

28. Chemistry of transition elements

28.2 General physical and chemical properties of the first set of transition elements, titanium to copper

Paper 4

Question Paper

- 1 (c) Tollens' reagent can be used to distinguish between aldehydes and ketones. Tollens' reagent contains $[\text{Ag}(\text{NH}_3)_2]\text{OH}$, which can be prepared in a two-step process.

step 1 Aqueous NaOH is added dropwise to aqueous AgNO_3 to form Ag_2O as a brown precipitate.

step 2 Aqueous NH_3 is added dropwise to Ag_2O to form a colourless solution containing $[\text{Ag}(\text{NH}_3)_2]\text{OH}$.

Construct equations for each of the steps in the preparation of $[\text{Ag}(\text{NH}_3)_2]\text{OH}$.

step 1

step 2 [2]

- (d) Name the shape of the complex ion $[\text{Ag}(\text{NH}_3)_2]^+$.

State the bond angle for H-N-Ag and for N-Ag-N.

shape

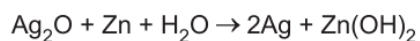
bond angle for H-N-Ag = °

bond angle for N-Ag-N = °

[2]

- (e) An electrochemical cell uses Ag_2O as the positive electrode and Zn as the negative electrode immersed in an alkaline electrolyte.

The overall cell reaction is shown.



Complete the half-equation for the reaction at each electrode.

at the positive electrode $\text{Ag}_2\text{O} + \dots\dots\dots$

at the negative electrode $\text{Zn} + \dots\dots\dots$

[2]

- (f) Coordination polymers are made when a bidentate ligand acts as a bridge between different metal ions.

Under certain conditions $\text{Ru}^{3+}(\text{aq})$ and the bidentate ligand *dps* can form a coordination polymer containing $([\text{Ru}(\textit{dps})\text{Cl}_4]^-)_n$ chains.

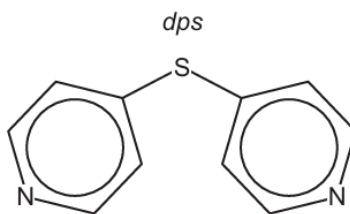


Fig. 2.2

The bidentate ligand *dps* uses each of the nitrogen atoms to bond to a different Ru^{3+} .

Complete Fig. 2.3 by drawing the structure for the coordination polymer $([\text{Ru}(\textit{dps})\text{Cl}_4]^-)_n$. Show **two** repeat units.

The *dps* ligand can be represented using N N.

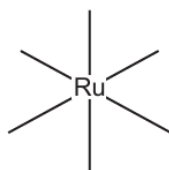
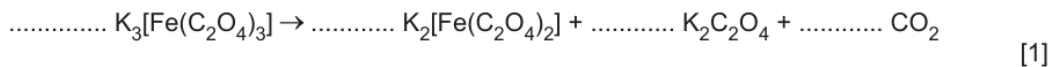


Fig. 2.3

- 2 (d)** The anhydrous iron(III) compound $K_3[Fe(C_2O_4)_3]$ decomposes on heating to form a mixture of $K_2[Fe(C_2O_4)_2]$, $K_2C_2O_4$ and CO_2 .

Complete the equation for the decomposition of $K_3[Fe(C_2O_4)_3]$.



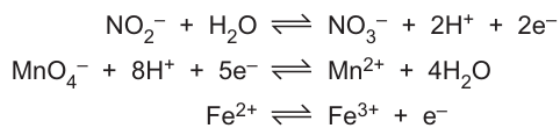
- 3 (b)** Acidified manganate(VII) ions, MnO_4^- , can be used to analyse solutions containing nitrite ions, NO_2^- , by titration.

X is a solution of $NaNO_2$.

250.0 cm³ of **X** is added to 50.0 cm³ of 0.125 mol dm⁻³ acidified MnO_4^- (aq). The MnO_4^- (aq) ions are in excess; all the NO_2^- ions are oxidised in the reaction.

The unreacted MnO_4^- (aq) required 22.50 cm³ of 0.0400 mol dm⁻³ Fe^{2+} (aq) to reach the end-point.

The relevant half-equations are shown.



Calculate the concentration, in mol dm⁻³, of $NaNO_2$ in **X**.

concentration of $NaNO_2$ in **X** = mol dm⁻³ [3]

- 4 (b)** Samples of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ are reacted separately with an excess of solution **A** and with an excess of solution **B**.

The reaction of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ with solution **A** is a precipitation reaction.

The reaction of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ with solution **B** is a ligand substitution reaction.

Suggest a possible identity for solution **A** and for solution **B**. Give relevant observations and the formula of the copper-containing product for each reaction.

solution **A**

observations

formula of the copper-containing product

solution **B**

observations

formula of the copper-containing product

[3]

- (d)** Two bidentate ligands are shown in Fig. 4.2.

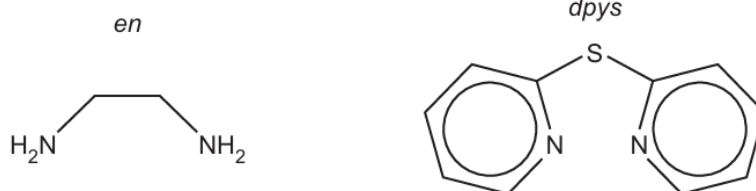


Fig. 4.2

Explain what is meant by a bidentate ligand.

.....

..... [2]

5 Transition metal atoms and transition metal ions form complexes by combining with species called ligands.

(a) When NaOH(aq) is added to an aqueous solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ a precipitation reaction occurs accompanied by a colour change.

In this reaction two of the water ligands each lose one H^+ ion. The H^+ ions are gained by OH^- ions from the NaOH(aq).

(i) State the colour change seen in this precipitation reaction.

from to [1]

(ii) Complete the ionic equation for this precipitation reaction.

$[\text{Co}(\text{H}_2\text{O})_6]^{2+} + \dots \rightarrow \dots + \dots$ [1]

(iii) This precipitation reaction can also be described as a **different** type of reaction.

Name this type of reaction.

..... [1]

(b) **L** is an uncharged tridentate ligand. **L** donates three lone pairs to a metal atom or ion.

Cobalt forms an octahedral complex ion, **E**, with **L**. Complex ion **E** has a 2+ charge.

(i) Give the formula of **E**.

..... [1]

(ii) Identify the oxidation state of cobalt in **E**.

..... [1]

(iii) The d-orbitals of the cobalt atom or ion present in **E** are split in energy.

