

**Q16.**

This question is about copper chemistry.

(a) Aqueous copper(II) ions  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$  are blue.

(i) With reference to electrons, explain why aqueous copper(II) ions are blue.

---

---

---

---

---

---

---

(3)

(ii) By reference to aqueous copper(II) ions, state the meaning of each of the **three** terms in the equation  $\Delta E = h\nu$ .

---

---

---

---

---

---

---

(3)

(iii) Write an equation for the reaction, in aqueous solution, between  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  and an excess of chloride ions.  
State the shape of the complex produced and explain why the shape differs from that of the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion.

---

---

---

---

---

---

---

(3)



- (b) Draw the structure of the ethanedioate ion ( $\text{C}_2\text{O}_4^{2-}$ ). Explain how this ion is able to act as a ligand.

---

---

---

---

---

(2)

- (c) When a dilute aqueous solution containing ethanedioate ions is added to a solution containing aqueous copper(II) ions, a substitution reaction occurs. In this reaction four water molecules are replaced and a new complex is formed.

- (i) Write an ionic equation for the reaction. Give the co-ordination number of the complex formed and name its shape.

---

---

---

---

---

---

---

(4)



- (ii) In the complex formed, the two water molecules are opposite each other. Draw a diagram to show how the ethanedioate ions are bonded to a copper ion and give a value for one of the O–Cu–O bond angles. You are **not** required to show the water molecules.

(2)

(Total 17 marks)

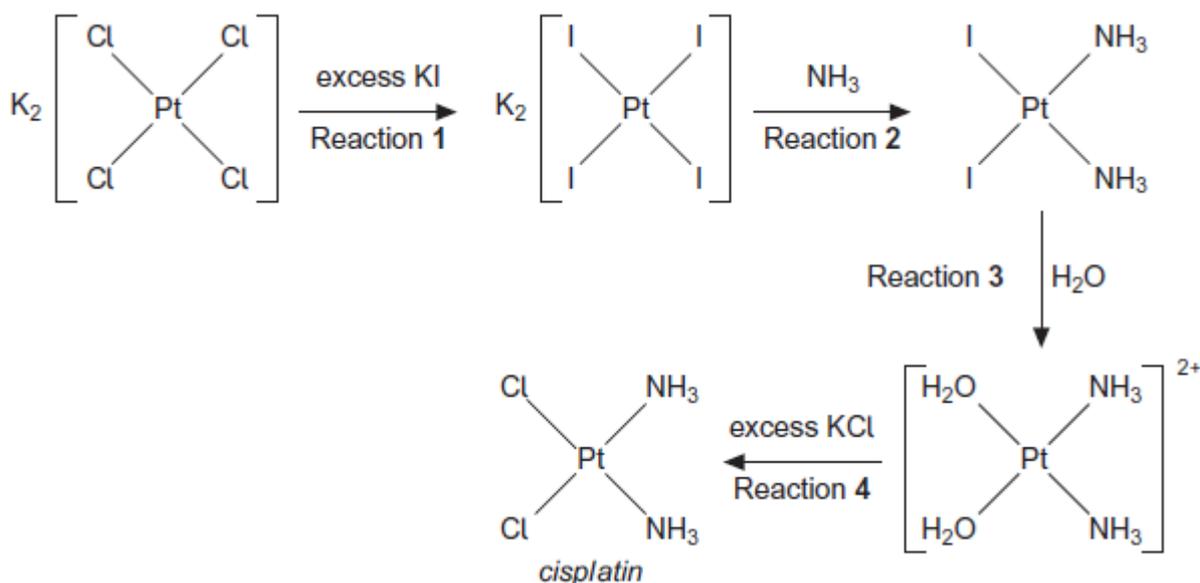
## Q17.

Complexes containing transition elements have a wide variety of uses including acting as dyestuffs like *Prussian Blue*.

*Cisplatin* is a platinum-based chemotherapy drug used to treat various types of cancers. It was the first member of a class of anti-cancer drugs that react with DNA in tumour cells.

*Cisplatin* is prepared from  $K_2PtCl_4$  according to the following scheme.

All the reactions shown are reversible.



- (a) Name the type of reaction occurring in all four steps of the scheme.

