12 An introduction to the chemistry of transition elements

This topic illustrates the physical and chemical properties of the transition elements.

12.1 General physical properties of the first set of transition elements, titanium to copper ☐

12.2 General characteristic chemical properties of the first set of transition elements, titanium to copper ☐

12.3 Colour of complexes ☐

12.4 Stereoisomerism in transition element complexes ☐

12.5 Stability constants, $\boldsymbol{K}_{\text{stab}}$ ☐

TRANSITION ELEMENTS

12 An introduction to the chemistry of transition elements

The physical and chemical properties of the transition elements are introduced in this topic.

Learning outcomes
Candidates should be able to:

12.1 General physical properties of the first set of transition elements, titanium to copper

a) explain what is meant by a *transition element*, in terms of d-block elements forming one or more stable ions with incomplete d orbitals

b) sketch the shape of a d orbital

c) state the electronic configuration of each of the first row transition elements and of their ions

d) contrast, qualitatively, the melting points and densities of the transition elements with those of calcium as a typical s-block element

e) describe the tendency of transition elements to have variable oxidation states

f) predict from a given electronic configuration, the likely oxidation states of a transition element

12.2 General characteristic chemical properties of the first set of transition elements, titanium to copper

a) describe and explain the reactions of transition elements with ligands to form complexes, including the complexes of copper(II) and cobalt(II) ions with water and ammonia molecules and hydroxide and chloride ions

b) (i) define the term *ligand* as a species that contains a lone pair of electrons that forms a dative bond to a central metal atom/ion including monodentate, bidentate and polydentate ligands

(ii) define the term *complex* as a molecule or ion formed by a central metal atom/ion surrounded by one or more ligands

(iii) describe transition metal complexes as linear, octahedral, tetrahedral or square planar

(iv) state what is meant by co-ordination number and predict the formula and charge of a complex ion, given the metal ion, its charge, the ligand and its co-ordination number

c) explain qualitatively that ligand exchange may occur, including the complexes of copper(II) ions with water and ammonia molecules and hydroxide and chloride ions

d) describe and explain the use of Fe^{3+}/Fe^{2+}, MnO_4^{-}/Mn^{2+} and $Cr_2O_7^{2-}/Cr^{3+}$ as examples of redox systems (see also Section 6.3)

e) predict, using $E^\ominus$ values, the likelihood of redox reactions

12.3 Colour of complexes	**a) describe the splitting of degenerate d orbitals into two energy levels in octahedral and tetrahedral complexes** **b) explain the origin of colour in transition element complexes resulting from the absorption of light energy as an electron moves between two non-degenerate d orbitals** **c) describe, in qualitative terms, the effects of different ligands on absorption, and hence colour, using the complexes of copper(II) ions with water and ammonia molecules and hydroxide and chloride ions as examples** **d) apply the above ideas of ligands and complexes to other metals, given information**
12.4 Stereoisomerism in transition element complexes	**a) describe the types of stereoisomerism shown by complexes, including those associated with bidentate ligands:** **(i) cis-trans isomerism, e.g. cis- and trans-platin $Pt(NH_3)_2Cl_2$** **(ii) optical isomerism, e.g. $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$** **b) describe the use of cisplatin as an anticancer drug and its action by binding to DNA in cancer cells, preventing cell division**
12.5 Stability constants, K_{stab}	**a) describe and explain ligand exchanges in terms of competing equilibria (also see Section 7)** **b) state that 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 or molecules** **c) deduce expressions for the stability constant of a ligand substitution** **d) explain ligand exchange in terms of stability constants, K_{stab}, and understand that a large K_{stab} is due to the formation of a stable complex ion**

D BLOCK ELEMENTS

The elements from scandium to zinc inclusive comprise the 3d block.

They are called d-block elements because the sub-shell being filled across this series is the 3d sub-shell.

The electronic configurations range from $[Ar]4s^23d^1$ for scandium to $[Ar]4s^23d^{10}$ for zinc.

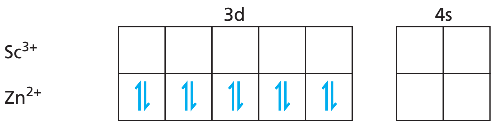
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$[Ar]4s^23d^1$	$[Ar]4s^23d^2$	$[Ar]4s^23d^3$	$[Ar]4s^13d^5$	$[Ar]4s^23d^5$	$[Ar]4s^23d^6$	$[Ar]4s^23d^7$	$[Ar]4s^23d^8$	$[Ar]4s^13d^{10}$	$[Ar]4s^23d^{10}$

TRANSITION ELEMENTS

Transition elements are d-block elements forming one or more stable ions with incomplete d orbitals.

According to this definition, scandium and zinc are not counted as transition elements, as the only ion formed by Sc is the 3^+ ion, with electronic configuration $1s^22s^22p^63s^23p^6$ (no d electrons), and that formed by Zn is the 2^+ ion, with electronic configuration $1s^22s^22p^63s^23p^63d^{10}$ (full d sub-shell). Scandium and zinc do not exhibit some of the characteristic properties of transition metals (e.g. they do not form coloured compounds).

Sc	$1s^2\ 2s^2\ 2p^6\ 3s2\ 3p^6\ 3d^1\ 4s^2$
Sc^{3+}	$1s^2\ 2s^2\ 2p^6\ 3s2\ 3p^6$
Zn	$1s^2\ 2s^2\ 2p^6\ 3s2\ 3p^6\ 3d^{10}\ 4s^2$
Zn^{2+}	$1s^2\ 2s^2\ 2p^6\ 3s2\ 3p^6\ 3d^{10}$



ELECTRONIC CONFIGURATION

As the proton number increases by one unit, an extra electron is usually added to the 3d sub-shell. There are two exceptions to this general trend:

- chromium is [Ar] $3d^5$ $4s^1$, and not [Ar] $3d^4$ $4s^2$
- copper is [Ar] $3d^{10}$ $4s^1$, and not [Ar] $3d^9$ $4s^2$.

This is because the $3d^5$ (with a half-filled sub-shell) and $3d^{10}$ (with a full sub-shell) are energetically preferred configurations, avoiding the inter-electron repulsion in the 4s orbital that occurs with the $4s^2$ configuration.

Both these configurations have a symmetrical 3d cloud of electrons that screens the nucleus more effectively than other configurations.

PHYSICAL PROPERTIES

ELEMENT	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1st I.E. / kJ mol^{-1}	590	632	661	648	653	716	762	757	736	745	908
Atomic radius / nm	0.197	0.144	0.132	0.122	0.117	0.117	0.116	0.116	0.115	0.117	0.125
Ionic radius / nm	0.099	0.081	0.090	0.090	0.085	0.080	0.076	0.078	0.078	0.069	0.074
density / g cm^{-3}	1.55	3	4.5	6	7.2	7.4	7.9	8.9	8.9	8.9	7

MELTING POINTS

The melting and boiling points of the 3d-block metals are generally much higher than those of the s- and p-block metals.

