

**Q9.**

Solution **A** contains the compound  $[\text{Cu}(\text{H}_2\text{O})_6]\text{Cl}_2$

- (a) State the type of bonding between the oxygen and hydrogen in this compound.

\_\_\_\_\_

(1)

- (b) State why the chloride ions in this compound are **not** considered to be ligands.

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

(1)

- (c) An excess of ammonia was added to a sample of solution **A** to form solution **B**.

Write an ionic equation for the reaction that occurs when solution **A** is converted into solution **B** and state the colour of solution **B**.

Equation \_\_\_\_\_

\_\_\_\_\_

Colour \_\_\_\_\_

(2)

- (d) Aqueous sodium carbonate was added to another sample of solution **A** to form a blue-green solid **C**.

Identify the blue-green solid **C**.

\_\_\_\_\_

(1)

- (e) Reagent **D** was added to another sample of solution **A** to form a yellow-green solution.

Identify reagent **D** and write an ionic equation for the reaction that occurs when the yellow-green solution is formed from solution **A**.

Identity of reagent **D** \_\_\_\_\_

Equation \_\_\_\_\_

\_\_\_\_\_

(2)



- (f) Explain why colorimetry cannot be used to determine the concentration of solutions containing  $[\text{CuCl}_2]^-$

In your answer refer to the electron configuration of the metal ion.

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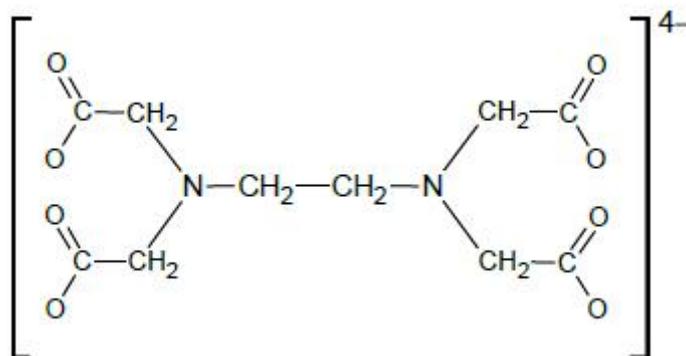


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(2)  
(Total 9 marks)

### Q10.

EDTA is a useful laboratory chemical and is found in a wide variety of commercial products including detergents. It is very soluble in water and is often used in its ionic form  $\text{EDTA}^{4-}$  as shown in the diagram below.



- (a)  $\text{EDTA}^{4-}$  can act as a multidentate ligand.

Explain the meanings of the terms **multidentate** and **ligand** with reference to the reaction of  $\text{EDTA}^{4-}$  with  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$  ions to form a complex ion.

Draw on the diagram above a separate circle around each atom that bonds to the  $\text{Cu}^{2+}$  ion in this complex ion.

Multidentate \_\_\_\_\_

\_\_\_\_\_

Ligand \_\_\_\_\_

\_\_\_\_\_

(3)



- (b) Copper(II) compounds may be used as fungicides in vineyards. When used in this way, copper(II) ions can enter the water supply and cause problems because they are toxic in high concentrations. The water supply near a vineyard can be tested for copper(II) ions by forming a blue aqueous complex with  $\text{EDTA}^{4-}$  ions. The concentration of this complex can be determined using a colorimeter.

Outline the practical steps that you would follow, using colorimetry, to determine the concentration of this complex in a sample of water.

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(3)

- (c) The concentration of copper(II) ions, in the sample of water, determined by colorimetry was  $7.56 \times 10^{-5} \text{ mol dm}^{-3}$ .

This result was checked by titrating a sample of the water with a solution containing  $\text{EDTA}^{4-}(\text{aq})$  ions.

The  $\text{EDTA}^{4-}(\text{aq})$  used in the titration had a concentration of  $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ .

Write an equation for the reaction between  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  and  $\text{EDTA}^{4-}$  ions.

Calculate the volume of the  $\text{EDTA}^{4-}$  solution needed to react with a  $25.0 \text{ cm}^3$  sample of the water.

Justify whether this titration will give an accurate value for the concentration of copper(II) ions. If necessary, suggest a practical step that would improve the accuracy.

