Chemistry of Transition elements - 2023 A2 Chemistry 9701

1. Nov/2023/Paper_9701/41/No.4(a)

(a) Cobalt(II) nitrate, $Co(NO_3)_2$, is a reddish-brown crystalline solid. It dissolves in water to form a solution containing $[Co(H_2O)_6]^{2+}$ complex ions.

(i) Complete Table 4.1 giving the formula of the cobalt-containing species that is formed in each of the three reactions described.

Table 4.1

reaction	reagent added to $[Co(H_2O)_6]^{2+}(aq)$	cobalt-containing species formed
1	NaOH(aq)	
2	an excess of $NH_3(aq)$	
3	an excess of conc. $HCl(aq)$	

[2]

(ii) Describe the colour change seen in reaction 3.

original colour of $[Co(H_2O)_6]^{2+}(aq)$ ....

final colour after addition of an excess of conc. $HCl(aq)$ ....

[1]

2. Nov/2023/Paper_9701/41/No.5(a _ d)

Transition elements behave as catalysts and can form complex ions.

(a) Explain why transition elements behave as catalysts.

....

....

.... [2]

(b) Silver forms the linear complex ion $[Ag(CN)_2]^-$.

Copper forms the tetrahedral complex ion $[Cu(CN)_4]^{3-}$.

Titanium forms the complex $[TiCl_4(\textit{diars})_2]$, where *diars* is a neutral bidentate ligand.

(i) State the oxidation state and the coordination number of titanium in $[TiCl_4(\textit{diars})_2]$.

oxidation state ....

coordination number ....

[1]

(ii) Draw three-dimensional diagrams to show the shapes of $[Ag(CN)_2]^-$ and $[Cu(CN)_4]^{3-}$, in the boxes.

Label one bond angle on each diagram.

Ag

Cu

[2]

(c) The numerical value of the stability constant, K_{stab}, of the copper(I) complex $[Cu(CN)_4]^{3-}$ is 2.0×10^{27}.

(i) Write an expression for the K_{stab} of $[Cu(CN)_4]^{3-}$.

K_{stab} =

[1]

(ii) In a solution the concentrations of CN^- and $[Cu(CN)_4]^{3-}$ are both 0.0010 mol dm^{-3}.

Use your expression from **(c)(i)** and the value of K_{stab} to calculate the concentration of $Cu^+(aq)$ in this solution.

concentration of $Cu^+(aq)$ = ... mol dm^{-3} [1]

(d) A piece of a copper-containing alloy has a mass of 0.567 g. It is dissolved in an acid giving 100.0 cm^3 of a blue solution in which all the copper is present as Cu^{2+} ions.

An excess of KI(aq) is added to a 25.0 cm^3 sample of this solution.

All of the copper is precipitated as white CuI(s).

Cu^{2+} ions are the only component in the solution that react with KI(aq). This is reaction 1.

reaction 1 $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

The liberated I_2 is then titrated with 0.0200 mol dm^{-3} $S_2O_3^{2-}$. This is reaction 2.

reaction 2 $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

The titration requires 20.10 cm^3 of 0.0200 mol dm^{-3} $S_2O_3^{2-}$ to reach the end-point.

(i) Calculate the number of moles of I_2 that are reduced in this titration.

number of moles of I_2 = ... mol [1]

(ii) Calculate the number of moles of copper in the original piece of alloy.

number of moles of copper = ... mol [1]

(iii) Calculate the percentage of copper in the alloy.

percentage of copper = ... % [1]

(iv) Suggest why a solution of Cu^{2+} is coloured but solid CuI is white.

....

....

.... [2]

[Total: 12]

3. Nov/2023/Paper_9701/41/No.6

(a) Five ligands are listed in Table 6.1.

Table 6.1

ligand	type of ligand
NH_3	
$EDTA^{4-}$	
CN^-	
$H_2NCH_2CH_2NHCH_2CH_2NH_2$	tridentate
$C_2O_4^{2-}$	

(i) Complete Table 6.1 using the words monodentate, bidentate and polydentate only.

Each of these three words may be used once, more than once, or not at all. [2]

(ii) The molecule $H_2NCH_2CH_2NHCH_2CH_2NH_2$ is a tridentate ligand.

Suggest the meaning of tridentate ligand.

....

.... [1]

(iii) Suggest how $H_2NCH_2CH_2NHCH_2CH_2NH_2$ acts as a tridentate ligand.

....

.... [1]

(b) Nickel forms the octahedral complex $[Ni(\mathit{en})_2(H_2O)_2]^{2+}$. This complex can exist in three isomeric forms, listed in Table 6.2.

One of these forms is a trans isomer, the other forms are two different cis isomers.