This is because not only the 4s electrons but also the 3d electrons are involved in the metallic bonding.

The conductivities of the 3d-block metals are similar to those of calcium; the conductivity of copper is particularly high.

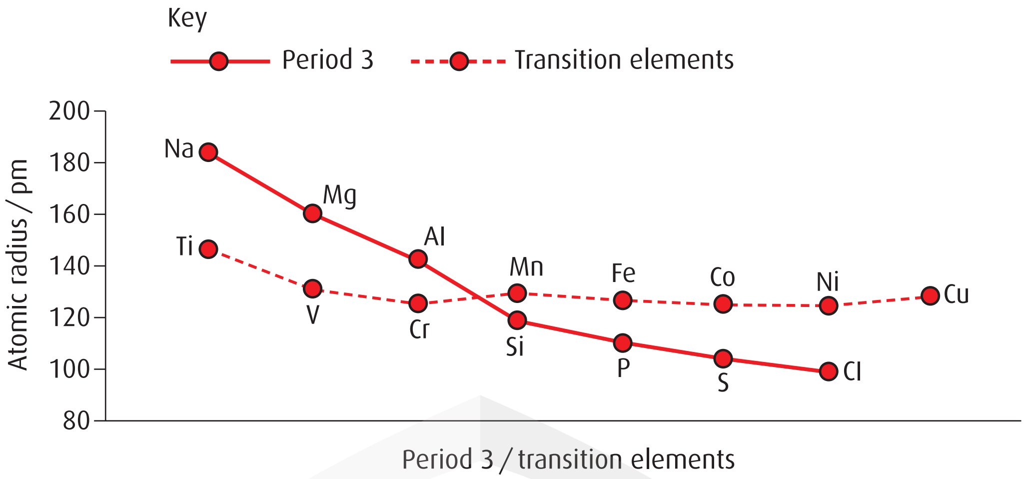
RADII AND DENSITIES

The atomic radii of transitional elements are relatively small and are roughly equal i.e. do not decrease as much as in other elements along a period.

Atomic radii are roughly equal because the electrons are entering the penultimate shell, which increases the shielding effect roughly counterbalancing the increasing nuclear charge thereby making the effective nuclear charge almost the same.

Densities of the transition metals are higher than that of calcium as they have the smallest atomic radii and the highest relative atomic masses.

RADII AND DENSITIES



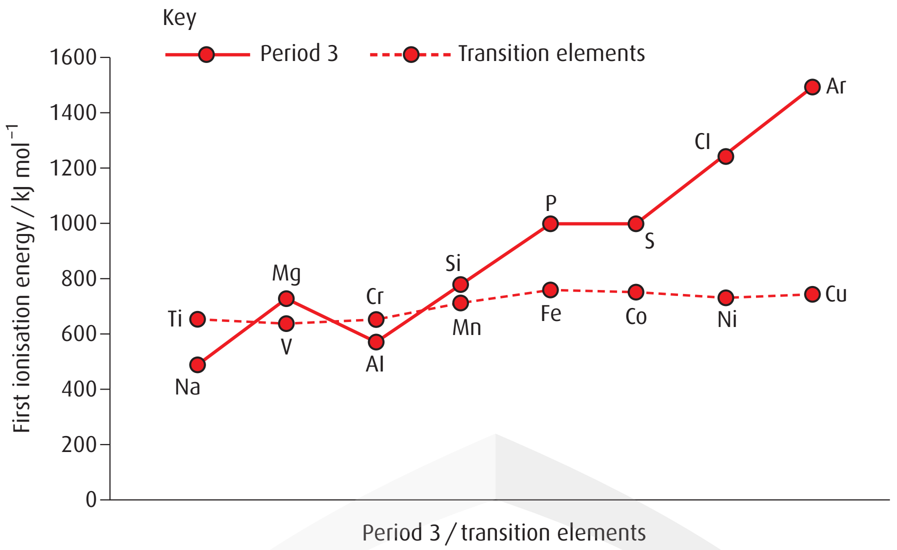
IONISATION ENERGIES

The first ionisation energy increase only slightly across the d block.

The first ionisation energies involve the removal of a 4s electron. This is outside the 3d sub-shell and is partially screened/shielded by it.

As the nuclear charge increases across the block, the additional d electrons shield the effect of the increasing nuclear charge so that the 4s electron experiences only a small extra attraction (because the increasing nuclear charge is almost counterbalanced by the increasing screening effect).

IONISATION ENERGIES



4s vs 3d

The 4s sub-shell is filled before the 3d sub-shell because it is lower in energy, even though the 4s sub-shell is part of a shell whose average distance is further away from the nucleus. The difference in energy between 4s and 3d is very small, however, which means that both s and d electrons may be involved in bonding.

The order of energy levels 4s < 3d holds only as far as calcium. With the increasing nuclear charge from 21 in scandium to 30 in zinc, the energy levels of both the 4s and 3d orbitals decrease, but the 3d level decreases faster than the 4s.

At scandium their energy levels are almost the same, but subsequently the order changes so that 3d is slightly lower than 4s. When an ion is formed, the 4s electrons are removed before the 3d electrons.

4s vs 3d

Up to calcium, the energy of the 4s orbital is lower than that of the 3d, even though, on average, the electron is further away from the nucleus. This is because the 4s electron spends some time very near to the nucleus, where it experiences the full attraction of the unscreened nuclear charge.

