

CHEMISTRY



EXAM QUESTION PACK

23 CHEMISTRY OF TRANSITION ELEMENTS

SCORE

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1. Nov/2020/Paper_41/No.5

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 $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

(a) (i) Write an expression for the K_{stab} of $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

$$K_{\text{stab}} =$$

[1]

(ii) State the colour of the solution of $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

..... [1]

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]

- (e) Explain why complexes **Y** and **Z** are coloured and why their colours are different.

.....

.....

.....

.....

.....

.....

.....

..... [5]

[Total: 12]

- (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]

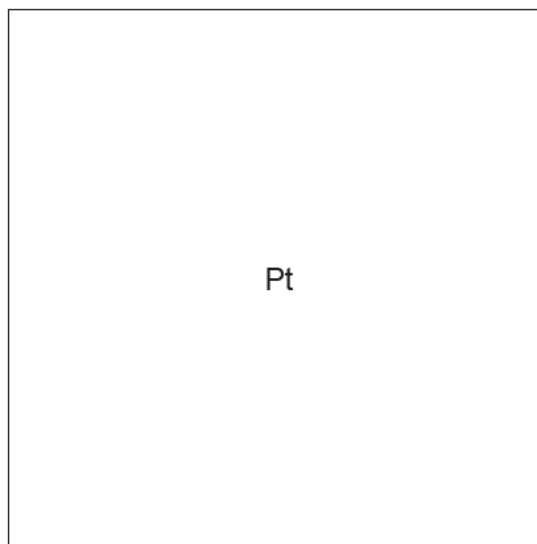
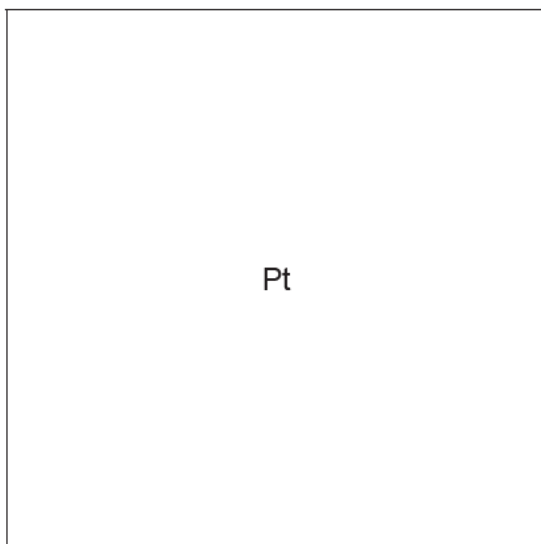
(iii) Name the type of reaction in which **P** forms **Q**.

..... [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]

[Total: 9]

(a) Define the term *transition element*.

.....
 [1]

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

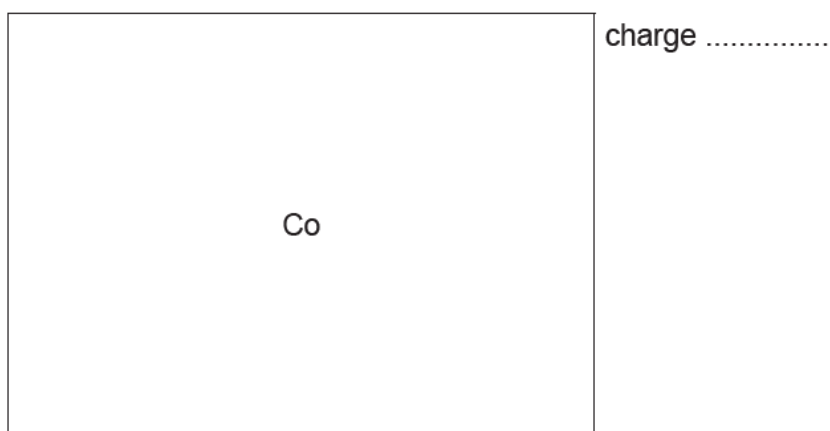
$1s^2$ [1]

(ii) Name **two** transition elements whose isolated gaseous **atoms** have the same number of electrons in the 3d subshell as an isolated gaseous Fe^{3+} ion.

..... [1]

(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]

(iii) Explain why solutions that contain transition element ions are often coloured.

.....

.....

.....

.....

.....

..... [4]

(iv) Explain why the colours of **P** and **Q** are different.

.....

.....

..... [2]

(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.

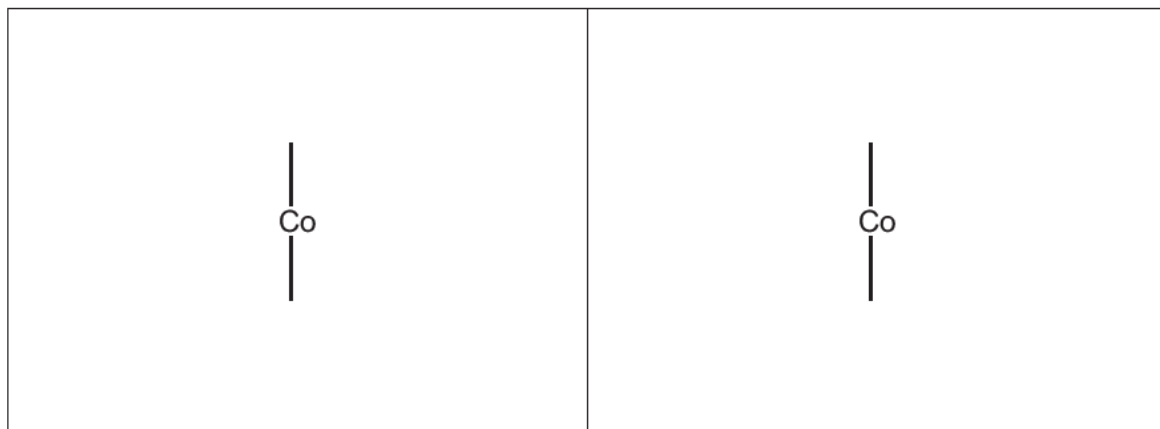
(i) In this reaction, cobalt undergoes **two** types of reaction. One type of reaction is the same as that described in (c)(ii).

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

..... [1]

(ii) Draw the three-dimensional structures of the two isomeric complexes in the boxes.

You may use  to represent a molecule of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.



[2]

(iii) Name the type of stereoisomerism shown by these two isomeric complexes.

..... [1]

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

..... [1]

(e) The stability constants, K_{stab} , of three complexes of mercury(II) are given in the table.

complex	K_{stab}
$[\text{Hg}(\text{CN})_4]^{2-}$	2.5×10^{41}
$[\text{HgCl}_4]^{2-}$	1.7×10^{16}
$[\text{HgI}_4]^{2-}$	2.0×10^{30}

(i) Write an expression for the K_{stab} of $[\text{Hg}(\text{CN})_4]^{2-}$.

$$K_{\text{stab}} =$$

[1]

(ii) An aqueous solution containing Hg^{2+} is added to a solution containing equal concentrations of $\text{CN}^-(\text{aq})$, $\text{Cl}^-(\text{aq})$ and $\text{I}^-(\text{aq})$. The mixture is left to reach equilibrium.

Predict which of the complexes $[\text{Hg}(\text{CN})_4]^{2-}$, $[\text{HgCl}_4]^{2-}$ and $[\text{HgI}_4]^{2-}$ is present in the resulting mixture in the highest concentration and which is present in the lowest concentration. Explain your answer.

.....

.....

.....

..... [2]

[Total: 20]

Iron is a transition element in the fourth period. Iron forms compounds containing the ions Fe^{2+} and Fe^{3+} .

(a) (i) Define the term *transition element*.

.....

.....

..... [1]

(ii) Compare the melting point and density of iron with those of calcium, an s-block element in the fourth period.

melting point

density [1]

(iii) Complete the electronic configuration of an isolated gaseous Fe^{2+} ion.

$1s^2$ [1]

(iv) Aqueous Fe^{3+} ions form coloured complexes.

Explain the origin of the colour in transition element complexes.

.....

.....

.....

.....

.....

..... [4]

- (b) When an excess of $\text{CN}^-(\text{aq})$ ions is added to green $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ ions, yellow $[\text{Fe}(\text{CN})_6]^{4-}$ complex ions are formed.

Heating $[\text{Fe}(\text{CN})_6]^{4-}$ with dilute nitric acid and then neutralising the product with $\text{Na}_2\text{CO}_3(\text{aq})$ produces red crystals, containing the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ complex ion.

NO is a neutral, monodentate ligand.

- (i) State the shape of the $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ complex ion.

..... [1]

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

..... [1]

- (iii) Deduce the oxidation states of iron in:

$[\text{Fe}(\text{CN})_6]^{4-}$ $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ [1]

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

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

- (v) Complete the diagram to show the three-dimensional structure of the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ complex ion.



[1]

- (vi) The two complex ions $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ are different colours.

Explain why the colours of the two complex ions are different.

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

(c) **E** is a complex ion, $[\text{Fe}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{4-}$, containing Fe^{2+} with a coordination number of 6.

(i) Define the term *coordination number*.