Table 6.2

isomer	polarity
trans isomer	
cis isomer 1	
cis isomer 2	

(i) Complete Table 6.2 using the terms polar or non-polar.

Each term may be used once, more than once, or not at all. [1]

(ii) Describe the difference between cis isomer 1 and cis isomer 2.

....

.... [1]

[Total: 6]

4. Nov/2023/Paper_9701/42/No.4

The structure of the polydentate ligand, $EDTA^{4-}$, is shown in Fig. 4.1.

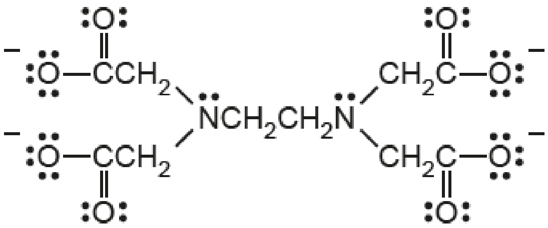


Fig. 4.1

The stability constants, at 298 K, of five octahedral complexes are given in Table 4.1.

Table 4.1

complex	K_{stab}
$[Cu(EDTA)]^{2-}$	6.31×10^{19}
$[Cr(EDTA)]^{2-}$	1.00×10^{13}
$[Cr(EDTA)]^{-}$	1.00×10^{24}
$[Fe(EDTA)]^{2-}$	2.00×10^{14}
$[Fe(EDTA)]^{-}$	1.26×10^{25}

(a) Define stability constant.

....

.... [1]

(b) Calculate the oxidation states of Cu in $[Cu(EDTA)]^{2-}$ and Cr in $[Cr(EDTA)]^{-}$.

Cu ....

Cr ....

[1]

(c) Deduce the number of lone pairs donated by each $EDTA^{4-}$ ligand in a single $[Fe(EDTA)]^{2-}$ complex ion.

.... [1]

(d) Identify the most stable complex in Table 4.1. Explain your choice.

....

.... [1]

(e) In a solution at equilibrium at 298 K, $[[Cu(H_2O)_6]^{2+}] = 3.00 \times 10^{-10}$ mol dm^{-3} and $[EDTA^{4-}] = 5.00 \times 10^{-12}$ mol dm^{-3}.

Use the expression for K_{stab} to calculate the concentration of $[Cu(EDTA)]^{2-}$ in this solution.

Show your working.

$[[Cu(EDTA)]^{2-}]$ = ... mol dm^{-3} [2]

(f) A solution of $[Cu(EDTA)]^{2-}$ ions is pale blue while a solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions is deep blue.

Explain this difference in colour.

....

....

.... [2]

[Total: 8]

5. Nov/2023/Paper_9701/42/No.6

(a) Phosphine, :PH_3, and carbon monoxide, :CO, are monodentate ligands found in some transition element complexes.

(i) Define monodentate ligand.

....

.... [1]

(ii) Define transition element complex.

....

.... [1]

(iii) Explain why transition elements form complexes.

....

.... [1]

(b) The formulae of six complexes are given in Table 6.1.

The abbreviation *en* is used for 1,2-diaminoethane.

The abbreviation *dien* is used for the tridentate ligand $H_2NCH_2CH_2NHCH_2CH_2NH_2$.

The *dien* ligand forms three bonds to the gold ion in $[Au(dien)(H_2O)_2Cl]^{2+}$ and $Au(dien)Cl_3$.

These three bonds all lie in the same plane.

The CO ligand coordinates through the carbon atom in $[Rh(CO)_2Cl_2]^{+}$.

Table 6.1

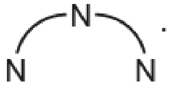
formula	isomerism shown	geometry
$[Rh(en)_2Cl_2]^{+}$	yes	
$[Rh(CO)_2Cl_2]^{+}$	yes	
$[Au(dien)(H_2O)_2Cl]^{2+}$		
$Au(dien)Cl_3$	no	octahedral
$Ni(PH_3)_2Cl_2$	no	
$[Ni(H_2O)_2(NH_3)_4]^{2+}$	yes	

(i) Complete Table 6.1 to state the geometry of the first three complexes. Each complex is either square planar, tetrahedral or octahedral. [1]

(ii) Use complexes $[Au(dien)(H_2O)_2Cl]^{2+}$ and $Au(dien)Cl_3$ to write an equation showing ligand exchange.