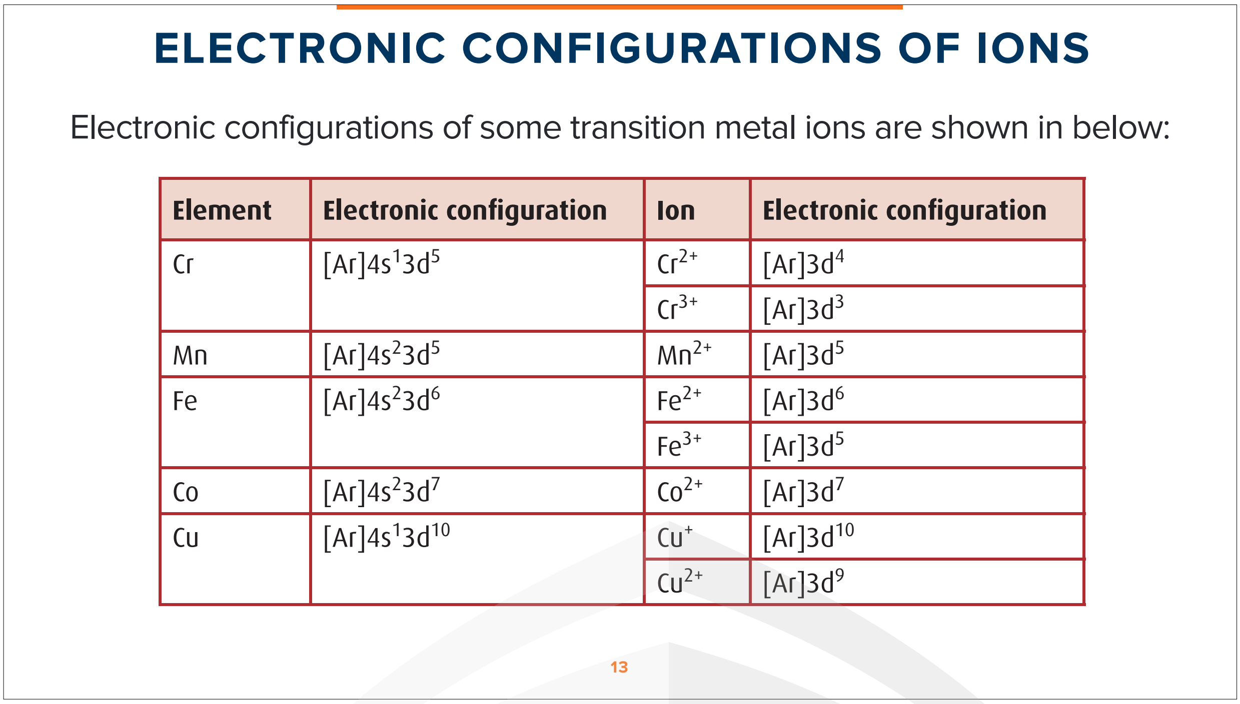
After calcium, the 4s electrons are screened from the effect of the increasing nuclear charge by the addition of the 3d electrons, which are nearer to the nucleus. The energy of the 4s electrons therefore decreases only slightly on crossing the 3d block.

The 3d electrons, however, are not screened to the same extent and so experience a greater effective nuclear charge, becoming progressively more tightly held by the nucleus.

IONS

Therefore, on forming ions, 4s electrons are removed before the 3d.

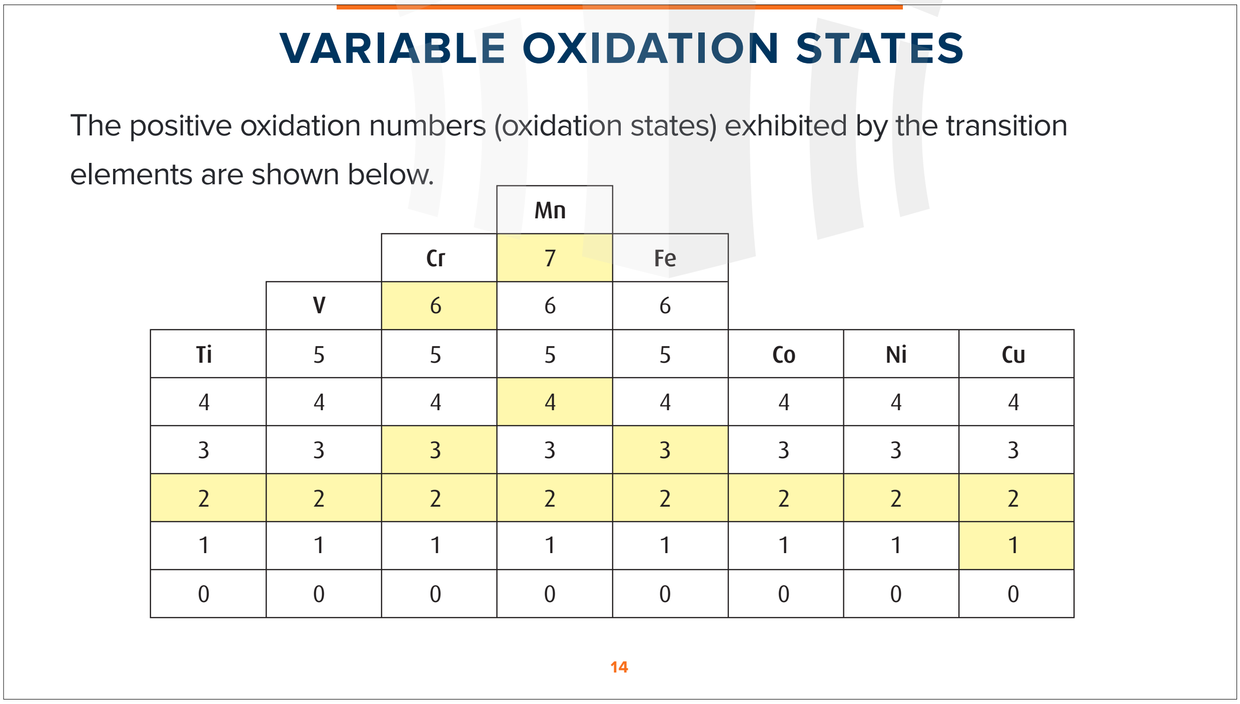
		3d					4s
Mn	[Ar]	↑	↑	↑	↑	↑	↑↓
Mn^{2+}	[Ar]	↑	↑	↑	↑	↑	
Mn^{3+}	[Ar]	↑	↑	↑	↑		
Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓
Fe^{2+}	[Ar]	↑↓	↑	↑	↑	↑	
Fe^{3+}	[Ar]	↑	↑	↑	↑	↑	



ELECTRONIC CONFIGURATIONS OF IONS

Electronic configurations of some transition metal ions are shown in below:

Element	Electronic configuration	Ion	Electronic configuration
Cr	[Ar]$4s^1 3d^5$	Cr^{2+}	[Ar]$3d^4$
		Cr^{3+}	[Ar]$3d^3$
Mn	[Ar]$4s^2 3d^5$	Mn^{2+}	[Ar]$3d^5$
Fe	[Ar]$4s^2 3d^6$	Fe^{2+}	[Ar]$3d^6$
		Fe^{3+}	[Ar]$3d^5$
Co	[Ar]$4s^2 3d^7$	Co^{2+}	[Ar]$3d^7$
Cu	[Ar]$4s^1 3d^{10}$	Cu^+	[Ar]$3d^{10}$
		Cu^{2+}	[Ar]$3d^9$



VARIABLE OXIDATION STATES

The positive oxidation numbers (oxidation states) exhibited by the transition elements are shown below.