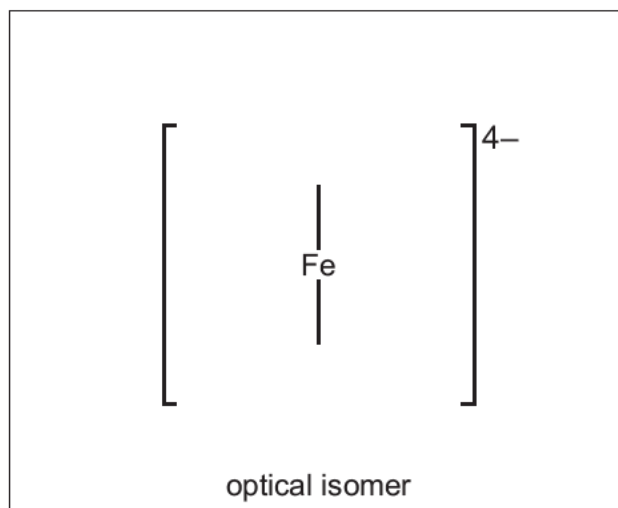
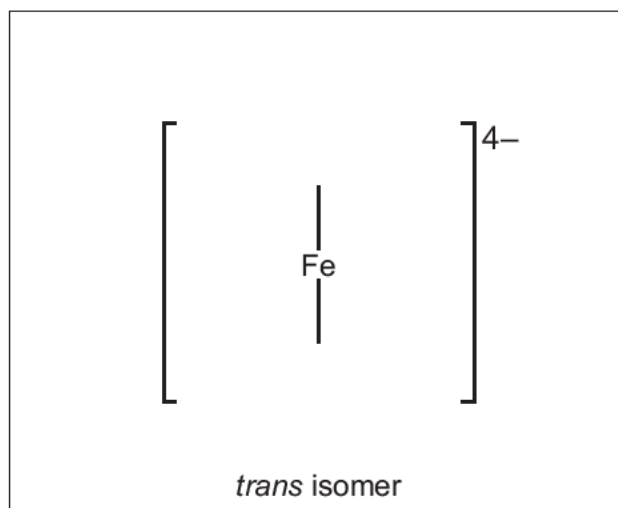
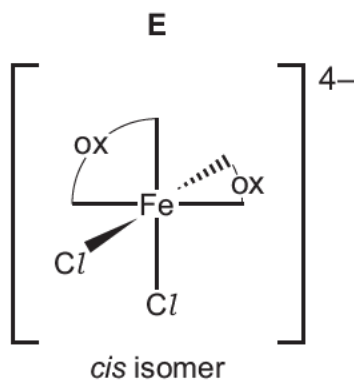
.....
..... [1]

(ii) **E** shows both optical isomerism and *cis-trans* isomerism.

One isomer of **E** is shown. The $\text{C}_2\text{O}_4^{2-}$ ion is represented as ox .

In the boxes, draw three-dimensional diagrams to show:

- the *trans* isomer of **E**
- the optical isomer of **E**.



[2]

(iii) $[\text{Fe}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{4-}$ contains ligands which are anions of ethanedioic acid, $\text{HO}_2\text{CCO}_2\text{H}$.

Complete the table to show any observations for the reactions of $\text{HO}_2\text{CCO}_2\text{H}$ with the named reagents.

Where no change is observed, write 'none'.

reagent	observations with $\text{HO}_2\text{CCO}_2\text{H}$
warm acidified manganate(VII)	
2,4-dinitrophenylhydrazine	
warm Tollens' reagent	

[2]

[Total: 20]

- (a) The electronic configuration of transition element **Q** is $[\text{Ar}] 3d^2 4s^2$.

Predict the likely oxidation states of element **Q** in compounds.

..... [1]

- (b) Suggest why transition elements often show variable oxidation states in their compounds, but typical s-block elements such as calcium do not.

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

- (c) Many enzymes contain transition element complexes.

Describe, with the aid of a suitably labelled diagram, how an enzyme catalyses the breakdown of a substrate molecule.

.....
.....
.....
..... [3]

[Total: 5]

EDTA⁴⁻, is a polydentate ligand.

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

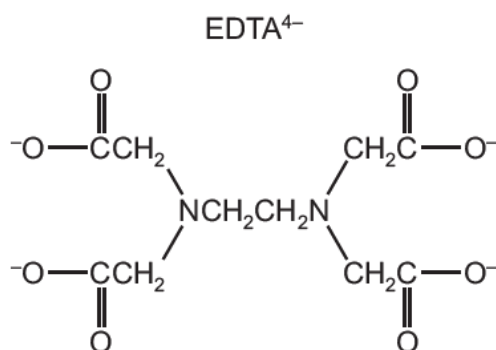
.....

 [2]

(ii) When a solution containing EDTA⁴⁻ is added to a solution containing [Cd(H₂O)₆]²⁺ a new complex is formed, [CdEDTA]²⁻.



Circle, on the structure of EDTA⁴⁻, the **six** atoms that form bonds with the metal ion.



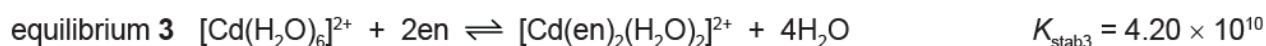
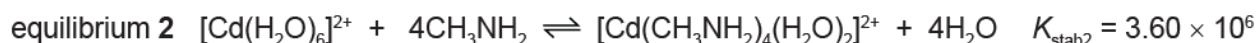
[1]

(iii) Write an expression for the stability constant, K_{stab1} , for equilibrium 1, and state its units.

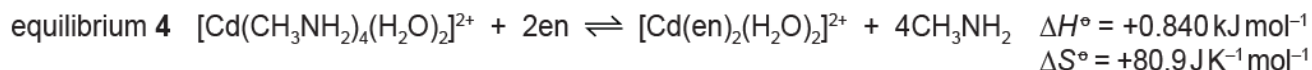
$$K_{\text{stab1}} =$$

units = ...
 [2]

(b) Cadmium ions form complexes with methylamine, CH_3NH_2 , and with 1,2-diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, as shown in equilibria 2 and 3. 1,2-diaminoethane is shown as en.



An equilibrium is set up between these two complexes as shown in equilibrium 4.



(i) K_{eq4} is the equilibrium constant for equilibrium 4.

Write an expression for K_{eq4} in terms of K_{stab2} and K_{stab3} .

$$K_{\text{eq4}} =$$

[1]

(ii) Calculate the value of the standard Gibbs free energy change, ΔG° , for equilibrium 4 at 298 K.

$$\Delta G^\circ = \dots\dots\dots \text{ kJ mol}^{-1} \quad [2]$$

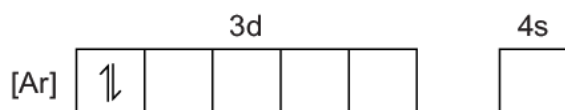
(iii) State how the value of ΔG° changes as the temperature increases. Explain your answer.

.....

 [1]

[Total: 9]

(a) Complete the electronic configuration of an isolated gaseous nickel(II) ion, Ni^{2+} .

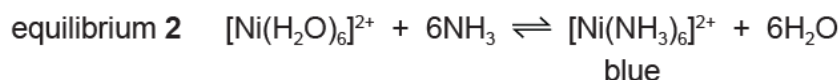
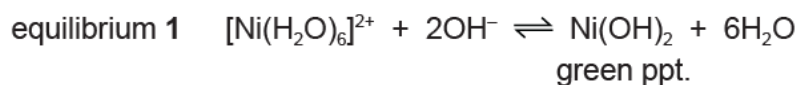


[1]

(b) Explain the origin of colour in transition element complexes.

..... [4]

(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.

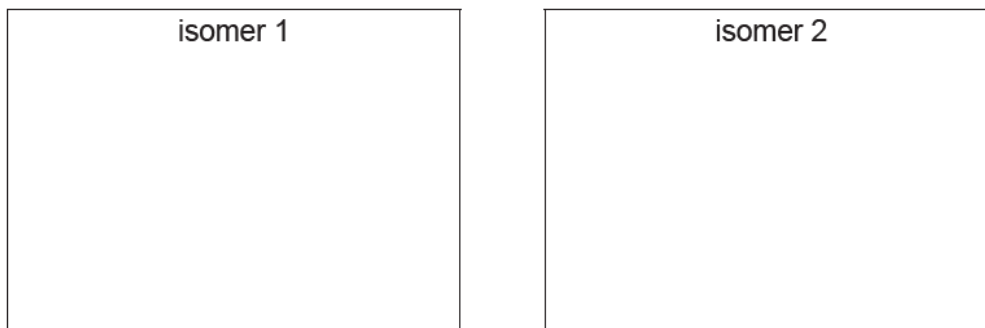
..... [1]

- (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]

- (d) The complex ion $[\text{NiBr}_2(\text{CN})_2]^{2-}$ shows stereoisomerism.

Draw diagrams to show the two isomers of $[\text{NiBr}_2(\text{CN})_2]^{2-}$. Name the type of stereoisomerism.



type of stereoisomerism

[2]

[Total: 9]

1. Nov/2021/Paper_41/No.5

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

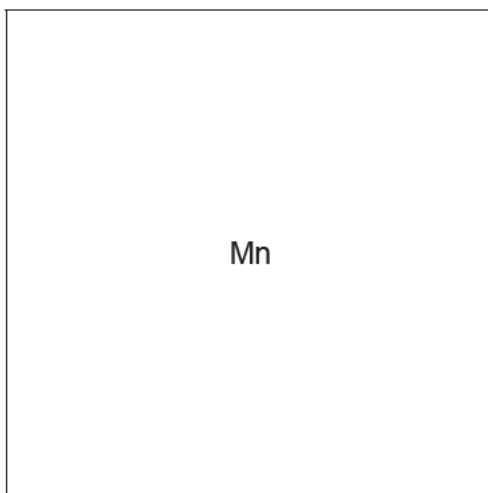
(i) Deduce the oxidation state of manganese in $[\text{MnCl}_4]^{2-}$.

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.

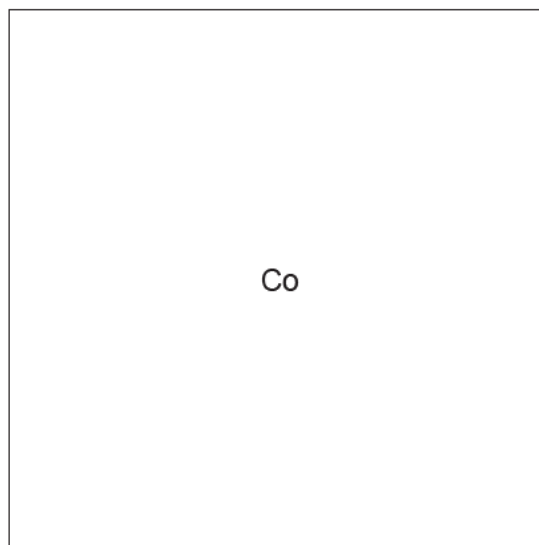
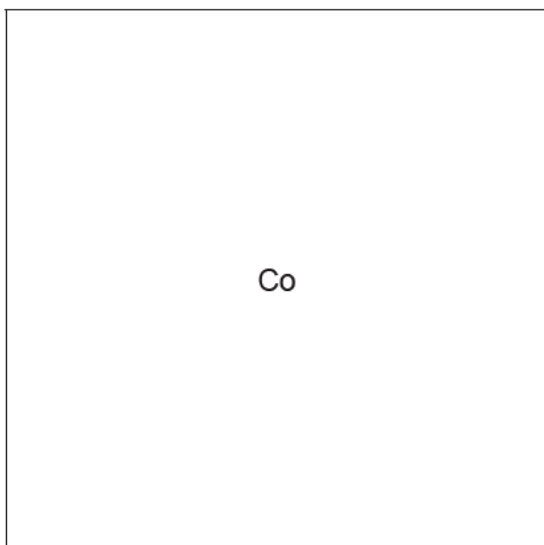
(i) Define the term *bidentate ligand*.