.... [1]

(iii) Draw the three-dimensional structure of Au(*dien*)$\mathrm{C}l_3$ in the box. The *dien* ligand can be drawn as



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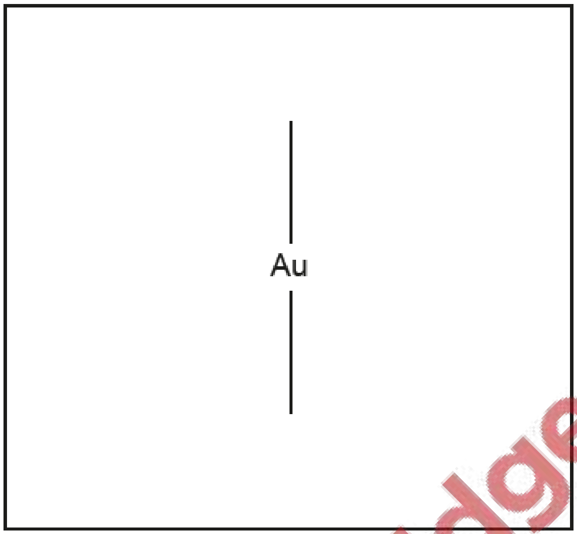
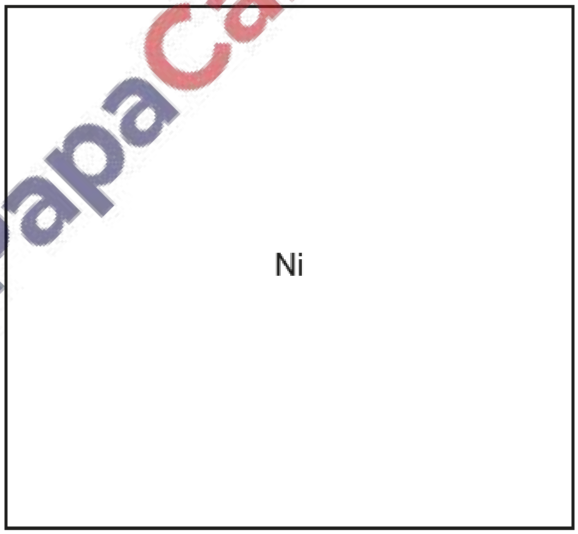


[1]

(iv) Draw the three-dimensional structure of $\mathrm{Ni(PH_3)_2C}l_2$ in the box.



[1]

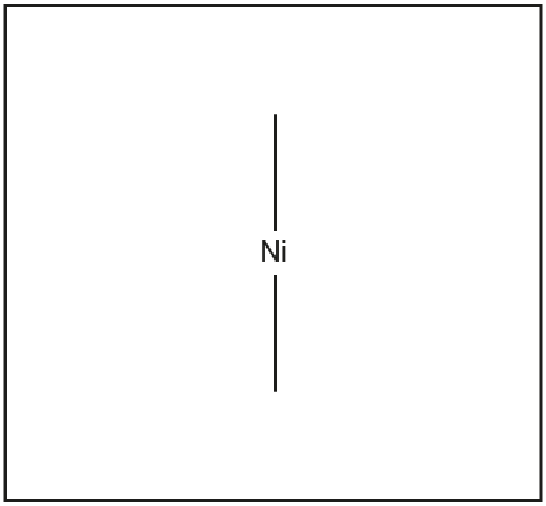
(v) One of the complexes, $[\mathrm{Rh}(en)_2\mathrm{C}l_2]^+$ or $[\mathrm{Rh(CO)_2C}l_2]^+$, can exist in three isomeric forms.

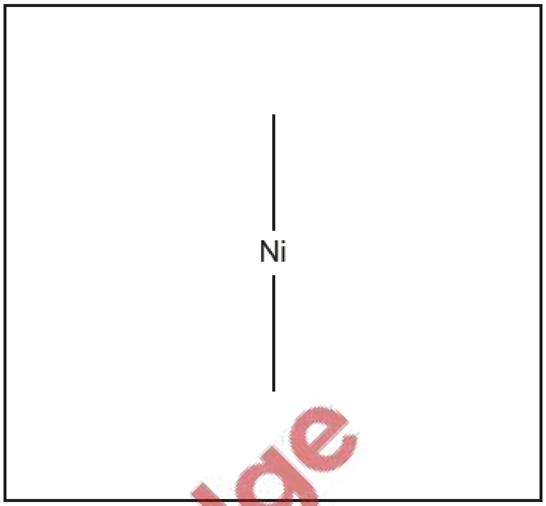
Identify this complex and the types of isomerism shown.

....

.... [1]

(vi) Draw the three-dimensional structures of the two isomers of $[Ni(H_2O)_2(NH_3)_4]^{2+}$ in the boxes and identify the type of isomerism shown.





type of isomerism shown ....