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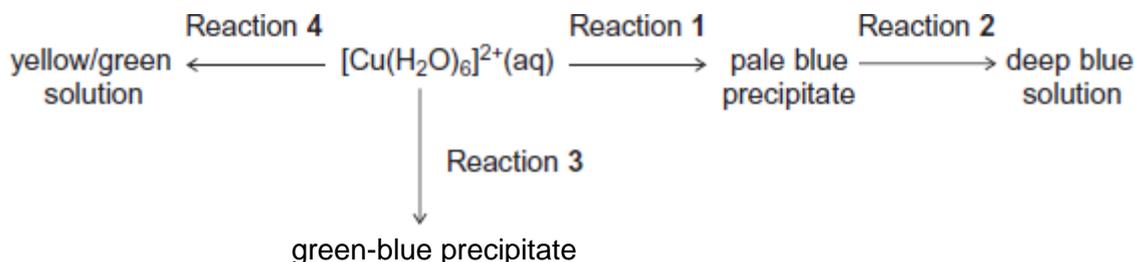
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(5)

(Total 11 marks)

**Q11.**

Consider the following reaction scheme that starts from aqueous  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ions.



For each of the reactions 1 to 4, identify a suitable reagent, give the formula of the copper-containing species formed and write an equation for the reaction.

(a) Reaction 1

Reagent \_\_\_\_\_

Copper-containing species \_\_\_\_\_

Equation \_\_\_\_\_

**(3)**

(b) Reaction 2

Reagent \_\_\_\_\_

Copper-containing species \_\_\_\_\_

Equation \_\_\_\_\_

**(3)**

(c) Reaction 3

Reagent \_\_\_\_\_

Copper-containing species \_\_\_\_\_

Equation \_\_\_\_\_

**(3)**

(d) Reaction 4

Reagent \_\_\_\_\_

Copper-containing species \_\_\_\_\_

Equation \_\_\_\_\_

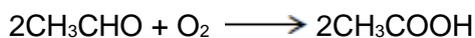
**(3)**

**(Total 12 marks)**

**Q12.**

This question explores some reactions and some uses of cobalt compounds.

- (a) Ethanal is oxidised to ethanoic acid by oxygen. The equation for this reaction is



This redox reaction is slow at room temperature but speeds up in the presence of cobalt compounds.

Explain why a cobalt compound is able to act as a catalyst for this process.

Illustrate your explanation with **two** equations to suggest how, in the presence of water and hydrogen ions,  $\text{Co}^{3+}$  and then  $\text{Co}^{2+}$  ions could be involved in catalysing this reaction.

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(4)

- (b) In aqueous solution, the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ion reacts with an excess of ethane-1,2-diamine to form the complex ion **Y**.

- (i) Write an equation for this reaction.

Explain, in terms of the chelate effect, why the complex ion **Y** is formed in preference to the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  complex ion.

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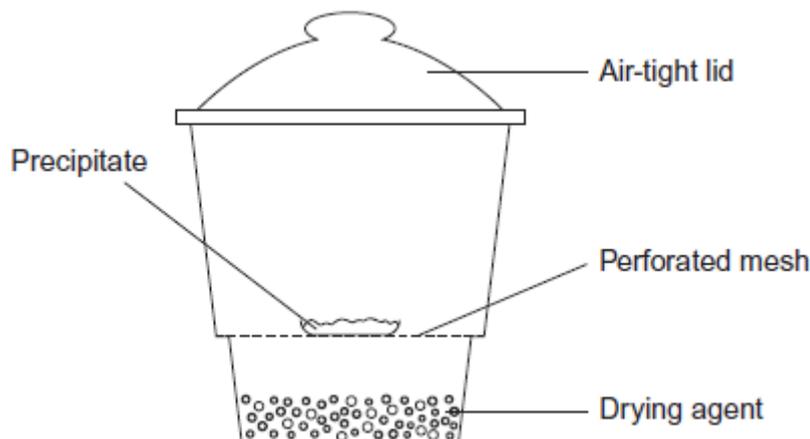
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(3)



**Q13.**

A desiccator can be used to dry precipitates as shown in the diagram.



- (a) Explain briefly how the precipitate in the desiccator becomes dry.

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**(1)**

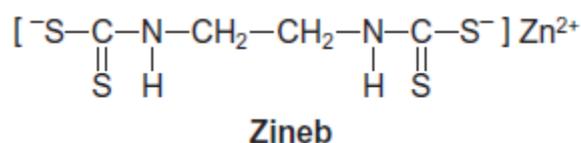
- (b) Anhydrous cobalt(II) chloride is blue. It is often added to the drying agent to indicate the amount of moisture in the drying agent.

State the colour change of this cobalt compound that you would observe as the drying process takes place.

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**(1)****(Total 2 marks)****Q14.**

- (a) Because of the toxic nature of the copper(II) ion, a wide range of alternative anti-fungal drugs has been developed for use in agriculture. One example is Zineb.