State the number of d-orbitals that are at a higher energy level and the number of d-orbitals that are at a lower energy level.

number of d-orbitals at a higher energy level	
number of d-orbitals at a lower energy level	

[1]

(iv) Define the term non-degenerate d-orbitals.

.....
 [1]

- (c) The mineral chromite contains a compound which has the formula FeCr_nO_4 . The oxidation state of iron in FeCr_nO_4 is +2.

A sample of 4.18 g of FeCr_nO_4 is dissolved in an excess of sulfuric acid. The resulting solution is made up to 250 cm^3 . This is solution **F**.

All the Fe^{2+} ions in 25.0 cm^3 of solution **F** are oxidised to Fe^{3+} ions by exactly 18.7 cm^3 of $0.0200\text{ mol dm}^{-3}$ KMnO_4 .

One MnO_4^- ion reacts with five Fe^{2+} ions. Assume no other oxidation reaction occurs.

- (i) Write an equation for the reaction of Fe^{2+} ions with MnO_4^- ions in acid solution.

..... [1]

- (ii) Calculate the number of moles of Fe^{2+} ions in 25.0 cm^3 of solution **F**.

number of moles of Fe^{2+} ions = [2]

- (iii) Calculate the M_r of FeCr_nO_4 and use your answer to deduce the value of n .

M_r of FeCr_nO_4 =

value of n =

[2]

- 6 (c) $\text{Cu}(\text{NO}_3)_2$ is added to water to form solution **A**.

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

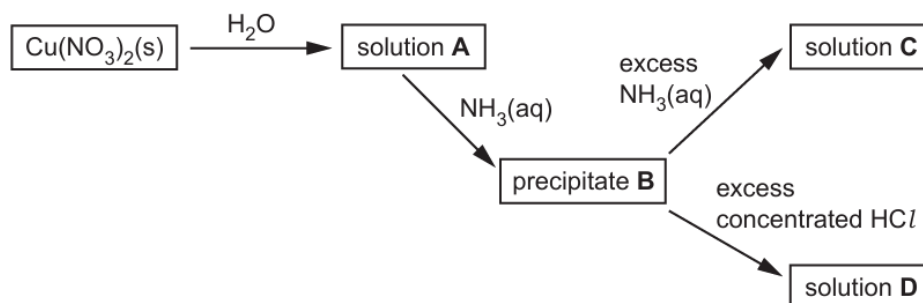


Fig. 1.1

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.

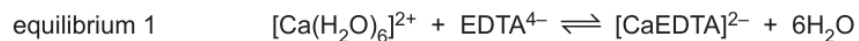
(i) Explain what is meant by a polydentate ligand.

.....

 [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 $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$ to form a new complex, $[\text{CaEDTA}]^{2-}$, as shown.



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

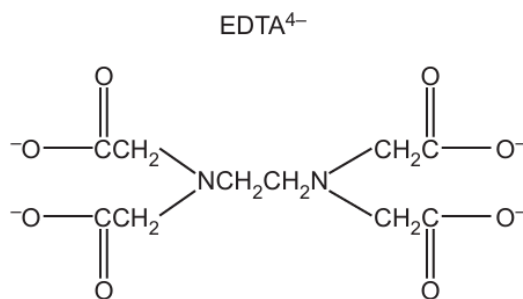


Fig. 1.2

[1]

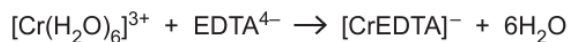
(iii) The calcium ions in $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{CaEDTA}]^{2-}$ have a coordination number of 6.

Explain what is meant by coordination number.

.....
 [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, $\text{Cr}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, 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 $0.00800 \text{ mol dm}^{-3}$ aqueous EDTA^{4-} ions to reach the end-point.

The reaction occurs as shown.



Use the data to calculate the value of n in the formula of $\text{Cr}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$.

Show your working.

$$n = \dots\dots\dots [3]$$

- 7 (b) The complexes $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pt}(\text{en})_2]^{2+}$ have the same geometry (shape) around the metal ion.

$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ exists as two stereoisomers whereas $[\text{Pt}(\text{en})_2]^{2+}$ only has one possible structure.

State the geometry around the metal ion.

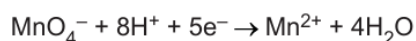
..... [1]

- 8 (c)** Potassium sulfite, K_2SO_3 , is used as a food additive.

The concentration of sulfite ions, SO_3^{2-} , can be determined by titration using aqueous acidified manganate(VII) ions, MnO_4^- .

- A 250 cm^3 solution contains 3.40 g of impure K_2SO_3 .
- 25.0 cm^3 of this solution requires 22.40 cm^3 of $0.0250\text{ mol dm}^{-3}$ acidified MnO_4^- to reach the end-point. All the SO_3^{2-} ions are oxidised. None of the other species in the impure K_2SO_3 are oxidised.

The reaction occurs as shown by the two half-equations.



- (i) Give the ionic equation for the reaction between SO_3^{2-} and acidified MnO_4^- .

..... [1]

- (ii) Calculate the percentage purity of the sample of K_2SO_3 .
Show your working.

percentage purity of K_2SO_3 = [3]

9 (b) Aqueous solutions of cobalt(II) salts contain the complex ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.

(i) Define complex ion.

.....
 [1]

(ii) Samples of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ are reacted separately with an excess of aqueous ammonia, with an excess of concentrated HCl and with an excess of aqueous sodium hydroxide, as shown in Fig. 2.1.

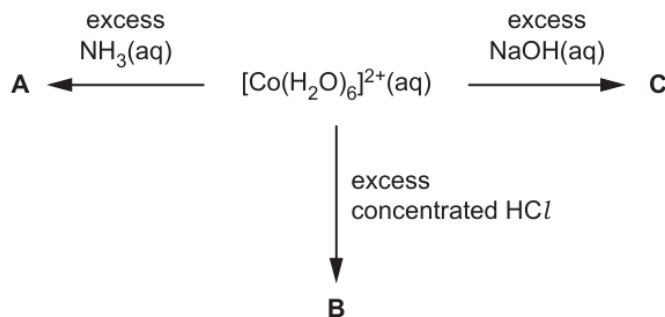


Fig. 2.1

Complete Table 2.1 about the reactions shown by $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.

Table 2.1

reagent added to $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$	formula of cobalt species formed	colour and state of cobalt species formed	type of reaction
an excess of $\text{NH}_3(\text{aq})$	A =		
an excess of concentrated HCl	B =		
an excess of $\text{NaOH}(\text{aq})$	C =		

[4]

(c) The ethanedioate ion, $\text{C}_2\text{O}_4^{2-}$, can act as a bidentate ligand.