---

(1)



- (b) Explain why an excess of potassium iodide is used in Reaction 1.

---

---

---

(2)

- (c) (i) Write an equation for Reaction 1.

---

---

(1)

- (ii) Calculate the percentage atom economy for the formation of  $K_2PtI_4$  in Reaction 1. Show your working.

---

---

---

---

(2)

- (d) In Reaction 3, silver nitrate solution is added to improve the yield of product.

- (i) Write the **simplest ionic** equation for the reaction of iodide ions with silver nitrate.

---

(1)

- (ii) Suggest why addition of silver nitrate improves the yield of product from Reaction 3.

---

---

(1)

- (e) Suggest two reasons, other than poor practical technique, why the overall yield of *cisplatin* in this synthesis may be low.

Reason 1 \_\_\_\_\_

---

Reason 2 \_\_\_\_\_

---

(2)



- (f) The *cisplatin* formed in Reaction 4 is impure. Outline how the impure solid is purified by recrystallisation.

---

---

---

---

---

(3)

- (g) Platinum compounds are highly toxic.

- (i) State why *cisplatin* is used in cancer treatment despite its toxicity.

---

---

(1)

- (ii) Suggest a suitable precaution that should be taken by medical staff when using *cisplatin*.

---

(1)

(Total 15 marks)

**Q18.**

- (a) Some metal ions are toxic to humans. A substance that can be used to treat such poisoning contains the ion  $\text{EDTA}^{4-}$ .  
 $\text{EDTA}^{4-}$  forms very stable complexes with metal ions. These complexes are **not** toxic.

- (i) Write an equation for the reaction of  $\text{EDTA}^{4-}$  with aqueous copper(II) ions,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ .

---

(1)



- (ii) A solution containing  $\text{EDTA}^{4-}$  can also be used in a titration to determine the concentration of metal ions in solution.  
A river was polluted with copper(II) ions. When a  $25.0 \text{ cm}^3$  sample of the river water was titrated with a  $0.0150 \text{ mol dm}^{-3}$  solution of  $\text{EDTA}^{4-}$ ,  $6.45 \text{ cm}^3$  were required for complete reaction.  
Calculate the concentration, in  $\text{mol dm}^{-3}$ , of copper(II) ions in the river water.  
Show your working.

---

---

---

(2)

- (b) The determination of the concentration of copper(II) ions in a single sample of river water gives an unreliable value for the copper(II) ion pollution in the river.  
Give one reason why this value is unreliable.

---

---

(1)

- (c) Silver complexes can be used to identify a particular organic functional group.  
Give **one** example of a silver complex that can be used in this way and state the organic functional group it identifies.

Silver complex \_\_\_\_\_

Organic functional group \_\_\_\_\_

(2)

(Total 6 marks)

### Q19.

Aqueous metal ions can be identified by test-tube reactions.

For each of the following, describe what you would observe.

Write an equation or equations for any reactions that occur.

- (a) The addition of aqueous sodium carbonate to a solution containing  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$  ions.

---

---

---

---

---

(4)



- (b) The addition of aqueous sodium hydroxide, dropwise until in excess, to a solution containing  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$  ions.

---

---

---

---

---

---

---

(4)

- (c) The addition of dilute aqueous ammonia, dropwise until in excess, to a solution containing  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$  ions.

---

---

---

---

---

---

---

(4)

- (d) The addition of concentrated hydrochloric acid, dropwise until in excess, to a solution containing  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$  ions.

---

---

---

---

---

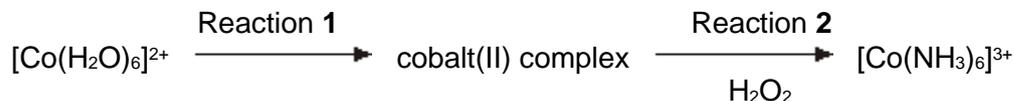
(2)

(Total 14 marks)

**Q20.**

Hydrogen peroxide is used as an oxidising agent in the preparation of transition metal complexes.

- (a) Consider the following reaction scheme. All the complexes are in aqueous solution.



- (i) Identify a reagent for Reaction 1 and describe the colour change that occurs.