[2]

[Total: 10]

6. June/2023/Paper_9701/41/No.1(c _ f)

(a) Group 2 nitrates decompose when heated.

(b) Copper(II) nitrate decomposes in a similar manner to Group 2 nitrates.

Write an equation for the decomposition of $Cu(NO_3)_2$.

.... [1]

(c) $Cu(NO_3)_2$ is added to water to form solution **A**.

Fig. 1.1 shows some reactions of solution **A**.

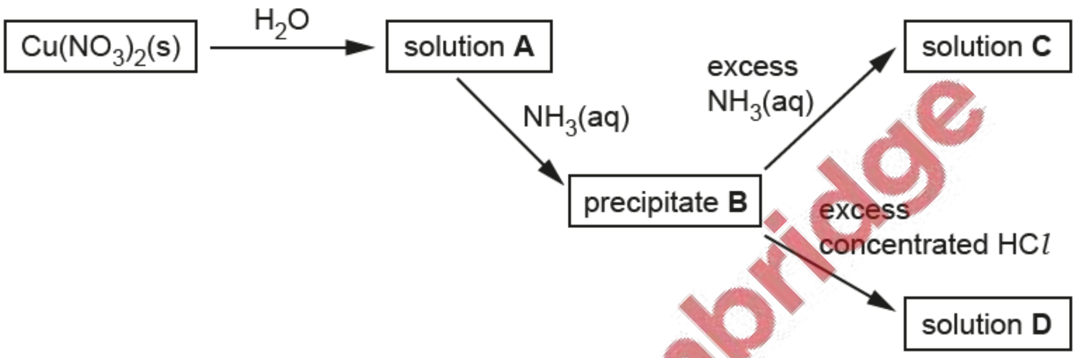


Fig. 1.1

Complete Table 1.1 to show the formula and colour of each of the copper-containing species present in **A**, **B**, **C** and **D**.

Table 1.1

	formula of copper-containing species formed	colour of copper-containing species formed
A		
B		
C		
D		

[4]

(d) $EDTA^{4-}$ is a polydentate ligand.

(i) Explain what is meant by a polydentate ligand.

....

....

.... [2]

(ii) Group 2 metal ions can form complexes similar to those of transition elements.

A solution of $EDTA^{4-}$ is added to water containing $[Ca(H_2O)_6]^{2+}$ to form a new complex, $[CaEDTA]^{2-}$, as shown.

equilibrium 1 $[Ca(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [CaEDTA]^{2-} + 6H_2O$

Circle on the structure of $EDTA^{4-}$ in Fig. 1.2 the **six** atoms that form bonds with the metal ion.

$EDTA^{4-}$

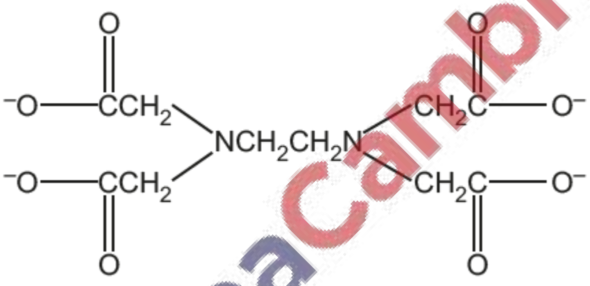


Fig. 1.2

[1]

(iii) The calcium ions in $[Ca(H_2O)_6]^{2+}$ and $[CaEDTA]^{2-}$ have a coordination number of 6.

Explain what is meant by coordination number.

....

.... [1]

(iv) The complex $[CaEDTA]^{2-}$ can be used to remove toxic metals from the body.

Table 1.2 shows the numerical values for the stability constants, K_{stab}, for some metal ions with $EDTA^{4-}$.

Table 1.2

complex	K_{stab}
$[CaEDTA]^{2-}$	5.0×10^{10}
$[CrEDTA]^{-}$	2.5×10^{23}
$[FeEDTA]^{-}$	1.3×10^{25}
$[PbEDTA]^{2-}$	1.1×10^{18}

An aqueous solution containing $[CaEDTA]^{2-}$ is added to a solution containing equal concentrations of $Cr^{3+}(aq)$, $Fe^{3+}(aq)$ and $Pb^{2+}(aq)$. The resulting mixture is left to reach a state of equilibrium.

State the type of reaction when $[CaEDTA]^{2-}$ reacts with $Cr^{3+}(aq)$, $Fe^{3+}(aq)$ and $Pb^{2+}(aq)$.

.... [1]

(v) Deduce the relative concentrations of $[CrEDTA]^{-}$, $[FeEDTA]^{-}$ and $[PbEDTA]^{2-}$ present in the resulting mixture.

Explain your answer.

.... > .... > ....

highest concentration lowest concentration

....

