# Transition metals and complex ions

What a transition metal is, variable oxidation states, ligands and complex ions, shapes, colour, the stability of complexes, and haemoglobin and cisplatin.

## Transition metals

A **transition metal** is a d-block element that forms **one or more stable ions with an incompletely filled d sub-shell**. Scandium ($Sc^{3+}$, empty 3d) and zinc ($Zn^{2+}$, full $3d^{10}$) are in the d-block but are **not** transition metals.

### Electronic configurations

The 4s fills before 3d, but the **4s electrons are lost first** when ions form.

| Atom or ion | Configuration |
|---|---|
| Ti | $[Ar]3d^2 4s^2$ |
| V | $[Ar]3d^3 4s^2$ |
| Cr | $[Ar]3d^5 4s^1$ |
| Mn | $[Ar]3d^5 4s^2$ |
| Fe | $[Ar]3d^6 4s^2$ |
| Cu | $[Ar]3d^{10} 4s^1$ |
| $Fe^{2+}$ | $[Ar]3d^6$ |
| $Fe^{3+}$ | $[Ar]3d^5$ |
| $Cu^{2+}$ | $[Ar]3d^9$ |
| $Zn^{2+}$ | $[Ar]3d^{10}$ |

### Variable oxidation numbers

Transition metals show **variable oxidation states** (e.g. iron +2 and +3, manganese +2 to +7), because the **4s and 3d electrons are close in energy**, so a different number of electrons can be lost, using a similar amount of energy for each successive ionisation.

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# Ligands and complex ions

A **ligand** is a species with a **lone pair** that it donates to a metal ion, forming a **dative covalent (coordinate) bond**. A **complex ion** is a central metal ion surrounded by ligands.

The **coordination number** is the number of dative bonds to the central metal ion (more precisely, the number of coordinate bonds from ligands).

| Ligand type | Bonds per ligand | Examples |
|---|---|---|
| **Monodentate** | 1 | $H_2O$, $NH_3$, $OH^-$, $Cl^-$, $CN^-$ |
| **Bidentate** | 2 | 1,2-diaminoethane (en) $NH_2CH_2CH_2NH_2$, ethanedioate |
| **Hexadentate (polydentate)** | 6 | $EDTA^{4-}$ |

## Shapes

| Coordination number | Shape | Examples |
|---|---|---|
| 6 | **Octahedral** (90°) | $[Cu(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$ |
| 4 | **Tetrahedral** (109.5°), with large ligands like $Cl^-$ | $[CuCl_4]^{2-}$, $[CoCl_4]^{2-}$ |
| 4 | **Square planar** (90°) | **cisplatin**, $[Pt(NH_3)_2Cl_2]$ |
| 2 | **Linear** | $[Ag(NH_3)_2]^+$ |

Six-fold coordination with small ligands ($H_2O$, $NH_3$, $OH^-$) is octahedral, which spaces the six ligands as far apart as possible. Larger chloride ligands cannot fit six round the ion, so four give a tetrahedral complex.

## Cisplatin

**Cisplatin** is a square planar complex with two $NH_3$ and two $Cl^-$ ligands on the same side (**cis**). It is an anti-cancer drug: it binds to DNA in cancer cells and prevents replication. It is supplied as the **cis isomer only**, because the **trans** isomer does not have the same effect.

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### Haemoglobin

**Haemoglobin** contains **iron(II)** held in an octahedral complex by a polydentate ligand (the haem group) and a protein, with the sixth position taken by an $O_2$ molecule (a ligand). **Carbon monoxide** is toxic because $CO$ bonds more strongly than oxygen, so **ligand exchange** occurs and the haemoglobin can no longer carry oxygen.

## Colour

Most transition metal ions in solution are **coloured**.

In an isolated ion the five 3d orbitals have the same energy. **Ligands split** them into two groups of slightly different energy. An electron can absorb a photon with energy equal to the difference $\Delta E = hv$ and move to the higher level (a **d–d transition**). The **remaining frequencies** are transmitted, giving the **complementary** colour.

$$\Delta E = hv = \frac{hc}{\lambda}$$

Ions with an **empty** ($Sc^{3+}$) or **full** ($Zn^{2+}$, $Cu^{+}$) d sub-shell have no d–d transitions so they are **colourless**.

The colour (and the size of $\Delta E$) changes with:

- the **oxidation number** of the metal ion ($Fe^{2+}$ pale green, $Fe^{3+}$ yellow-brown),
- the **ligand** ($[Cu(H_2O)_6]^{2+}$ is pale blue and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is deep blue),
- the **coordination number** ($[CuCl_4]^{2-}$ is yellow-green).

## Ligand exchange and the stability of complexes

A ligand may be replaced by another: **ligand exchange**.

$$[Cu(H_2O)_6]^{2+} + 4Cl^{-} \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

Blue changes to yellow-green. The coordination number changes from 6 to 4 because chloride ions are bigger.

### The chelate effect

Replacing monodentate ligands with **bidentate or hexadentate** ligands gives a **more stable** complex.

$$[Cu(H_2O)_6]^{2+} + 3en \rightarrow [Cu(en)_3]^{2+} + 6H_2O$$

There are 4 moles of reactant particles and 7 of products. The number of particles in solution **increases**, so $\Delta S_{system}$ is **positive**. The enthalpy change is close to zero, since the same number of bonds is made and broken, so $\Delta S_{total}$ is positive and the reaction is feasible. The $K$ value is large.

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**Explain the chelate effect with entropy: more particles released, so more disorder in the system, so $\Delta S_{total}$ becomes more positive and the complex is more stable.**

**TRY IT**

Explain why the substitution of six $H_2O$ ligands by $EDTA^{4-}$ is favourable.

One $EDTA^{4-}$ replaces six water molecules. The number of dissolved particles increases from 2 (one metal ion, one EDTA) to 7 (one complex, six water molecules), so $\Delta S_{system}$ is large and positive, and $\Delta H$ is about zero. $\Delta S_{total}$ is positive, so the reaction is feasible and the complex is very stable.

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