---

---

---

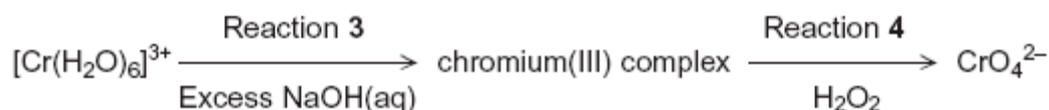
(3)

- (ii) State the colour of the final solution formed in Reaction 2.

---

(1)

- (b) Consider the following reaction scheme. All the complexes are in aqueous solution.



- (i) For Reaction 3, state the colour of the initial and of the final solution and write an equation for the reaction.

---

---

---

(4)

- (ii) Write a half-equation for the reduction of hydrogen peroxide to hydroxide ions.  
Deduce an overall equation for Reaction 4 and state the colour of the final solution.

---

---

---

---

---

(4)





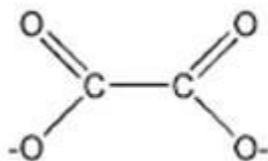
## Mark Scheme

### Q16.

- (a) (i) absorbs (certain frequencies of) (white) light / photons  
*not absorbs white / u.v. light* 1
- d electrons excited / promoted  
*or d electrons move between levels / orbitals*  
*d electrons can be implied elsewhere in answer* 1
- the colour observed is the light not absorbed / light  
 reflected / light transmitted  
*allow blue light transmitted*  
*penalise emission of light in M3* 1
- (ii)  $\Delta E$  is the energy gained by the (excited) electrons (of  $\text{Cu}^{2+}$ )  
*allow:*
- *energy difference between orbitals / sub-shells*
  - *energy of photon / light absorbed*
  - *change in energy of the electrons energy lost by excited electrons*
  - *energy of photon / light emitted*
- 1
- h (Planck's) constant 1
- $\nu$  frequency of light (absorbed by  $\text{Cu}^{2+}(\text{aq})$ )  
*do not allow wavelength*  
*If energy lost / photon lost / light emitted in M1 do not penalised*  
*light emitted* 1
- (iii)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}$   
*note that  $[\text{CuCl}_4]^{2-}$  is incorrect*  
*penalise charges shown separately on the ligand and overall*  
*penalise HCl* 1
- tetrahedral 1
- $\text{Cl}^-$  / Cl / chlorine too big (to fit more than 4 round Cu)  
*allow*  
*water smaller than  $\text{Cl}^-$*   
*explanation that change in shape is due to change in*  
*co-ordination number* 1



(b)

*allow:*

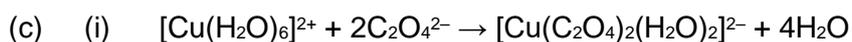
- ion drawn with any bond angles
- ion in square brackets with overall / 2- charge shown outside the brackets
- ion with delocalised O=C–O bonds in carboxylate group(s)

1

lone pair(s) on O<sup>-</sup> / O

*allow position of lone pair(s) shown on O in the diagram even if the diagram is incorrect.*

1



product correct

1

equation balanced

1

6

*note can only score M3 and M4 if M1 awarded or if complex in equation has 2 waters and 2 ethanedioates*

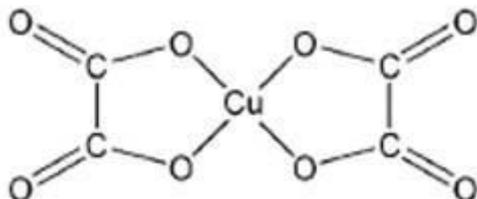
1

octahedral

*If this condition is satisfied the complex can have the wrong charge(s) to allow access to M3 and M4 but not M1*

1

(ii)

*ignore charges**diagram must show both ethanedioates with correct bonding**ignore water*

1

90°

*allow 180°**mark bond angle independently but penalise if angle incorrectly*



*labelled / indicated on diagram*

1

[17]

