M1.(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 $[Cu(H_2O)_{\epsilon}]^{2+}$ except in part (b) Mark reagent, species and equation independently

ammonia (NH₃) (solution) / NaOH

1

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+ /$$

$$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$$

Do not allow OH for reagent
Product 1, balanced equation 1
Allow either equation for ammonia

2

(b) Reaction 2

Ammonia (conc / xs)

1

[Cu(H₂O)₄(OH)₂] + 4NH₃
$$\rightarrow$$
 [Cu(H₂O)₂(NH₃)₄]²⁺ + 2H₂O + 2OH⁻
Product 1, balanced equation 1
Note that the equation must start from the hydroxide
[Cu(H₂O)₄(OH)₂]

2

(c) Reaction 3

Na₂CO₃ / any identified soluble carbonate / NaHCO₃

Do not allow NaCO₃ or any insoluble carbonate but mark on

$$\begin{split} & [Cu(H_2O)_6]^{2^+} + CO_3^{2^-} \to CuCO_3 + 6H_2O \\ & OR \ [Cu(H_2O)_6]^{2^+} + Na_2CO_3 \to CuCO_3 + 6H_2O + 2Na^+ \\ & OR \ 2[Cu(H_2O)_6]^{2^+} + 2CO_3^{2^-} \to Cu(OH)_2.CuCO_3 + 11H_2O + CO_2 \\ & OR \ with \ NaHCO_3 \\ & [Cu(H_2O)_6]^{2^+} + HCO_3^- \to CuCO_3 + 6H_2O + H^+ \\ & \qquad \qquad Product \ 1, \ balanced \ equation \ 1 \end{split}$$

2

2

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1

1

1

1

$$[Cu(H2O)6]2+ + 4Cl- → [CuCl4]2- + 6H2O$$
Product 1, balanced equation 1

Allow any identified soluble chloride

M2.(a) Cobalt has variable oxidation states

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

HCI (conc / xs) / NaCl

(It can act as an intermediate that) lowers the activation energy Allow (alternative route with) lower E_a

CH₃CHO + 2Co³⁺ + H₂O \rightarrow CH₃COOH + 2Co²⁺ + 2H⁺

Allow multiples; allow molecular formulae

Allow equations with H₃O+

$$\frac{1}{2}O_2 + 2Co^{2+} + 2H^+ \rightarrow 2Co^{3+} + H_2O$$

(b) (i) $[Co(H_2O)_6]^{2+} + 3H_2NCH_2CH_2NH_2 \rightarrow [Co(H_2NCH_2CH_2NH_2)_3]^{2+} + 6H_2O$ Do not allow en in equation, allow $C_2H_8N_2$ 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 H_2N ----- NH_2 Allow linkage as -C-C- or just a line.

1

Minimum for ${\bf M3}$ 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 AgCl₂ or AgNO₃), lose this mark and can only score **M1, M4** and **M5**

Ratio = 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 [Co(NH₃)₆]Cl₃ (square brackets not essential) 1 Difference due to incomplete oxidation in the preparation Allow incomplete reaction. Allow formation [Co(NH₃)₅Cl]Cl₂ etc. Some chloride ions act as ligands / replace NH₃ in complex. Do not allow 'impure sample' or reference to practical deficiencies [15] **M3.**(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] **M4.**(a) Electron pair donor Allow lone <u>pair</u> donor 1 (b) $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow Cu(H_2O)_4(OH)_2 + 2NH_4^+$

(Blue solution) gives a (pale) blue precipitate/solid M2 only awarded if M1 shows Bronsted-Lowry reaction 1 (c) $[Cu(H_2O)_6]^{2+}$ + 4NH₃ \rightarrow $[Cu(H_2O)_2(NH_3)_4]^{2+}$ + 4H₂O 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 Fe(H₂O)₄(OH)₂ / Fe(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 Fe(OH)₂ oxidised to Fe(OH)₃ by air / O₂ Ignore equations even if incorrect 1

(e) (i) $2[AI(H_2O)_6]^{3+} + 3H_2NCH_2CH_2NH_2 \rightarrow 2AI(H_2O)_3(OH)_3 + 3[H_3NCH_2CH_2NH_3]^{2+}$ For correct AI species

1 For correct balanced equation Allow equation with formation of 3[H₂NCH₂CH₂NH₃] + from 1 mol [AI(H₂O)₆]³⁺ 1 White precipitate 1 $[Co(H_2O)_6]^{2+} + 3H_2NCH_2CH_2NH_2 \rightarrow [Co(H_2NCH_2CH_2NH_2)_3]^{2+} + 6H_2O$ (ii) 1 Complex with 3 en showing 6 correct bonds from N to Co Ignore charge Accept N – N for ligand Ignore incorrect H If C shown, must be 2 per ligand 1 Co-ordinate bonds (arrows) shown from N to Co Can only score M3 if M2 correct 1 $4[Co(H_2NCH_2CH_2NH_2)_3]^{2+} + O_2 + 2H_2O \rightarrow 4[Co(H_2NCH_2CH_2NH_2)_3]^{3+} 4OH^{-}$ For Co(III) species 1

For balanced equation (others are possible)

Allow + O_2 + $4H^+ \rightarrow 2H_2O$ If en used can score M4 and M5 only

If Cu not Co, can only score M2 and M3
Allow N₂C₂H₈ in equations

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M5. (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 / 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 <u>comparison</u> with standard using chromatography) If method completely inappropriate, only M1 is accessible	1