.....

..... [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]

[Total: 14]

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]

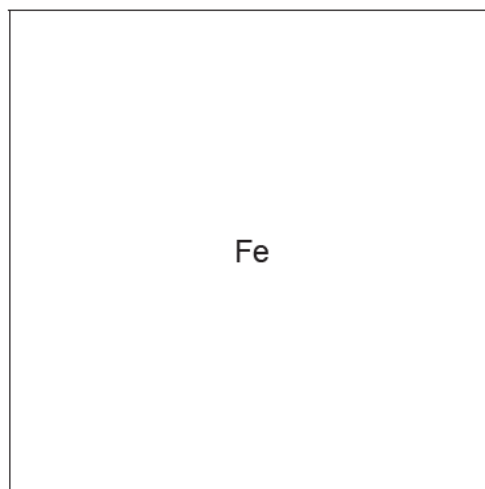
- (ii) Complete the table by stating the formulae and charges of the complexes described.

	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]

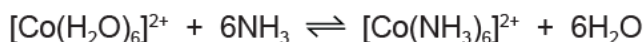
(v) Explain why the colour of a solution of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ is different from the colour of a solution of **Z**. You should refer to the energies of the orbitals involved in your answer.

.....

..... [1]

[Total: 15]

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]

(b) Write an expression for the stability constant, K_{stab} , of $[\text{Co}(\text{NH}_3)_6]^{2+}$.

$$K_{\text{stab}} =$$

[1]

(c) The numerical value of K_{stab} of $[\text{Co}(\text{NH}_3)_6]^{2+}$ is 7.7×10^4 .

What deduction about the properties of $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ can be made from this K_{stab} value?

..... [1]

(d) Oxygen can oxidise $[\text{Co}(\text{NH}_3)_6]^{2+}$ to $[\text{Co}(\text{NH}_3)_6]^{3+}$ under standard conditions in alkaline solutions.



(i) Use this information and the *Data Booklet* to calculate the E°_{cell} value for this oxidation of $[\text{Co}(\text{NH}_3)_6]^{2+}$.

.....

$$E^\circ_{\text{cell}} = \dots\dots\dots \text{ V}$$

[1]

(ii) Write an ionic equation for this oxidation of $[\text{Co}(\text{NH}_3)_6]^{2+}$.

..... [1]

(iii) Predict, by selecting suitable data from the *Data Booklet*, whether oxygen can oxidise $\text{Co}^{2+}(\text{aq})$ in **acidic** solution, in the absence of ammonia. Explain your answer.

.....
 [2]

(a) The most common oxidation states of cobalt are +2 and +3.

Complete the electronic configurations of the following free ions.

- Co^{2+} [Ar]
- Co^{3+} [Ar]

[1]

(b) Co^{2+} and Co^{3+} both form complexes with edta^{4-} .

half-equation	E°/V
$\text{Co}^{3+} + \text{e}^- \rightleftharpoons \text{Co}^{2+}$	+1.82
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.23
$[\text{Co}(\text{edta})]^- + \text{e}^- \rightleftharpoons [\text{Co}(\text{edta})]^{2-}$	+0.38
$\text{Co}^{2+} + 2\text{e}^- \rightleftharpoons \text{Co}$	-0.28

Use the data in the table to predict what happens, if anything, when separate aqueous solutions of Co^{3+} and $[\text{Co}(\text{edta})]^-$ are left to stand in the air.

aqueous solution of Co^{3+}

.....

aqueous solution of $[\text{Co}(\text{edta})]^-$

.....

[3]

- (c) Hydrated cobalt(II) nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, is a red solid that behaves like hydrated magnesium nitrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, when heated.

Describe in detail what you would expect to observe when crystals of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are heated in a boiling tube, gently at first and then more strongly.

.....

.....

.....

..... [2]

- (d) Explain why the thermal stability of the Group 2 nitrates increases down the group.

.....

.....

.....

..... [2]

[Total: 8]

The transition elements are able to form stable complexes with a wide range of molecules and ions.

(a) State the meaning of *transition element*.

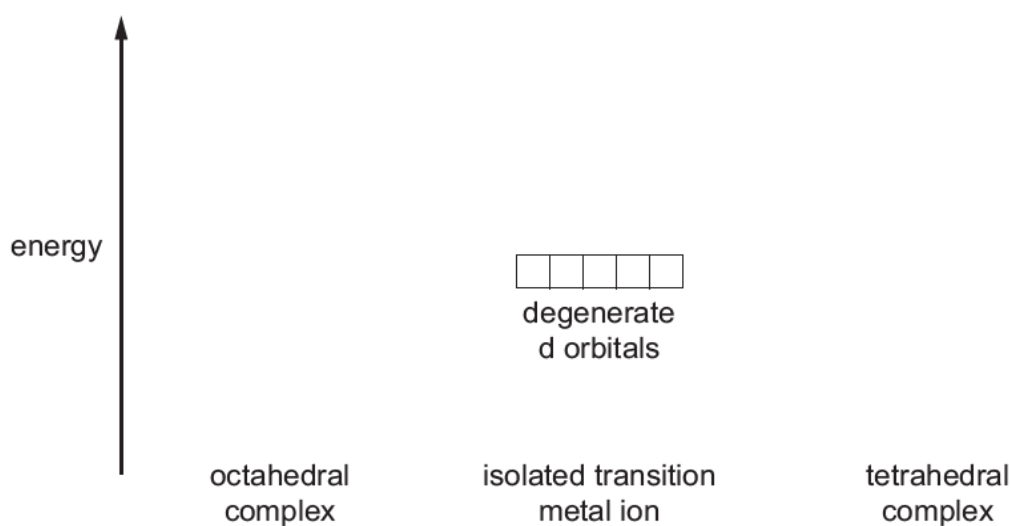
.....

.....

..... [1]

(b) The d orbitals in an isolated transition metal ion are degenerate. In complexes, the d orbitals occupy two energy levels.

(i) Complete the diagram to show the arrangement of d orbital energy levels in octahedral and in tetrahedral complexes.



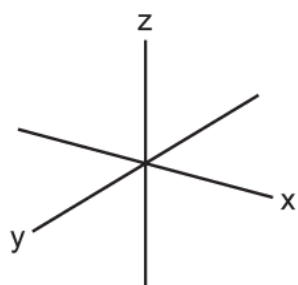
[1]

(ii) Sketch the shape of **two** d orbitals:

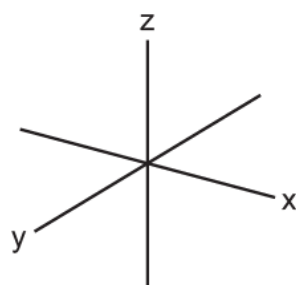
- one d orbital from the lower energy level in an octahedral complex
- one d orbital from the higher energy level in an octahedral complex.

Use the axes below.

lower energy level

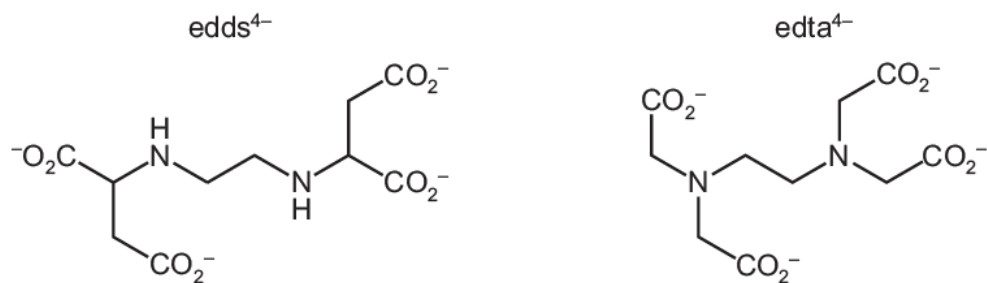


higher energy level



[2]

(c) Edds^{4-} and edta^{4-} are polydentate ligands that form octahedral complexes with $\text{Fe}^{3+}(\text{aq})$.



The formulae of the complexes are $[\text{Fe}(\text{edds})]^-$ and $[\text{Fe}(\text{edta})]^-$ respectively.

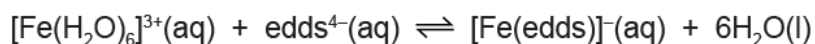
(i) On the diagram of edds^{4-} , circle each atom that forms a bond to the Fe^{3+} ion in $[\text{Fe}(\text{edds})]^-$.
[1]

(ii) $[\text{Fe}(\text{edds})]^-$ is red and $[\text{Fe}(\text{edta})]^-$ is yellow.

Explain why the two complexes have different colours.

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

(iii) When $\text{edds}^{4-}(\text{aq})$ is added to $\text{Fe}^{3+}(\text{aq})$, the following reaction occurs.



State the type of reaction that occurs.

..... [1]

(iv) Write an expression for the stability constant, K_{stab} , of $[\text{Fe}(\text{edds})]^{-}(\text{aq})$.

$$K_{\text{stab}} =$$

[1]

(v) The table shows the values for the stability constants, K_{stab} , of both complexes.

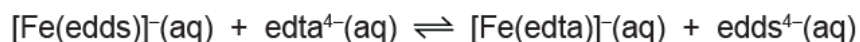
complex	$K_{\text{stab}} / \text{mol}^{-1} \text{dm}^3$
$[\text{Fe}(\text{edds})]^{-}$	3.98×10^{20}
$[\text{Fe}(\text{edta})]^{-}$	1.26×10^{25}

Predict which of the $[\text{Fe}(\text{edds})]^{-}$ and $[\text{Fe}(\text{edta})]^{-}$ complexes is more stable.

Explain your answer with reference to the K_{stab} value for each complex.

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

(vi) When an excess of $\text{edta}^{4-}(\text{aq})$ is added to $[\text{Fe}(\text{edds})]^{-}(\text{aq})$, the following equilibrium is established.