....

.... [1]

(e) The number of moles of water of crystallisation in a hydrated ionic salt can be determined by titration using aqueous $EDTA^{4-}$ ions with a suitable indicator.

- 0.255 g of hydrated chromium(III) sulfate, $Cr_2(SO_4)_3{\bullet}nH_2O$, is dissolved in water and made up to 100 cm^3 in a volumetric flask.
- 25.0 cm^3 of this solution requires 26.2 cm^3 of 0.00800 mol dm^{-3} aqueous $EDTA^{4-}$ ions to reach the end-point.

The reaction occurs as shown.

$$[Cr(H_2O)_6]^{3+} + EDTA^{4-} \longrightarrow [CrEDTA]^{-} + 6H_2O$$

Use the data to calculate the value of n in the formula of $Cr_2(SO_4)_3{\bullet}nH_2O$.

Show your working.

n = ... [3]

(f) A solution of $Cr^{3+}(aq)$ and a solution of $Fe^{3+}(aq)$ have different colours.

Explain why the two complexes have different colours.

....

....

....

.... [2]

7. June/2023/Paper_9701/41/No.2

(a) Some transition element complexes can show stereoisomerism.

State **two** types of stereoisomerism shown by transition element complexes.

1 ....

2 ....
[1]

(b) The complexes $[Pt(NH_3)_2Cl_2]$ and $[Pt(en)_2]^{2+}$ have the same geometry (shape) around the metal ion.

$[Pt(NH_3)_2Cl_2]$ exists as two stereoisomers whereas $[Pt(en)_2]^{2+}$ only has one possible structure.

State the geometry around the metal ion.

.... [1]

(c) The complex $[Cr(en)_3]^{2+}$ exists as two stereoisomers whereas the complex $[Cr(OCH_2CH_2NH_2)_3]^-$ exists as four stereoisomers.

Complete the three-dimensional diagrams in Fig. 2.1 to show the four stereoisomers of $[Cr(OCH_2CH_2NH_2)_3]^-$.

Represent the ligand $^-OCH_2CH_2NH_2$ by using  .

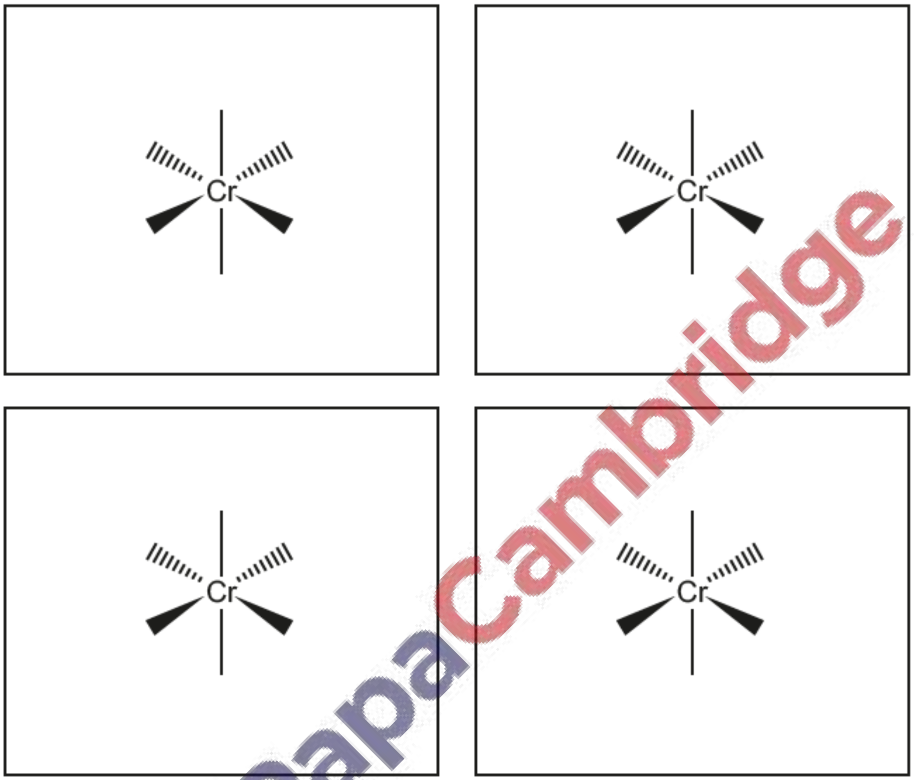


Fig. 2.1

[3]

(d) The complex $[Cr(OCH_2CH_2NH_2)_3]^-$ is formed by reacting $Cr^{2+}(aq)$ with the conjugate base of 2-aminoethanol.

