

1 This question looks at properties of transition elements, ions and complexes.

(a) What is the oxidation number of Cr in the complex ion $[\text{CrOCl}_5]^{2-}$?

..... [1]

(b) Write the equation for a reaction catalysed by a named transition element, compound or ion.

Equation:

Catalyst: [1]

(c) An octahedral complex ion **A**, $\text{C}_9\text{H}_{30}\text{N}_6\text{Ni}^{3+}$, exists as two optical isomers.

In complex ion **A**, Ni^{3+} is bonded to three molecules of a bidentate ligand **B**.

(i) State what is meant by a *bidentate ligand*.

.....
.....
..... [1]

(ii) What is the molecular formula of the bidentate ligand **B**?

..... [1]

(iii) Draw a possible structure for **B** and explain how **B** is able to act as a bidentate ligand.

.....
.....
..... [2]

(iv) What is the coordination number of complex ion **A**?

..... [1]

2 Elements in the d-block of the Periodic Table form ions that combine with ligands to form complex ions. Most d-block elements are also classified as transition elements.

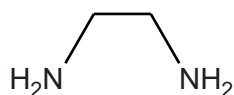
(a) Explain why two of the Period 4 d-block elements (Sc–Zn) are **not** also transition elements.

In your answer you should link full electron configurations to your explanations.

.....
.....
.....
.....
..... [6]

(b) The cobalt(III) ion, Co^{3+} , forms a complex ion **A** with two chloride ligands and two ethanediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, ligands.

The structure of ethanediamine is shown below.



(i) Explain how ethanediamine is able to act as a bidentate ligand.

.....
.....
..... [2]

(ii) Write the formula of complex ion **A**.

..... [1]

(iii) What is the coordination number of cobalt in complex ion **A**?

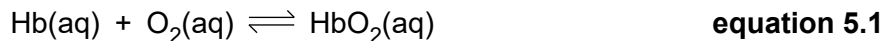
..... [1]

(iv) Complex ion **A** has *cis* and *trans* stereoisomers. One of these stereoisomers also has an optical isomer.

Draw 3-D diagrams to show the three stereoisomers.

[3]

- (c) The equilibrium reaction for the transport of oxygen by haemoglobin (Hb) in blood can be represented as **equation 5.1**.



- (i) Explain how ligand substitution reactions allow haemoglobin to transport oxygen in blood.

.....
.....
..... [2]

- (ii) Write an expression for the stability constant, K_{stab} , for the equilibrium involved in the transport of oxygen by haemoglobin.

Use the simplified species in **equation 5.1**.

[1]

- (iii) In the presence of carbon monoxide, less oxygen is transported in the blood.

Suggest why, in terms of bond strength and stability constants.

.....
.....
.....
..... [2]

[Total: 18]

- 3 Iron is heated with chlorine to form an orange–brown solid, **A**.
Solid **A** is dissolved in water to form an orange–brown solution, **X**, containing the complex ion $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.

Separate portions of solution **X** are reacted as shown in **Experiments 1–4** below.

Experiment 1

Aqueous sodium hydroxide is added to solution **X**. An orange–brown precipitate **B** forms.

Experiment 2

Excess zinc powder is added to solution **X** and the mixture is heated. The excess zinc is removed leaving a pale-green solution containing the complex ion **C** and aqueous Zn^{2+} ions.

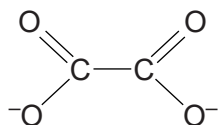
Experiment 3

An excess of aqueous potassium cyanide, $\text{KCN}(\text{aq})$, is added to solution **X**.
The solution turns a yellow colour and contains the complex ion **E**.
E has a molar mass of 211.8 g mol^{-1} .

Experiment 4

An aqueous solution containing ethanedioate ions, $(\text{COO}^-)_2$, is added to solution **X**.
A coloured solution forms containing a mixture of optical isomers **F** and **G**.