Calculate the equilibrium constant, K_{c} , for this equilibrium, using the K_{stab} values given in the table in (c)(v).

$$K_{\text{c}} = \dots\dots\dots [1]$$

[Total: 11]

(a) Explain why chromium complexes are coloured.

.....

.....

.....

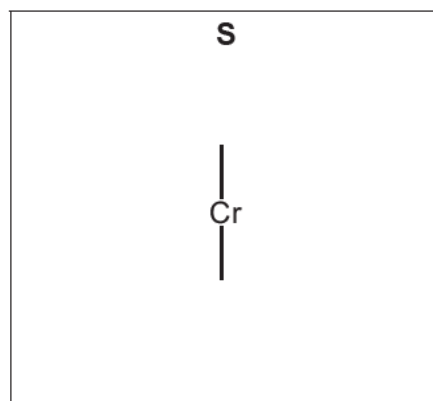
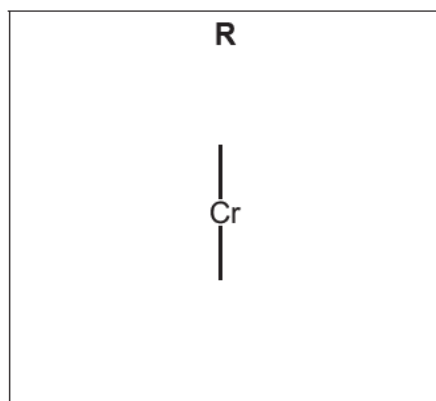
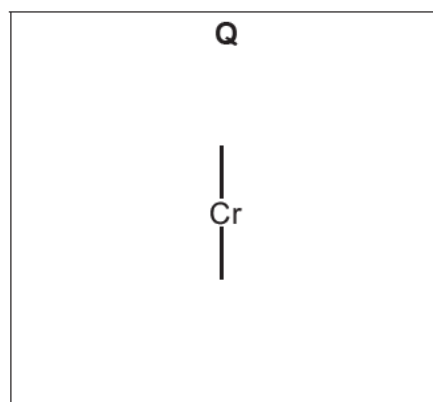
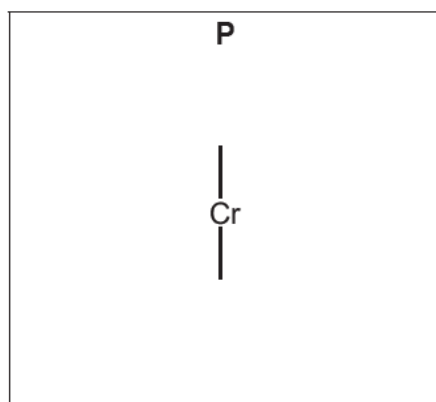
.....

..... [4]

(b) Four different compounds can be obtained when anhydrous chromium(III) chloride reacts with water under various conditions. When samples of each compound are reacted separately with aqueous silver nitrate, different amounts of silver chloride are precipitated. The precipitation leaves the complex ions **P**, **Q**, **R** and **S** in solution.

formula of compound	moles of AgCl precipitated per mole of complex ion	complex ion	property of complex ion
$\text{CrCl}_3(\text{H}_2\text{O})_6$	3	P	non-polar
$\text{CrCl}_3(\text{H}_2\text{O})_5$	2	Q	polar
$\text{CrCl}_3(\text{H}_2\text{O})_4$	1	R	polar
$\text{CrCl}_3(\text{H}_2\text{O})_4$	1	S	non-polar

- (i) Draw three-dimensional diagrams for the structures of complex ions **P**, **Q**, **R** and **S**. Include the charges for each complex ion.

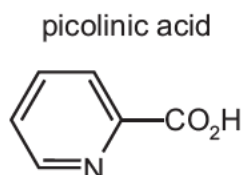


[4]

- (ii) Suggest why complex ion **S** is non-polar.

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

- (c) The structure of picolinic acid is shown.



The conjugate base of picolinic acid is a bidentate ligand, **Z**.

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

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

- (ii) Draw the structure of **Z**.

[1]

- (iii) **Z** reacts with aqueous chromium(III) ions, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, in a 3 : 1 ratio to form a new neutral complex.

State the coordination number and the geometry of the chromium(III) centre in the complex.

coordination number geometry [1]

- (d) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ decomposes readily on heating to form Cr_2O_3 , steam and an inert colourless gas.

- (i) Deduce the oxidation numbers of chromium in $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and in Cr_2O_3 .

$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ Cr_2O_3 [1]

- (ii) Construct an equation for the thermal decomposition of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

..... [1]

[Total: 15]

(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]

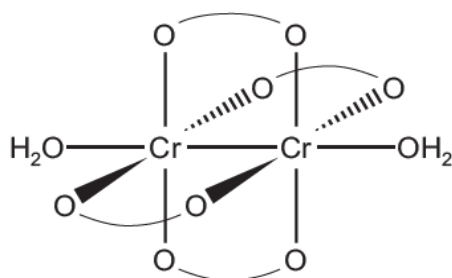
(c) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ are both complexes of chromium(II) and have different colours.

Explain why the colours of these complexes are different.

.....

 [2]

- (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]

- (e) The $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ complex reacts with aqueous acid to form $\text{Cr}^{2+}(\text{aq})$ ions.

$\text{Cr}^{2+}(\text{aq})$ ions react with $\text{O}_2(\text{aq})$ under acidic conditions. $\text{Cr}^{3+}(\text{aq})$ ions are formed.

Use the *Data Booklet* to answer the following questions.

- (i) Construct an ionic equation for the reaction of $\text{Cr}^{2+}(\text{aq})$ with $\text{O}_2(\text{aq})$ under acidic conditions.

..... [2]

- (ii) Calculate $E^\ominus_{\text{cell}}$ for the reaction in (e)(i).

$$E^\ominus_{\text{cell}} = \dots\dots\dots \text{V} \quad [1]$$

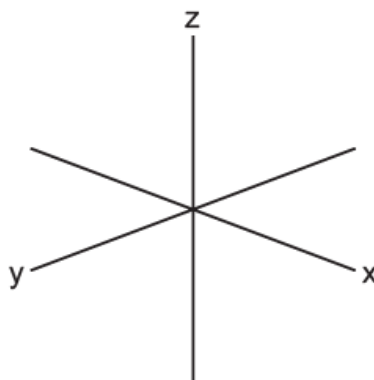
[Total: 15]

1. June/2022/Paper_41/No.2(a, b)

(a) Define transition element.

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

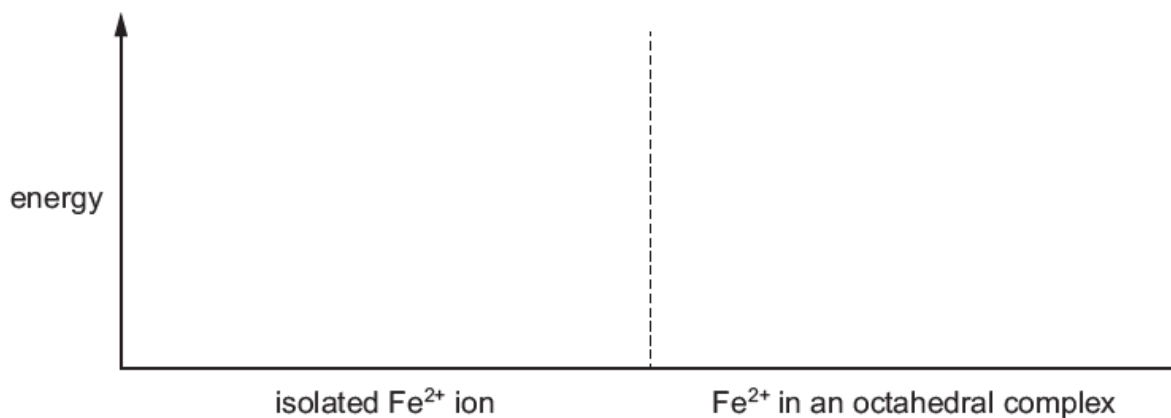
(b) Sketch the shape of a $3d_{z^2}$ orbital.



[1]

(a) The 3d orbitals in an isolated Fe^{2+} ion are degenerate.

Complete the diagram to show the splitting of the 3d orbital energy levels in an isolated Fe^{2+} ion and when Fe^{2+} forms an octahedral complex.



[2]

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

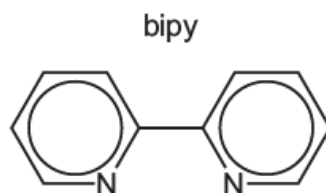


Fig. 4.1

Explain what is meant by bidentate ligand.

.....

.....

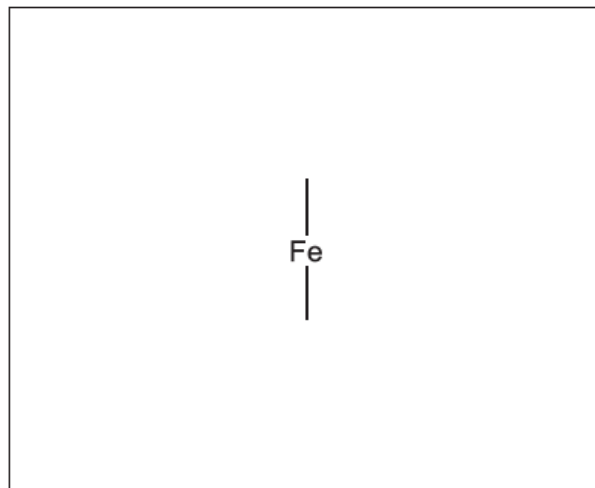
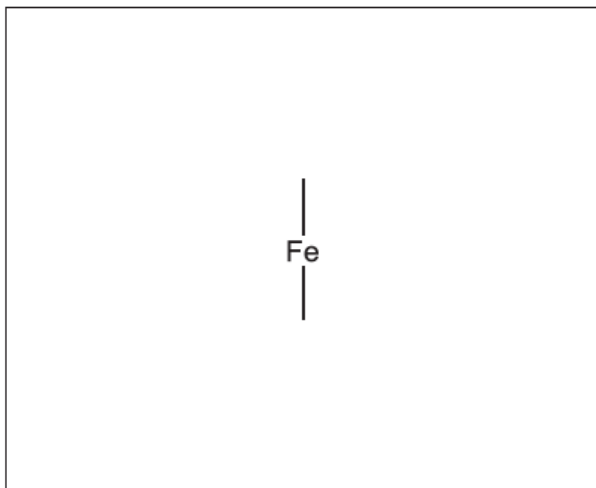
..... [2]

(ii) The complex $[\text{Fe}(\text{bipy})_3]^{2+}$ exists as two stereoisomers.