- (i) The negative ion in Zineb could act as a bidentate ligand.

On the structure above, draw a ring around each of **two** atoms that could provide the lone pairs of electrons when this ion acts as a bidentate ligand.

**(1)**



- (ii) Calculate the  $M_r$  of Zineb. Give your answer to the appropriate precision.

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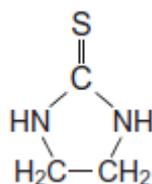
(1)

- (iii) Name the functional group formed at each end of the negative ion when all the sulfur atoms in the structure of Zineb are replaced by oxygen atoms.

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(1)

- (b) Zineb has been investigated for harmful effects. Generally, Zineb has been found to be safe to use in agriculture. It is only slightly soluble in water and is sprayed onto plants. A breakdown product of Zineb is ethylene thiourea (ETU), which is very soluble in water. The structure of ETU is shown below.



Determine the percentage, by mass, of sulfur in ETU ( $M_r = 102.1$ ).

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(1)





- (c) Write an equation for a different reaction between aqueous copper(II) ions ( $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ) and ammonia in which ammonia acts as a Lewis base but **not** as a Brønsted–Lowry base. State what you would observe.

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(2)

- (d) An excess of dilute ammonia solution is added to an aqueous solution containing iron(II) ions in a test tube that is then left to stand for some time. State and explain what you would observe.

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(4)

- (e) Diaminoethane ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ), like ammonia, can react as a base and as a ligand.

- (i) Write an equation for the reaction that occurs between an aqueous solution of aluminium chloride and an excess of aqueous diaminoethane. Describe the appearance of the aluminium-containing reaction product.

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(3)





## Mark Scheme

## Q9.

- (a) Covalent

*Do not allow dative covalent or coordinate (covalent)*

1

- (b)
- $\text{Cl}^{-}$
- not donating lone pair (to
- $\text{Cu}^{2+}$
- )

$\text{Cl}^{-}$  does not form a coordinate/dative bond (to  $\text{Cu}^{2+}$ )

*Allow without charges but penalise incorrect charges*

*Cl/it is bonded ionically (to  $\text{Cu}^{2+}$ )*

1

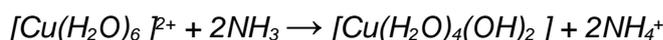
- (c)
- $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + 4\text{H}_2\text{O}$

1

Deep blue / Royal blue / Dark blue (solution)

1

*Allow combination of:*



*Do not penalise missing square brackets*

*Ignore initial colour of  $\text{Cu}^{2+}$  (aq)*

- (d)
- $\text{CuCO}_3$
- or copper carbonate

*Penalise incorrect oxidation state*

*Allow correct formula for basic copper carbonate*

1

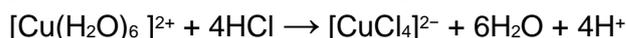
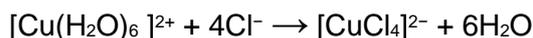
- (e) HCl/ hydrochloric acid

*Ignore concentration*

*Allow soluble chloride salt*

*Also allow any reagent which leads to a change in colour of solution due to a change in ligands (e.g.  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) or change in oxidation state (e.g.  $\text{SO}_2$ ) and associated correct equations.*

1



*Mark independently*

1

- (f) (3)d
- <sup>10</sup>
- or has full (3)d (sub) shell/orbital

*Penalise incorrect principal quantum number*

1

It is colourless/cannot absorb (frequencies of) visible light

*Ignore clear*

1



[9]

**Q10.**

(a) Multidentate – EDTA can form many / six dative bonds with central cation. 1

Ligand – lone pair (on N or O of EDTA) can form dative bond with copper(II) ions. 1

6 circles drawn on EDTA<sup>4-</sup> structure – 2 × N and 4 × –O 1

(b) Calibrate a colorimeter / produce a calibration curve. 1

By testing the colorimeter with solutions of copper-EDTA complex of known concentration. 1

Add excess EDTA salt to the sample. 1

(c)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + \text{EDTA}^{4-} \rightarrow [\text{Cu}(\text{EDTA})]^{2-} + 6\text{H}_2\text{O}$  1

Amount of copper(II) =  $(25.0 \times 7.56 \times 10^{-5}) / 1000 = 1.89 \times 10^{-6}$  mol 1

Volume of EDTA<sup>4-</sup> =  $(1.89 \times 10^{-6} / 0.001) \times 1000 = 1.89$  cm<sup>3</sup> 1

