

Transition Elements

Properties

A **transition element** is a d-block element that forms one or more ions with incompletely filled d-orbitals. This definition excludes scandium which only forms 3+ ions, 3d⁰, and zinc which only forms 2+ ions, 3d¹⁰.

Electronic configurations of d-block atoms

The 4s sub-shell is **filled before** the 3d sub-shell. **Cr and Cu have 4s¹ configurations**, allowing a d sub-shell to be filled or half filled, a more stable arrangement.

Scandium	Sc	[Ar] 3d ¹ 4s ²	iron	Fe	[Ar] 3d ⁶ 4s ²
Titanium	Ti	[Ar] 3d ² 4s ²	cobalt	Co	[Ar] 3d ⁷ 4s ²
Vanadium	V	[Ar] 3d ³ 4s ²	nickel	Ni	[Ar] 3d ⁸ 4s ²
Chromium	Cr	[Ar] 3d⁵ 4s¹	copper	Cu	[Ar] 3d¹⁰ 4s¹
Manganese	Mn	[Ar] 3d ⁵ 4s ²	zinc	Zn	[Ar] 3d ¹⁰ 4s ²

When ions are formed, 4s electrons are **lost before** 3d electrons

Variable oxidation states Transition elements occur in several oxidation states, with ions of similar stability because the 3d and 4s electrons are very close in energy.

Electronic Configurations of d-block ions

e.g. Fe²⁺ is [Ar] 3d⁶
 Fe³⁺ is [Ar] 3d⁵
 Cu⁺ is [Ar] 3d¹⁰
 Cu²⁺ is [Ar] 3d⁹

Coloured ions

Aqueous solutions of transition metal ions with **partly filled d-orbitals** are coloured.

e.g. Fe²⁺ **pale** green, Fe³⁺ yellow, **Cu⁺ colourless**, Cu²⁺ blue, Co²⁺ pink

Catalytic behaviour

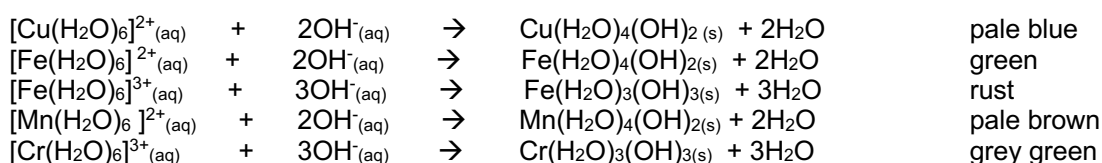
Transition metals and their compounds are good catalysts for two reasons:

1. Transfer of electrons between two different ions provides a different reaction pathway with a lower activation energy eg V₂O₅ in the contact process SO₂ + ½ O₂ → SO₃
2. Reacting molecules can be held on the surface of a solid catalyst, so their bonds are weakened. e.g. Finely divided **iron** in the Haber Process.

Practical examples of catalytic behaviour include: Cu²⁺ for reaction of Zn with acids; MnO₂ for decomposition of H₂O₂.

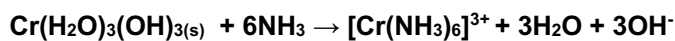
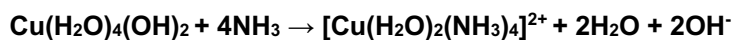
Transition metal catalysts lower energy requirements for reactions but are often toxic.

Precipitation Reactions - Reaction with aqueous sodium hydroxide and ammonium hydroxide produces a gelatinous precipitate e.g.



Note: With excess NaOH, only $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_{3(s)}$ reacts further forming $[\text{Cr}(\text{OH})_6]^{3-}$.

With excess NH_3 , only $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_{3(s)}$ and $\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2$ react:



Ligands and Complex Ions

A **complex ion** is a transition metal ion surrounded by ligands.

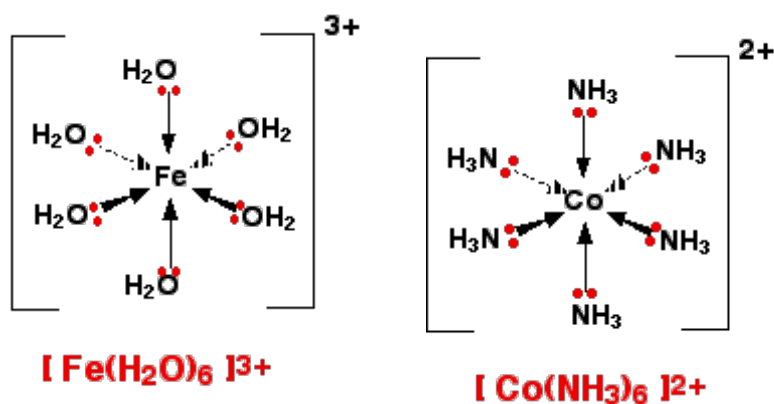
A **ligand** is an electron-pair donor that forms a co-ordinate (or dative) bond with a transition metal cation. Ligands can be anions or molecules eg Cl^- , H_2O , NH_3 .