Ti	V	Cr	Mn	Fe	Co	Ni	Cu
			7				
		6	6	6			
	5	5	5	5			
4	4	4	4	4	4	4	4
3	3	3	3	3	3	3	3
2	2	2	2	2	2	2	2
1	1	1	1	1	1	1	1
0	0	0	0	0	0	0	0

SKILL CHECK

Q. State the electronic configurations of the following atoms or ions:

i Cr^{3+}

ii Co

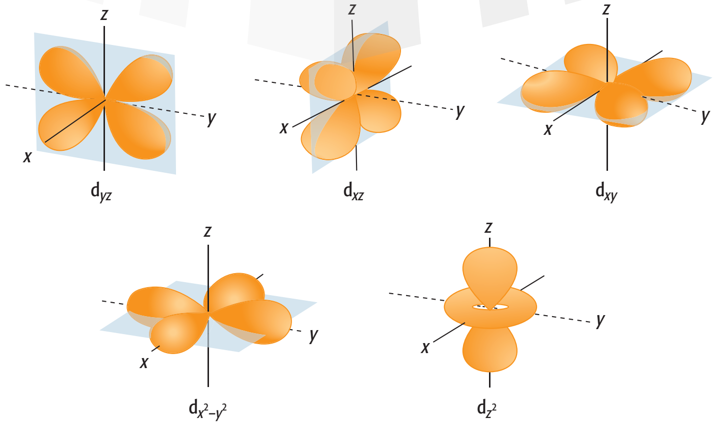
iii Fe^{3+}

iv Ni^{2+}

v Cu^{+}

D ORBITALS

The five d orbitals in an isolated transition metal atom or ion are described as degenerate, meaning they are all at the same energy level.



COMPLEX IONS

The 3d metal ions are relatively small and have a high charge density. They therefore attract groups containing lone pairs of electrons. These groups are known as ligands.

Ligands are bases. For common ligands an approximate order of attraction is as follows:

H_2O < halide ions < NH_3 < CN^-

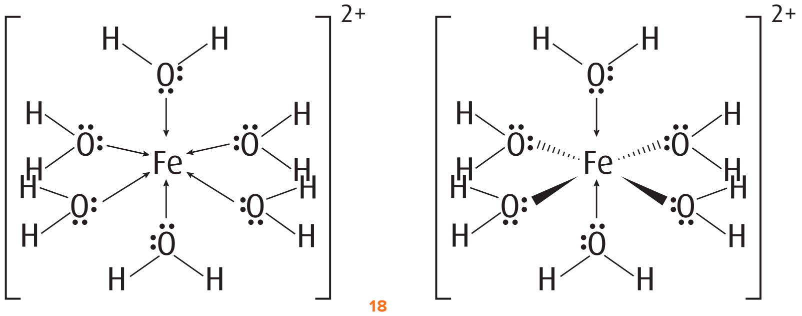
The ligand bonds to the metal ion to form a complex ion. Six, four or two ligands combine with one metal ion, so the formation of a complex ion may be represented as the donation of six or four or two pairs of electrons to the metal ion.

A dative covalent bond (co-ordinate bond) is formed between each ligand and the metal ion.

COMPLEX IONS

Ligands are negative ions or neutral molecules that use lone pairs of electrons to bond to a transition metal ion to form a **complex ion**. Dative covalent bonds (coordinate links) are formed between the ligand and the transition metal ion.

The structure of $[Fe(H_2O)_6]^{2+}$ is shown below. H_2O is the ligand in this complex ion. The shape of this complex ion is octahedral and it is called the hexaaquairon (II) ion.



COMPLEX IONS

The oxidation number of a transition metal in a complex ion may be worked out from the charges on the ligands. Ligands may be either neutral or negatively charged.

In $[Fe(H_2O)_6]^{2+}$ all the ligands are neutral. The overall charge on the ion is just due to the Fe, so the oxidation number of Fe must be 2+.

In $[Ni(CN)_4]^{2-}$ all the ligands have a 1– charge, so the total charge on all four ligands is 4–. The overall charge on the ion is 2–; therefore, the oxidation state of Ni must be +2 to cancel out 2– from the 4– charge.

COMPLEX IONS

If a simple formula does not make it clear which groups are attached to the metal ion, it is common practice to enclose the complex ion in square brackets.

An example of this is $Cr(H_2O)_6Cl_3$, which does not make it clear which ligands are attached to the chromium ion.

- It could, for example, be $[Cr(H_2O)_6]Cl_3$ (which has no chlorine ligands but has three free chloride ions) or
- $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (which has one chlorine ligand and two free chloride ions).

SHAPES OF COMPLEX IONS

Transition metal complexes do not obey always valence shell electron pair repulsion (VSEPR) theory rules, so although six coordinate complexes are virtually always octahedral, four coordinate complexes may be tetrahedral or square planar.

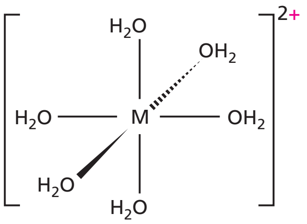
The number of atoms surrounding a central atom is called the co-ordination number. Thus a complex such as $[Cr(H_2O)_6]^{3+}$ has a co-ordination number of 6.

SHAPES OF COMPLEX IONS

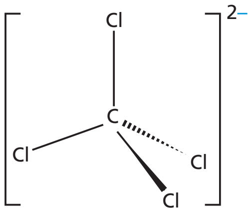
If the complex contains two ligands (co-ordination number 2), it is linear; examples are the $CuCl_2^-$ and $[Ag(NH_3)_2]^+$ ions. With four ligands, VSEPR arguments predict that the complex is tetrahedral and this is usually the case; examples are the $CoCl_4$ and $[Zn(NH_3)_4]^{2+}$ ions.

However, there are complexes with four ligands that are square planar, which shows that factors other than electron repulsion must be taken into account.

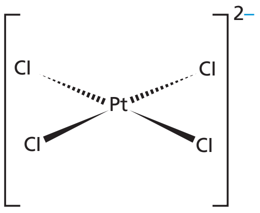
SHAPES OF COMPLEX IONS



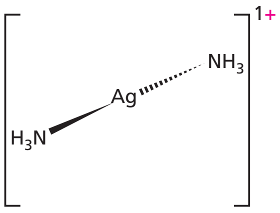
octahedral



tetrahedral

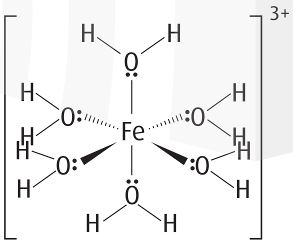
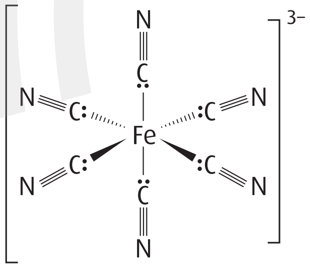


square planar

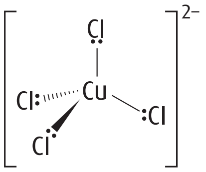
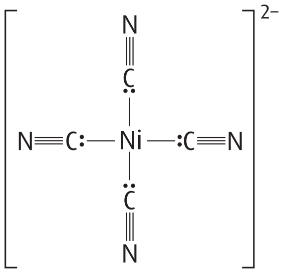


linear

SHAPES OF COMPLEX IONS

Complex ion		
Formula	$[Fe(H_2O)_6]^{3+}$	$[Fe(CN)_6]^{3-}$
Shape	octahedral	octahedral
Oxidation number of metal	+3	+3
Name	hexaaquairon(III) ion	hexacyanoferrate(III) ion

