

28.2 GENERAL CHARACTERISTICS AND CHEMICAL PROPERTIES OF TRANSITION ELEMENTS

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Learning outcomes

Candidates should be able to:

1. describe and explain the reactions of transition elements with ligands to form complexes, including the complexes of copper(II) and cobalt(II) ions with water and ammonia molecules and hydroxide and chloride ions
2. define the term ligand as a species that contains a lone pair of electrons that forms a dative covalent bond to a central metal atom / ion
3. understand and use the terms:
 - (a) monodentate ligand including as examples H_2O , NH_3 , Cl^- and CN^-
 - (b) bidentate ligand including as examples 1,2-diaminoethane, *en*, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ and the ethanedioate ion, $\text{C}_2\text{O}_4^{2-}$
 - (c) polydentate ligand including as an example EDTA^{4-}
4. define the term complex as a molecule or ion formed by a central metal atom / ion surrounded by one or more ligands
5. describe the geometry (shape and bond angles) of transition element complexes which are linear, square planar, tetrahedral or octahedral
6.
 - (a) state what is meant by coordination number
 - (b) predict the formula and charge of a complex ion, given the metal ion, its charge or oxidation state, the ligand and its coordination number or geometry
7. explain qualitatively that ligand exchange can occur, including the complexes of copper(II) ions and cobalt(II) ions with water and ammonia molecules and hydroxide and chloride ions
8. predict, using $E^\ominus$ values, the feasibility of redox reactions involving transition elements and their ions
9. describe the reactions of, and perform calculations involving:
 - (a) $\text{MnO}_4^- / \text{C}_2\text{O}_4^{2-}$ in acid solution given suitable data
 - (b) $\text{MnO}_4^- / \text{Fe}^{2+}$ in acid solution given suitable data
 - (c) $\text{Cu}^{2+} / \text{I}^-$ given suitable data
10. perform calculations involving other redox systems given suitable data

Initial assessment

1. Draw a dot-and-cross diagram to show the bonding in an ammonium ion, NH_4^+ . Only include the outer shell electrons.

Ligands

Ligand is a species that contains a lone pair of electrons that forms a dative covalent bond to a central metal atom/ion

Ligands are bases, and also nucleophiles

monodentate ligand: H_2O , NH_3 , Cl^- and CN^-

bidentate ligand: 1,2-diaminoethane, *en*, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ and the ethanedioate ion, $\text{C}_2\text{O}_4^{2-}$

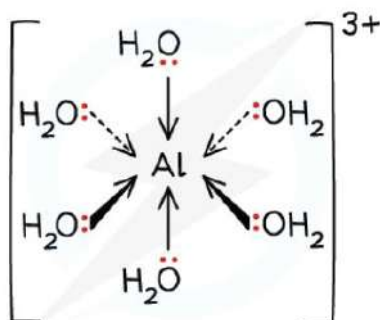
polydentate ligand: EDTA^{4-}

Complex

A complex ion is a species that consists of a central metal ion with a specific number of ions or molecules surrounding it, bound by coordinate bonds.

The molecules or ions surrounding the metal ion are called **ligands**, which always contain at least one lone pair of electrons.

e.g., $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$



Coordination number = ?

Coordination number = the number of coordinate bonds formed by ligands with a transition element ion in a complex.

Geometry

Name of ligand	Formula	Example of complex	Co-ordination number	Shape of complex
water	H ₂ O	[Fe(H ₂ O) ₆] ²⁺	6	octahedral (see Figure 24.4)
ammonia	NH ₃	[Co(NH ₃) ₆] ³⁺	6	octahedral
chloride ion	Cl ⁻	[CoCl ₄] ²⁻	4	tetrahedral (see Figure 24.5b)
cyanide ion	CN ⁻	[Ni(CN) ₄] ²⁻	4	square planar (see Figure 24.5a)
hydroxide ion	OH ⁻	[Cr(OH) ₆] ³⁻	6	octahedral
thiocyanate ion	SCN ⁻	[FeSCN] ²⁺ or [Fe(SCN)(H ₂ O) ₅] ²⁺	6	octahedral
ethanedioate ion (abbreviated to 'ox' – oxalate – in the formulae of complexes)	⁻ OOC–COO ⁻	[Mn(ox) ₃] ³⁻	6	octahedral
1,2-diaminoethane (abbreviated to 'en' in the formulae of complexes)	NH ₂ CH ₂ CH ₂ NH ₂	[Co(en) ₃] ³⁺	6	octahedral (see Figure 24.6)

Linear

Central metal atoms or ions with **two coordinate bonds** form **linear** complexes

