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 $[Cu(H_2O)_6]^{2+}$ except in part (b) Mark reagent, species and equation independently

ammonia (NH₃) (solution) / NaOH

1

2

1

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

$$\begin{split} [Cu(H_2O)_6]^{2*} + 2OH^{\cdot} &\rightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O \\ Do \ not \ allow \ OH^{\cdot} \ for \ reagent \\ Product \ 1, \ balanced \ equation \ 1 \\ Allow \ either \ equation \ for \ ammonia \end{split}$$

(b) Reaction 2

Ammonia (conc / xs)

$$\begin{split} & [Cu(H_2O)_4(OH)_2] + 4NH_3 \rightarrow [Cu(H_2O)_2(NH_3)_4]^{2*} + 2H_2O + 2OH^- \\ & Product \ 1, \ balanced \ equation \ 1 \\ & Note \ that \ the \ equation \ must \ start \ from \ the \ hydroxide \\ & [Cu(H_2O)_4(OH)_2] \end{split}$$

2

(c) Reaction 3

Na₂CO₃ / any identified soluble carbonate / NaHCO₃ Do not allow NaCO₃ or any insoluble carbonate but mark on

1

$$\begin{split} & [\operatorname{Cu}(\operatorname{H}_2\operatorname{O})_6]^{2^+} + \operatorname{CO}_3^{2^-} \rightarrow \operatorname{Cu}\operatorname{CO}_3 + 6\operatorname{H}_2\operatorname{O} \\ & \operatorname{OR} [\operatorname{Cu}(\operatorname{H}_2\operatorname{O})_6]^{2^+} + \operatorname{Na}_2\operatorname{CO}_3 \rightarrow \operatorname{Cu}\operatorname{CO}_3 + 6\operatorname{H}_2\operatorname{O} + 2\operatorname{Na}^+ \\ & \operatorname{OR} 2[\operatorname{Cu}(\operatorname{H}_2\operatorname{O})_6]^{2^+} + 2\operatorname{CO}_3^{2^-} \rightarrow \operatorname{Cu}(\operatorname{OH})_2.\operatorname{Cu}\operatorname{CO}_3 + 11\operatorname{H}_2\operatorname{O} + \operatorname{CO}_2 \\ & \operatorname{OR} \text{ with } \operatorname{Na}\operatorname{HCO}_3 \\ & [\operatorname{Cu}(\operatorname{H}_2\operatorname{O})_6]^{2^+} + \operatorname{HCO}_3^- \rightarrow \operatorname{Cu}\operatorname{CO}_3 + 6\operatorname{H}_2\operatorname{O} + \operatorname{H}^+ \\ & \quad Product \ 1, \ balanced \ equation \ 1 \end{split}$$

(d) Reaction 4

$$\label{eq:cull_2O_6} \begin{split} & [Cu(H_2O)_6]^{2*} + 4Cl^{\cdot} \rightarrow [CuCl_4]^{2*} + 6H_2O \\ & Product \ 1, \ balanced \ equation \ 1 \end{split}$$

1

1

1

1

1

2

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

 $CH_{3}CHO + 2Co^{3+} + H_{2}O \rightarrow CH_{3}COOH + 2Co^{2+} + 2H^{+}$ Allow multiples; allow molecular formulae Allow equations with $H_{3}O+$

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

(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 H₂NNH₂ Allow linkage as −C−C− or just a line.	1
		Minimum for M3 is one bidentate ligand showing two arrows from separate nitrogens to cobalt	1
(c)	Mole	es of cobalt = (50 × 0.203) / 1000 = <u>0.01015</u> mol <i>Allow 0.0101 to 0.0102</i>	1
	Mole	es 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	1

Ratio = CI⁻ 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)₅]Cl₃ (square brackets not essential)

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

1

1

1

1

1

[2]

[15]

M3.(a) <u>Water in the gaseous state</u> from the precipitate <u>absorbed by drying agent</u>

OR

<u>Water vapour</u> from the precipitate <u>absorbed by drying agent</u> Allow 'water vapour <u>reacts with drying agent'</u>. Do not allow 'absorb water' without qualification.

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

M4.(a) Electron pair donor

Allow lone pair donor

(b) $[Cu(H_2O)_6]^{2*} + 2NH_3 \longrightarrow Cu(H_2O)_4(OH)_2 + 2NH_4^*$

	(Blue solution) gives a (pale) <u>blue precipitate/solid</u> M2 only awarded if M1 shows Bronsted–Lowry reaction	1
(c)	$[Cu(H_2O)_6]^{2*}$ + $4NH_3 \longrightarrow [Cu(H_2O)_2(NH_3)_4]^{2*}$ + $4H_2O$ Allow formation in two equations via hydroxide	1
	(Blue solution) gives a <u>dark/deep blue solution</u> 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
	<u>Green precipitate</u> of Fe(H ₂ O) ₄ (OH) ₂ / Fe(OH) ₂ / iron(II) hydroxide Do not allow observation if compound incorrect or not given	1
	Slowly changes to <u>brown solid</u> 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) $2[AI(H_2O)_3]^{3*} + 3H_2NCH_2CH_2NH_2 \rightarrow 2AI(H_2O)_3(OH)_3 + 3[H_3NCH_2CH_2NH_3]^{2*}$ For correct AI species	

	For correct balanced equation Allow equation with formation of 3[H₂NCH₂CH₂NH₃] + from 1 mol [Al(H₂O)₅]³*	1
	White precipitate	1
(ii)	$[Co(H_2O)_6]^{2*} + 3H_2NCH_2CH_2NH_2 \longrightarrow [Co(H_2NCH_2CH_2NH_2)_3]^{2*} + 6H_2O$	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 <i>Can only score M3 if M2 correct</i>	1
	$4[Co(H_2NCH_2CH_2NH_2)_3]^{2*} + O_2 + 2H_2O \longrightarrow 4[Co(H_2NCH_2CH_2NH_2)_3]^{3*} + 4OH^{-}$ 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 $N_2C_2H_8$ in equations	1

[17]

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	2.1 / 102.1) = 31.4% Do not penalise precision but do not allow 1 significant figure.	1
(c)	Zin	eb is mixed with a <u>solvent / water</u> <i>Max=2 if M1 missed</i>	1
	Use	e of column / paper / TLC Lose M1 and M2 for GLC	1
		Appropriate collection of the ETU fraction 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
		thod of identification of ETU (by <u>comparison</u> with standard using omatography) <i>If method completely inappropriate, only M1 is accessible</i>	1