A synthesis of 2-aminoethanol is shown in Fig. 2.2.

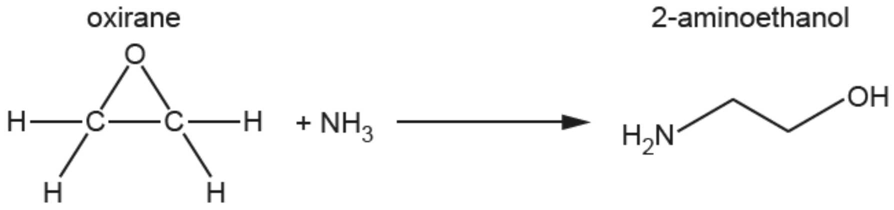


Fig. 2.2

(i) Suggest the mechanism for step 1 of the reaction of oxirane with ammonia in Fig. 2.3.

Include all relevant curly arrows, lone pairs of electrons, charges and partial charges.

Draw the structure of the organic intermediate.

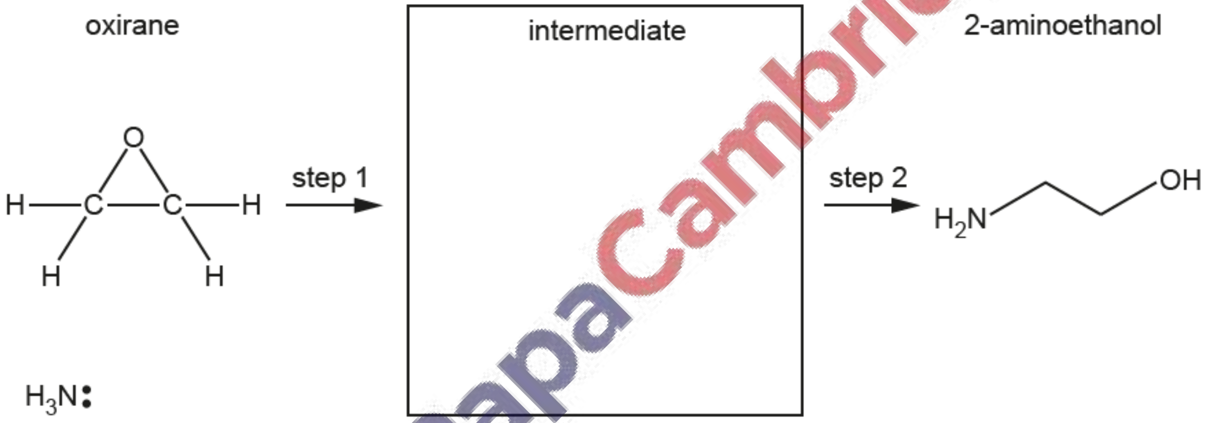


Fig. 2.3

[3]

(ii) A small amount of by-product **E**, shown in Fig. 2.4, is produced during the reaction shown in Fig. 2.2.

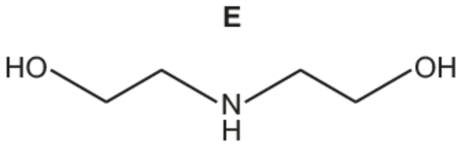


Fig. 2.4

Suggest how the formation of by-product **E** can be minimised.

....

.... [1]

(iii) Compound **F**, C_4H_9NO, can be formed from the reaction of by-product **E**, $C_4H_{11}NO_2$, with concentrated H_2SO_4.

Compound **F** is a **saturated** and basic organic compound.

Suggest a structure for compound **F**. State the type of reaction undergone by **E** to form **F**.

F

type of reaction ....

[2]

[Total: 11]

8. June/2023/Paper_9701/42/No.2

(a) State **two** typical chemical properties of a transition element.

1 ....

2 .... [1]

(b) Aqueous solutions of cobalt(II) salts contain the complex ion $[Co(H_2O)_6]^{2+}$.

(i) Define complex ion.

....

.... [1]

(ii) Samples of $[Co(H_2O)_6]^{2+}$ are reacted separately with an excess of aqueous ammonia, with an excess of concentrated HC*l* and with an excess of aqueous sodium hydroxide, as shown in Fig. 2.1.