The bond angles in these complexes are 180°

The most common examples are a copper (I) ion, (Cu), or a silver (I) ion, (Ag), as the central metal ion with two coordinate bonds formed to two ammonia ligands

Tetrahedral

When there are **four coordinate bonds** the complexes often have a **tetrahedral** shape

Complexes with four **chloride ions** most commonly adopt this geometry

Chloride ligands are large, so only four will fit around the central metal ion

The bond angles in tetrahedral complexes are 109.5

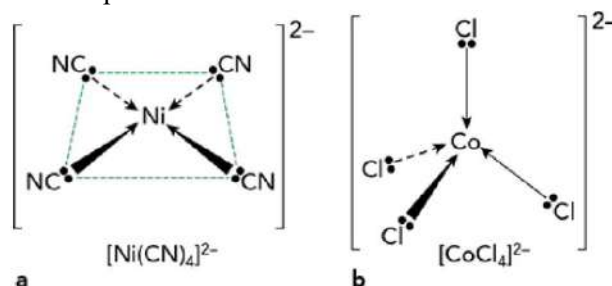


Figure: The complex ion formed between a transition metal ion and a larger ligand can only fit four, not six, ligands around the central ion. These are arranged in either a square planar shape (as in **a** [Ni(CN)₄]²⁻) or a tetrahedral shape (as in **b** [CoCl₄]²⁻).

Square planar

Sometimes, complexes with **four coordinate bonds** may adopt a **square planar** geometry instead of a tetrahedral one

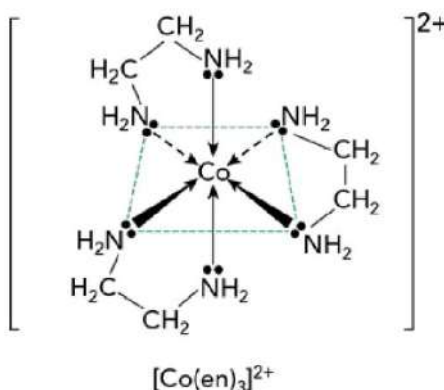
Cyanide ions (CN) are the most common ligands to adopt this geometry

An example of a square planar complex is **cisplatin**

The bond angles in a square planar complex are 90

Octahedral

Octahedral complexes are formed when a central metal atom or ion forms **six coordinate bonds**



Ligand Exchange Reactions

The ligands in a complex can be exchanged, wholly or partially, for other ligands.

This is a type of substitution reaction.

It happens if the new complex formed is more stable than the original complex.

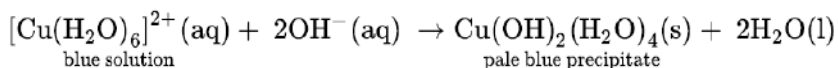
The complexes of copper(II) ions can be used to show ligand substitution reactions, also called **ligand exchange reactions**.

Copper complexes

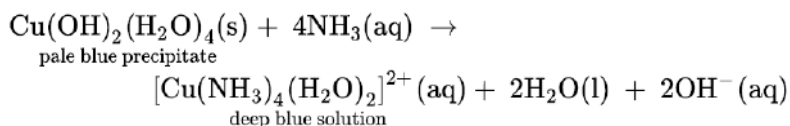
Whenever we write $\text{Cu}^{2+}(\text{aq})$ we are really referring to the complex ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. This ion gives a solution of copper sulfate its blue colour.

On adding sodium hydroxide solution, we see a light blue precipitate forming.

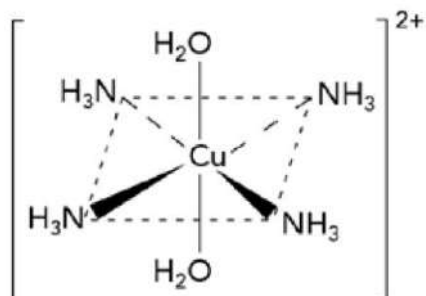
Two water ligands are replaced by two hydroxide ligands in the reaction:



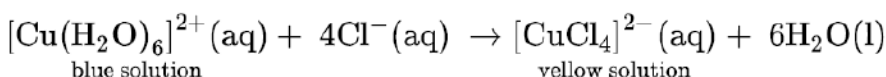
If you now add concentrated ammonia solution, the pale blue precipitate dissolves and we get a deep blue solution:



The first reaction can also be achieved by adding concentrated ammonia solution to copper sulfate solution drop by drop or by adding a dilute solution of ammonia. The pale blue precipitate formed will then dissolve and form the deep blue solution when excess ammonia is added. The structure of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$ is shown in Figure



Water ligands in $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ can also be exchanged for chloride ligands if we add concentrated hydrochloric acid drop by drop. A yellow solution forms, containing the complex ion $[\text{CuCl}_4]^{2-}$:



The mixture of blue and yellow solutions in the reaction mixture gives it a greenish colour

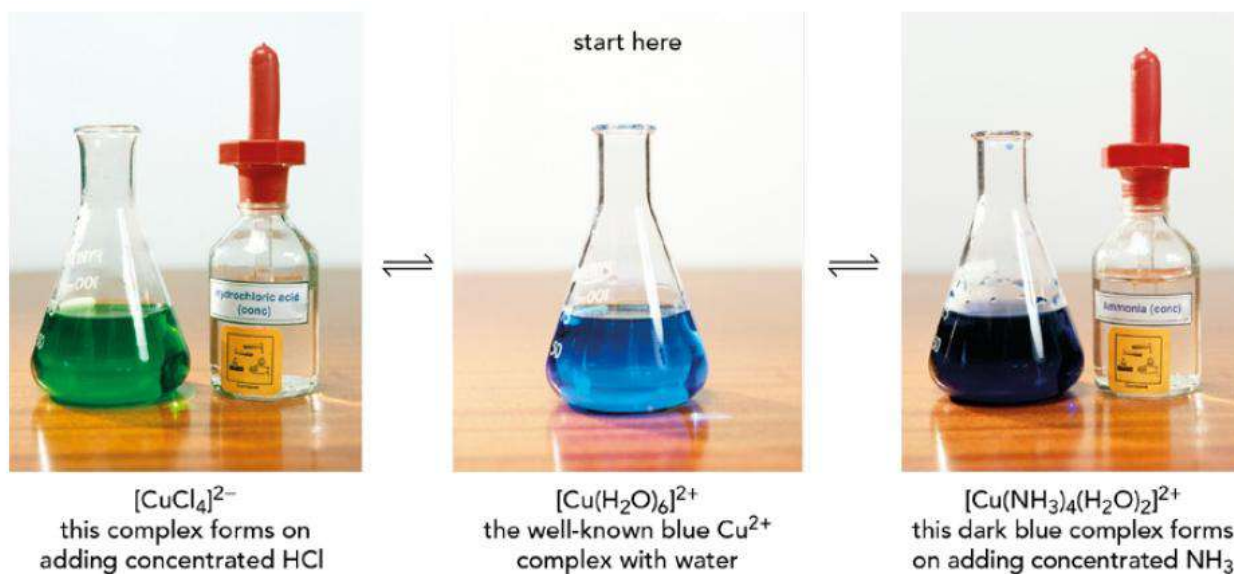
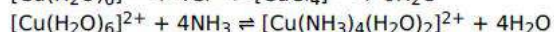
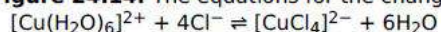
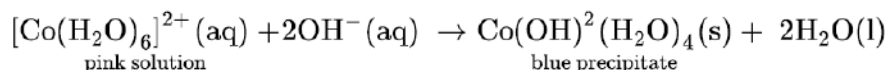


Figure 24.14: The equations for the changes are:

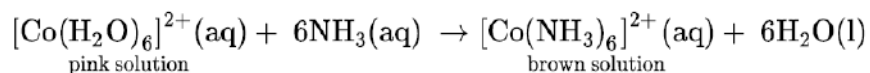


Cobalt complexes

Aqueous cobalt(II) compounds also form complex ions. Whenever we write $\text{Co}^{2+}(\text{aq})$, we are referring to the complex ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. This ion gives an aqueous solution of cobalt(II) sulfate its pink colour. On adding sodium hydroxide solution, we see a blue precipitate of cobalt(II) hydroxide forming, which turns red when warmed if the alkali is in excess.



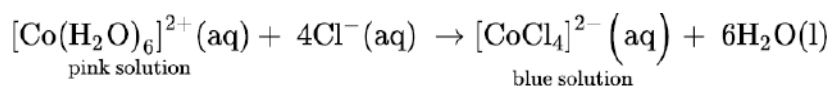
Water ligands in $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ can also be exchanged for ammonia ligands if we add concentrated aqueous ammonia drop by drop.



The brown cobalt(II) complex ion is oxidised by oxygen in the air to $[\text{Co}(\text{NH}_3)_6]^{3+}(\text{aq})$, a cobalt(III) complex ion.

Adding concentrated hydrochloric acid drop by drop to an aqueous solution of cobalt(II) ions results in the

formation of a blue solution containing the tetrahedral complex $[\text{CoCl}_4]^{2-}(\text{aq})$.



Aqueous cobalt(II) ions usually form tetrahedral complexes with monodentate anionic ligands such as Cl^{-} ,

SCN^{-} and OH^{-} .

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