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

.....

 [2]

10 (a) Cobalt(II) nitrate, $\text{Co}(\text{NO}_3)_2$, is a reddish-brown crystalline solid. It dissolves in water to form a solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ 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 $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$	cobalt-containing species formed
1	$\text{NaOH}(\text{aq})$	
2	an excess of $\text{NH}_3(\text{aq})$	
3	an excess of conc. $\text{HCl}(\text{aq})$	

[2]

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

original colour of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$

final colour after addition of an excess of conc. $\text{HCl}(\text{aq})$

[1]

11 Transition elements behave as catalysts and can form complex ions.

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

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

Titanium forms the complex $[\text{TiCl}_4(\text{diars})_2]$, where *diars* is a neutral bidentate ligand.

(i) State the oxidation state and the coordination number of titanium in $[\text{TiCl}_4(\text{diars})_2]$.

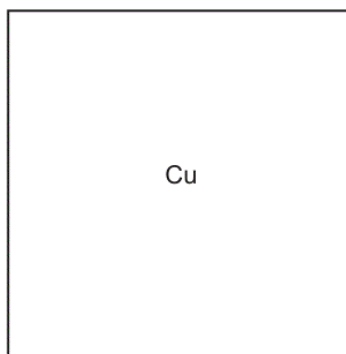
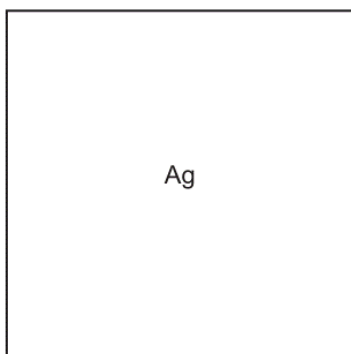
oxidation state

coordination number

[1]

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

Label one bond angle on each diagram.



[2]

- (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.

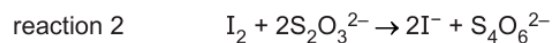
An excess of $\text{KI}(\text{aq})$ is added to a 25.0 cm^3 sample of this solution.

All of the copper is precipitated as white $\text{CuI}(\text{s})$.

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



The liberated I_2 is then titrated with $0.0200\text{ mol dm}^{-3} \text{S}_2\text{O}_3^{2-}$. This is reaction 2.



The titration requires 20.10 cm^3 of $0.0200\text{ mol dm}^{-3} \text{S}_2\text{O}_3^{2-}$ 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]

- 12 (a)** Five ligands are listed in Table 6.1.

Table 6.1

ligand	type of ligand
NH_3	
EDTA^{4-}	
CN^-	
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$	tridentate
$\text{C}_2\text{O}_4^{2-}$	

- (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 $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ is a tridentate ligand.

Suggest the meaning of tridentate ligand.

.....
 [1]

- (iii) Suggest how $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ acts as a tridentate ligand.

.....
 [1]

- 13 The structure of the polydentate ligand, EDTA⁴⁻, is shown in Fig. 4.1.

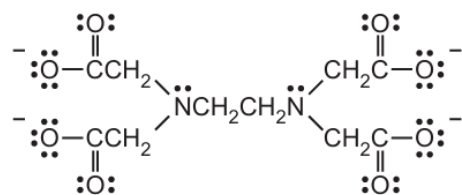


Fig. 4.1

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

Table 4.1

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

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

Cu

Cr

[1]

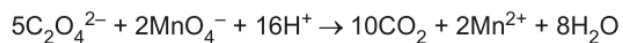
- (c) Deduce the number of lone pairs donated by each EDTA⁴⁻ ligand in a single $[\text{Fe}(\text{EDTA})]^{2-}$ complex ion.

..... [1]

- 14** Some of the ionic compounds of Group 2 elements undergo thermal decomposition.

Thermal decomposition of solid anhydrous magnesium ethanedioate, MgC_2O_4 , occurs above 650°C . The products are magnesium oxide and a mixture of two different gases, one of which gives a white precipitate with saturated calcium hydroxide solution.

- (c) The ethanedioate ion is oxidised by acidified KMnO_4 .



An experiment is performed to find the solubility of MgC_2O_4 in water.

A 40.0 cm^3 sample of saturated aqueous MgC_2O_4 requires 27.05 cm^3 of $0.00200\text{ mol dm}^{-3}$ acidified KMnO_4 to oxidise all the $\text{C}_2\text{O}_4^{2-}$ ions.

Calculate the solubility, in mol dm^{-3} , of MgC_2O_4 in water. Show your working.

solubility = mol dm^{-3} [3]

15 (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 $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$.

The *dien* ligand forms three bonds to the gold ion in $[\text{Au}(\textit{dien})(\text{H}_2\text{O})_2\text{Cl}]^{2+}$ and $\text{Au}(\textit{dien})\text{Cl}_3$.

These three bonds all lie in the same plane.

The CO ligand coordinates through the carbon atom in $[\text{Rh}(\text{CO})_2\text{Cl}_2]^+$.

Table 6.1

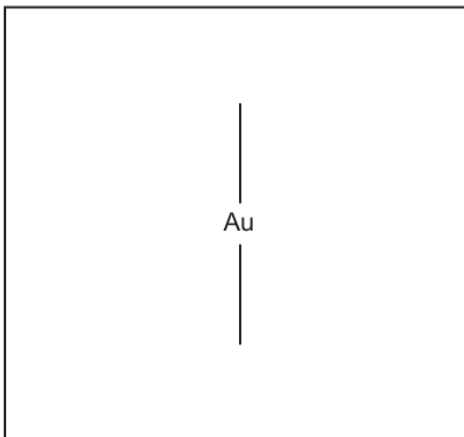
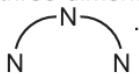
formula	isomerism shown	geometry
$[\text{Rh}(\textit{en})_2\text{Cl}_2]^+$	yes	
$[\text{Rh}(\text{CO})_2\text{Cl}_2]^+$	yes	
$[\text{Au}(\textit{dien})(\text{H}_2\text{O})_2\text{Cl}]^{2+}$		
$\text{Au}(\textit{dien})\text{Cl}_3$	no	octahedral
$\text{Ni}(\text{PH}_3)_2\text{Cl}_2$	no	
$[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$	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 $[\text{Au}(\textit{dien})(\text{H}_2\text{O})_2\text{Cl}]^{2+}$ and $\text{Au}(\textit{dien})\text{Cl}_3$ to write an equation showing ligand exchange.

