413 TERM 4

INTRODUCTION to TRANSITION METALS — LIGANDS

6

GENERAL PROPERTIES

INCOMPLETED SUBSHELL

Transition metals have atoms or ions with an incomplete d subshell.

The electron structure of a vanadium (V) atom is:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$

'core' of electrons, the same as argon — different for each transition metal

This can also be written as:

$[Ar]\ 3d^3\ 4s^2$

All of the atoms and ions of period 4 transition metals (Ti to Cu) have the same inner electrons as an argon atom, plus electrons in:

- the partially filled 3d subshell
- the 4s orbital

Transition metals form ions with an incomplete (partially full) d subshell. Sc and Zn are not transition metals because Sc^{3+} has an empty d subshell Zn^{2+} and has a full d subshell.

VARIABLE OXIDATION STATE

All transition metals can form ions with different charges. An excellent example is vanadium, which can form V^{5+}, V^{4+}, V^{3+} and V^{2+} ions. Each ion has a different number of electrons.

CATALYTIC ACTIVTY

Transition metals can often catalyse reactions, meaning that they can **make a reaction occur faster.**

Chemical reactions involve the movement of electrons, and transition metals can give and take electrons due to their **variable oxidation states.**

COLOURED IONS

Many transition metals form brightly coloured solutions.

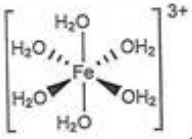
TRANSITION METAL COMPLEXES

The general formula of a complex is:

$[M(L)_x]^n$

- M is the transition metal
- L is the ligand
- x is the number of ligands
- n is the charge of the complex

e.g. the complex formed by iron(III) with six water ligands is: $[Fe(H_2O)_6]^{3+}$



EXAM TIP

Make sure you draw the coordinate bond from the correct atom, i.e. O in H_2O and N in NH_3.

COORDINATE BONDS

The bonds between ligands and the metal ion are called **coordinate bonds.** A coordinate bond is a type of covalent bond where both electrons come from one species.

In transition metal complexes, **both electrons in the bond come from a lone pair of electrons on the ligand.**

COMMON LIGANDS

Ions or molecules which have formed complexes with transition metal ions are known as ligands.

H_2O
A small, uncharged ligand. One lone pair on the oxygen atom forms a coordinate bond with a transition metal.

$H_2O{:}\rightarrow M$

NH_3
Another small, uncharged ligand. The coordinate bond forms from the lone pair on the nitrogen atom.

$H_3N{:}\rightarrow M$

Cl^-
A large, negatively charged ion. Cl^- forms a coordinate bond from one of its four lone pairs.

$Cl^-{:}\rightarrow M$

COORDINATION NUMBER

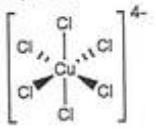
The coordination number of a complex is the number of dative covalent bonds present in the complex.

TYPES OF LIGAND

Different ligands can form different numbers of coordinate bonds with the transition metal ion. To form multiple coordinate bonds, a ligand must have multiple atoms with lone pairs available to donate.

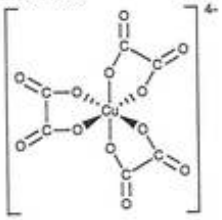
MONODENTATE

Monodentate ligands, such as Cl^-, H_2O and NH_3, can form **one** coordinate bond in complexes.



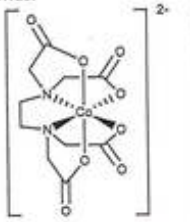
BIDENTATE

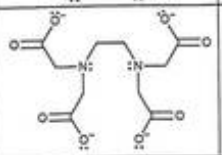
Bidentate ligands can form **two** coordinate bonds with metal ions.



MULTIDENTATE

Multidentate ligands can form **multiple** coordinate bonds.



Ligand	Formula	Bonds
Ethanedioate ion		2
1,2-diaminoethane		2
EDTA		6

EXAM TIP

Exam questions might involve ligands you've never seen before.

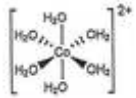
SUBSTITUTION

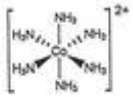
When a metal ion is in solution, it forms a complex with the water molecules around it. Commonly these are called hexaaqua ions because they contain six H_2O ligands. When other ions are added to the solution, the H_2O ligands may be substituted with new ions.

WITH NH_3

Like H_2O, NH_3 is small and uncharged. Each H_2O is replaced with an NH_3.

$[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$

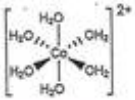


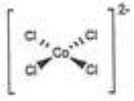


WITH Cl^-

Unlike H_2O, Cl^- is **large** and **charged.** When Cl^- substitutes H_2O, there is a change in coordination number from 6 to 4.

$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$





CHELATE EFFECT

A metal ion will form a complex with ligands, which form more bonds. This is 'entropically favourable'.

Enthalpy	Entropy
Generally, **if more bonds are formed than broken then the reaction is enthalpically favourable,** since bond formation is exothermic.	Reactions where there are **more species in the product than in the reactants** are **entropically favourable.**



- The coordination number stays the same, so the enthalpy change is very small.
- There are more species on the right than on the left, so the entropy change is positive.

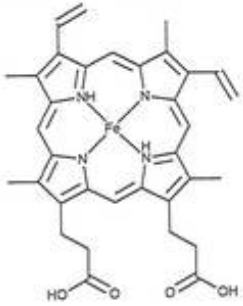
$[Cu(H_2O)_6]^{2+} + EDTA^{2-} \rightarrow Cu(EDTA) + 6H_2O$

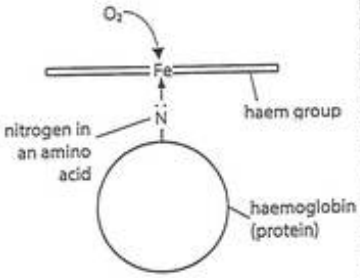
Number of species: 2 → 7

The reaction occurs because it is entropically favourable and the enthalpy change is too small to matter.

HAEMOGLOBIN

Blood contains haemoglobin, which is a protein with an iron(II) complex with a multidentate (four coordinate bonds) ligand called a **haem group.**





Oxygen is a ligand for the iron(II) ion in the haemoglobin, allowing it to be transported in blood.

CARBON MONOXIDE

Carbon monoxide forms a very strong coordinate bond with iron in haemoglobin, preventing oxygen from binding. This is why carbon monoxide is toxic.

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