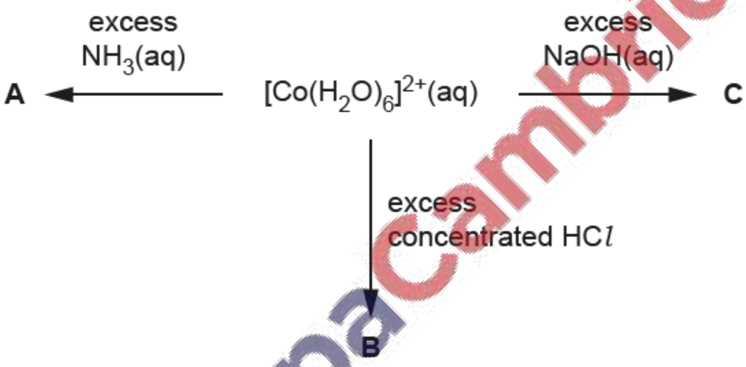


Fig. 2.1

Complete Table 2.1 about the reactions shown by $[Co(H_2O)_6]^{2+}$.

Table 2.1

reagent added to $[Co(H_2O)_6]^{2+}(aq)$	formula of cobalt species formed	colour and state of cobalt species formed	type of reaction
an excess of $NH_3(aq)$	**A** =		
an excess of concentrated HC*l*	**B** =		
an excess of NaOH(aq)	**C** =		

[4]

(c) The ethanedioate ion, $C_2O_4^{2-}$, can act as a bidentate ligand.

(i) Explain what is meant by a bidentate ligand.

....

....

.... [2]

(ii) The complex $[Co(H_2O)_2(C_2O_4)BrCl]^-$ exists as stereoisomers.

Complete the three-dimensional diagrams in Fig. 2.2 to show **four** stereoisomers of $[Co(H_2O)_2(C_2O_4)BrCl]^-$.

The $C_2O_4^{2-}$ ligand is represented using O⌒O.

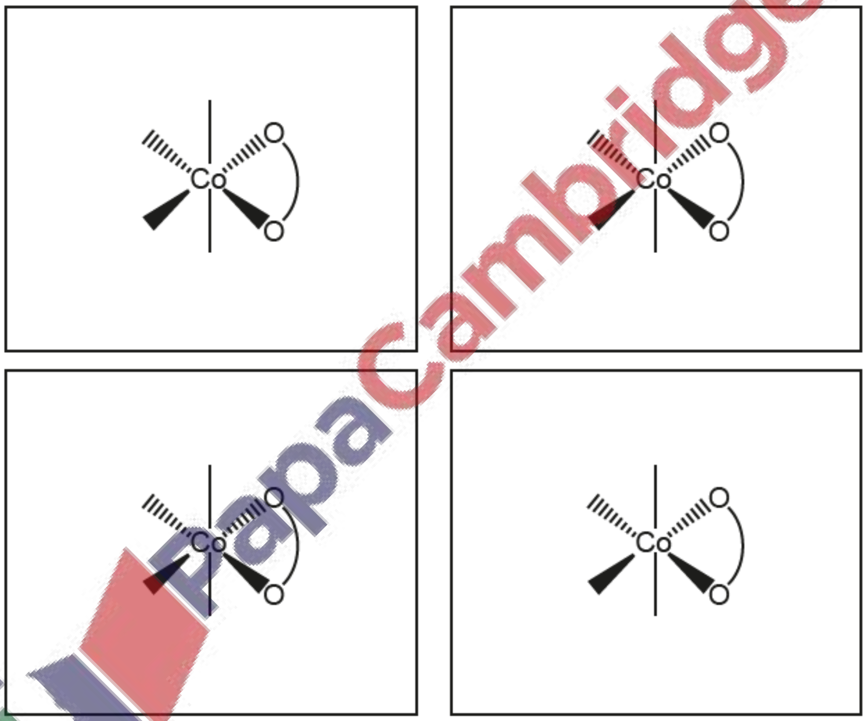


Fig. 2.2

[3]

(iii) State the oxidation state of cobalt in this complex and a type of stereoisomerism shown.

oxidation state of cobalt ....

type of stereoisomerism ....
[1]

[Total: 12]

9. March/2023/Paper_9701/42/No.3

Vanadium is a transition element in Period 4 of the Periodic Table.

(a) Define transition element.

....

.... [1]

(b) Vanadium shows typical chemical properties of transition elements, including variable oxidation states.

(i) State **two** other typical chemical properties of transition elements.

1 ....

2 ....
[1]

(ii) Explain why transition elements have variable oxidation states.

....

.... [1]

(c) VO_2^+ can be reduced to V^{2+} by $C_2O_4^{2-}$ in acidic conditions.

equation 2 $$2VO_2^+ + 3C_2O_4^{2-} + 8H^+ \rightarrow 2V^{2+} + 6CO_2 + 4H_2O$$

(i) In a titration, 25.00 cm³ of 0.0300 mol dm⁻³ $VO_2^+(aq)$ is added to 10 cm³ of dilute sulfuric acid.