Complete the three-dimensional diagrams to show the two stereoisomers of $[\text{Fe}(\text{bipy})_3]^{2+}$.

State the type of stereoisomerism shown.

Use  to represent bipy in your diagrams.



type of stereoisomerism [3]

(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°/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]

- (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.

(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

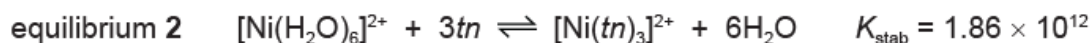
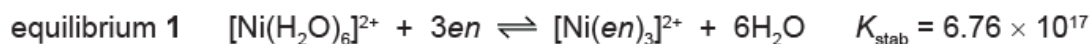
complex ion	shape	coordination number	polar or non-polar
<i>cis</i> - $[\text{Pt}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)\text{Cl}_2]$	square planar		
$[\text{Ag}(\text{NH}_3)_2]^+$			non-polar
$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$		6	

[2]

(e) (i) Define stability constant, K_{stab} .

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

(ii) Nickel can form complexes with the ligands *en*, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, and *tn*, $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, as shown.



Construct an expression for the stability constant, K_{stab} , for equilibrium 1.
State the units for K_{stab} .

$K_{\text{stab}} =$

units = ...
[2]

(iii) Describe what the K_{stab} values indicate about the position of equilibrium for equilibrium 1 and 2. Use the K_{stab} values to deduce which complex, $[\text{Ni}(\text{en})_3]^{2+}$ or $[\text{Ni}(\text{tn})_3]^{2+}$, is more stable.

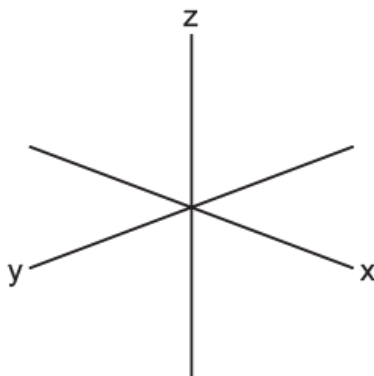
.....
..... [1]

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

.....

..... [1]

(b) Sketch the shape of a $3d_{xy}$ orbital.



[1]

(c) Explain why transition elements form coloured compounds.

.....

.....

.....

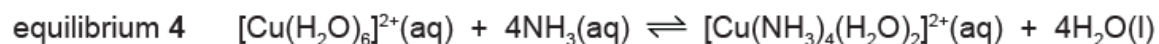
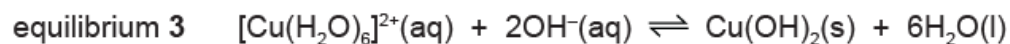
.....

.....

..... [3]

(d) Aqueous solutions of copper(II) salts contain $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions.

Equilibrium 3 and equilibrium 4 show two reactions of these ions.



(i) State the colour of $\text{Cu}(\text{OH})_2(\text{s})$ and $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$.

colour of $\text{Cu}(\text{OH})_2(\text{s})$

colour of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$

[1]

(ii) Use Le Chatelier's principle to explain why a precipitate is formed when $\text{NaOH}(\text{aq})$ is added dropwise to $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$.

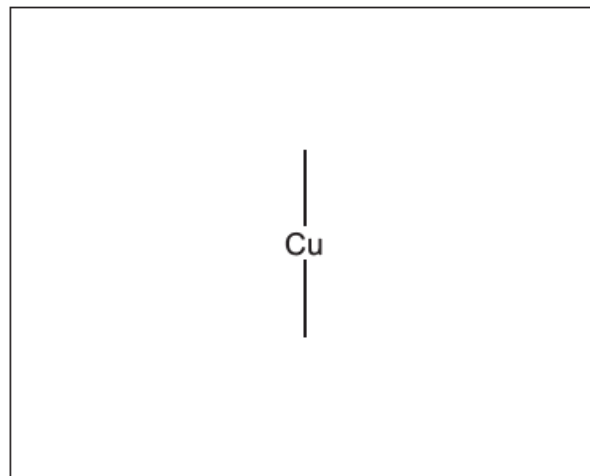
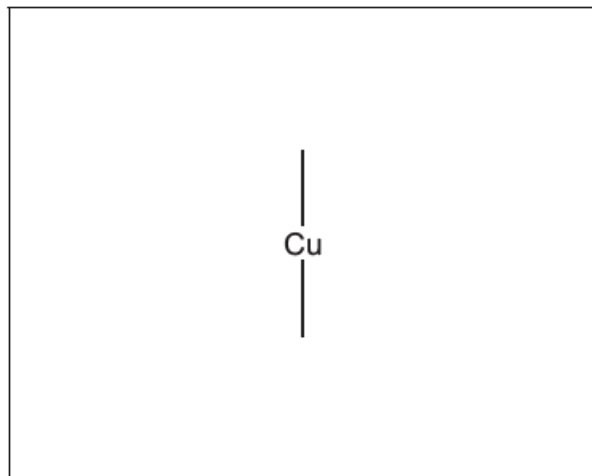
.....

.....

..... [1]

(e) There are two possible stereoisomers with the formula $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

Draw three-dimensional diagrams to show the two stereoisomers.



[2]

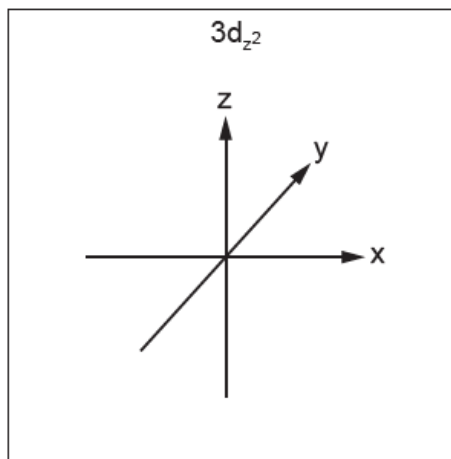
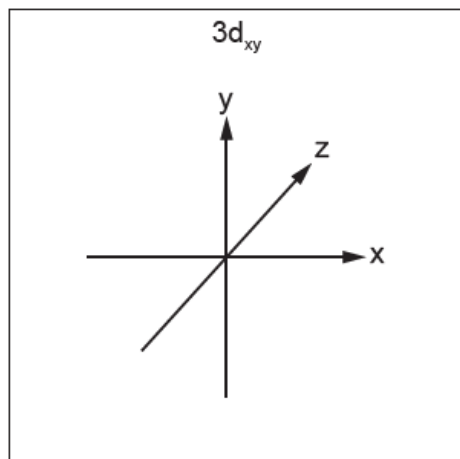
[Total: 9]

1. Nov/2022/Paper_41/No.5

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

- (a) Two of the 3d orbitals are the $3d_{xy}$ orbital and the $3d_{z^2}$ orbital.

Sketch the shapes of these two orbitals.



[1]

- (b) The Ni^{2+} ion forms many different complexes. A solution containing the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex ion is green. When an excess of 1,2-diaminoethane, *en*, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, is added, the colour of the solution changes to blue. This is due to the formation of the $[\text{Ni}(\text{en})_3]^{2+}$ complex ion.

- (i) Explain why the two solutions are coloured, and why the colours are different.

.....

.....

.....

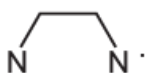
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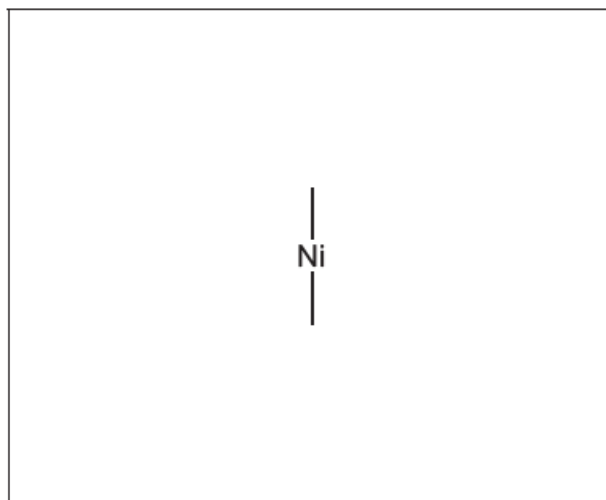
.....

..... [4]

(ii) The $[\text{Ni}(\text{en})_3]^{2+}$ complex can exist as a mixture of two stereoisomers.

Complete the three-dimensional diagram to show one of the stereoisomers.

Each *en* ligand can be represented using .



[1]

(iii) Name the geometry of the complex ion drawn in (b)(ii) and the type of stereoisomerism shown by $[\text{Ni}(\text{en})_3]^{2+}$.

geometry

stereoisomerism shown

[1]

(c) Iron(II) carbonate, FeCO_3 , and nickel(II) carbonate, NiCO_3 , both decompose when heated.

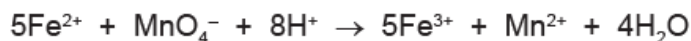
FeCO_3 decomposes at a lower temperature than NiCO_3 .

Suggest a possible reason for this difference. Explain your answer.

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

- (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]

[Total: 12]

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 .

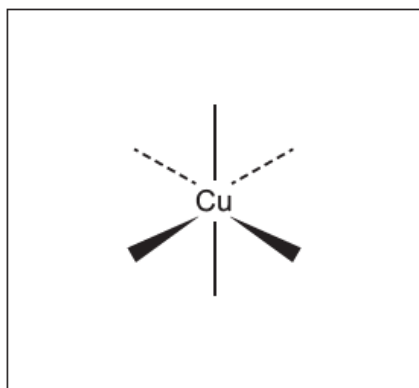
..... [1]

- (b) If an excess of ammonia is added to a solution of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ a deep blue solution containing $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ complex ions is formed.

