1 Iron, copper and platinum are examples of transition elements.

(a) Define the term *transition element*.

Show that iron fits this definition by use of full electron configurations of iron as the element and in its common oxidation states.

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..... **[4]**

(b) Describe **one** precipitation reaction and **one** ligand substitution reaction of copper in the +2 oxidation state.

Your answer should include reagents, relevant observations and balanced equations.

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

(c) Platinum is an extremely unreactive transition element. However, platinum does take part in a redox reaction with '*aqua regia'*, a mixture of concentrated hydrochloric and nitric acids. Two products of this reaction are hexachloroplatinic acid, H_2PtCl_6, and nitrogen dioxide, NO_2.

(i) Use oxidation states to show that this is a redox reaction.

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

(ii) Write an equation for the reaction of platinum metal with *aqua regia*.

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

(d) Ammonium hexachloroplatinate, $(NH_4)_2PtCl_6$, is a complex of platinum used in platinum plating. Ammonium hexachloroplatinate contains the hexachloroplatinate ion.

Draw a 3-D diagram to show the shape of a hexachloroplatinate ion.

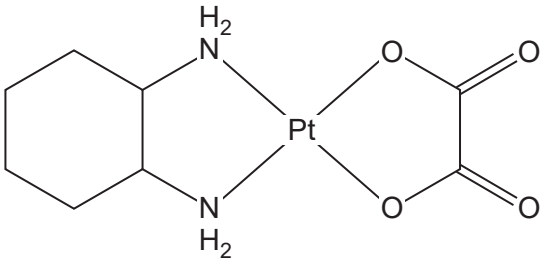
On your diagram, show

- the charge on the ion
- the value of the bond angle.

[3]

(e) Oxaliplatin is a neutral complex of platinum(II) used in cancer treatment.

A molecule of oxaliplatin has a square planar shape about the metal ion with two bidentate ligands. The structure of oxaliplatin is shown below.



(i) What is meant by a *bidentate ligand*?

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

(ii) In the boxes below, show the structures of the two bidentate ligands in oxaliplatin.

[2]

[Total: 21]

2 Nickel is a typical transition element in the d-block of the Periodic Table. Many nickel ions are able to interact with ligands to form complex ions, such as $[Ni(H_2O)_6]^{2+}$.

(a) Using the information about nickel above, explain the meaning of the terms *d-block element*, *transition element*, *ligand* and *complex ion*.

Include electron structures and diagrams in your answer.

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..... **[7]**

(b) A student dissolves nickel(II) sulfate in water. A green solution forms containing the complex ion $[Ni(H_2O)_6]^{2+}$.

The student then reacts separate portions of the green solution of nickel(II) sulfate as outlined below.

- Concentrated hydrochloric acid is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a lime-green colour and contains the four-coordinate complex ion **A**.

- Aqueous sodium hydroxide is added to the green solution of nickel(II) sulfate. A pale-green precipitate **B** forms.

- Concentrated aqueous ammonia is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a violet colour and contains the complex ion **C**.
  C has a molar mass of $160.7\,g\,mol^{-1}$.

(i) Draw a 3-D diagram for the $[Ni(H_2O)_6]^{2+}$ ion.
Show a value for the bond angles on your diagram.

[2]

(ii) Suggest the formulae of **A** and **B**.

A .....

B ..... **[2]**

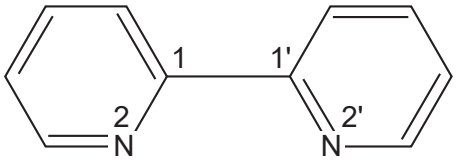
(iii) Deduce the formula of **C**.

C ..... **[1]**

(iv) Write an equation for the formation of **C** from $[Ni(H_2O)_6]^{2+}$.

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

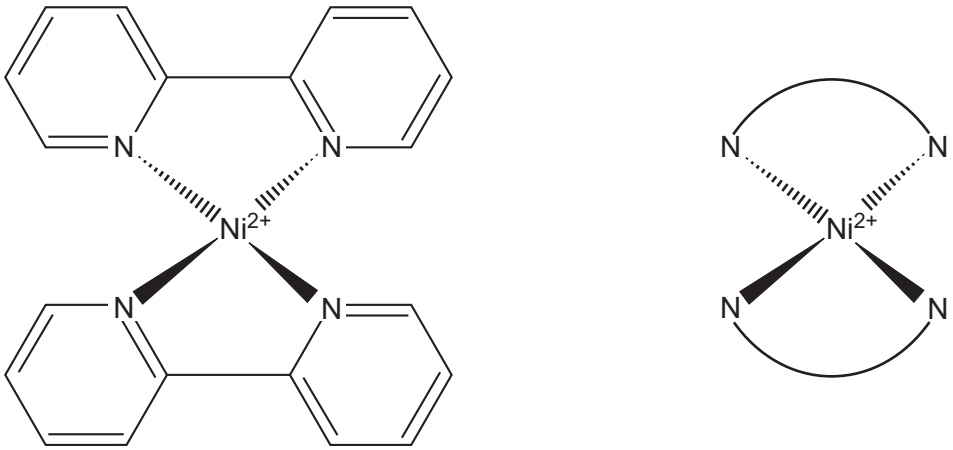
(c) 2,2'-Bipyridine (or 'bipy') is a bidentate ligand that forms complexes with many transition metals. The structure of 2,2'-bipyridine is shown below.



2,2'-bipyridine

In the naming of bipyridines, the numbering starts at the carbon atom that links to the other ring.

