

3.4 – Transition metals

A **transition metal** is an element that possesses a partially filled d sub-shell in its atom or stable ions.

Electronic configurations

Although 4s orbitals are filled before 3d orbitals (apart from Cr and Cu), when electrons are removed the 4s electrons are lost first.

Cr and Cu end in $4s^1$ not $4s^2$ – shells are more stable if they are filled or half-filled.

We can use [Ar] to represent $1s^2 2s^2 2p^6 3s^2 3p^6$

Sc [Ar]3d¹4s² Sc³⁺ [Ar]

Scandium is a transition metal because its atom has an incomplete d sub-shell

Cu [Ar]3d¹⁰4s² Cu²⁺ [Ar]3d⁹4s⁰

Copper is a transition metal because its 2+ ion has an incomplete d sub-shell

Zn [Ar]3d¹⁰4s² Zn²⁺ [Ar]3d¹⁰4s⁰

Zinc is not a transition metal because neither its atom nor its ion has an incomplete d sub-shell

1. Variable oxidation states

They can form different oxidation states because the energies of the 4s and 3d orbitals are very similar, so the energy required to remove any of these electrons is similar.

Important oxidation states are:

Cr +3 Cr₂O₃ and +6 Na₂Cr₂O₇ (orange), Na₂CrO₄ (yellow)

Mn +2 MnSO₄, +4 MnO₂ and +7 KMnO₄ (purple)

Fe +2 FeI₂ and +3 FeCl₃

Co +2 CoCl₂

Cu +1 CuI (white) and +2 CuSO₄

3. Form complex ions

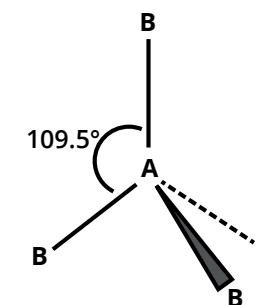
A complex ion is a metal ion surrounded by co-ordinately bonded ligands. A ligand is a small molecule or ion with a lone pair of electrons. Typically, complexes are either **tetrahedral** with 4 ligands arranged around the metal ion.

Examples:

[CoCl₄]²⁻ blue

[CuCl₄]²⁻ yellow/green

Remember, the structures must be represented in 3D.



or **octahedral** with 6 ligands

[Fe(H₂O)₆]²⁺ pale green

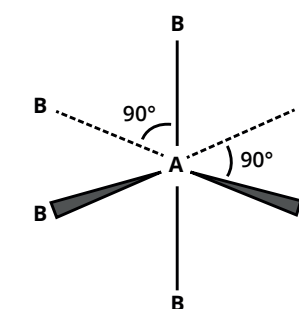
[Fe(H₂O)₆]³⁺ yellow

[Cr(H₂O)₆]³⁺ dark green

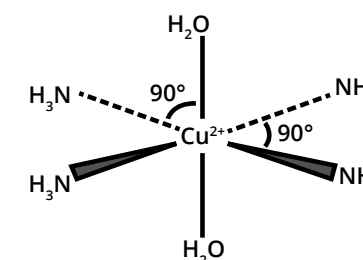
[Co(H₂O)₆]²⁺ pink

[Cu(H₂O)₆]²⁺ blue

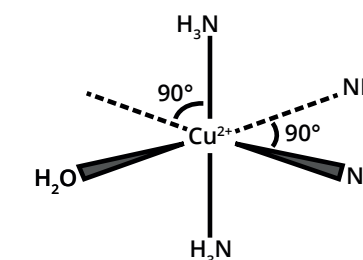
[Cu(NH₃)₄(H₂O)₂]²⁺ royal blue



Since [Cu(NH₃)₄(H₂O)₂]²⁺ contains two different ligands, there could be two arrangements of ligands.



Water molecules opposite each other (common isomer)



Water molecules next to each other

2. Act as catalysts

Transition metals and their compounds are good catalysts. Examples include:

Fe in the Haber process, Ni in the hydrogenation of alkenes, V₂O₅ in the contact process and MnO₂ in the decomposition of H₂O₂.

