

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

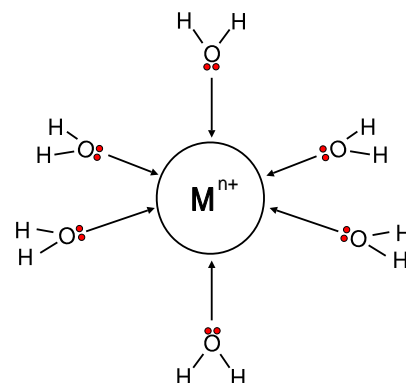
cation	charge	ionic radius	reaction with water and trend in pH of chloride
Na	1+	0.095 nm	
Mg	2+	0.065 nm	
Al	3+	0.050 nm	

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.

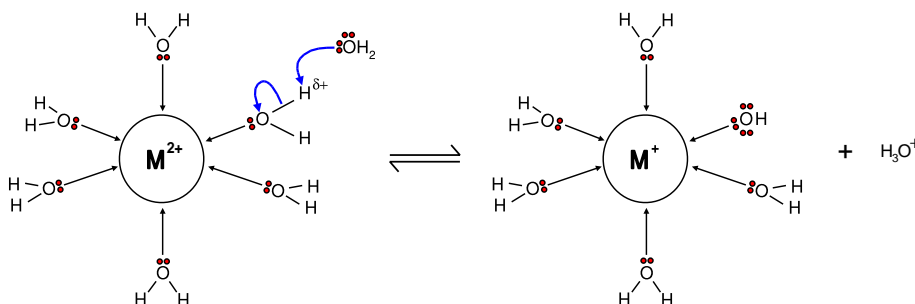
Theory

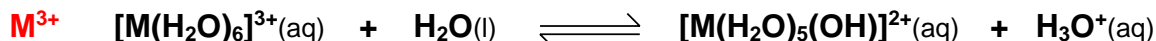
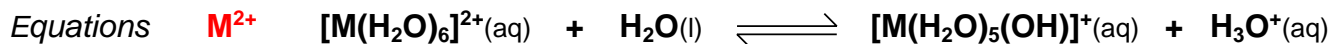
- aqueous metal ions attract water molecules
- many have **six water molecules** surrounding
- these are known as **hexaaqua ions**
- they are **octahedral** in shape
- water acts as a Lewis Base - lone pair donor
- water forms a co-ordinate bond to the metal ion
- metal ions accept the lone pair - Lewis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



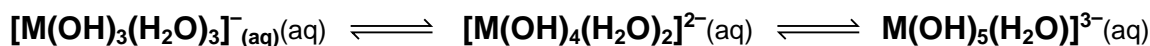
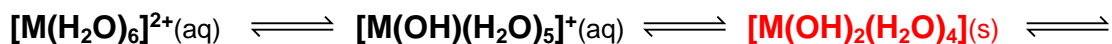


- the **resulting solution is acidic** as there are more protons in the water
- the greater the charge density of the cation, the more the equilibrium lies to RHS
- the reaction is known as **hydrolysis** - the water causes the substance to split up

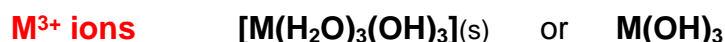
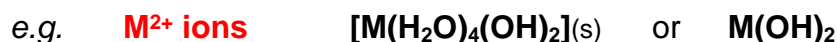
Stronger bases (e.g. CO_3^{2-} , NH_3 and OH^-) **can remove further protons ...**

- Lewis bases can attack the water molecules co-ordinated to metal ions.
- protons 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.

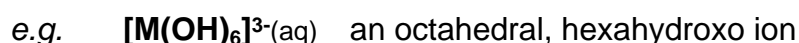
ADD BASE - EQUILIBRIUM MOVES TO THE RIGHT
ADD ACID - EQUILIBRIUM MOVES TO THE LEFT



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



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



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

Stability Constant - K_{stab}

Definition The stability constant, K_{stab} , of a complex ion is the equilibrium constant for the formation of the complex ion in a solvent from its constituent ions.