Co-ordination number is the number of co-ordinate bonds formed between the ligands and the transition metal ion.

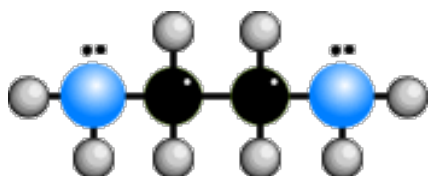
Complexes show **4-fold** co-ordination with either a planar or tetrahedral shape.

Complexes show **6-fold** co-ordination with an octahedral shape.

The charge on the complex ion is the sum of the charges on the cation plus ligands. e.g. The complex consisting of a Cu^{2+} ion and six water molecules has the formula $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$



Bidentate ligands form two co-ordinate bonds e.g. $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (ethanediamine known as 'en')



Stereoisomerism

1. **Cis-trans isomerism** occurs in:

Octahedral complexes with 4 of one monodentate ligand and 2 of another



TRANS



CIS

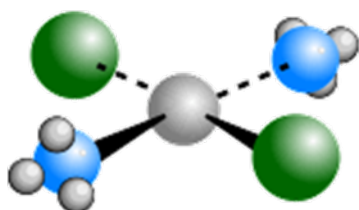
Bond angles:

trans = 180°

cis = 90°

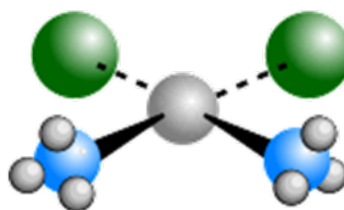
Square planar complexes, e.g. $[Ni(NH_3)_2Cl_2]$ and cis-platin $[Pt(NH_3)_2Cl_2]$. Cis-platin is an anti-cancer drug that binds to the DNA in fast-growing cancer cells, preventing division.

trans platin



Bond angles: trans = 180°

cis platin



cis = 90°

If a bidentate ligand is involved then only the cis isomer is possible eg $[Ni(en)Cl_2]$. A bidentate ligand will always occupy two neighbouring sites.

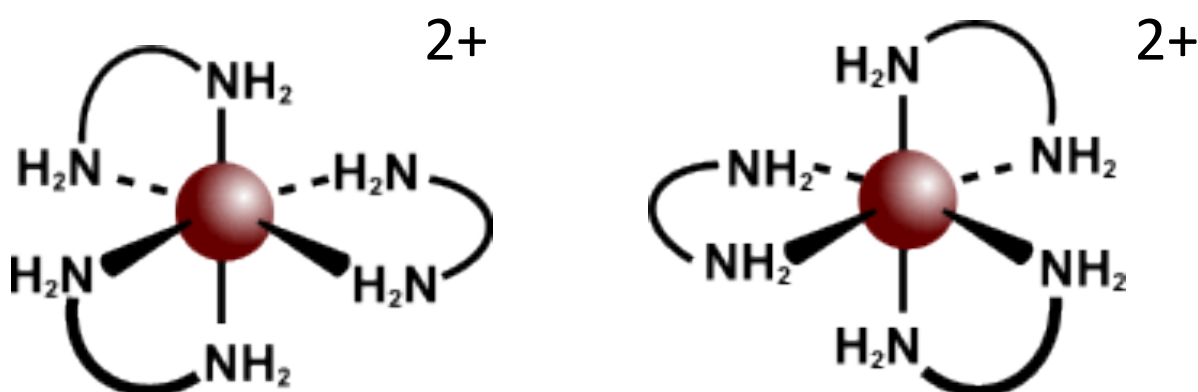
Note – you should know the shapes for

Octahedral: many hexaaqua complexes, e.g. $[Cu(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$

Tetrahedral: many tetrachloro complexes, e.g. $CuCl_4^{2-}$ and $CoCl_4^{2-}$

Square planar: complexes of Pt, e.g. platin: $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$

2. **Optical isomerism** occurs in octahedral complexes with 3 bidentate ligands, e.g. $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{2+}$.

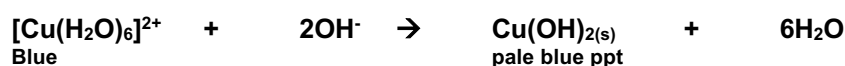


Ligand Substitution

Ligand substitution One ligand can replace another to form a more stable complex. These reactions give a colour change because different ligands change the colour of the metal ion in soln.