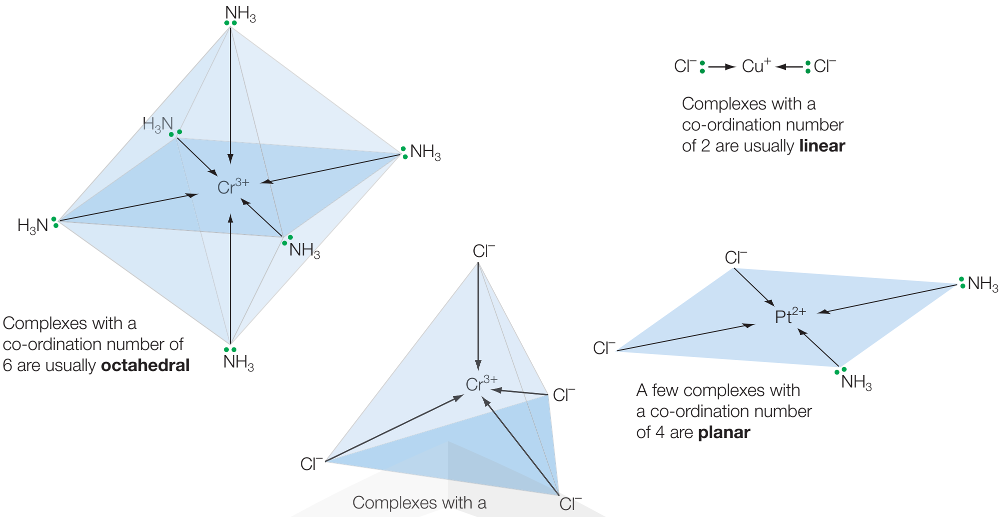
SHAPES OF COMPLEX IONS

Complex ion		
Formula	$[CuCl_4]^{2-}$	$[Ni(CN)_4]^{2-}$
Shape	tetrahedral	square planar
Oxidation number of metal	+2	+2
Name	tetrachlorocuprate(II) ion	tetracyanonickellate(II) ion

SHAPES OF COMPLEX IONS

Complex ion	$[H_3N\!:\!—Ag—\!:\!NH_3]^+$
Formula	$[Ag(NH_3)_2]^+$
Shape	linear
Oxidation number of metal	+1
Name	diamminesilver(I) ion

SHAPES OF COMPLEX IONS



$Cl^- : \rightarrow Cu^+ \leftarrow : Cl^-$

Complexes with a co-ordination number of 2 are usually **linear**

Complexes with a co-ordination number of 6 are usually **octahedral**

A few complexes with a co-ordination number of 4 are **planar**

Complexes with a co-ordination number of 4 are usually **tetrahedral**

LIGANDS

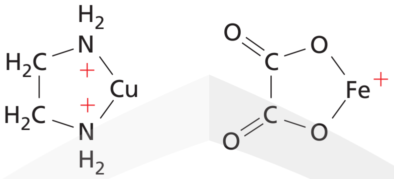
Name of ligand	Formula	Example of complex	Co-ordination number	Shape of complex
water	H_2O	$[Fe(H_2O)_6]^{2+}$	6	octahedral
ammonia	NH_3	$[Co(NH_3)_6]^{3+}$	6	octahedral
chloride ion	Cl^-	$[CuCl_4]^{2-}$	4	tetrahedral
cyanide ion	CN^-	$[Ni(CN)_4]^{2-}$	4	square planar
hydroxide ion	OH^-	$[Cr(OH)_6]^{3-}$	6	octahedral
thiocyanate ion	SCN^-	$[FeSCN]^{2+}$ or $[Fe(SCN)(H_2O)_5]^{2+}$	6	octahedral
ethanedioate ion (abbreviated as ‘ox’ in the formulae of complexes)	$^-OOC{-}COO^-$	$[Mn(ox)_3]^{3-}$	6	octahedral
1,2-diaminoethane (abbreviated as ‘en’ in the formulae of complexes)	$NH_2CH_2CH_2NH_2$	$[Co(en)_3]^{3+}$	6	octahedral

BIDENTATE LIGANDS

Ligands such as H_2O and CN^- are attached by one coordinate bond to the metal ion. If the ligand contains two groups that have a lone pair of electrons, it may form two bonds to the metal atom, forming a ring.

Such a ligand is called a chelate, a name derived from the Greek word for a crab's claw.

Stable complexes result if five- or six- membered rings are produced by the chelate and the metal ion.



BIDENTATE LIGANDS

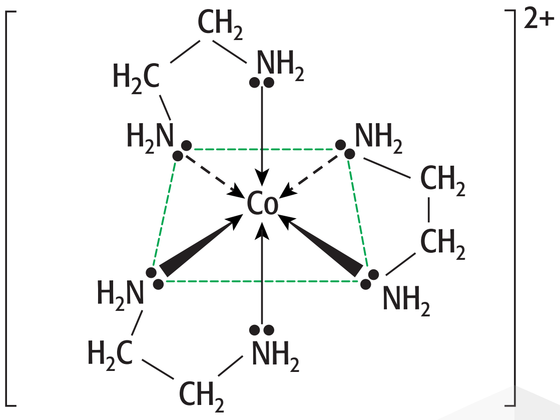
Two ligands that readily form chelates are 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, and the ethanedioate ion, $^-O_2CCO_2^-$. These form five-membered rings and are called **bidentate ligands** because they join by two bonds.

Chelates form particularly stable complex ions, partly because they form strong bonds to the metal ion, but also because there is an additional entropy effect that adds to their stability.

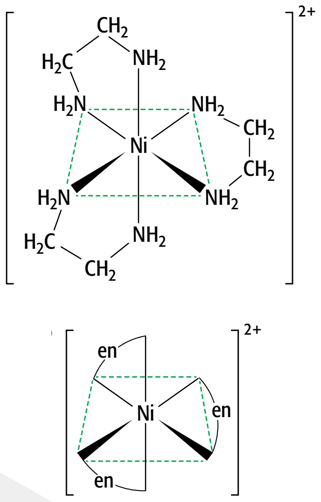
For example, a chelate is formed in which three ethanedioate ions bond to Fe^{3+}. Four species become seven after the reaction, so the formation of this chelate is accompanied by an increase in entropy:

$$Fe(H_2O)_6^{3+} + 3C_2O_4^{2-} \longrightarrow Fe(C_2O_4)_3^{3-} + 6H_2O$$

BIDENTATE LIGANDS

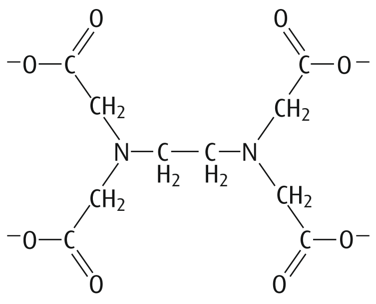


$[Co(en)_3]^{2+}$

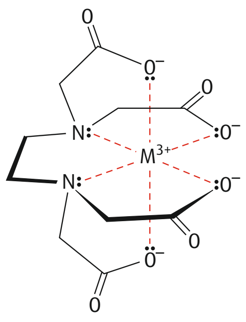


POLYDENTATE LIGANDS – EDTA

Some chelates form more than two bonds with the metal ion. A particularly important one is ethylene diamine tetraacetic acid, abbreviated as **edta.** This has six pairs of electrons able to bond to a metal ion, and so forms a hexadentate chelate.



edta



The $[EDTA]^{4-}$ ion bound to a central metal ion in an octahedral coordination complex.