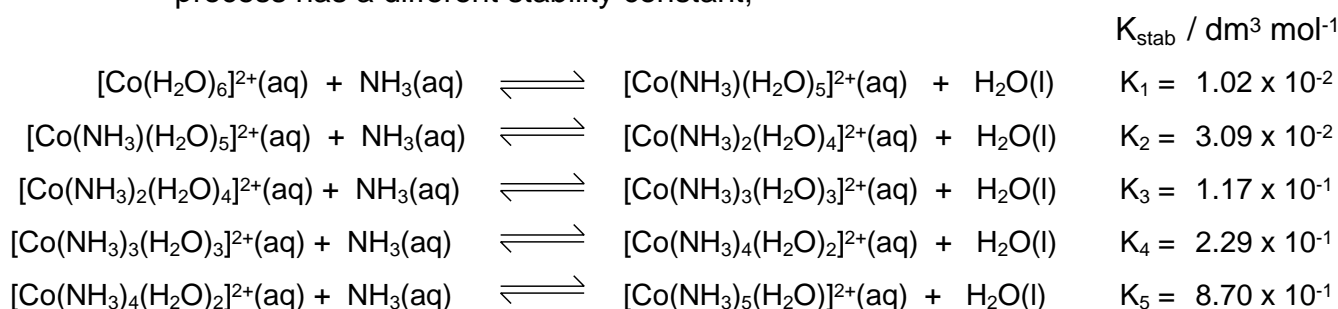


the expression for the stability constant is
$$K_{\text{stab}} = \frac{[\text{MX}_6^{4-}(\text{aq})]}{[\text{M}(\text{H}_2\text{O})_6^{2+}(\text{aq})][\text{X}^{-}(\text{aq})]^6}$$

Note that the water isn't included

The **LARGER** the value of K_{stab} - the more the equilibrium lies to the right
- the more stable the complex ion formed

Because ligand exchange involves a series of equilibria, each step in the process has a different stability constant;



The **overall stability constant** is simply the equilibrium constant for the total reaction. It is found by multiplying the individual stability constants... $k_1 \times k_2 \times k_3 \times k_4 \dots$ etc

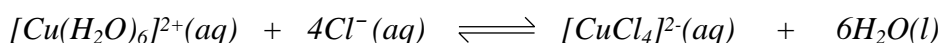
K_{stab} or $\text{p}K_{\text{stab}}$?

For an easier comparison, the expression $\text{p}K_{\text{stab}}$ is often used.

$$\text{p}K_{\text{stab}} = -\log_{10} K_{\text{stab}}$$

Q.2

Write an expression for the stability constant for the following reaction



Summary

- The larger the stability constant, the further the reaction lies to the right
- Complex ions with large stability constants are more stable
- Stability constants are often given as $\text{p}K_{\text{stab}}$
- Complex ions with smaller $\text{p}K_{\text{stab}}$ values are more stable

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 Sc to Zn filling the 3d orbitals.

Q.3 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.

	4s	3d	
Sc			$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$ or $[\text{Ar}] 3d^1 4s^2$
Ti			
V			
Cr			
Mn			
Fe			
Co			
Ni			
Cu			
Zn			

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
- **higher melting** and **boiling points** and **higher densities** than s-block metals

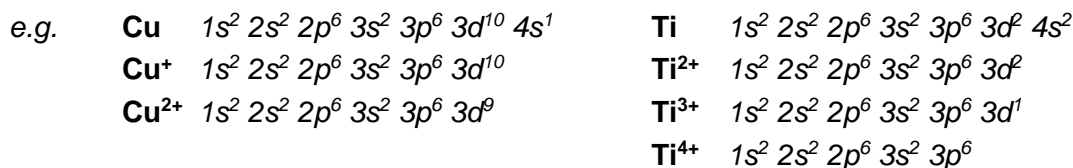
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	etc.
<i>m. pt / °C</i>	63	850	1400	1677	1917	1903	1244	1539	1495	
<i>density / g cm⁻³</i>	0.86	1.55	3	4.5	6.1	7.2	7.4	7.9	8.9	

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
- then falls as the energy required to remove more electrons becomes very high
- all (except scandium) have an M^{2+} ion
- stability of the +2 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



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.4 Find out the colours of the following ions in aqueous solution