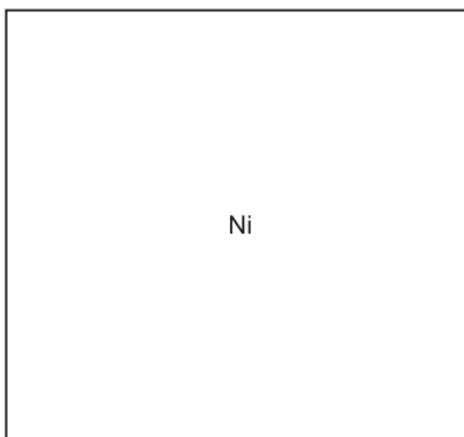
..... [1]

- (iii) Draw the three-dimensional structure of $\text{Au}(\text{dien})\text{Cl}_3$ in the box. The *dien* ligand can be drawn as



[1]

- (iv) Draw the three-dimensional structure of $\text{Ni}(\text{PH}_3)_2\text{Cl}_2$ in the box.



[1]

- 16 (d)** Manganese(VII) oxide, Mn_2O_7 , can be made by treatment of KMnO_4 with concentrated sulfuric acid (reaction 1).

Mn_2O_7 readily decomposes at room temperature to form manganese(IV) oxide and a colourless diatomic gas (reaction 2).

Construct equations for **both** the reactions described.

reaction 1

reaction 2

[2]

- (e)** Aqueous manganese(II) ions show similar chemical properties to aqueous copper(II) ions when reacted separately with $\text{NaOH}(\text{aq})$ and with concentrated HCl .

- (i)** Write the ionic equation, and state the type of reaction, for the reaction of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ with $\text{NaOH}(\text{aq})$.

ionic equation

type of reaction

[2]

- (ii)** Write the ionic equation, and state the type of reaction, for the reaction of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ with concentrated HCl .

ionic equation

type of reaction

[2]

- (iii)** Table 2.1 lists relevant electrode potentials for some electrode reactions.

Table 2.1

electrode reaction	E^\ominus/V
$\text{Mn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mn}$	-1.18
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36
$2\text{HOCl} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Cl}_2 + 2\text{H}_2\text{O}$	+1.64
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$	+1.67

Suggest the formula of the manganese species formed when $\text{Mn}^{2+}(\text{aq})$ reacts with Cl_2 .

State the type of reaction.

formula of manganese species formed

type of reaction

[1]

- 17 (b) (i) Bipyridine, bipy, is a bidentate ligand.

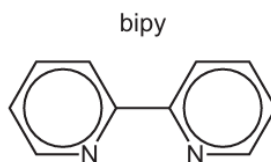


Fig. 4.1

Explain what is meant by bidentate ligand.

.....

.....

..... [2]

- (c) Standard electrode potentials can be used to compare the stability of different complex ions for a given transition element.

Table 4.1 lists electrode potentials for some electrode reactions for $\text{Fe}^{3+}/\text{Fe}^{2+}$ systems.

Table 4.1

electrode reaction	E^\ominus/V
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	+0.77
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	+0.36
$[\text{Fe}(\text{bipy})_3]^{3+} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{bipy})_3]^{2+}$	+0.96

Use relevant data from Table 4.1 to state which iron(III) complex is hardest to reduce. Explain your choice.

iron(III) complex

explanation

..... [1]

18 (c) $\text{Be}(\text{OH})_2$ is soluble in aqueous solutions containing an excess of hydroxide ions and forms the complex ion $[\text{Be}(\text{OH})_4]^{2-}$. This complex ion has a similar shape to that of $[\text{CuCl}_4]^{2-}$.

(i) Define the term complex ion.

.....
 [1]

(ii) Draw a three-dimensional diagram to show the structure of the complex ion $[\text{Be}(\text{OH})_4]^{2-}$. Name the shape of the $[\text{Be}(\text{OH})_4]^{2-}$ complex ion.

shape [1]

(d) (i) Explain why transition elements can form complex ions.

.....
 [1]

(ii) Complete Table 1.1 to show the coordination number of each metal ion, and the shapes and overall polarities of the complex ions listed.

Table 1.1

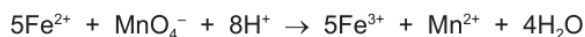
complex ion	shape	coordination number	polar or non-polar
<i>cis</i> - $[\text{Pt}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)\text{Cl}_2]$	square planar		
$[\text{Ag}(\text{NH}_3)_2]^+$			non-polar
$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$		6	

[2]

- 19** A transition element is a d-block element which forms one or more stable ions with incomplete d-orbitals.

(d) **A** is a pale green salt containing Fe^{2+} ions. A sample of 2.62 g of **A** is dissolved in water and the solution is made up to exactly 100 cm^3 with water. 25.0 cm^3 samples of this solution are placed in conical flasks and titrated against $0.0100\text{ mol dm}^{-3}$ acidified potassium manganate(VII).

The equation for the only reaction that occurs is shown.



The average titre value is 35.0 cm^3 of $0.0100\text{ mol dm}^{-3}$ acidified potassium manganate(VII).

- (i)** Describe the colour change that is seen in the conical flask at the end-point of this titration.

The colour changes from to [1]

- (ii)** Calculate the percentage by mass of iron in **A**.

[A_r : Fe, 55.8]

percentage by mass of iron = % [2]

20 An aqueous solution of copper(II) sulfate is a blue colour due to the presence of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ions.

(a) (i) Write an equation for the reaction between $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions and $\text{NaOH}(\text{aq})$.

..... [1]

(ii) Write an equation for the reaction between $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions and an excess of conc. HCl .

..... [1]

(d) Phenanthroline, $\text{C}_{12}\text{H}_8\text{N}_2$, and ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, are bidentate ligands.

Ruthenium(III) ions, Ru^{3+} , form an octahedral complex with phenanthroline and chloride ions. The complex ion contains two phenanthroline molecules.

Iron(III) ions, Fe^{3+} , form an octahedral complex with ethanedioate ions only.

Deduce the formula and charge of each of these complex ions.

Ru^{3+} complex

Fe^{3+} complex

[2]

21 Copper is a transition element. It forms a wide variety of compounds.

(a) Define transition element.

.....
 [1]

(c) Cu^{2+} forms a complex ion containing water molecules and ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, as ligands. The formula of the complex is $[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$. The ethanedioate ion is a bidentate ligand.