SKILL CHECK

What is the oxidation number of the transition metal in each of the following complexes?

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

ii $[Ni(CN)_4]^{2-}$

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

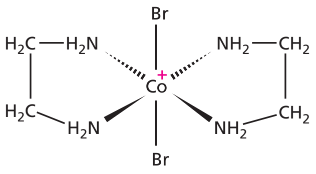
iv $[Co(en)_3]^{3+}$

v $Cu(OH)_2(H_2O)_4$

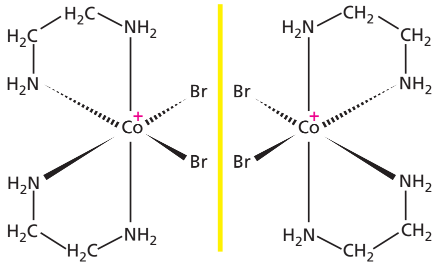
STEREOISOMERISM

Complexes can show stereochemistry. A good example of this is the complex ion $[Co(en)_2(NH_3)_2]^{2+}$, where 'en' is used as an abbreviation for 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$.

This complex can exist in cis and trans forms. The cis form (but not the trans) has a chiral centre (the nickel atom) and can be resolved into optical isomers.



trans form



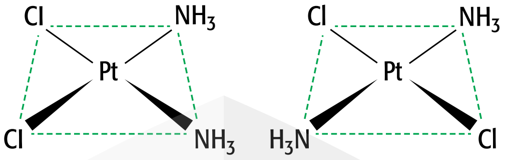
cis form

CIS TRANS

An important example of cis/trans isomerism is the drug cisplatin. This has a Pt atom joined to two chlorine atoms and two ammonia molecules, $Pt(NH_3)_2Cl_2$

It is a square planar complex and can, therefore, exist in both cis and trans forms.

In *cis*-platin, the chlorine atoms are next to each other in the square complex but in *trans*-platin, they are opposite. The properties of these geometrical isomers are slightly different.



cis-platin *trans*-platin

CIS-PLATIN AND CANCER

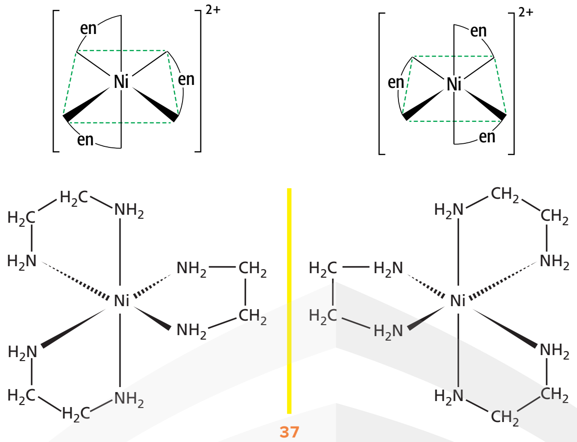
Cis-platin (but not *trans*-platin) is very effective in treating some forms of cancer.

One of the chlorine ions in cis-platin is easily hydrolysed to give the $[Pt(NH_3)_2Cl(H_2O)]^+$ ion. This ion binds to one of the four bases in DNA, usually guanine.

This ion can cross-link with another DNA chain by displacement of the chlorine from the complex. The cross-linking inhibits DNA replication, particularly in cancer cells that are undergoing rapid cell division, and the cell dies.

OPTICAL ISOMERISM

Ni^{2+} forms a complex with three 1,2-diaminoethane ligands and can also be resolved into optical isomers.

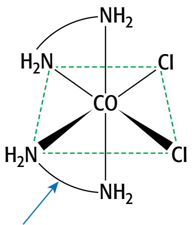


SKILL CHECK

Cobalt forms a complex with the simplified structure:

i Give the co-ordination number in this complex.

ii Draw the stereoisomers of this complex.



the curve represents $—CH_2—CH_2—$

SKILL CHECK

Draw the two geometrical isomers of $[Ni(CN)_2(Cl)_2]^{2-}$. Label the cis-isomer and the trans-isomer.

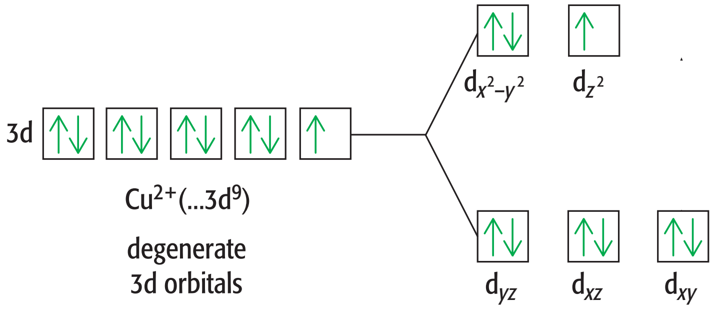
BONDING IN COMPLEXES

In aqueous solution, Cu^{2+} ions hydrate to give the $Cu(H_2O)_6^{2+}$ ion. Each water molecule is bonded to the central Cu^{2+} ion by a dative covalent bond, resulting in six lone pairs from the six water molecules forming six dative bonds.

Under the influence of the ligand lone pairs, the five 3d orbitals in Cu^{2+} split into two groups with different energies.

In the simple Cu^{2+} ion, the five 3d orbitals all have the same energy (they are said to be **degenerate**), but in the presence of six ligands spaced octahedrally, the orbitals divide into two groups.