Splitting of d orbitals

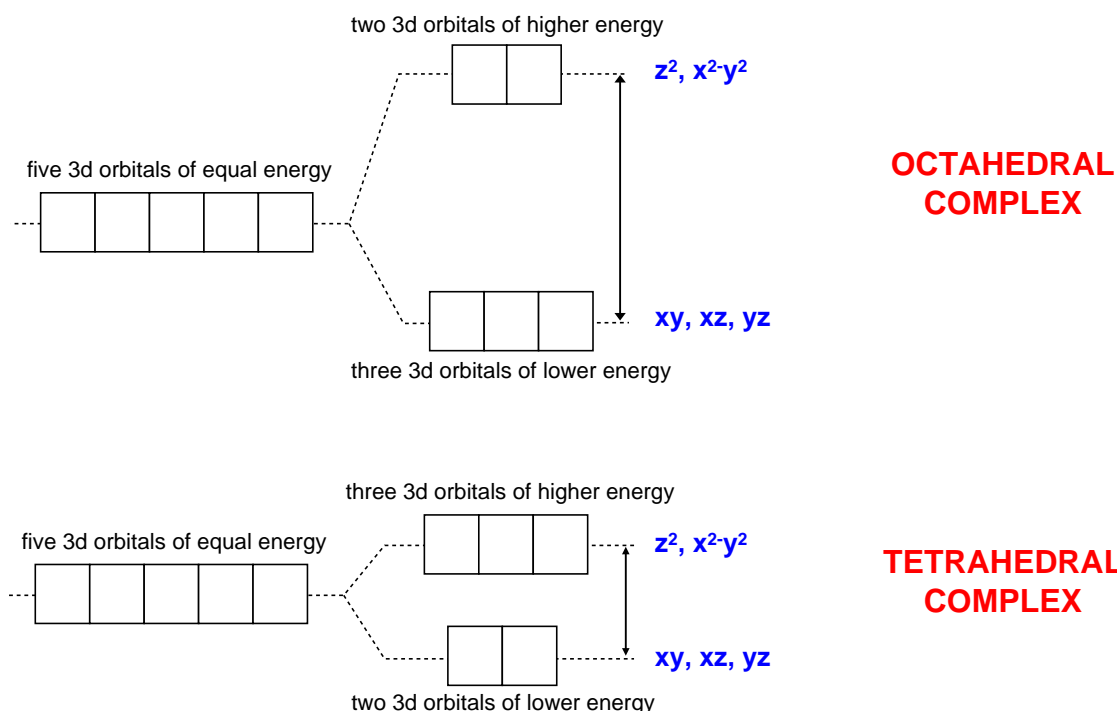
Placing ligands around a central metal ion changes the energies of the d orbitals. Some of the d orbitals gain energy and some lose energy

The amount of splitting depends on the

- central ion
- ligand

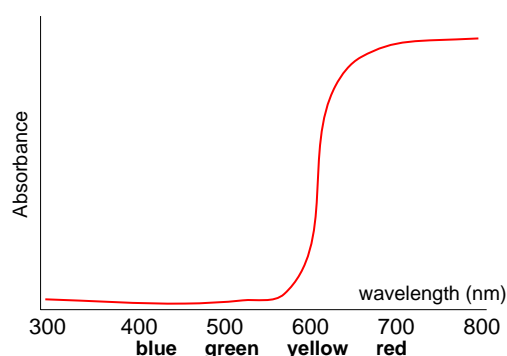
The difference in energy between the new levels affects how much energy will be absorbed when an electron is promoted to a higher level.

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

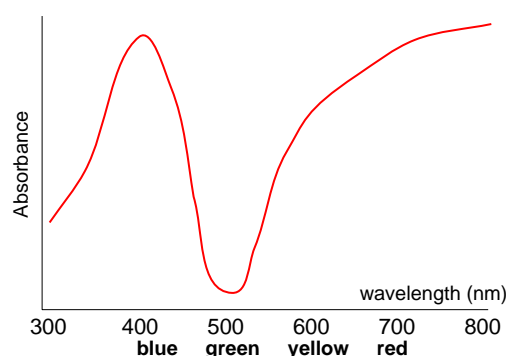


Absorbed colour	λ nm	Observed colour	λ nm
VIOLET	400	GREEN-YELLOW	560
BLUE	450	YELLOW	600
BLUE-GREEN	490	RED	620
YELLOW-GREEN	570	VIOLET	410
YELLOW	580	DARK BLUE	430
ORANGE	600	BLUE	450
RED	650	GREEN	520

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

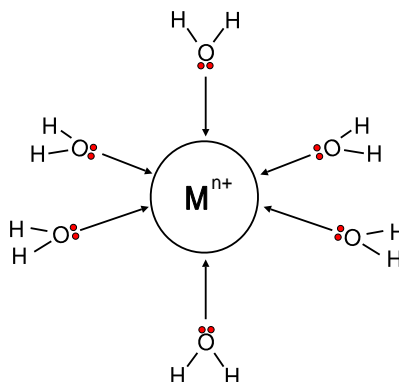


What colour is this hexaaqua complex?