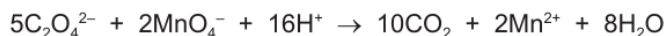
(i) Explain what is meant by bidentate.

.....
 [1]

22 Copper is a transition element. It forms a wide variety of compounds.

- (d) A solution contains 3.70g of $\text{Na}_2[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ dissolved in 100cm^3 of solution. A 25.0cm^3 sample of this solution is warmed and then oxidised by 0.0100mol dm^{-3} acidified potassium manganate(VII).

The equation for the redox reaction is shown.



Calculate the minimum volume of 0.0100mol dm^{-3} acidified potassium manganate(VII) needed to oxidise all of the ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, in the 25.0cm^3 sample. Show all your working.

[M_r : $\text{Na}_2[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$, 321.5]

minimum volume = cm^3 [3]

23 An aqueous solution of cobalt(II) chloride is a pink colour due to the presence of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex ions.

- (a) (i) Complete Table 6.1 to describe what is observed when the named reagent is added to an aqueous solution of cobalt(II) chloride.

Table 6.1

reagent	colour of cobalt-containing product	state of cobalt-containing product
NaOH(aq)		
an excess of conc. HCl		

[2]

- (ii) Write an equation for the reaction between $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions and NaOH(aq).

..... [1]

- (iii) Write an equation for the reaction between $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions and an excess of conc. HCl.

..... [1]

24 (a) An aqueous solution of chromium(III) contains the green $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ complex ion.

(i) Complete the electronic configuration of an isolated, gaseous Cr^{3+} ion.

$1s^2$ [1]

(ii) Define the term *complex ion*.

.....
 [1]

(b) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ shows some similar chemical properties to $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$.

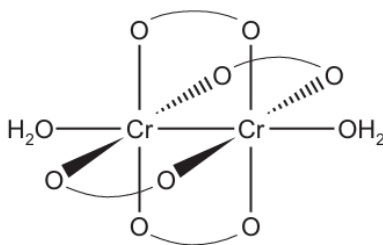
Samples of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ are reacted separately with either $\text{NaOH}(\text{aq})$, $\text{H}_2\text{O}_2(\text{aq})$, or excess $\text{NH}_3(\text{aq})$.

Use this information and the *Data Booklet* to suggest the formula of the chromium species formed. State the type of reaction taking place in each case.

reagent added to $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$	formula of chromium species formed	type of reaction
$\text{NaOH}(\text{aq})$		
$\text{H}_2\text{O}_2(\text{aq})$		
an excess of $\text{NH}_3(\text{aq})$		

[5]

- (d) The structure of $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ is shown. Ethanoate ions act as ligands in this complex. The ethanoate ligand, CH_3CO_2^- , is shown as $\text{O} \text{---} \text{O}$.



- (i) Water and ethanoate ions behave as different types of ligand in this complex.

Suggest an explanation for this statement.

.....
 [1]

- (ii) Deduce the coordination number of Cr and the geometry around each Cr atom in this structure.

coordination number
 geometry around Cr atom
 [1]

- (iii) State the type of bond between the two atoms in the Cr–Cr bond.

..... [1]

- 25 (c) (i)** Barium ethanedioate, BaC_2O_4 , decomposes on heating to produce barium oxide and a mixture of two different gases.

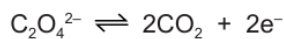
Construct an equation for the decomposition of barium ethanedioate.

..... [1]

- (ii)** An impure sample of BaC_2O_4 , of mass 0.500 g, is added to 50.0 cm³ of 0.0200 mol dm⁻³ acidified MnO_4^- (aq), an excess. A redox reaction takes place and all the BaC_2O_4 reacts.

The resulting solution, containing unreacted acidified MnO_4^- , is titrated with 0.0500 mol dm⁻³ Fe^{2+} (aq).

The end-point is reached when 30.40 cm³ of 0.0500 mol dm⁻³ Fe^{2+} (aq) has been added.

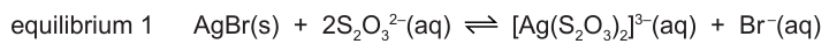


Calculate the percentage by mass of BaC_2O_4 in the 0.500 g impure sample. Show your working.

[M_r : BaC_2O_4 , 225.3]

percentage by mass of BaC_2O_4 = [4]

- 26 (c)** Silver bromide, AgBr, dissolves in an aqueous solution of $\text{S}_2\text{O}_3^{2-}$ ions to form the complex ion $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$. The $\text{S}_2\text{O}_3^{2-}$ ions act as monodentate ligands.



- (i) Define the term *ligand*.

.....
..... [1]

- (ii) Write an expression for the equilibrium constant, K_c , for equilibrium 1.

$K_c =$

[1]

27 (a) $[\text{MnCl}_4]^{2-}$ is a complex ion.

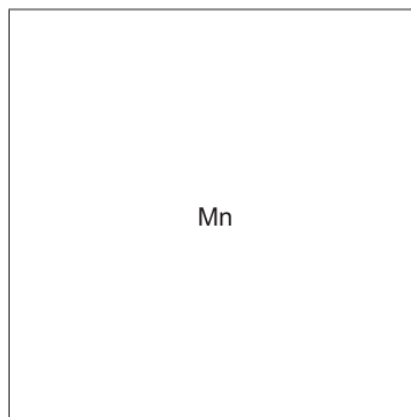
(i) Deduce the oxidation state of manganese in $[\text{MnCl}_4]^{2-}$.

oxidation state = [1]

(ii) The $[\text{MnCl}_4]^{2-}$ complex does **not** contain any 180° bond angles.

Draw a three-dimensional diagram to show the shape of the $[\text{MnCl}_4]^{2-}$ complex.

State one bond angle on your diagram.



[2]

(b) A solution of cobalt(II) sulfate contains the complex ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.

A solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is reacted separately with an excess of each of $\text{NaOH}(\text{aq})$, $\text{NH}_3(\text{aq})$ and $\text{NaCl}(\text{aq})$.

Write an equation for each of these reactions. State **one** observation that can be made immediately after the reaction, include the colour and state of the cobalt-containing product.

(i) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and an excess of $\text{NaOH}(\text{aq})$

equation

observation

[2]

(ii) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and an excess of $\text{NH}_3(\text{aq})$

equation

observation

[2]

(iii) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and an excess of $\text{NaCl}(\text{aq})$

equation

observation

[2]

(iv) Name the type of reaction that occurs in (b)(iii).

..... [1]


(c) Cobalt forms the complex ion $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{2+}$. The abbreviation en is used for the bidentate ligand 1,2-diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$. The complex ion shows both geometrical and optical isomerism.