A solution of 0.0400 mol dm⁻³ $C_2O_4^{2-}(aq)$ is then added from a burette until the end-point is reached.

The titration is repeated and concordant results obtained, as shown in Table 3.1.

Table 3.1

	1	2
volume of $C_2O_4^{2-}(aq)$ added / cm³	28.15	28.10

Show that these results are consistent with the stoichiometry of equation 2.

[2]

(ii) An excess of $C_2O_4^{2-}$ reacts with VO_2^+ to form a mixture of two octahedral complex ions. The complex ions are stereoisomers of each other.

Each complex ion contains a V^{2+} cation and three $C_2O_4^{2-}$ ions.

Complete the diagram to show the three-dimensional structure of **one** of the complex ions.

Include the charge of the complex ion.

Use O⌒O to represent a $C_2O_4^{2-}$ ion.

[2]

(d) V^{2+}(aq) can be oxidised by H_2O_2(aq).

Table 3.2 gives some relevant data.

Table 3.2

	half-equation	$E^\ominus$ / V
1	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
2	$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00
3	$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
4	$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	–0.26

(i) Identify the vanadium species that forms when an excess of H_2O_2(aq) reacts with V^{2+}(aq) under standard conditions.

Explain your answer with reference to the data in Table 3.2.

....

....

.... [1]

(ii) Concentrated acidified H_2O_2 can react with V^{2+} to form red VO_2^{3+} ions.

VO_2^{3+} contains vanadium combined with the peroxide anion, O_2^{2-}.

Deduce the oxidation state of vanadium in VO_2^{3+}.

.... [1]

[Total: 9]

10. March/2023/Paper_9701/42/No.4(e, f)

(e) Methylamine, CH_3NH_2, is another primary amine. CH_3NH_2 can act as a monodentate ligand.

(i) Define monodentate ligand.

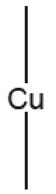
....

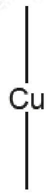
....

.... [2]

(ii) Cu^{2+}(aq) reacts with CH_3NH_2 to form $[Cu(CH_3NH_2)_2(H_2O)_4]^{2+}$.

Draw three-dimensional diagrams to show the two geometrical isomers of $[Cu(CH_3NH_2)_2(H_2O)_4]^{2+}$.





[2]

(iii) State the coordination number of copper in $[Cu(CH_3NH_2)_2(H_2O)_4]^{2+}$.

.... [1]

(f) Cd^{2+}(aq) ions form tetrahedral complexes with CH_3NH_2, OH^- and Cl^- ions, as shown in equilibria 1, 2 and 3.

equilibrium 1 $Cd^{2+}(aq) + 4CH_3NH_2(aq) \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}(aq)$ $K_{stab} = 3.3 \times 10^6$

equilibrium 2 $Cd^{2+}(aq) + 4OH^-(aq) \rightleftharpoons Cd(OH)_4{}^{2-}(aq)$ $K_{stab} = 5.0 \times 10^8$

equilibrium 3 $Cd^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CdCl_4{}^{2-}(aq)$ $K_{stab} = 6.3 \times 10^2$

(i) Give the units of K_{stab} for equilibrium 1.

.... [1]

(ii) Write an expression for K_{stab} for equilibrium 3.

K_{stab} =

[1]

(iii) A solution of Cl^-(aq) is added to Cd^{2+}(aq) and allowed to reach equilibrium. The equilibrium concentrations are given.

$$[Cd^{2+}(aq)] = 0.043\,mol\,dm^{-3}$$

$$[Cl^-(aq)] = 0.072\,mol\,dm^{-3}$$

Use your expression in **(f)(ii)** to calculate the concentration of $CdCl_4^{2-}$(aq) in the equilibrium mixture.

$[CdCl_4^{2-}(aq)]$ = ... mol dm^{-3} [1]

(iv) When CH_3NH_2(aq) is added to Cd^{2+}(aq), a mixture of $[Cd(CH_3NH_2)_4]^{2+}$(aq) and $[Cd(OH)_4]^{2-}$(aq) forms.

Suggest how the $[Cd(OH)_4]^{2-}$(aq) is formed.

....

.... [1]

(v) Cd^{2+}(aq) exists as a complex ion, $[Cd(H_2O)_6]^{2+}$(aq).

Identify the most stable and the least stable of the complexes in Table 4.1 by placing **one** tick (✓) in each column.

Explain your answer.

Table 4.1

complex	most stable	least stable
$[Cd(H_2O)_6]^{2+}$(aq)		
$[Cd(OH)_4]^{2-}$(aq)		
$[Cd(CH_3NH_2)_4]^{2+}$(aq)		
$[CdCl_4]^{2-}$(aq)		

explanation ....

....

.... [2]