2,2'-Bipyridine forms a complex, $[Ni(bipy)_2]^{2+}$. The structure of $[Ni(bipy)_2]^{2+}$ is shown in **Fig 6.1** below.



structure simplified diagram

$[Ni(bipy)_2]^{2+}$

Fig 6.1

(i) What is the molecular formula of 2,2'-bipyridine?

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

(ii) What is the coordination number of the $[Ni(bipy)_2]^{2+}$ complex ion?

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

(iii) 2,2'-Bipyridine forms a complex with the transition metal ruthenium with the formula $[Ru(bipy)_3]^{2+}$. This complex exists as two stereoisomers.

Draw 3-D diagrams to predict the structures for these stereoisomers of $[Ru(bipy)_3]^{2+}$. You can represent the 2,2'-bipyridine ligands as in the simplified diagram for $[Ni(bipy)_2]^{2+}$ in **Fig 6.1**.

[2]

(iv) 4,4'-Bipyridine (4,4'-bipy) can also form complexes with transition metal ions. Because of its structure, 4,4'-bipyridine can bridge between metal ions to form 'coordination polymers'. For example, nickel(II) can form a coordination polymer with 4,4'-bipyridine containing $\{[Ni(H_2O)_4(4,4'\text{-bipy})]^{2+}\}_n$ chains.

Draw a 3-D diagram to predict the repeat unit in this coordination polymer of nickel(II). Your diagram should show the complete structure of 4,4'-bipyridine and all coordinate bonds.

[3]

[Total: 21]

3 Brass is an alloy which contains copper.
The percentage of copper in brass can be determined using the steps below.

Step 1 2.80 g of brass is reacted with an excess of concentrated nitric acid, HNO_3.
The half-equations taking place are shown below.

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$
$$2HNO_3(l) + e^- \longrightarrow NO_3^-(aq) + NO_2(g) + H_2O(l)$$

Step 2 Excess aqueous sodium carbonate is added to neutralise any acid. The mixture effervesces and a precipitate forms.

Step 3 The precipitate is reacted with ethanoic acid to form a solution which is made up to 250 cm^3 with water.

Step 4 A 25.0 cm^3 sample of the solution is pipetted into a conical flask and an excess of aqueous potassium iodide is added.
A precipitate of copper(I) iodide and a solution of iodine, $I_2(aq)$, forms.

Step 5 The resulting mixture is titrated with 0.100 mol dm^{-3} sodium thiosulfate to estimate the iodine present:

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Step 6 **Steps 4** and **5** are repeated to obtain an average titre of 29.8 cm^3.

- For **steps 1**, **2** and **4**, write ionic equations, including state symbols, for the reactions taking place.
- Determine the percentage, by mass, of copper in the brass.
  Give your answer to **one** decimal place.

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[9]

[Total: 9]

4 Chromium shows typical properties of a transition element. The element's name comes from the Greek word 'Chroma' meaning colour because of its many colourful compounds.

(a) Write down the electron configuration of

(i) a Cr atom, ... **[1]**

(ii) a Cr^{3+} ion. ..... **[1]**

(b) An acidified solution containing orange $Cr_2O_7^{2-}$ ions reacts with zinc in a redox reaction to form a solution containing Zn^{2+} ions and blue Cr^{2+} ions.

The unbalanced half-equations are shown below.

$$Zn \longrightarrow Zn^{2+} + e^-$$

$$Cr_2O_7^{2-} + H^+ + e^- \longrightarrow Cr^{2+} + H_2O$$

Balance these equations and construct an overall equation for this reaction.

..... **[3]**

(c) Aqueous solutions of Cr^{3+} ions contain ruby-coloured $[Cr(H_2O)_6]^{3+}$ complex ions. If an excess of concentrated ammonia solution is added, the solution changes to a violet colour as the hexaammine chromium(III) complex ion forms.

(i) What type of reaction has taken place?

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

(ii) Suggest an equation for this reaction.

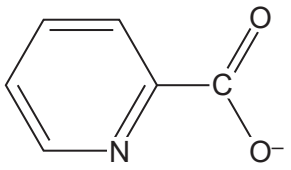
..... **[2]**

(d) Chromium picolinate, $Cr(C_6H_4NO_2)_3$, is a bright red complex, used as a nutritional supplement to prevent or treat chromium deficiency in the human body.

In this complex,

- chromium has the +3 oxidation state,
- picolinate ions, $C_6H_4NO_2^-$, act as bidentate ligands.

The structure of the picolinate ion is shown below.



$Cr(C_6H_4NO_2)_3$ exists as a mixture of stereoisomers.

(i) What is meant by the term *ligand*?

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

(ii) How is the picolinate ion able to act as a **bidentate** ligand?

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

(iii) Why does $Cr(C_6H_4NO_2)_3$ exist as a mixture of stereoisomers?
Draw diagrams of the stereoisomers as part of your answer.

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..... **[3]**

(e) Compound **A** is an orange ionic compound of chromium with the percentage composition by mass N, 11.11%; H, 3.17%; Cr, 41.27%; O, 44.45%. Compound **A** does **not** have water of crystallisation.

On gentle heating, compound **A** decomposes to form three products, **B**, **C** and water.
B is a green oxide of chromium with a molar mass of 152.0 g mol^{-1}.
C is a gas. At RTP, each cubic decimetre of **C** has a mass of 1.17 g.

In the steps below, show all your working.

- Calculate the empirical formula of compound **A**.
- Deduce the ions that make up the ionic compound **A**.
- Identify substances **B** and **C**.
- Write an equation for the decomposition of compound **A** by heat.

[8]

[Total: 22]