This is too small to be accurate. 1

Dilute the EDTA<sup>4-</sup> solution / use larger volume of river water. 1

[11]

**Q11.**

(a) **Reaction 1**

**General principles in marking this question**

*Square brackets are not essential*

*Penalise charges on individual ligands rather than on the whole complex*

*Reagent and species can be extracted from the equation*

*Ignore conditions such as dilute, concentrated, excess*

*Reagent must be a compound NOT just an ion*

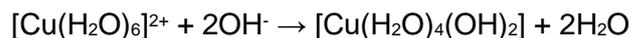
*Equations must start from  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  except in part (b)*

*Mark reagent, species and equation independently*

ammonia (NH<sub>3</sub>) (solution) / NaOH

1





*Do not allow OH<sup>-</sup> for reagent*

*Product 1, balanced equation 1*

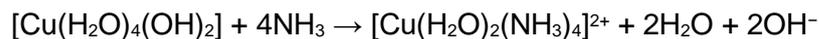
*Allow either equation for ammonia*

2

(b) **Reaction 2**

Ammonia (conc / xs)

1



*Product 1, balanced equation 1*

*Note that the equation must start from the hydroxide*

*[Cu(H<sub>2</sub>O)<sub>4</sub>(OH)<sub>2</sub>]*

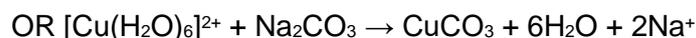
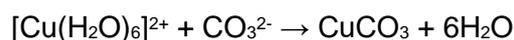
2

(c) **Reaction 3**

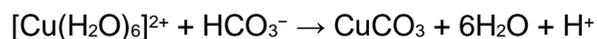
Na<sub>2</sub>CO<sub>3</sub> / any identified soluble carbonate / NaHCO<sub>3</sub>

*Do not allow NaCO<sub>3</sub> or any insoluble carbonate but mark on*

1



OR with NaHCO<sub>3</sub>



*Product 1, balanced equation 1*

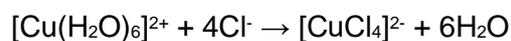
2

(d) **Reaction 4**

HCl (conc / xs) / NaCl

*Allow any identified soluble chloride*

1



*Product 1, balanced equation 1*

2

[12]

**Q12.**

(a) Cobalt has variable oxidation states

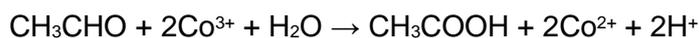
*Allow exists as Co(II) and Co(III)*

1

(It can act as an intermediate that) lowers the activation energy

*Allow (alternative route with) lower E<sub>a</sub>*

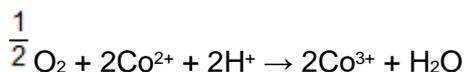
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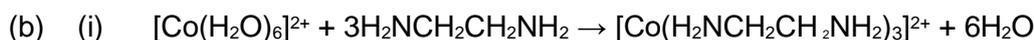
*Allow multiples; allow molecular formulae*

*Allow equations with  $\text{H}_3\text{O}^+$*

1



1



*Do not allow en in equation, allow  $\text{C}_2\text{H}_8\text{N}_2$*

1

The number of particles increases / changes from 4 to 7

*Can score M2 and M3 even if equation incorrect or missing provided number of particles increases*

1

So the entropy change is positive / disorder increases / entropy increases

1

(ii) Minimum for **M1** is 3 bidentate ligands bonded to Co

*Ignore all charges for M1 and M3 but penalise charges on any ligand in M2*

1

Ligands need not have any atoms shown but diagram must show 6 bonds from ligands to Co, 2 from each ligand

Minimum for **M2** is one ligand identified as  $\text{H}_2\text{N}-----\text{NH}_2$

*Allow linkage as  $-\text{C}-\text{C}-$  or just a line.*

1

Minimum for **M3** is one bidentate ligand showing two arrows from separate nitrogens to cobalt

1

(c) Moles of cobalt =  $(50 \times 0.203) / 1000 = \underline{0.01015}$  mol

*Allow 0.0101 to 0.0102*

1

Moles of AgCl =  $4.22/143.4 = 0.0294$

*Allow 0.029*

*If not AgCl (eg  $\text{AgCl}_2$  or  $\text{AgNO}_3$ ), lose this mark and can only score **M1**, **M4** and **M5***

1

Ratio =  $\text{Cl}^-$  to Co = 2.9 : 1

*Do not allow 3 : 1 if this is the only answer but if 2.9:1 seen somewhere in answer credit this as **M3***