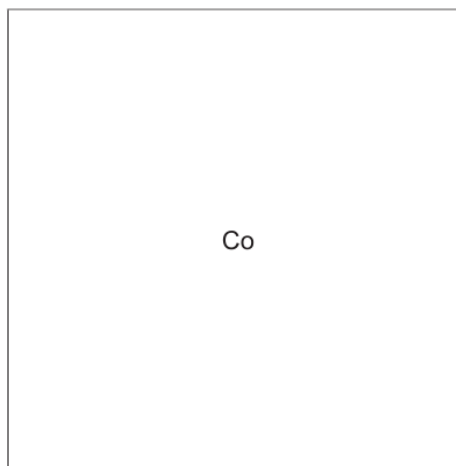
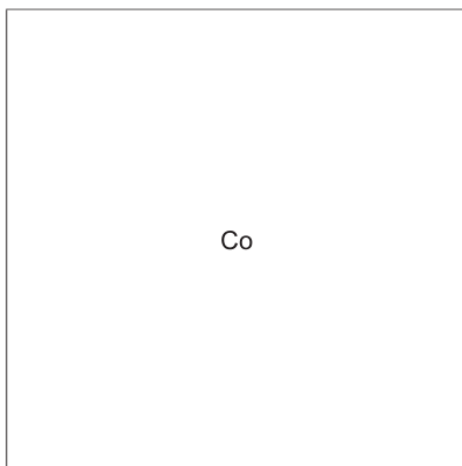
(i) Define the term *bidentate ligand*.

.....

..... [2]

(ii) Draw three-dimensional diagrams for the two **optical** isomers of $[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{2+}$.

Each en ligand can be represented using .



[2]

28 Transition elements form complexes.

- (a) Molybdenum, Mo, forms an octahedral complex consisting of one Mo atom surrounded by carbon monoxide, CO, molecules. CO is a monodentate ligand. Iron forms an octahedral complex consisting of one Fe^{3+} and a number of cyanide, CN^- , ions. CN^- is a monodentate ligand.

- (i) Define the term *monodentate ligand*.

.....
 [1]

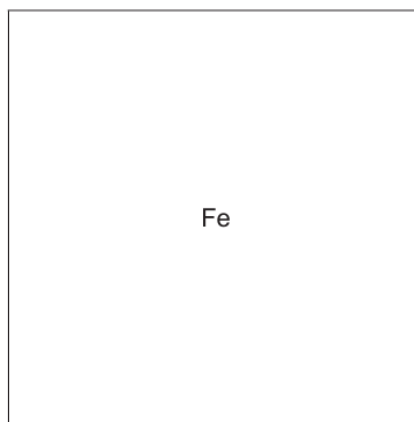
- (ii) Complete the table by stating the formulae and charges of the complexes described.

	formula	charge
molybdenum complex		
iron(III) complex		

[2]

- (iii) Draw a three-dimensional diagram to show the shape of this iron(III) complex.

Label one 180° bond angle on your diagram.



[1]

- (b) An excess of aqueous ammonia is added to dilute copper(II) sulfate solution. A dark blue complex, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$, is formed.

- (i) Write an ionic equation for this reaction.

..... [1]

- (ii) Explain the origin of colour in copper(II) complexes.

.....

 [4]

- (c) An excess of concentrated hydrochloric acid is added to the dark blue solution of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$. A new complex, **Z**, is formed. The colour of the solution changes.

- (i) Write an equation for the formation of **Z** from the solution of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$. Include the formula and charge of **Z**.

..... [2]

- (ii) Name the type of reaction when **Z** forms from $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

..... [1]

- (iii) State the geometry of **Z**.

..... [1]

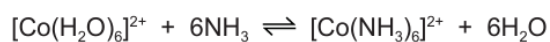
- (iv) State the colour of a solution of **Z**.

..... [1]

- (v) Explain why the colour of a solution of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ is different from the colour of a solution of **Z**. You should refer to the energies of the orbitals involved in your answer.

.....
 [1]

- 29** An excess of aqueous ammonia is added to a solution containing the complex ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.



- (a) Complete the sentence to describe the colour change that will be seen during this reaction.

The colour changes from to [1]

30 (a) An aqueous solution of cobalt(II) contains the $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex ion.

(i) Define the term *complex ion*.

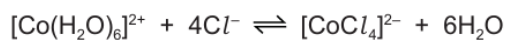
.....
 [1]

(ii) Samples of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ are reacted separately with aqueous sodium hydroxide and with an excess of aqueous ammonia.

Give the following information about these reactions.

- the reaction of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ with aqueous sodium hydroxide
 colour and state of the cobalt-containing species
 ionic equation
 type of reaction
- the reaction of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ with an excess of aqueous ammonia
 colour and state of the cobalt-containing species
 ionic equation
 type of reaction [6]

(b) When concentrated hydrochloric acid is added to a solution containing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, a blue solution of $[\text{CoCl}_4]^{2-}$ is formed and the following equilibrium is established.

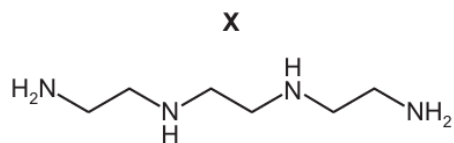


Use Le Chatelier's principle to suggest the expected observations when silver nitrate solution is added dropwise to the blue solution of $[\text{CoCl}_4]^{2-}$. Explain your answer.

.....

 [2]

(d) Compound **X**, $C_6H_{18}N_4$, is a tetradentate ligand.



(i) Suggest why one molecule of **X** can form four dative bonds.

.....

 [1]

(ii) $C_6H_{18}N_4$ reacts with aqueous cobalt(II) ions, $[Co(H_2O)_6]^{2+}$, in a 1:1 ratio to form a new complex ion.

Construct an equation for this reaction.

..... [1]

31 $EDTA^{4-}$, is a polydentate ligand.

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

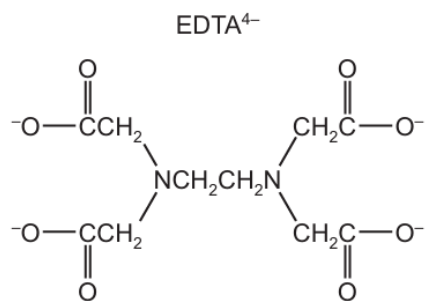
.....

