

Transition Elements

The d block

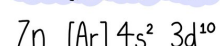
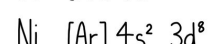
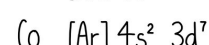
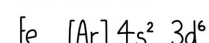
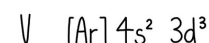
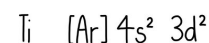
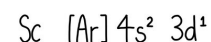
Transition elements are elements which form **ions** with a **partially-filled d-orbital** – their outermost electron is found in a d sub-shell. This means that all the transition elements are found in the **d-block** in the middle of the periodic table.

		GROUP												3 4 5 6 7 8					
		S-BLOCK		D-BLOCK										P-BLOCK					
		1	2											B	C	N	O	F	Ne
PERIOD	1	H	He																
	2	Li	Be																
	3	Na	Mg											Al	Si	P	S	Cl	Ar
	4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rc	Cn	Nh	Fl	Mc	Lv	Ts	Og

However, **not all d-block elements are technically transition metals.**

Some elements, such as **scandium** and **zinc**, form ions that have an empty d-orbital (Sc) or a full d-orbital (Zn). Only elements that form ions with partially filled d-orbitals are classed as transition elements.

To the right are the electron configurations of the elements in the first row of the d-block. Notice how the configurations for chromium and copper aren't what you'd expect. To **increase stability**, they will have just one electron in the 4s orbital so that they can have either five (Cr) or ten (Cu) electrons in their 3d orbitals.



Electron configuration of transition metal ions

The **4s** electrons have **less energy** than the 3d electrons, so the 4s orbitals will be **filled before** the 3d orbitals. This means that the **4s electrons will be removed before the 3d electrons** when forming ions. For instance, when manganese forms an ion (Mn^{2+}), the two electrons are lost from the 4s orbital.

- **Mn:** $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
- **Mn^{2+} :** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

If we have a look at the electron configurations of **scandium** and **zinc**, we can see why they are **not classed as transition** elements. Even though their atoms have an incomplete d sub-shell, their ions don't so they are not technically transition metals.

- **Sc:** $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
- **Sc^{3+} :** $1s^2 2s^2 2p^6 3s^2 3p^6$
- **Zn:** $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$
- **Zn^{2+} :** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

Properties of transition elements

Transition elements have **unique properties** not found in other elements:

- They exist in **various oxidation states** e.g. iron (II) and iron (III) can exist in a +2 or +3 oxidation state respectively.
- They form **coloured compounds** e.g. copper sulfate is a blue solid.
- They act as **catalysts** e.g. nickel is used as a catalyst in hydrogenation reaction to convert alkenes into alkanes.

Various oxidation states

The 4s and 3d sub-shells are close together and **only slightly differ in energy**. This means similar amounts of energy can be used to remove different numbers of electrons, resulting in **variable oxidation states**.

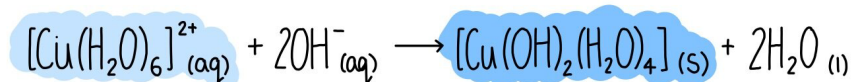
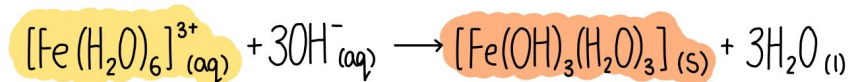
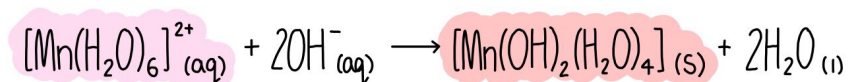
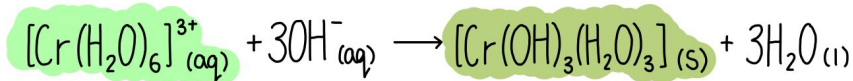
The table below shows the various oxidation states of transition metal ions:

TRANSITION ELEMENT	OXIDATION STATE
TITANIUM	Ti ²⁺ Ti ³⁺
VANADIUM	V ²⁺ V ³⁺ VO ₂ ⁺ VO ₂ ²⁺
CHROMIUM	Cr ₂ O ₇ ²⁻ Cr ³⁺
MANGANESE	MnO ₄ ⁻ MnO ₄ ²⁻ Mn ²⁺
IRON	Fe ²⁺ Fe ³⁺

Coloured compounds

When added to water, transition metals will form a **hydrated complex ion** with the formula **[M(H₂O)₆]ⁿ⁺**. This can be simplified and written as **Mⁿ⁺ (aq)** if the only thing it is attached to is water molecules.