BONDING IN COMPLEXES



3d

$Cu^{2+}(...3d^9)$

degenerate
3d orbitals

$d_{x^2-y^2}$ d_{z^2}

d_{yz} d_{xz} d_{xy}

splitting the
d orbitals to give
non-degenerate
orbitals

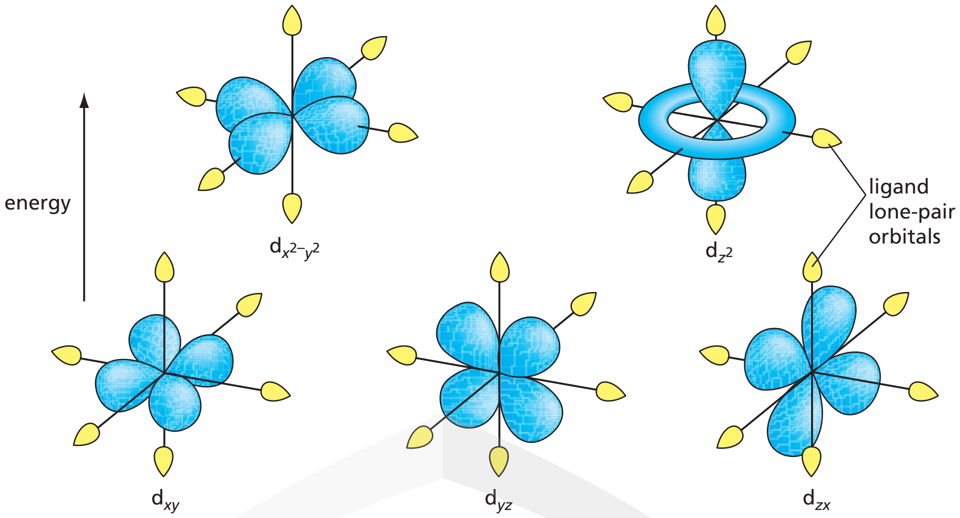
SPLITTING IN D SUBSHELL

The lobes of the three orbitals, d_{xy}, d_{xz} and d_{yz}, are directed in between the six ligands, and their energy is only slightly increased when the complex is formed.

The two orbitals, d_{x2-y2} and d_{z2}, however, have lobes which point in the direction of the six ligands;

this means that any electrons in these orbitals will experience inter-electron repulsion with the ligand lone pairs when the complex is formed, and so their energy is higher than that of electrons in the d_{xy}, d_{xz} and d_{yz} orbitals.

SPLITTING IN D SUBSHELL



SPLITTING IN D SUBSHELL

In tetrahedral complexes, the changes in the energy levels of the ***d_{xy}***, ***d_{xz}*** and ***d_{yz}*** and ***$d_{x^2-y^2}$*** and ***d_{z^2}*** orbitals is reversed. The ***d_{xy}***, ***d_{xz}*** and ***d_{yz}*** orbitals now point towards the ligands.

This means that they can be used to form strong bonds, but it also means that any electrons that are already in the orbitals will be strongly repelled.

The ***d_{yz}*** and ***$d_{x^2-y^2}$*** orbitals now lie between the ligands and any electrons in them are relatively unaffected by the formation of a complex.

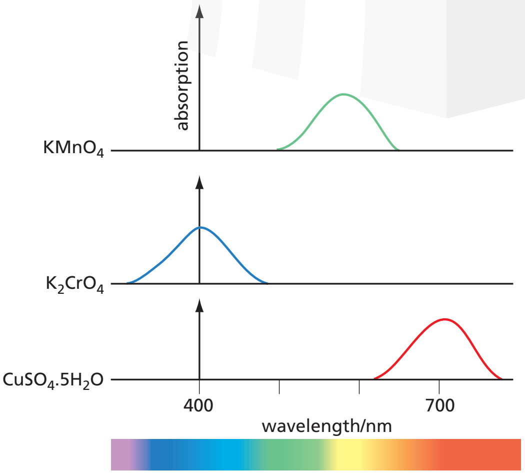
THE ORIGIN OF COLOUR

All atoms and molecules absorb in the ultraviolet region of the spectrum because this radiation has enough energy to excite their outer electrons. The ultraviolet region is outside the visible range of the spectrum, so absorption in the ultraviolet leaves a substance colourless.

Some substances, however, also have outer electron levels that are sufficiently close together for visible radiation to have enough energy to bring about electronic excitation. Under these circumstances, the substance appears coloured.

The resulting colour seen is white light minus the colour being absorbed. The colour we see is therefore the complementary colour to the colour being absorbed.

THE ORIGIN OF COLOUR



Example	Absorption spectrum	Colour absorbed	Colour observed (complementary)
$KMnO_4$		green	purple
K_2CrO_4		blue	yellow
$CuSO_4.5H_2O$		red	blue

COLOUR IN COMPLEX IONS

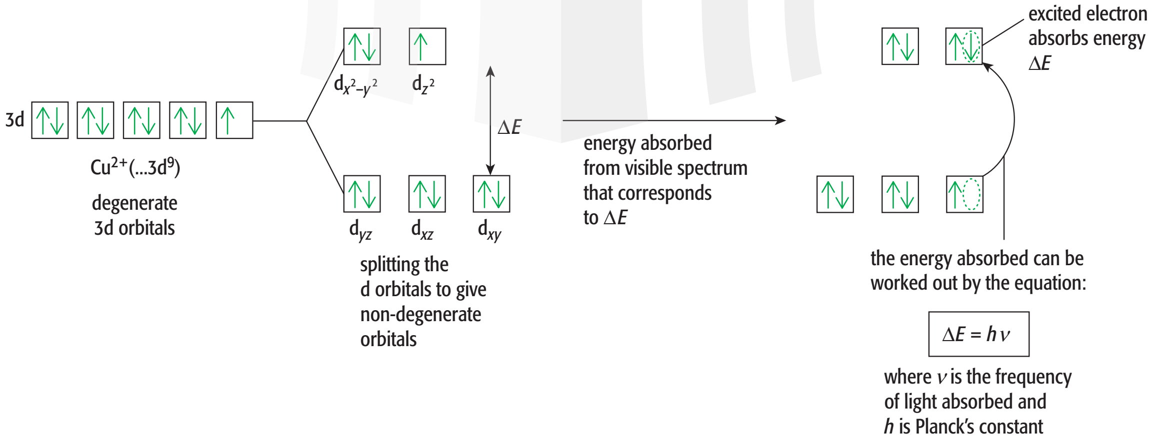
Cu^{2+} has the nine d electrons distributed between the non-degenerate orbitals formed in a complex with ligands.

The difference in the energy between the non-degenerate d orbitals is ΔE.

So, when light shines on the solution containing the $[Cu(H_2O)_6]^{2+}$ complex, an electron absorbs this amount of energy and jumps into the higher of the two non-degenerate energy levels.

In copper complexes, the rest of the visible spectrum that passes through the solution makes it appear blue in colour.

COLOUR IN COMPLEX IONS



degenerate 3d orbitals

splitting the d orbitals to give non-degenerate orbitals

energy absorbed from visible spectrum that corresponds to ΔE

the energy absorbed can be worked out by the equation:

$$\boxed{\Delta E = h\nu}$$

where ν is the frequency of light absorbed and h is Planck's constant

COLOUR IN COMPLEX IONS

The exact energy difference (ΔE), and therefore the colour absorbed and seen, between the non-degenerate d orbitals in a transition metal ion is affected by many factors.