 [2]

(ii) When a solution containing $EDTA^{4-}$ is added to a solution containing $[Cd(H_2O)_6]^{2+}$ a new complex is formed, $[CdEDTA]^{2-}$.

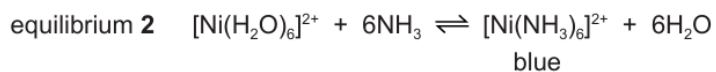
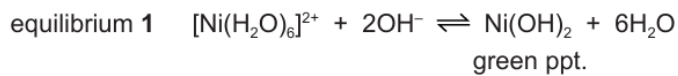


Circle, on the structure of $EDTA^{4-}$, the **six** atoms that form bonds with the metal ion.



[1]

- 32 (c)** Hexaaquanickel(II) ions are green. They form a green precipitate with hydroxide ions, OH^- , in equilibrium **1** and a blue complex with ammonia, NH_3 , in equilibrium **2**.



Use Le Chatelier's principle to suggest explanations for the following observations.

- (i) Explain why when aqueous NH_3 is added dropwise to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ a green precipitate is formed.

.....

 [1]

- (ii) Explain why when a large excess of aqueous NH_3 is added to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, the green precipitate dissolves and a blue solution is formed.

.....

 [1]

- 33** A solution is made by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in an excess of aqueous ammonia. This solution contains the copper complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

The solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is heated gently in a fume cupboard so that NH_3 is released. Some NH_3 remains in solution and some forms NH_3 gas. The colour of the solution changes; a precipitate of $\text{Cu}(\text{OH})_2$ forms and is collected.

A sample of $\text{Cu}(\text{OH})_2$ is added to concentrated hydrochloric acid. A reaction takes place forming a coloured copper complex, **Y**.

A sample of $\text{Cu}(\text{OH})_2$ is added to dilute sulfuric acid. A reaction takes place forming a coloured copper complex, **Z**.

$[\text{Cu}(\text{NH}_3)_4]^{2+}$, **Y** and **Z** are different colours.

- (b) Suggest an equation for the reaction of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ to form $\text{Cu}(\text{OH})_2$ as the aqueous solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is heated.

..... [1]

- (c) Suggest an equation for the reaction of $\text{Cu}(\text{OH})_2$ with concentrated hydrochloric acid, forming **Y**.

..... [2]

- (d) Complete the table with the colour and geometry of complex **Y** and the colour, geometry and formula of complex **Z**.

	Y	Z
colour of complex		
geometry of complex		
formula of complex		

[2]

34 (a) When $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3(\text{aq})$ is added to a solution containing $\text{Ag}^+(\text{aq})$ ions, a linear complex, **P**, is formed. $\text{S}_2\text{O}_3^{2-}$ ions are present in **P** as monodentate ligands.

(i) Define the term *monodentate ligand*.

.....
..... [2]

(ii) Give the formula of **P**, including its charge.

..... [1]

(b) When $1.0 \text{ mol dm}^{-3} \text{ NaCN}(\text{aq})$ is added to a solution of **P**, a mixture which includes a second linear complex, **Q**, is formed. In this mixture the concentration of **Q** is much greater than the concentration of **P**.

(i) Write an equation for the reaction that occurs when $\text{NaCN}(\text{aq})$ is added to a solution of **P**.

..... [1]

(ii) Suggest a reason why the concentration of **Q** is much greater than the concentration of **P** in the mixture.

.....
.....
..... [1]

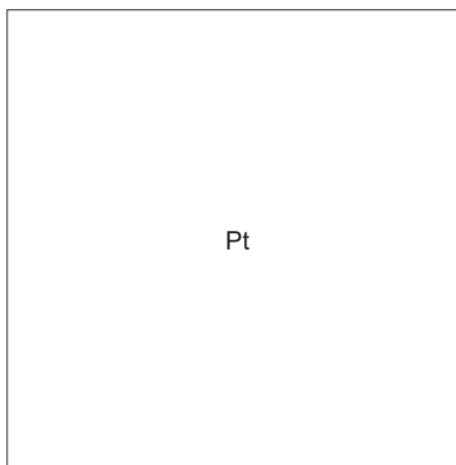
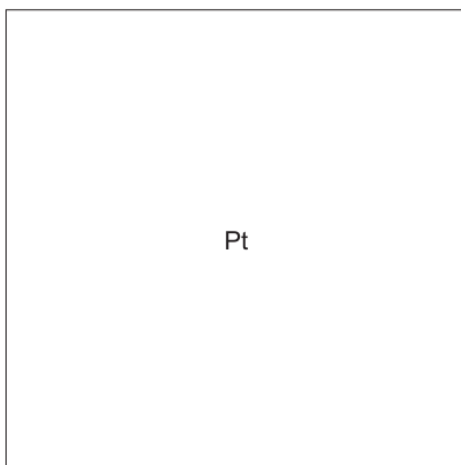
(iii) Name the type of reaction in which **P** forms **Q**.

..... [1]

(c) Platinum forms a complex ion with the formula $[\text{Pt}(\text{CN})_2\text{Cl}_2]^{2-}$. In this complex ion the carbon atom of each CN^- ligand bonds to the platinum ion. This complex shows stereoisomerism.

(i) There are only two isomers of this complex.

Draw structures of these two isomers in the boxes below.



[1]

(ii) Describe the geometry of $[\text{Pt}(\text{CN})_2\text{Cl}_2]^{2-}$.

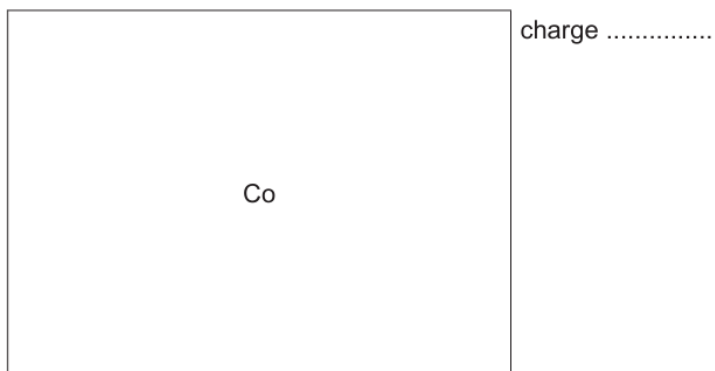
..... [1]

(iii) Name the type of stereoisomerism shown by $[\text{Pt}(\text{CN})_2\text{Cl}_2]^{2-}$.