1

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  (square brackets not essential)

1

Difference due to incomplete oxidation in the preparation



*Allow incomplete reaction.*

*Allow formation  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  etc.*

*Some chloride ions act as ligands / replace  $\text{NH}_3$  in complex.*

*Do not allow 'impure sample' or reference to practical deficiencies*

1

[15]

**Q13.**

- (a) Water in the gaseous state from the precipitate absorbed by drying agent

**OR**

Water vapour from the precipitate absorbed by drying agent

*Allow 'water vapour reacts with drying agent'.*

*Do not allow 'absorb water' without qualification.*

1

- (b) (Blue to) pink / pink colour observed

1

[2]

**Q14.**

- (a) (i) Two rings only around nitrogen or sulfur

*Lose this mark if more than 2 atoms are ringed.*

*Do not allow two atoms at the same end of the ion.*

1

- (ii) 275.8

*Accept this answer only. Do not allow 276*

1

- (iii) Carboxylate /  $\text{COO}^-$

*Allow salt of carboxylic acid or just carboxylic acid.*

1

- (b)  $(32.1 / 102.1) = 31.4\%$

*Do not penalise precision but do not allow 1 significant figure.*

1

- (c) Zineb is mixed with a solvent / water

*Max=2 if M1 missed*

1

Use of column / paper / TLC

*Lose M1 and M2 for GLC*

1

Appropriate collection of the ETU fraction

**OR** Appropriate method of detecting ETU

*Allow ETU is an early fraction in a column or collecting a range of samples over time, lowest retention time / travels furthest on paper or TLC (allow 1 mark for having the longest retention time in GLC).*



1

Method of identification of ETU (by comparison with standard using chromatography)

*If method completely inappropriate, only M1 is accessible*

1

[8]

## Q15.

(a) Electron pair donor

*Allow lone pair donor*

1

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

1

(Blue solution) gives a (pale) blue precipitate/solid

*M2 only awarded if M1 shows Bronsted–Lowry reaction*

1

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

*Allow formation in two equations via hydroxide*

1

(Blue solution) gives a dark/deep blue solution

*If (b) and (c) are the wrong way around allow one mark only for each correct equation with a correct observation (max 2/4)*

*M2 only awarded if M1 shows Lewis base reaction*

1

(d) (Start with) green (solution)

1

Green precipitate of  $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2$  /  $\text{Fe}(\text{OH})_2$  / iron(II) hydroxide

*Do not allow observation if compound incorrect or not given*

1

Slowly changes to brown solid

*Allow red-brown ppt*

*Allow turns brown or if precipitate implied*

*Can only score M3 if M2 scored*

1

(Iron(II) hydroxide) oxidised by air (to iron(III) hydroxide)

*Allow  $\text{Fe}(\text{OH})_2$  oxidised to  $\text{Fe}(\text{OH})_3$  by air /  $\text{O}_2$*

*Ignore equations even if incorrect*

1

(e) (i)  $2[\text{Al}(\text{H}_2\text{O})_6]^{3+} + 3\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \rightarrow 2\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3 + 3[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3]^{2+}$

*For correct Al species*

1

*For correct balanced equation*

*Allow equation with formation of  $3[\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_3]$  + from 1 mol*



$[Al(H_2O)_6]^{3+}$	1
White precipitate	1
(ii) $[Co(H_2O)_6]^{2+} + 3H_2NCH_2CH_2NH_2 \rightarrow [Co(H_2NCH_2CH_2NH_2)_3]^{2+} + 6H_2O$	1
Complex with 3 en showing 6 correct bonds from N to Co <i>Ignore charge</i> <i>Accept N – N for ligand</i> <i>Ignore incorrect H</i> <i>If C shown, must be 2 per ligand</i>	1
Co–ordinate bonds (arrows) shown from N to Co <i>Can only score M3 if M2 correct</i>	1
$4[Co(H_2NCH_2CH_2NH_2)_3]^{2+} + O_2 + 2H_2O \rightarrow 4[Co(H_2NCH_2CH_2NH_2)_3]^{3+} + 4OH^-$ <i>For Co(III) species</i>	1
<i>For balanced equation (others are possible)</i> <i>Allow + O<sub>2</sub> + 4H<sup>+</sup> → 2H<sub>2</sub>O</i> <i>If en used can score M4 and M5 only</i> <i>If Cu not Co, can only score M2 and M3</i> <i>Allow N<sub>2</sub>C<sub>2</sub>H<sub>8</sub> in equations</i>	1

[17]