A-Level Chemistry

Ligand Substitution

Mark Scheme

Time available: 69 minutes
Marks available: 63 marks

1.

(a) Covalent

Do not allow dative covalent or coordinate (covalent)

1

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

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

Allow without charges but penalise incorrect charges

Cl^-/it is bonded ionically (to Cu^{2+})

1

(c) $[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

1

Deep blue / Royal blue / Dark blue (solution)

1

Allow combination of:

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

$[Cu(H_2O)_4(OH)_2] + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2H_2O + 2OH^-$

Do not penalise missing square brackets

Ignore initial colour of Cu^{2+} (aq)

(d) $CuCO_3$ 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. $NH_2CH_2CH_2NH_2$) or change in oxidation state (e.g. SO_2) and associated correct equations.

1

$[Cu(H_2O)_6]^{2+} + 4Cl^- \longrightarrow [CuCl_4]^{2-} + 6H_2O$

$[Cu(H_2O)_6]^{2+} + 4HCl \longrightarrow [CuCl_4]^{2-} + 6H_2O + 4H^+$

Mark independently

1

(f) $(3)d^{10}$ 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]

2. (a) $[Fe(H_2O)_6]^{3+} + 4Cl^- \longrightarrow FeCl_4^- + 6H_2O$

1

(b) Cl^- is a bigger ligand

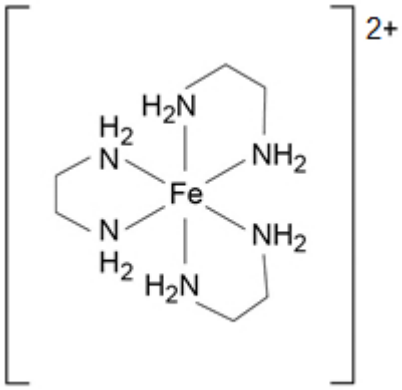
1

So only $4Cl^-$ can fit around the metal

Allow fewer Cl^- can fit around the metal

1

(c)



M1 for structure of complex

M2 for correct charge

1

1

(d) Change in entropy is positive

1

(e) $5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

1

(f) Amount of manganate (VII) = 6.50×10^{-4} mol

1

Amount of iron(II) = 3.25×10^{-3} mol

ie M1 × 5

1

Mass of iron = 0.181 g = 181 mg

Allow M2 × 55.8

1

Percentage Fe = 181/1980 × 100 = 9.14(%) 3 sf

1

(g) Colourless to pale pink

1

[12]

3. (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 $EDTA^{4-}$ 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) $[Cu(H_2O)_6]^{2+} + EDTA^{4-} \longrightarrow [Cu(EDTA)]^{2-} + 6H_2O$

1

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

1

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

1

This is too small to be accurate.

1

Dilute the $EDTA^{4-}$ solution / use larger volume of river water.

1

[11]

4. (a) (i) $EDTA^{4-} + [Cu(H_2O)_6]^{2+} \rightarrow [Cu(EDTA)]^{2-} + 6H_2O$

1

(ii) (Mol EDTA = (6.45/1000) × 0.015 =)9.68×10^{-5} mol Cu(II)

1

Conc. Cu(II) = $((9.68 \times 10^{-5}) / 0.025 =) 0.00387$ mol dm^{-3}

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) $[Ag(NH_3)_2]^+$

Accept name eg diamminesilver(I) ion.

1

aldehyde

Allow CHO.

1

[6]

5. (a) Ligand: -
atom, ion or molecules which can donate a pair of electrons to a metal ion.

1

co-ordinate bond:- a covalent bond

1

in which both electrons are donate by one atom

1

(b) (i) Two correct complex ions

1

Balanced equation

1

Two correct colours

2

(ii) Complex with a bidentate ligand

1

Balanced equation

NB en *not allowed as a ligand unless structure also given*

1

More molecules/ions formed

1

Increase in entropy

1

more stable complex formed

1

Max 2

(c) ΔE; energy absorbed by electron, ground to excited state (QoL)

1

h; Planck's constant or a constant

1

Change in

Oxidation state

1

Ligand

1

Co-ordination number

Apply list principle to incorrect additional answers

1

[16]

6. (a) $C_2O_4^{2-}$ or $H_2NCH_2CH_2NH_2$ **(1)**

1

(b) $[AgCl_2]^-$ or $[Ag(CN)_2]^-$ or $[Ag(NH_3)_2]^+$ **(1)**

1

(c) e.g. $[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$
Correct complex species **(1),** Balanced **(1),** Only allow if species correct

2

(d) e.g. $[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$
Correct complex species **(1),** Balanced **(1),** Only allow if species correct

2

(e) *Equation:* $[Co(H_2O)_6]^{2+} + EDTA^{4-} \rightarrow [Co(EDTA)]^{2-} + 6H_2O$ **(1)**
Explanation: More molecules on right hand side **(1)**
Entropy increases **(1)**

3

[9]