The hydrated ion reacts with **hydroxide ions** (i.e. from sodium hydroxide) to form **coloured precipitates of metal hydroxides**. Coloured metal hydroxides are also formed when the hydrated ion reacts with ammonia.



Catalytic behaviour

Because transition metals can exist in a variety of oxidation states, they can switch oxidation state by gaining or losing electrons from their d-orbital. This means that they can **transfer electrons** to or from other molecules to **speed up reactions** - in other words, they act as **catalysts**.

They work by **adsorbing** molecules on their surface, **lowering the activation energy** of reactions. They are **heterogeneous** catalysts. Here's some examples of some reactions that transition metals catalyse:

- **Iron** is a catalyst in the **Haber process** (the reaction between nitrogen and hydrogen to form ammonia in the manufacture of fertilisers).
- **Nickel** is a catalyst in **hydrogenation** reactions (adding hydrogen to alkenes to form alkanes).
- **Manganese oxide** is a catalyst in the **decomposition of hydrogen peroxide** into water and oxygen.

Transition metals are therefore useful from a **commercial** point of view since they allow industrial reactions to happen **quickly and cheaply** (since less energy is required).

However, they can give rise to health problems since transition metals and their compounds are **toxic**. For example, excess exposure to manganese can lead to psychiatric problems.

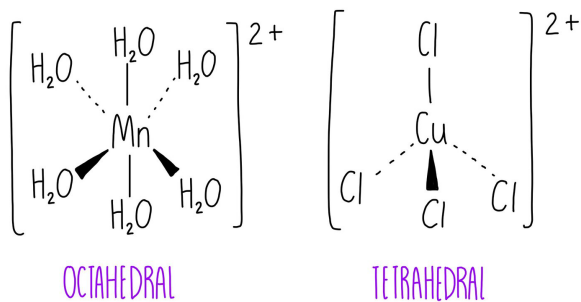
Ligands and complex ions

Transition metals often form something called **complex ions**, which is where the **transition metal ion** is bound to **ligands** through **coordinate bonds**.

- **Coordinate bond** - a type of covalent bond in which **both bonding electrons** have come from the **same atom**. It is also called dative covalent bonding.
- **Ligand** - an atom, ion or molecule with a **lone pair of electrons** to donate to a central metal ion.

Ligands donate their lone pair electrons to the transition metal ion to form a **coordinate bond**. Several ligands are present in a complex ion, each forming a coordinate bond. The **coordination number** is the number of coordinate bonds that are formed with the transition metal ion.

For **smaller ligands**, such as water, ammonia, or cyanide ions, **six** molecules can fit around the central metal ion, producing complex ions with a coordination number of 6. These have an **octahedral** geometry around the central metal ion, just like other types of molecules with six bond pairs. For **larger ligands**, such as chloride ions, only **four** molecules can fit around the metal ion, forming complex ions with a coordination number of 4. These complex ions usually have a **tetrahedral** geometry, but some assume a **square planar** shape.



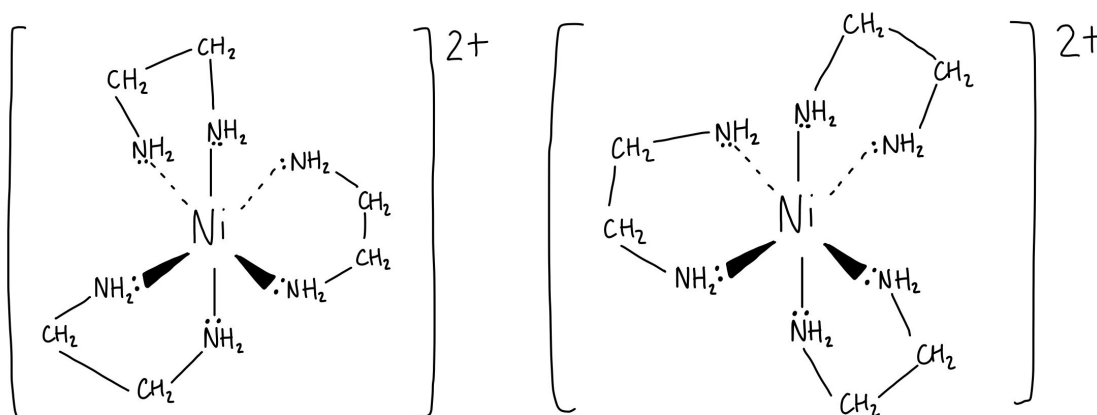
Ligands can have **one or more lone pairs**:

- **Monodentate** ligands are ligands with **one** lone pair. Each ligand forms one coordinate bond.
- **Bidentate** ligands are ligands with **two** lone pairs. Each ligand forms two coordinate bonds.
- **Multidentate** ligands are ligands with **two or more** lone pairs. Some of these ligands can form multiple coordinate bonds.