**Q17.**

- (a) (ligand) substitution

*Allow 'ligand exchange'.*

1

- (b) To displace the equilibrium to the right

*To ensure reaction goes to completion.*

1

To improve the yield

*Allow 'to replace all chlorines'.*

1

- (c) (i)  $K_2PtCl_4 + 4KI \rightarrow K_2PtI_4 + 4KCl$

*Allow correct ionic equations  $PtCl_4^{2-} + 4I^- \rightarrow PtI_4^{2-} + 4Cl^-$*

*Allow multiples and fractions.*

1

- (ii)  $= (780.9) \times 100 / (415.3 + 664)$

*Working must be clearly shown.*

*Allow one mark for correct relationship even if  $M_r$  values are incorrect eg using values from ionic equation.*

1

$= 72.4$

*Allow 72%*

1

- (d) (i)  $Ag^+ + I^- \rightarrow AgI$

*Ignore state symbols even if incorrect.*

*This equation only.*

1

- (ii) Stops the reverse reaction / equilibrium displaced to the right

1

- (e) Number of steps in the process

*Allow 'equilibrium may lie on the reactant side' / side reactions / isomer formation.*

1

Losses at each stage of the synthesis

*Equilibrium losses or practical losses or yield not 100% for each step.*

1

- (f) Minimum amount of hot solvent

*Accept 'small' for minimum.*

*Accept water.*

1



- Cool / crystallise 1
- Filter 1
- (g) (i) Small amounts are more likely to kill cancer cells rather than the patient 1
- (ii) Wear gloves / wash hands after use  
Ignore masks.  
Apply the list principle if more than one answer. 1
- [15]**

**Q18.**

- (a) (i)  $\text{EDTA}^{4-} + [\text{Cu}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{Cu}(\text{EDTA})]^{2-} + 6\text{H}_2\text{O}$  1
- (ii) (Mol EDTA =  $(6.45/1000) \times 0.015 = 9.68 \times 10^{-5}$  mol Cu(II)) 1
- Conc. Cu(II) =  $((9.68 \times 10^{-5}) / 0.025 = 0.00387$  mol dm<sup>-3</sup>  
Correct answer without working gains M2 only. 1
- (b) Samples may not be consistent throughout the river  
OR  
Concentration may vary over time  
Ignore comments on technique. 1
- (c)  $[\text{Ag}(\text{NH}_3)_2]^+$   
Accept name eg diamminesilver(I) ion. 1
- aldehyde  
Allow CHO. 1

**[6]****Q19.**

- (a) Brown ppt/solid 1
- Gas evolved/effervescence 1
- $2[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 3\text{CO}_3^{2-} \rightarrow 2\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3 + 3\text{CO}_2 + 3\text{H}_2\text{O}$   
Must be stated, Allow CO<sub>2</sub> evolved. Do not allow CO<sub>2</sub> alone  
Correct iron product (1) allow Fe(OH)<sub>3</sub> and in equation  
Balanced equation (1) 2

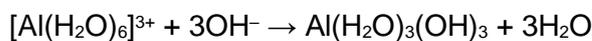


(b) White ppt/solid 1

Colourless Solution

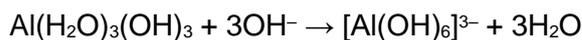
*Only award M2 if M1 given or initial ppt mentioned*

1



*Allow  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} + 3\text{OH}^- \rightarrow \text{Al}(\text{OH})_3 + 6\text{H}_2\text{O}$*

1



*Allow formation of  $[\text{Al}(\text{H}_2\text{O})_{6-x}(\text{OH})_x]^{(x-3)-}$  where  $x = 4, 5, 6$*

*Allow product without water ligands*

*Allow formation of correct product from  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$*

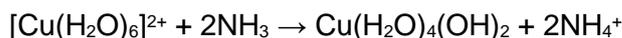
1

(c) Blue ppt/solid 1

(Dissolves to give a) deep blue solution

*Only award M2 if M1 given or initial ppt mentioned*

1

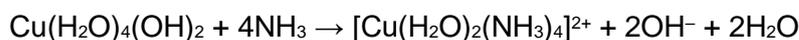


*Allow  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 2\text{NH}_3 \rightarrow \text{Cu}(\text{OH})_2 + 2\text{NH}_4^+ + 4\text{H}_2\text{O}$*