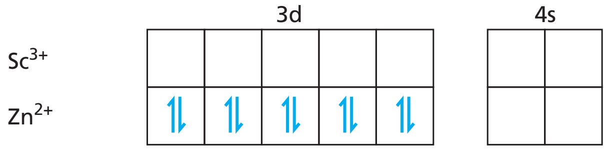
1. The identity of the ligands that surround the transition metal ion.
2. the shape of the complex ion, and
3. the identity of the central metal cation

The size of ΔE changes and this results in a slightly different amount of energy being absorbed by electrons jumping up to the higher orbitals. Therefore a different colour is absorbed from visible light, so a different colour is seen.

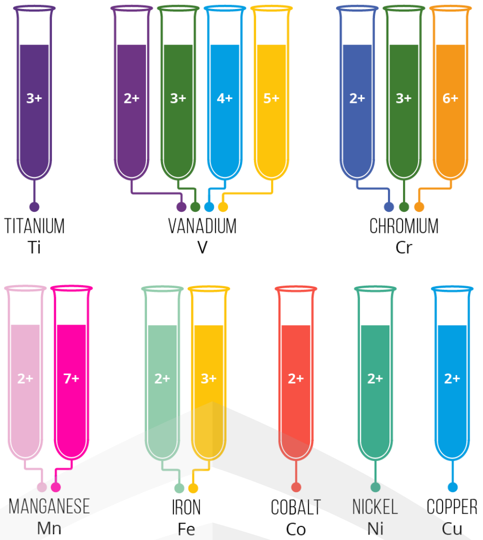
COLOURLESS

Ions that have no 3d electrons, for example $Sc(H_2O)_6^{3+}$, are colourless because there are no 3d electrons to promote.

Similarly d^{10} ions, for example $Zn(H_2O)_6^{2+}$, are also colourless because there is no empty space in the ***d_{yz}*** and ***$d_{x^2-y^2}$*** orbitals to receive an extra electron.

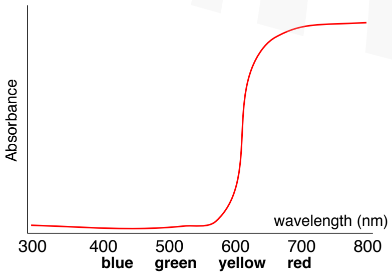


COLOURS OF IONS OF TRANSITION ELEMENTS

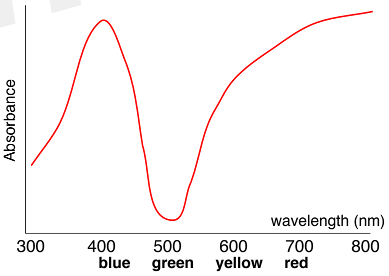


ABSORPTION SPECTRA

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



What colour is this hexaaqua complex?



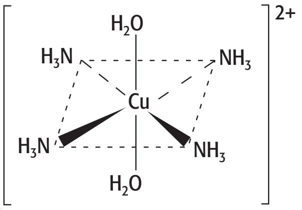
COPPER WITH ALKALIS

When sodium hydroxide solution is added to a solution containing $Cu^{2+}(aq)$ ions, a precipitate of copper(II) hydroxide, $Cu(OH)_2(s)$, is formed.

$$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \longrightarrow Cu(OH)_2(s) + 6H_2O_{(l)}$$

When ammonia is added to a solution containing aqueous Cu^{2+} ions, four of the water molecules are substituted by ammonia. This is an example of a ligand-exchange reaction, the substitution of one ligand by another:

$$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 4NH_3{}_{(aq)} \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}{}_{(aq)} + 4H_2O_{(l)}$$



LIGAND-EXCHANGE REACTIONS

$$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 4NH_3{}_{(aq)} \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}{}_{(aq)} + 4H_2O_{(l)}$$

This is a reversible reaction and if the dark blue complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (aq)] is diluted, the pale blue colour of the $[Cu(H_2O)_6]^{2+}$(aq)] ion is restored.

There is competition between the H_2O and NH_3 molecules to attach themselves to the copper ion.

We have an equilibrium with a constant given by the expression:

$$K = \frac{[[Cu(NH_3)_4(H_2O)_2]^{2+}][H_2O]^4}{[Cu(H_2O)_6]^{2+}[NH_3]^4}$$

STABILITY CONSTANT

As [H_2O] is in large excess and virtually a constant, we can include it in the equilibrium constant and write:

$$K_{\text{stab}} = \frac{[[\mathrm{Cu(NH_3)_4(H_2O)_2}]^{2+}]}{[\mathrm{Cu(H_2O)_6}][\mathrm{NH_3}]^4}$$

where **K_{stab}** is known as the **stability constant**. Strictly speaking, there are stability constants for each of the equilibria as H_2O molecules are progressively substituted by NH_3 molecules, but here we will only consider the overall constant.

The value of **K_{stab}** depends on how firmly the ligands bind to the metal atom.

STABILITY CONSTANT

In general, atoms with high electronegativity bond weakly and those with lower electronegativity bind more strongly.

Thus water (which binds via the very electronegative oxygen atom) forms weak bonds while the CN^- ion (which binds via the carbon atom that has much lower electronegativity) forms strong bonds and will have a large value of **K_{stab}**.

A high charge on the metal ion also makes **K_{stab}** larger;

e.g. compare

$$\frac{[[\mathrm{Fe(CN)_6}]^{3-}]}{[\mathrm{Fe^{3+}}][\mathrm{CN^-}]^6} \text{ and } \frac{[[\mathrm{Fe(CN)_6}]^{4-}]}{[\mathrm{Fe^{2+}}][\mathrm{CN^-}]^6}$$

STABILITY CONSTANT

Values of $\mathbf{K}_{\mathbf{stab}}$ for some complexes. The values are usually so large that they are often given in the form log $\mathbf{K}_{\mathbf{stab}}$.

Complex	K_{stab}	**log** K_{stab}
$[CuCl_4]^{2-}$	4.2×10^5	5.62
$[Cu(NH_3)_4]^{2+}$	1.3×10^{13}	13.1
$[Fe(CN)_6]^{3-}$	10×10^{31}	31
$[Fe(CN)_6]^{4-}$	1.0×10^{24}	24
$[Ag(NH_3)_2]^+$	1.7×10^7	7.23

LIGAND-EXCHANGE REACTIONS

A more complicated ligand-exchange reaction occurs when concentrated hydrochloric acid is added to aqueous Cu^{2+} ions. Here, four H_2O ligands are replaced by Cl^- ions, but the remaining two water molecules are expelled, leaving the tetrahedral tetrachlorocopper(II) ion, coloured yellow/green.

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