There are two types of catalysts – homogeneous and heterogeneous.

Homogeneous catalysts are in the same physical state as the reactions they catalyse. They work by using their **variable oxidation states** to oxidise/reduce a reactant which makes it more reactive. The transition metal can then be returned to its original oxidation state by reaction with another molecule.

Heterogeneous catalysts are in a different physical state from the reactions that they catalyse. They provide a surface for molecules to be adsorbed and come closer together for reaction. Molecules can form coordinate bonds to the metal atom because there are empty d orbitals to accept electron pairs due to the **d orbitals** only being **partially filled**.

3.4 – Transition metals

Ligand exchange

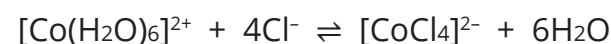
When a transition metal ion is exposed to a mixture of ligands, the ligands can be exchanged to form a new complex. This is an equilibrium process, e.g.



If more ammonia is added, the equilibrium shifts to the right, forming more $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ and giving a royal blue colour.

If more water is added, the equilibrium shifts to the left, forming more $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and giving a pale blue colour.

Ligand exchange can lead to a change in geometry of the complex ion.



If a large amount of chloride is used, such as by adding concentrated hydrochloric acid, the equilibrium shifts from the pink octahedral complex to the blue tetrahedral complex.

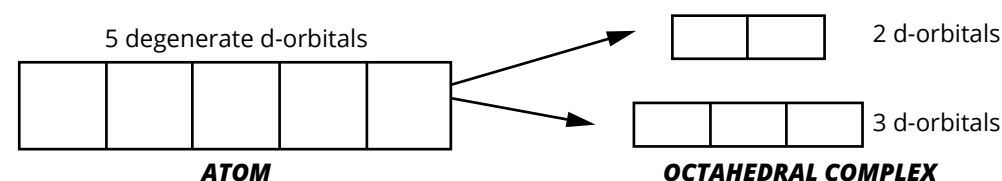
Reactions with hydroxide ions

Transition metal ion	Addition of some OH^-	Addition of excess OH^-
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	grey-green ppt of $[\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3]$	ppt dissolves giving a deep green solution of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	dark green ppt of $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]$	no further reaction
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	red-brown ppt of $[\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3]$	no further reaction
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	pale blue ppt of $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2]$	no further reaction

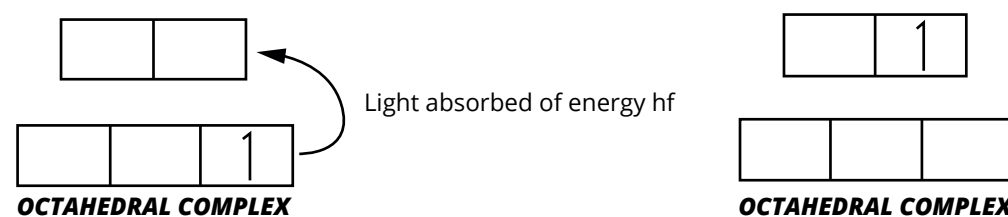
4. Form coloured complexes

Transition metal complexes are almost always coloured. However, in the absence of any ligands around the metal ion, the compound would be colourless.

Without ligands, a transition metal atom has five degenerate d orbitals, i.e. they all have the same energy. When ligands approach the metal ion, they cause the energy of three d orbitals to become different to the other two. This splits the d orbitals to give two sets of orbitals close together in energy.



Electrons in the lower 3d orbitals absorb energy from visible light, which promotes them to the higher 3d orbitals. Only one frequency (colour) of light is absorbed, which corresponds to the energy gap between the orbitals. The rest of the frequencies are transmitted; hence, the complementary colour is observed. Compounds containing the complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ are typically blue as they absorb all colours apart from blue.



The energy difference, ΔE , between the split 3d orbitals (and hence the colour) depends on the oxidation state of the metal and the nature and number of ligands.

Copper(I) complexes have an electronic configuration with a full d sub-shell which means that there are no empty orbitals to allow electrons to move between energy levels, so copper(I) complexes appear colourless.