*Allow two equations:  $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$*

*then  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 2\text{OH}^- \rightarrow \text{Cu}(\text{OH})_2 + 4\text{H}_2\text{O}$  etc*

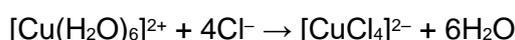
1



*Allow  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+} + 4\text{H}_2\text{O}$*

1

(d) Green/yellow solution 1



1

[14]

## Q20.

(a) (i) Ammonia 1  
*If reagent is missing or incorrect cannot score M3*

Starts as a pink (solution) 1

Changes to a yellow/straw (solution)

*Allow pale brown*

*Do not allow reference to a precipitate*

1



- (ii) (dark) brown  
*Do not allow pale/straw/yellow-brown (i.e. these and other shades except for dark brown)*  
 1
- (b) (i) Ruby/red-blue/purple/violet/green  
*Do not allow red or blue*  
*If ppt mentioned contradiction/CE =0*  
 1
- Green  
*If ppt mentioned contradiction/CE =0*  
 1
- $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} + 6\text{OH}^- \rightarrow [\text{Cr}(\text{OH})_6]^{3-} + 6\text{H}_2\text{O}$   
 1
- Formula of product  
*Can score this mark in (b) (ii)*  
 1
- (ii)  $\text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$   
 1
- $2[\text{Cr}(\text{OH})_6]^{3-} + 3\text{H}_2\text{O}_2 \rightarrow 2\text{CrO}_4^{2-} + 8\text{H}_2\text{O} + 2\text{OH}^-$   
*Allow 1 mark out of 2 for a balanced half-equation such as Cr(III)  $\rightarrow$  Cr(VI) + 3e<sup>-</sup>*  
*or Cr<sup>3+</sup> + 4H<sub>2</sub>O  $\rightarrow$  CrO<sub>4</sub><sup>2-</sup> + 8H<sup>+</sup> + 3e<sup>-</sup> etc*  
*also for 2Cr(III) + 3H<sub>2</sub>O<sub>2</sub>  $\rightarrow$  2CrO<sub>4</sub><sup>2-</sup> (unbalanced)*  
 2
- Yellow  
*Do not allow orange*  
 1
- (c)  $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{H}_2\text{O}_2 \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{O}_2$   
*if no equation and uses given ratio can score M2, M3, M4 & M5*  
 1
- Moles  $\text{MnO}_4^- = (24.35/1000) \times 0.0187 = \underline{4.55 \times 10^{-4}}$   
*Note value must be quoted to at least 3 sig. figs.*  
*M2 is for  $4.55 \times 10^{-4}$*   
 1
- Moles  $\text{H}_2\text{O}_2 = (4.55 \times 10^{-4}) \times \underline{5/2} = 1.138 \times 10^{-3}$   
*M3 is for  $\times 5/2$  (or 7/3)*  
*Mark consequential on molar ratio from candidate's equation*  
 1
- Moles  $\text{H}_2\text{O}_2$  in 5 cm<sup>3</sup> original  
*M4 is for  $\times 10$*   
 1
- $= (1.138 \times 10^{-3}) \times \underline{10} = 0.01138$



$$\text{Original } [\text{H}_2\text{O}_2] = 0.01138 \times \frac{1000}{5} = 2.28 \text{ mol dm}^{-3}$$

(allow 2.25-2.30)

*M5 is for consequentially correct answer from (answer to mark 4)  $\times (1000/5)$*

*Note an answer of between 2.25 and 2.30 is worth 4 marks)*

*If candidate uses given ratio 3/7 max 4 marks:*

**M1:** Moles of  $\text{MnO}_4^- = \underline{4.55 \times 10^{-4}}$

**M2:** Moles  $\text{H}_2\text{O}_2 = (4.55 \times 10^{-4}) \times \frac{7}{3} = 1.0617 \times 10^{-3}$

**M3:** Moles  $\text{H}_2\text{O}_2$  in  $5 \text{ cm}^3$  original

$$= (1.0617 \times 10^{-3}) \times 10 = 0.01062$$

**M4:** Original  $[\text{H}_2\text{O}_2] = 0.01062 \times (1000/5) = 2.12 \text{ mol dm}^{-3}$

(allow 2.10 to 2.15)

1

[17]