..... [1]

35 (c) Cobalt(II) sulfate is added to water to form a pink solution containing complex ion **P**. An excess of concentrated hydrochloric acid is added to this solution to form a blue solution containing complex ion **Q**.

- (i) Complete the diagram to show the three-dimensional structure of **Q**.
State the charge on this complex ion.



[2]

- (ii) Name the type of reaction in which **P** forms **Q**.

..... [1]

- 36 (d)** A solution of the bidentate ligand 1,2-diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, is added to an aqueous solution of cobalt(II) sulfate. Oxygen is then bubbled into the mixture forming a complex ion with the formula $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$.

This complex ion exists as a mixture of two isomers. The geometry of both of these isomeric complexes is octahedral.

- (i) In this reaction, cobalt undergoes **two** types of reaction. One type of reaction is the same as that described in (c)(ii).

Name the **other** type of reaction that cobalt undergoes.

..... [1]

- (iv) State the co-ordination number of cobalt in these two isomeric complexes.

..... [1]

- 37 (a)** Aqueous solutions of copper(II) salts contain the blue-coloured $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ion. Separate portions of this blue solution react with aqueous sodium hydroxide and with concentrated hydrochloric acid.

Give the following information for each of these reactions.

- reaction with aqueous sodium hydroxide

ionic equation

type of reaction

colour and state of the copper-containing product

- reaction with concentrated hydrochloric acid

ionic equation

type of reaction

colour and state of the copper-containing product

[6]

38 (c) Methylamine, CH_3NH_2 , is a monodentate ligand.

(i) State what is meant by the term *monodentate* in this context.

.....
 [1]

39 (a) Sketch the shape of a d orbital.

[1]

(b) (i) Explain what is meant by the term *transition element*.

.....
 [1]

Transition elements can form complex ions which contain ligands.

(ii) Name the *type of bonding* that occurs between a ligand and a transition element.

..... [1]

(d) CO and CN^- are monodentate ligands.

Complete the table for the following two complexes.

metal ion	ligand	co-ordination number	formula of complex ion	charge of complex ion
Ni^{2+}	CO	4		
Fe^{3+}	CN^-			3-

[2]

40 Manganese, chromium and ruthenium are all transition elements.

(b) MnO_4^- (aq) and $\text{Cr}_2\text{O}_7^{2-}$ (aq) act as oxidising agents in acidic solution. Both these oxidising agents will oxidise a solution of Sn^{2+} to give a solution of Sn^{4+} . Solutions containing Sn^{2+} and solutions containing Sn^{4+} are colourless.

(i) Describe the colour change seen when an excess of Sn^{2+} (aq) is added separately to

- dilute acidified MnO_4^- (aq)

from to

- dilute acidified $\text{Cr}_2\text{O}_7^{2-}$ (aq).

from to

[1]

(ii) Write an equation for the reaction between Sn^{2+} (aq) and acidified $\text{Cr}_2\text{O}_7^{2-}$ (aq).

..... [1]

(c) Ruthenium, Ru, forms complex ions. In one such complex ion, **X**, the ruthenium ion has a co-ordination number of six. Each complex ion **X** contains one Ru^{2+} ion, one Cl^- ion, one SO_2 molecule and the remaining ligands are NH_3 molecules.

The SO_2 molecule acts as a monodentate ligand and is attached to the Ru^{2+} ion via the sulfur atom. **X** exists in two isomeric forms.

(i) State what is meant by a *co-ordination number of six*.

..... [1]

(ii) State the formula of **X**. Include its charge.

..... [1]

41 Many copper compounds, such as CuSO_4 and $\text{Cu}(\text{NO}_3)_2$ contain Cu^{2+} ions. Aqueous solutions of this ion contain the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ion, in which water behaves as a monodentate ligand.

(a) Explain what is meant by the term *monodentate ligand*.

.....
 [1]

(b) Copper(II) sulfate solution, $\text{CuSO}_4(\text{aq})$, undergoes visible changes with certain reagents.

Complete the table below.

reagent added to a solution of $\text{CuSO}_4(\text{aq})$	observations	formula of the copper(II) compound or complex ion that is formed
a few drops of $\text{NH}_3(\text{aq})$		
an excess of $\text{NH}_3(\text{aq})$		
an excess of $\text{NaOH}(\text{aq})$		
an excess of concentrated $\text{HCl}(\text{aq})$		

[4]

42 Copper is a transition element with atomic number 29.

(b) Cu^+ ions form a linear complex with Cl^- ions, which are monodentate ligands.

Draw the structure of this complex and include its overall charge.

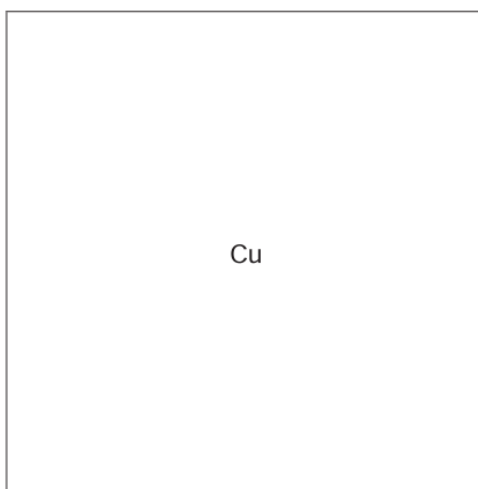
[2]

(c) Cu^{2+} ions exist as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ions in aqueous solution.

Complete a three-dimensional diagram to show the shape of this complex.

Name its shape.

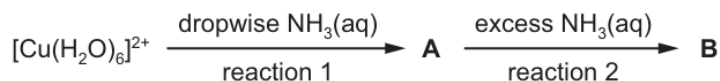
Label and state the value of one bond angle.



name of shape

[2]

- (d) When $\text{NH}_3(\text{aq})$ is added to $\text{Cu}^{2+}(\text{aq})$, dropwise at first and then in excess, two chemical reactions occur as shown.



For each reaction, describe what you would see and write an equation.

reaction 1

observation

.....

equation

reaction 2

observation

.....

equation

[4]

- (f) Ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, can act as a bidentate ligand.

- (i) Explain what is meant by the term *bidentate ligand*.

.....

.....

.....

..... [2]

- (ii) When ethanedioate ions are added to a solution of zirconium ions, Zr^{4+} , a complex ion containing four $\text{C}_2\text{O}_4^{2-}$ ions and one Zr^{4+} ion is formed. All four ethanedioate ions act as bidentate ligands in this complex.

Give the formula of this complex ion and explain why this complex is not octahedral.

.....

.....

.....

..... [2]