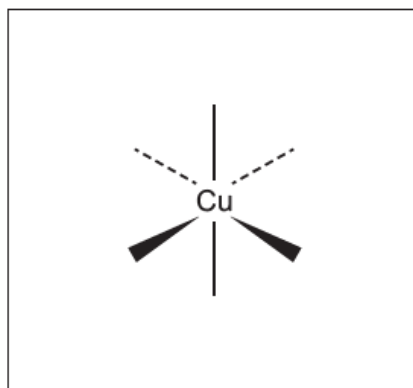
- (i) There are two possible stereoisomers with the formula $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

Complete the diagrams to show the two stereoisomers in the boxes below.

isomer 1



isomer 2



[1]

- (ii) Use your answer in (b)(i) to deduce whether each of these isomers is polar or non-polar.

polarity of isomer 1

polarity of isomer 2

[1]

- (c) The numerical value of the stability constant, K_{stab} , of the $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ complex ion is 1.40×10^{13} .

- (i) Define stability constant.

.....

..... [1]

- (ii) Compare the stabilities of the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ complex ions. Explain your answer.

.....
 [1]

- (iii) Write an expression for the stability constant, K_{stab} , of the $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ complex ion. State the units of the stability constant.

$$K_{\text{stab}} =$$

units = ...
 [2]

- (iv) In a particular solution the concentration of the $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ complex ion is $0.0074 \text{ mol dm}^{-3}$ and the concentration of NH_3 is 0.57 mol dm^{-3} .

Use your expression in (c)(iii) and the K_{stab} value of 1.40×10^{13} to calculate the concentration of the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ion in this solution.

concentration of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} = \dots\dots\dots \text{mol dm}^{-3}$ [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]

[Total: 11]

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

(a) Define transition element.

.....
 [1]

(b) An aqueous solution of copper(II) sulfate, CuSO_4 , contains $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ions. If an excess of concentrated hydrochloric acid is added to this solution a ligand exchange reaction occurs and $[\text{CuCl}_4]^{2-}$ complex ions are formed.

(i) Complete Table 5.1 to state the geometry, the coordination number of copper, and one bond angle in each of the two complex ions.

Table 5.1

complex ion	geometry	coordination number	bond angle
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$			
$[\text{CuCl}_4]^{2-}$			

[3]

(ii) In an isolated Cu^{2+} ion the d-orbitals are all degenerate. In a complex ion such as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ the d-orbitals are non-degenerate.

Define degenerate and non-degenerate in this context.

degenerate

non-degenerate

[1]

(iii) Explain why the solutions of the two complex ions in Table 5.1 are **different** colours.

.....
 [1]

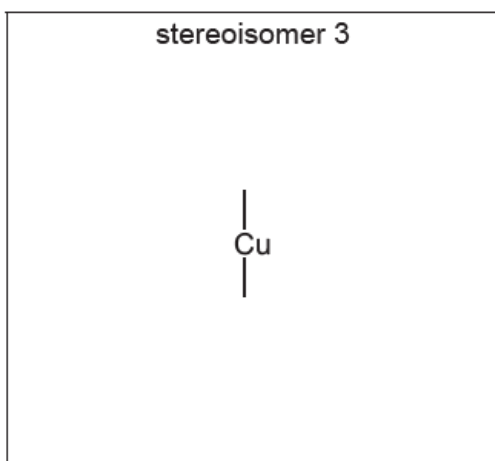
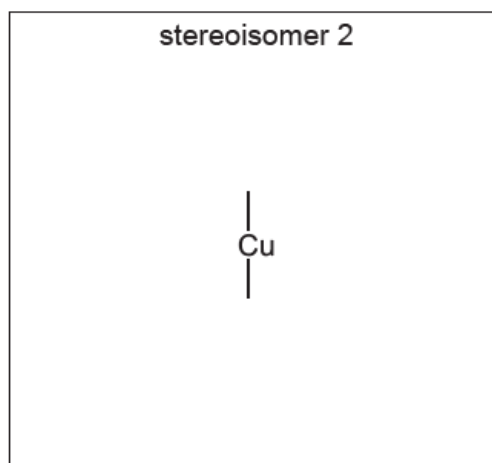
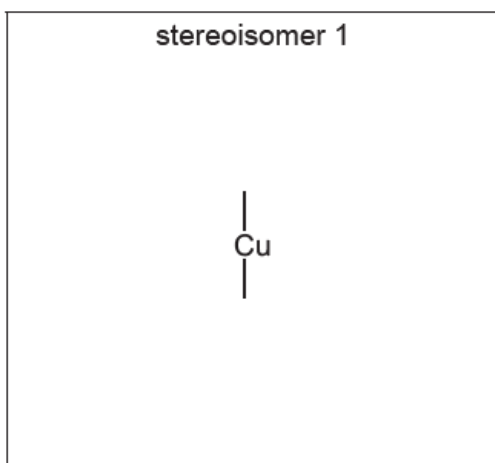
(c) Cu^{2+} forms a complex ion containing water molecules and ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, as ligands. The formula of the complex is $[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$. The ethanedioate ion is a bidentate ligand.

(i) Explain what is meant by bidentate.

.....
 [1]

(ii) There are three stereoisomers with the formula $[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$.

Complete the three-dimensional diagrams to show these three stereoisomers.



[2]

(iii) Use your answer to (c)(ii) to answer this question.

Stereoisomers 1, 2 and 3 show two different types of isomerism.

Name these two types of isomerism.

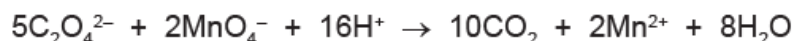
For each type of isomerism identify the pair of stereoisomers that demonstrate this isomerism.

type of isomerism	pair of stereoisomers
	and
	and

[2]

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

The equation for the redox reaction is shown.



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

- (e) Copper(II) nitrate, $\text{Cu}(\text{NO}_3)_2$, and barium nitrate, $\text{Ba}(\text{NO}_3)_2$, both decompose when heated.

Copper(II) nitrate decomposes at a lower temperature than barium nitrate.

Suggest a reason for this difference. Explain your answer.

.....

 [2]

[Total: 16]

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]

- (b) (i) Define stability constant.

.....

..... [1]

- (ii) Write an expression for the stability constant, K_{stab} , of the $[\text{Co}(\text{NH}_3)_6]^{2+}$ complex ion.

$$K_{\text{stab}} =$$

[1]

- (iii) Give the units of the stability constant, K_{stab} , of the $[\text{Co}(\text{NH}_3)_6]^{2+}$ complex ion.

units = ... [1]

- (iv) The numerical value of the stability constant, K_{stab} , of the $[\text{Co}(\text{NH}_3)_6]^{2+}$ complex ion is 7.7×10^4 .

In an aqueous solution the concentration of the $[\text{Co}(\text{NH}_3)_6]^{2+}$ complex ion is $0.0740 \text{ mol dm}^{-3}$ and the concentration of NH_3 is $0.480 \text{ mol dm}^{-3}$ at equilibrium.

Calculate the concentration of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ in this solution.

concentration = ... mol dm^{-3} [1]

[Total: 8]

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

(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]

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 $[\text{Ag}(\text{CN})_2]^-$.

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 $[\text{TiCl}_4(\text{diars})_2]$.

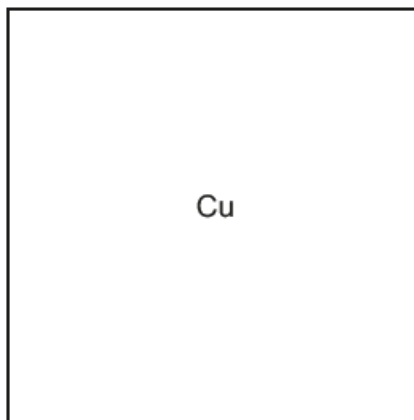
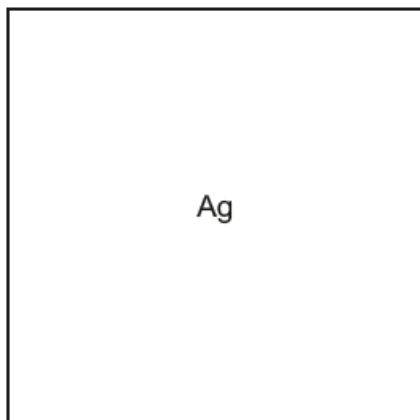
oxidation state

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]

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

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

$$K_{\text{stab}} =$$

[1]

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

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

concentration of $\text{Cu}^+(\text{aq}) = \dots\dots\dots \text{mol dm}^{-3}$ [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.

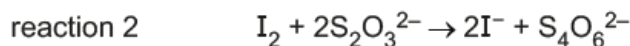
An excess of $\text{KI}(\text{aq})$ is added to a 25.0 cm^3 sample of this solution.

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 $\text{I}_2 = \dots\dots\dots \text{mol}$ [1]

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

number of moles of copper = $\dots\dots\dots \text{mol}$ [1]

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

percentage of copper = $\dots\dots\dots \%$ [1]

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

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

[Total: 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]

- (b) Nickel forms the octahedral complex $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$. 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]

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

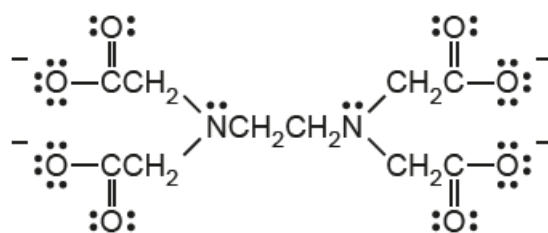


Fig. 4.1

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}

(a) Define stability constant.

.....
 [1]

(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]

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

.....
 [1]

- (e) In a solution at equilibrium at 298 K, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} = 3.00 \times 10^{-10} \text{ mol dm}^{-3}$ and $[\text{EDTA}^{4-}] = 5.00 \times 10^{-12} \text{ mol dm}^{-3}$.

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

Show your working.

$$[\text{Cu}(\text{EDTA})]^{2-} = \dots\dots\dots \text{ mol dm}^{-3} \quad [2]$$

- (f) A solution of $[\text{Cu}(\text{EDTA})]^{2-}$ ions is pale blue while a solution of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ ions is deep blue.

Explain this difference in colour.

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

[Total: 8]

(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 $[\text{Au}(\text{dien})(\text{H}_2\text{O})_2\text{Cl}]^{2+}$ and $\text{Au}(\text{dien})\text{Cl}_3$.

