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2002

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CHEMISTRY

**OCR
AS & A LEVEL**

Topic Questions

**Module 5: Physical chemistry and
transition elements**

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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, $(\text{NH}_4)_2\text{PtCl}_6$, 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.

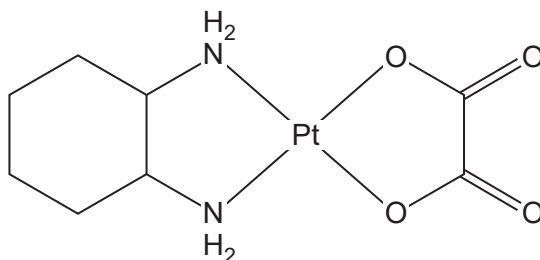
On your diagram, show

- 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.

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[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 $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.
- (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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- (b) A student dissolves nickel(II) sulfate in water. A green solution forms containing the complex ion $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

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 $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ion.
Show a value for the bond angles on your diagram.

[2]

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

A

B [2]

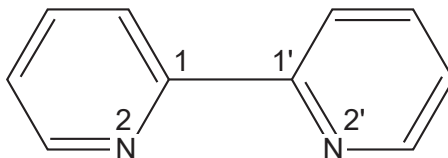
- (iii) Deduce the formula of **C**.

C [1]

- (iv) Write an equation for the formation of **C** from $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

..... [2]

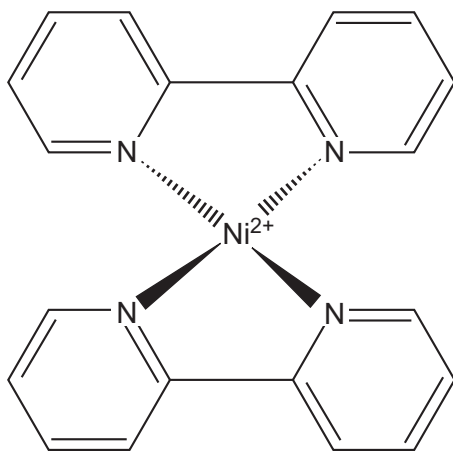
- (c) 2,2'-Bipyridine (or 'bipy') is a bidentate ligand that forms complexes with many transition metals. The structure of 2,2'-bipyridine is shown below.



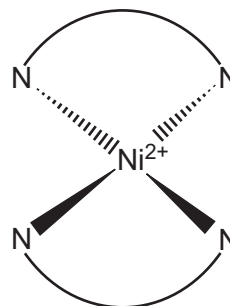
2,2'-bipyridine

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

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



structure



simplified diagram



Fig 6.1

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

..... [1]

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

..... [1]

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

Draw 3-D diagrams to predict the structures for these stereoisomers of $[\text{Ru}(\text{bipy})_3]^{2+}$. You can represent the 2,2'-bipyridine ligands as in the simplified diagram for $[\text{Ni}(\text{bipy})_2]^{2+}$ 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 $\{[\text{Ni}(\text{H}_2\text{O})_4(4,4'\text{-bipy})]^{2+}\}_n$ chains.

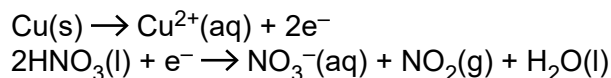
Draw a 3-D diagram to predict the repeat unit in this coordination polymer of nickel(II). Your diagram should show the complete structure of 4,4'-bipyridine and all coordinate bonds.

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

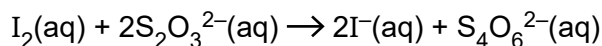


Step 2 Excess aqueous sodium carbonate is added to neutralise any acid. The mixture effervesces and a precipitate forms.

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, $\text{I}_2(\text{aq})$, forms.

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



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.

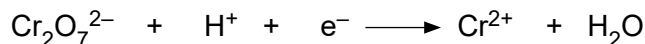
(a) Write down the electron configuration of

(i) a Cr atom, [1]

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

- (b) An acidified solution containing orange $\text{Cr}_2\text{O}_7^{2-}$ 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.



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

..... [3]

- (c) Aqueous solutions of Cr^{3+} ions contain ruby-coloured $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ 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.

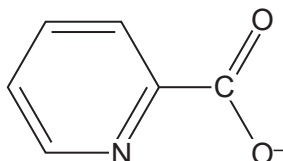
..... [2]

- (d) Chromium picolinate, $\text{Cr}(\text{C}_6\text{H}_4\text{NO}_2)_3$, 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, $\text{C}_6\text{H}_4\text{NO}_2^-$, act as bidentate ligands.

The structure of the picolinate ion is shown below.



$\text{Cr}(\text{C}_6\text{H}_4\text{NO}_2)_3$ exists as a mixture of stereoisomers.

- (i) What is meant by the term *ligand*?
 [1]

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

 [2]

- (iii) Why does $\text{Cr}(\text{C}_6\text{H}_4\text{NO}_2)_3$ exist as a mixture of stereoisomers?
 Draw diagrams of the stereoisomers as part of your answer.

.....

 [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]