

**Q.5** *Fill in the missing names for metals in anionic complexes.*

| | | | |
|---|---|---|---|
| *aluminium* | ***aluminate*** | *chromium* | ***chromate*** |
| *cobalt* | | *copper* | |
| *iron* | | *lead* | |
| *manganese* | | *silver* | |
| *nickel* | | *zinc* | |

**Q.6** *Name the following complex ions.*

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

$[CuCl_4]^{2-}$

$[Co(NH_3)_6]^{3+}$

$[Al(OH)_6]^{3-}$

$MnO_4^{-}$

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

$[Cr(H_2O)_4Cl_2]^{+}$

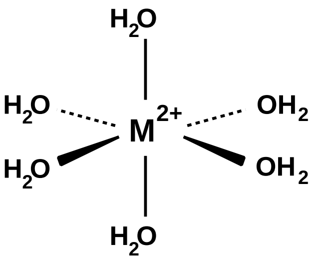
**SHAPE**

- the shape of a complex is **governed by the number of ligands** around the central ion
- shapes are based on electron pair repulsion theory
- **a change of ligand can affect the shape**

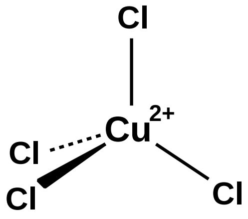
**COORDINATION NUMBER**

- the **number of co-ordinate bonds formed to the central ion**
- if monodentate ligands are present it will equal the number of ligands
- **a change of ligand can affect the co-ordination number**

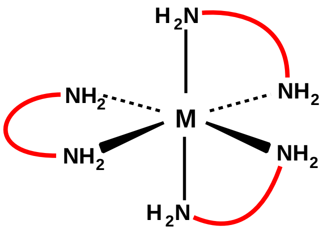
| *Co-ordination No.* | *Shape* | *Example(s)* |
|---|---|---|
| **6** | **Octahedral** | **$[Cu(H_2O)_6]^{2+}$** |
| **4** | **Tetrahedral** | **$[CuCl_4]^{2-}$** |
| | **Square planar** | **$[NiCl_4]^{2-}$** |
| **2** | **Linear** | **$[Ag(NH_3)_2]^+$** |



**CN = 6**



**CN = 4**



**CN = 6**

***Q.7*** *What is the co-ordination number and shape of the following complex ions?*

$[Cr(H_2O)_6]^{3+}$ $[CuCl_4]^{2-}$

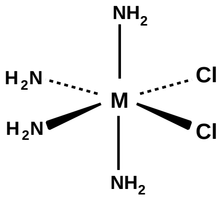
$[Co(H_2O)_6]^{2+}$ $[CoCl_4]^{2-}$

$[Cu(NH_3)_2]^{+}$ $[Al(OH)_6]^{3-}$

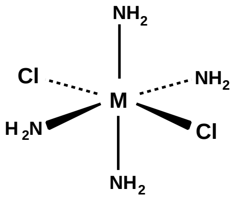
$MnO_4^{-}$ $[Cu(NH_3)_4(H_2O)_2]^{2+}$

# ISOMERISM IN COMPLEXES

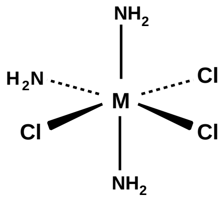
**Octahedral** Some octahedral complexes; e.g. $[MA_4B_2]^{n+}$ or $[MA_3B_3]^{n+}$ can exist in more than one form

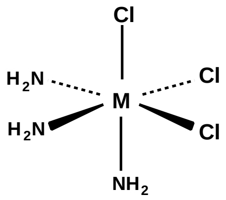


*CIS*

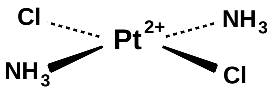


*TRANS*

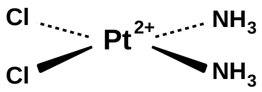




**Cis-trans** Square planar complexes of the form $[MA_2B_2]^{n+}$ exist in two forms

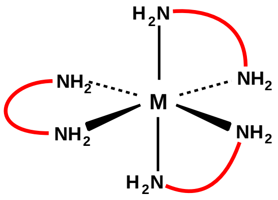


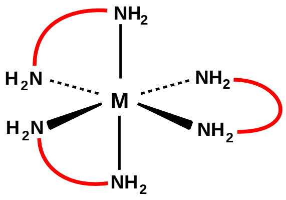
**trans platin**



**cis platin**
**(ANTI CANCER DRUG)**

**Optical** Octahedral complexes with bidentate ligands can exists as a pair of enantiomers (optical isomers)





**Catalysis**
- transition metals and their compounds show great catalytic activity...
- partly filled d-orbitals can be used to **form bonds with adsorbed reactants**
- due to their ability to exist in **more than one oxidation state**

***Q.8*** *In which reactions are the following catalysts used ?*

$V_2O_5$

*Fe*

$MnO_2$

*Ni*

*Pt/Rh*

*Cu*

# The first row transition elements

**Introduction** The examples aim to show typical properties of transition metals and their compounds.

- Variable oxidation states
- Formation of complex ions
- The importance of variable oxidation state in catalysis
- Definitions of Lewis Acids and Bases

One typical properties of transition elements is their ability to **form complex ions**. Complex ions consist of a **central metal ion surrounded by** co-ordinated ions or molecules known as **ligands**.

Ligand substitution can lead to changes in ...

- colour
- co-ordination number
- shape
- stability to oxidation or reduction

**Reactions** When investigating the reactions of selected transition metal ions, look for...

- **substitution** reactions of complex ions
- variation in **oxidation state** of transition metals
- the effect of ligands on **co-ordination number** and **shape**
- the increased acidity of $M^{3+}$ over $M^{2+}$ due to the increased charge density
- any difference in reactivity of $M^{3+}$ and $M^{2+}$ ions in reactions with $OH^-$ and $NH_3$
- the reason why $M^{3+}$ ions don't form carbonates
- **amphoteric character** in some metal hydroxides e.g. $Al^{3+}$ and $Cr^{3+}$
- the effect a ligand has on the **stability of an oxidation state**

## HEXAAQUA IONS

**Acidity** Lewis bases can attack the water molecules co-ordinated to transition metal ions. Protons can be removed from each water molecule turning the ligand from a neutral molecule to a negatively charged hydroxide ion. This will affect the overall charge on the complex ion.

$[M(H_2O)_6]^{2+}{}_{(aq)}$
$[M(OH)(H_2O)_5]^{+}{}_{(aq)}$
$\mathbf{[M(OH)_2(H_2O)_4]_{(s)}}$
$[M(OH)_3(H_2O)_3]^{-}{}_{(aq)}$
$[M(OH)_4(H_2O)_2]^{2-}{}_{(aq)}$
$[M(OH)_5(H_2O)]^{3-}{}_{(aq)}$
$[M(OH)_6]^{4-}{}_{(aq)}$

Species with no overall charge are insoluble and a precipitate is observed.

| | | |
|---|---|---|
| Very weak bases | $H_2O$ | remove few protons |
| Weak bases | $NH_3$, $CO_3^{2-}$ | remove protons until precipitation |
| Strong bases | $OH^-$ | can remove all the protons |

**Amphoteric character** Metal ions of 3+ charge have a high charge density and their hydroxides can dissolve in both acid and alkali.