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

<i>Ligand</i>	<i>Formula</i>	<i>Name of ligand</i>
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	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, $\text{C}_2\text{O}_4^{2-}$
Multidentate	form several co-ordinate bonds	EDTA , Haem

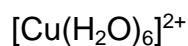
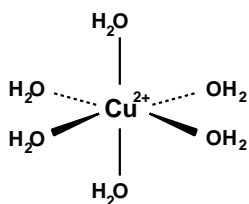
Q.5 Draw structures for some bidentate and multidentate ligands

- SHAPES**
- the shape 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

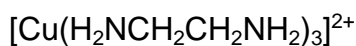
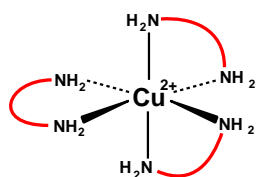
- the **number of co-ordinate bonds formed to the central ion**
- if monodentate ligands are present it will equal the number of ligands
- **a change of ligand can affect the co-ordination number**

<i>Co-ordination No.</i>	<i>Shape</i>	<i>Example(s)</i>
6	Octahedral	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
4	Tetrahedral	$[\text{CuCl}_4]^{2-}$
	Square planar	$[\text{NiCl}_4]^{2-}$
2	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$



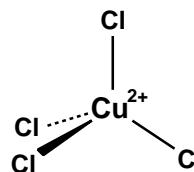
octahedral

CN = 6



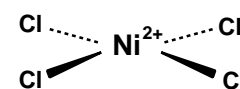
octahedral

CN = 6



tetrahedral

CN = 4



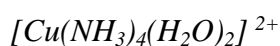
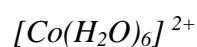
square planar

CN = 4

Q.6 What is the co-ordination number and shape of the following complex ions?

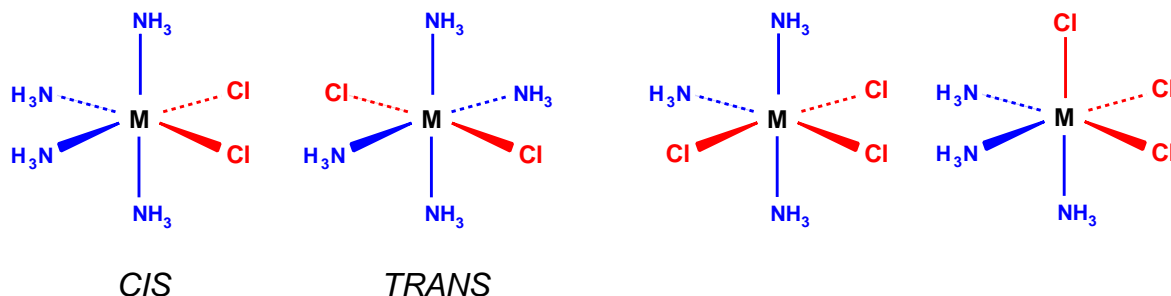
Coordination No.

Shape



ISOMERISM IN COMPLEXES

Octahedral Some complexes; e.g. $[\text{MA}_4\text{B}_2]^{n+}$ or $[\text{MA}_3\text{B}_3]^{n+}$ can exist in more than one form.

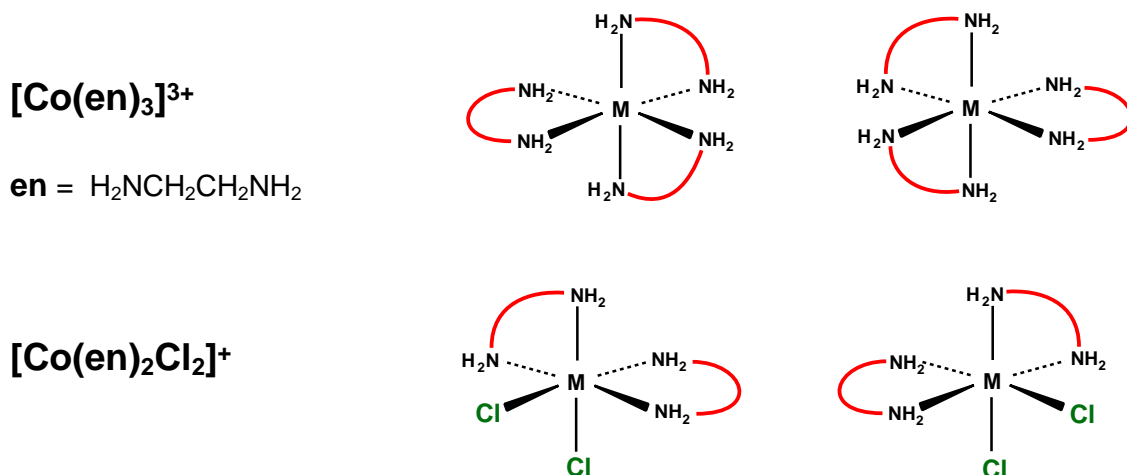


Cis-trans Square planar complexes of the form $[\text{MA}_2\text{B}_2]^{n+}$ exist in two forms



Q.7 Why is the cis isomer more effective than the trans?

Optical Octahedral complexes with bidentate ligands can exist as a pair of enantiomers (optical isomers). $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$



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

Q.8 Give details of reactions where the following catalysts are used ?



The first row transition elements

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**

Amphoteric character

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