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

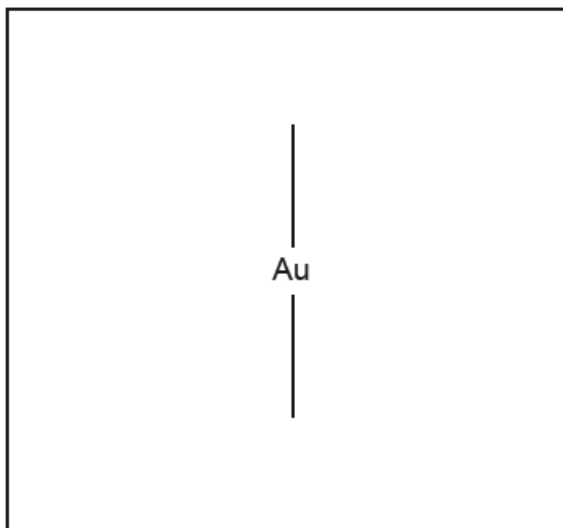
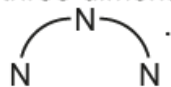
formula	isomerism shown	geometry
$[\text{Rh}(\text{en})_2\text{Cl}_2]^+$	yes	
$[\text{Rh}(\text{CO})_2\text{Cl}_2]^+$	yes	
$[\text{Au}(\text{dien})(\text{H}_2\text{O})_2\text{Cl}]^{2+}$		
$\text{Au}(\text{dien})\text{Cl}_3$	no	octahedral
$\text{Ni}(\text{PH}_3)_2\text{Cl}_2$	no	
$[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$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

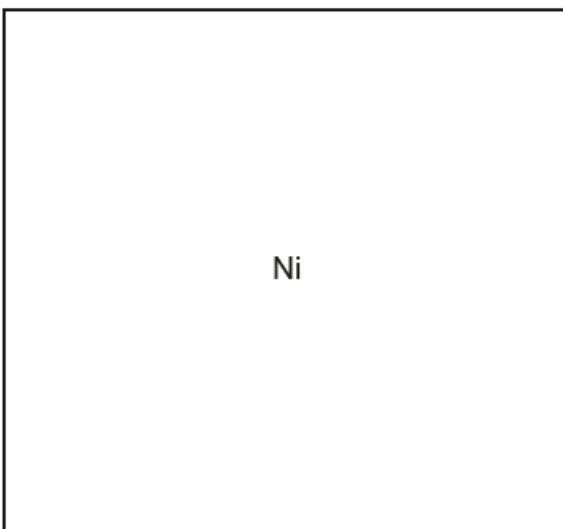
..... [1]

- (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.

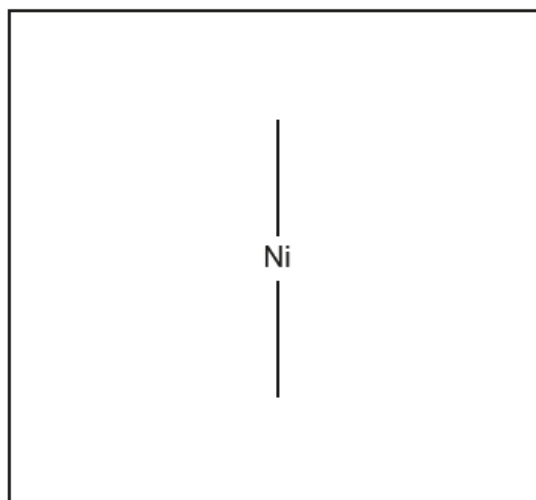
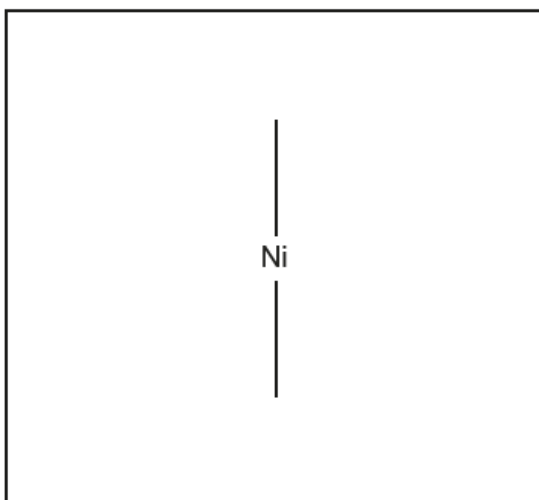


[1]

- (v) One of the complexes, $[\text{Rh}(\text{en})_2\text{Cl}_2]^+$ or $[\text{Rh}(\text{CO})_2\text{Cl}_2]^+$, 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 $[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$ in the boxes and identify the type of isomerism shown.



type of isomerism shown

[2]

[Total: 10]

(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 $\text{Cu}(\text{NO}_3)_2$.

..... [1]

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

Fig. 1.1 shows some reactions of solution A.

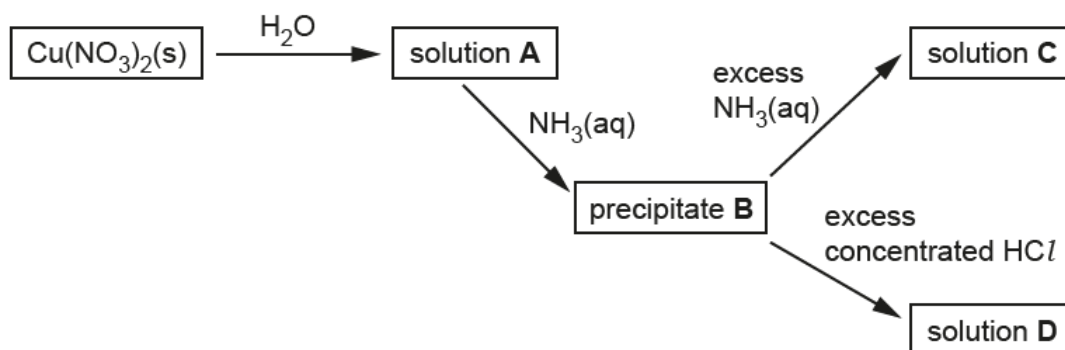


Fig. 1.1

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]

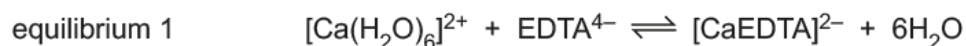
(d) EDTA^{4-} is a polydentate ligand.

(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.

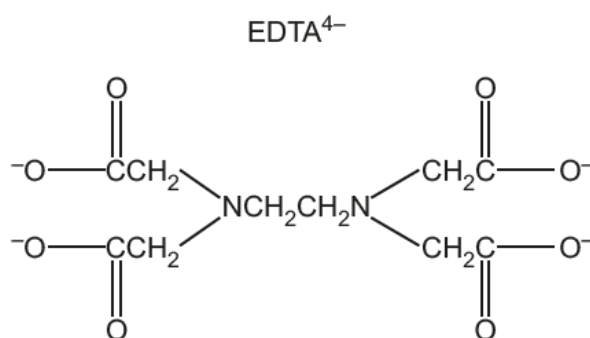


Fig. 1.2

[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]

- (iv) The complex $[\text{CaEDTA}]^{2-}$ 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}
$[\text{CaEDTA}]^{2-}$	5.0×10^{10}
$[\text{CrEDTA}]^{-}$	2.5×10^{23}
$[\text{FeEDTA}]^{-}$	1.3×10^{25}
$[\text{PbEDTA}]^{2-}$	1.1×10^{18}

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

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

..... [1]

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

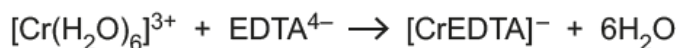
Explain your answer.

..... > >
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, $\text{Cr}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, 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]

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

Explain why the two complexes have different colours.

.....

.....

.....

..... [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 $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ 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]

- (c) The complex $[\text{Cr}(\text{en})_3]^{2+}$ exists as two stereoisomers whereas the complex $[\text{Cr}(\text{OCH}_2\text{CH}_2\text{NH}_2)_3]^-$ exists as four stereoisomers.

Complete the three-dimensional diagrams in Fig. 2.1 to show the four stereoisomers of $[\text{Cr}(\text{OCH}_2\text{CH}_2\text{NH}_2)_3]^-$.

Represent the ligand $^-\text{OCH}_2\text{CH}_2\text{NH}_2$ by using .

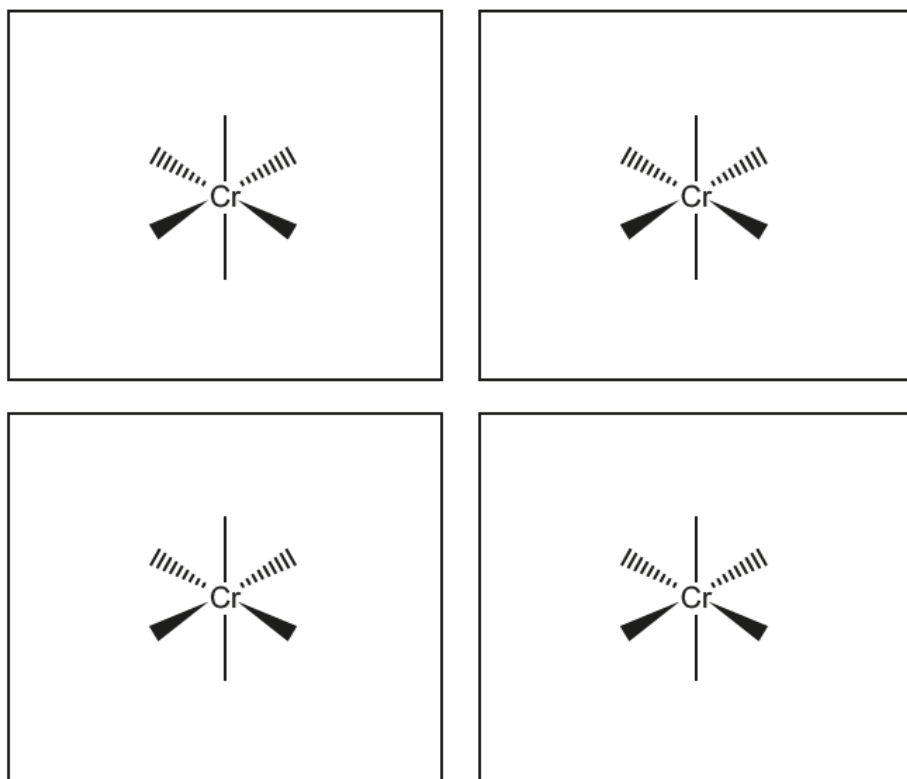


Fig. 2.1

[3]

- (d) The complex $[\text{Cr}(\text{OCH}_2\text{CH}_2\text{NH}_2)_3]^-$ is formed by reacting $\text{Cr}^{2+}(\text{aq})$ with the conjugate base of 2-aminoethanol.