Copper (II)

When conc aqueous ammonia is added drop-wise to aqueous copper(II)sulphate, the pale blue ppt of copper(II) hydroxide forms initially.



This dissolves to a deep blue soln with **excess** ammonia. Overall four ammonia molecules replace four water molecules as ligands.



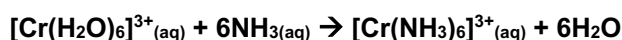
When **concentrated** HCl is added to copper sulphate soln, four chloride ions replace all the water molecules as ligands: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightleftharpoons [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}$

Chromium (III)

When chromium (III) potassium sulphate $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is dissolved in water, the complex ion $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is formed (violet solution). When chromium (III) sulphate is dissolved in water $[\text{Cr}(\text{H}_2\text{O})_5(\text{SO}_4)]^+$ is formed (green solution) where one water ligand has been replaced by a sulphate ion.

Reaction with ammonia.

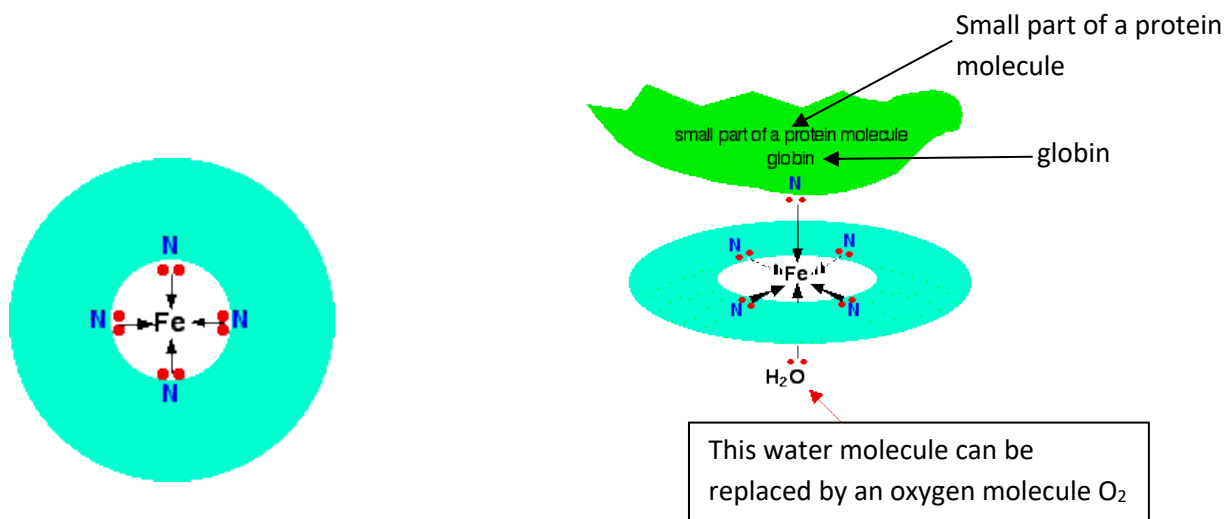
When ammonia is added drop-wise to the chromium (III) solution, initially a grey green precipitate of $\text{Cr}(\text{OH})_3$ is formed. This precipitate then dissolves in excess ammonia to form the complex ion $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (purple solution).



Biological importance of iron

Haemoglobin acts as a transport for oxygen in the blood. The active part of the haemoglobin complex is the Fe^{2+} ion. The iron forms 4 co-ordinate bonds with the haem, but still has space to form two more - one above and one below the plane of the ring.

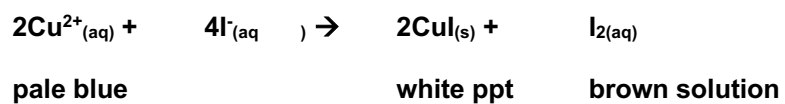
The protein **globin** attaches to one of these positions using a lone pair on one of the nitrogens in one of its amino acids.



Overall, the complex ion has a co-ordination number of 6 because the central metal ion is forming 6 co-ordinate bonds.

The water molecule which is bonded to the bottom position in the diagram is easily replaced by an oxygen molecule (via a lone pair on one of the oxygens in O_2) - and this is how oxygen gets carried around the blood by the haemoglobin. When the oxygen gets to where it is needed, it breaks away from the haemoglobin and replaced by H_2O .

Carbon monoxide is poisonous because it reacts with haemoglobin. It bonds to the same site that would otherwise be used by the oxygen - but it forms a very stable complex. The carbon monoxide



Disproportionation of Copper (I)