The structure of the ethanedioate ion is shown below.



- (a) Write an equation for the formation of solid **A**.
..... [1]
- (b) In **Experiment 1**, write an ionic equation for the formation of precipitate **B**.
..... [1]
- (c) In **Experiment 2**,
- (i) write an equation for the formation of complex ion **C**
..... [2]
- (ii) state the type of reaction taking place.
..... [1]

(d) In **Experiment 3**,

(i) write an equation for the formation of complex ion **E**

..... [2]

(ii) state the type of reaction taking place.

..... [1]

(e) In **Experiment 4**, optical isomers **F** and **G** are formed.

Show the 3-D shapes of **F** and **G**.

In your diagrams, show the ligand atoms that are bonded to the metal ions and any overall charges.

[3]

(f) In a separate experiment, iron metal is heated with potassium nitrate, KNO_3 , a strong oxidising agent. A reaction takes place and the resulting mixture is poured into water. A dark red solution forms containing ferrate(VI) ions. The ferrate(VI) ion has a 2- charge.

Suggest a possible formula for the ferrate(VI) ion.

..... [1]

[Total: 12]

4 Dimethylglyoxime, DMGH, can be used to analyse nickel(II)

An excess of a solution of DMGH is added to an acidic solution of a nickel(II) compound. Aqueous ammonia is added which precipitates out a nickel(II) complex, Ni(DMG)₂, as a red solid.

A sample of a hydrated nickel(II) salt is analysed using the procedure below.

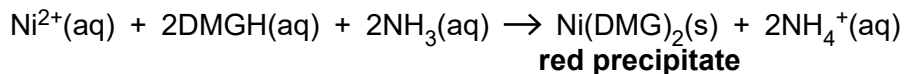
Step 1

2.50 g of the hydrated nickel(II) salt is dissolved in dilute acid.
An excess of an aqueous solution of DMGH is added.

Step 2

An excess of aqueous ammonia is added and the mixture is heated.
A red precipitate of Ni(DMG)₂ forms.

An equation for the reaction is shown below.



Step 3

The red precipitate is filtered, washed with water, dried and then weighed.
The precipitate of Ni(DMG)₂ has a mass of 2.57 g.
Assume that all Ni²⁺(aq) ions have been converted into Ni(DMG)₂(s).
 $M[\text{Ni}(\text{DMG})_2] = 288.7 \text{ g mol}^{-1}$.

Step 4

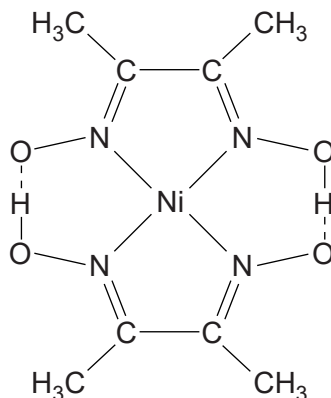
A second 2.50 g sample of the hydrated nickel(II) salt is heated in a crucible to remove the water of crystallisation.
1.38 g of the anhydrous salt remains.

(a) Complete the electron configurations of nickel as the element and in the +2 oxidation state.

nickel as the element: $1s^2 2s^2 2p^6$

nickel in the +2 oxidation state: $1s^2 2s^2 2p^6$ **[2]**

(b) The structure of $\text{Ni}(\text{DMG})_2$ is shown below.



(i) State and explain the role of ammonia in **step 2** of this experiment.

.....
.....
..... [1]

(ii) State the coordination number of Ni in $\text{Ni}(\text{DMG})_2$.

..... [1]

(iii) Why does the $\text{Ni}(\text{DMG})_2$ complex have no overall charge?

.....
..... [1]

(iv) Draw the structure of dimethylglyoxime, DMGH.

[1]

(c) Determine a possible formula of the hydrated nickel(II) salt.

Your answer **must** show relevant working.

[7]

[Total: 13]