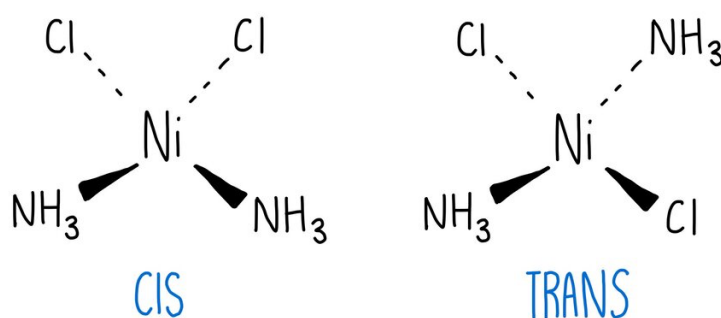
Isomerism in complex ions

Octahedral complex ions with **three bidentate ligands**, as shown in the image below, can exist as **optical isomers**. Optical isomers are isomers which are non-superimposable mirror

images of each other. They rotate plane-polarised light in opposite directions (clockwise vs anticlockwise).



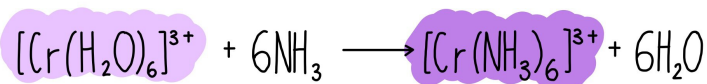
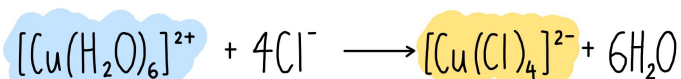
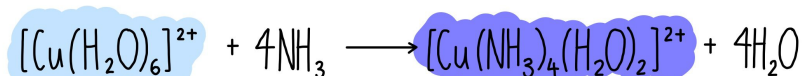
Other complex ions form **cis-trans isomers**, if two different groups are attached to the central metal ion. If the groups are on the **same side** of the complex ion, the complex ion exists in a **cis** conformation. **Trans** isomers have groups on **opposite sides** of the complex ion.



Cis-platin is an example of a complex ion which exists as a **cis** isomer with identical groups on the same side of the complex ion. It has a platinum (II) ion as the central ion, two ammonia ligands above the metal ion and two chloride ligands below the central metal ion. It is used as an **anti-cancer drug** and works by binding to DNA. The nitrogen atoms in DNA displace the chloride ligands of cis-platin. With cis-platin bound, DNA cannot replicate, and the cancer cell cannot divide. The cis conformation is important to its anti-cancer properties as the trans conformation has a different effect on the body.

Ligand substitution

A complex ion can react with substances such as water, ammonia, and chlorine in **ligand substitution** reactions, in which the ligands in the complex ion are replaced by different ligands. If the ligands are of the same size, the coordination number and geometry of the complex ion remains the same. If the ligands are a different size, then the coordination and geometry of the complex ion will change. Sometimes all the ligands are replaced and other times only some of them are – this is called **partial substitution**. Here's some examples of ligand substitution reactions:



Water ligands and **cyanide** (CN) ligands are small, which means that six of them will fit around the central metal ion, forming an **octahedral** complex. **Chloride ions** are bigger, with only four fitting around the metal ion, forming a **tetrahedral** complex.

Reactions of transition metal ions

Transition metals form ions with **various oxidation states**, which means they can change between oxidation states by gaining electrons (reduction) or losing electrons (oxidation) in redox reactions. In redox reactions involving transition metal ions, a **colour change** is often seen. For example:

- Fe^{2+} is a **pale green** colour but turns **yellow** when it is oxidised to Fe^{3+} .
- $\text{Cr}_2\text{O}_7^{2-}$ (dichromate ions) are **orange** in colour but turn **green** when they are reduced to Cr^{3+} . This is the colour change that occurs when potassium dichromate is used to oxidise primary and secondary alcohols.

Identifying transition metal ions

When reacted with **aqueous sodium hydroxide**, most of the transition metal ions form a **metal hydroxide** which appears as a **coloured precipitate**. This means that NaOH can be used to test for which transition metal ions are present in a solution.

- **Copper** hydroxide, $\text{Cu}(\text{OH})_2$ = **blue** precipitate
- **Iron (II)** hydroxide, $\text{Fe}(\text{OH})_2$ = **green** precipitate
- **Iron (III)** hydroxide, $\text{Fe}(\text{OH})_3$ = **brown** precipitate
- **Manganese** hydroxide, $\text{Mn}(\text{OH})_2$ = **pink** precipitate
- **Chromium** hydroxide, $\text{Cr}(\text{OH})_3$ = **grey/green** precipitate