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

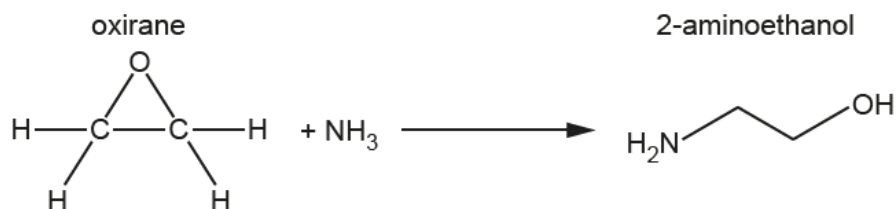


Fig. 2.2

- (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.

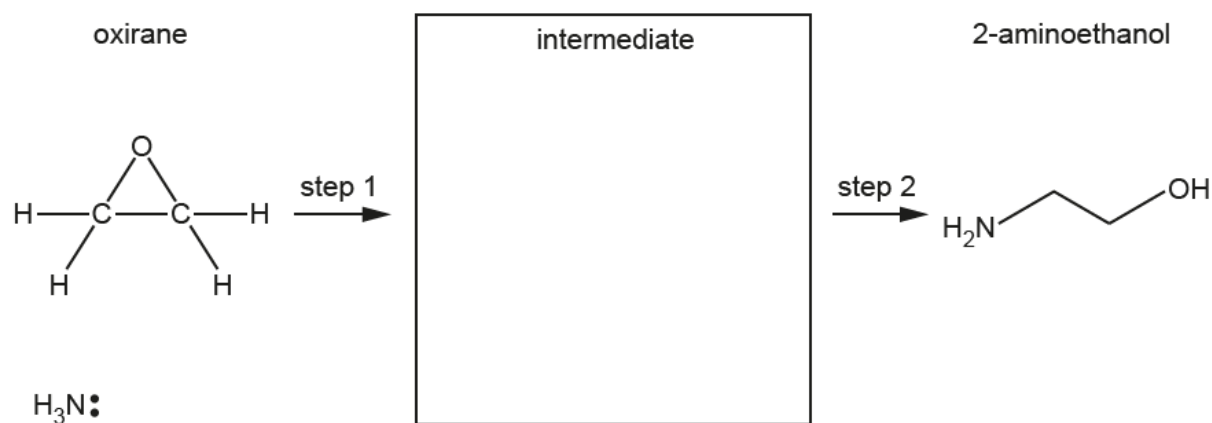


Fig. 2.3

[3]

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

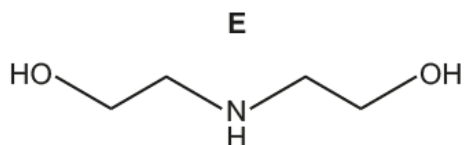


Fig. 2.4

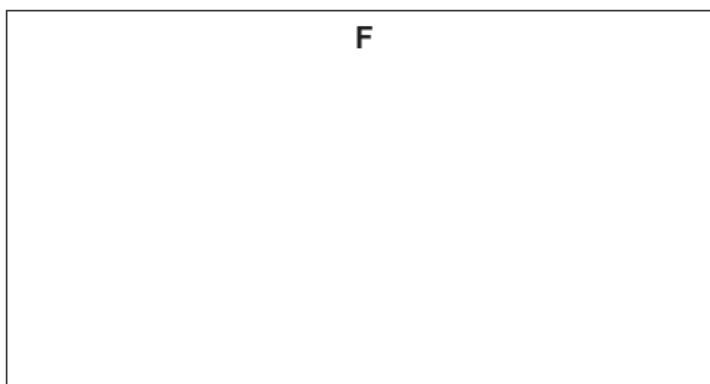
Suggest how the formation of by-product **E** can be minimised.

.....
..... [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**.



type of reaction [2]

[Total: 11]

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

1

2 [1]

(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.

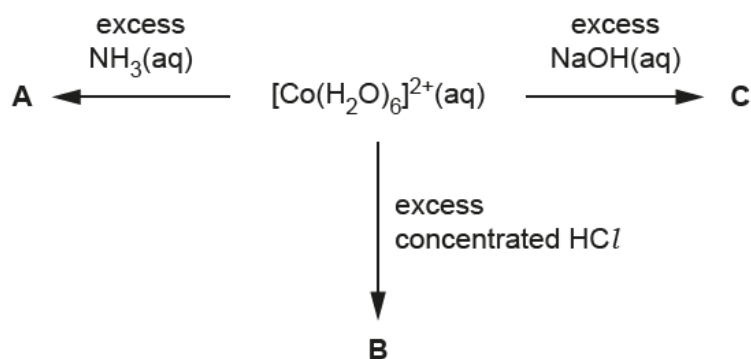


Fig. 2.1

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]

(ii) The complex $[\text{Co}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)\text{BrCl}]^-$ exists as stereoisomers.

Complete the three-dimensional diagrams in Fig. 2.2 to show **four** stereoisomers of $[\text{Co}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)\text{BrCl}]^-$.

The $\text{C}_2\text{O}_4^{2-}$ ligand is represented using $\text{O} \text{---} \text{O}$.

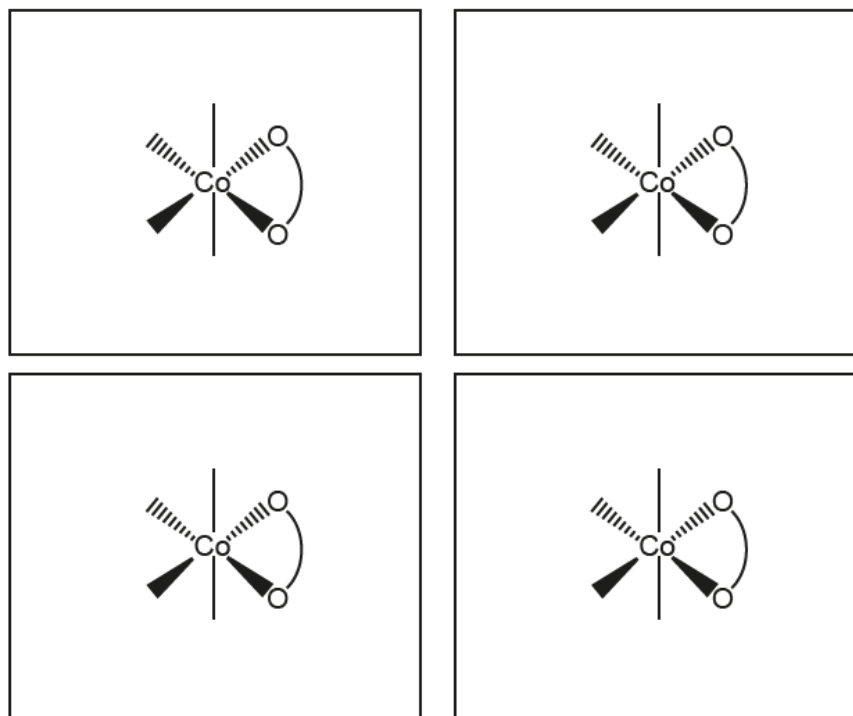


Fig. 2.2

[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]

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.

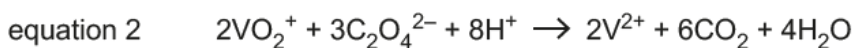
(i) State **two** other typical chemical properties of transition elements.

1
2
[1]

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

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

(c) VO_2^+ can be reduced to V^{2+} by $\text{C}_2\text{O}_4^{2-}$ in acidic conditions.



- (i) In a titration, 25.00 cm^3 of $0.0300\text{ mol dm}^{-3}$ $\text{VO}_2^+(\text{aq})$ is added to 10 cm^3 of dilute sulfuric acid.

A solution of $0.0400\text{ mol dm}^{-3}$ $\text{C}_2\text{O}_4^{2-}(\text{aq})$ 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 $\text{C}_2\text{O}_4^{2-}(\text{aq})$ added/ cm^3	28.15	28.10

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

[2]

- (ii) An excess of $\text{C}_2\text{O}_4^{2-}$ 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 $\text{C}_2\text{O}_4^{2-}$ ions.

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

Include the charge of the complex ion.

Use $\text{O} \text{---} \text{O}$ to represent a $\text{C}_2\text{O}_4^{2-}$ 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]

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

(i) Define monodentate ligand.

.....

 [2]

(ii) $\text{Cu}^{2+}(\text{aq})$ reacts with CH_3NH_2 to form $[\text{Cu}(\text{CH}_3\text{NH}_2)_2(\text{H}_2\text{O})_4]^{2+}$.

Draw three-dimensional diagrams to show the two geometrical isomers of $[\text{Cu}(\text{CH}_3\text{NH}_2)_2(\text{H}_2\text{O})_4]^{2+}$.

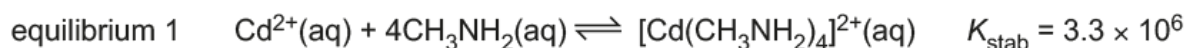


[2]

(iii) State the coordination number of copper in $[\text{Cu}(\text{CH}_3\text{NH}_2)_2(\text{H}_2\text{O})_4]^{2+}$.

..... [1]

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



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

..... [1]

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

$$K_{\text{stab}} =$$

[1]

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

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

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

Use your expression in (f)(ii) to calculate the concentration of $\text{CdCl}_4^{2-}(\text{aq})$ in the equilibrium mixture.

$$[\text{CdCl}_4^{2-}(\text{aq})] = \dots\dots\dots \text{ mol dm}^{-3} \quad [1]$$

- (iv) When $\text{CH}_3\text{NH}_2(\text{aq})$ is added to $\text{Cd}^{2+}(\text{aq})$, a mixture of $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}(\text{aq})$ and $[\text{Cd}(\text{OH})_4]^{2-}(\text{aq})$ forms.

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

.....
 [1]

- (v) $\text{Cd}^{2+}(\text{aq})$ exists as a complex ion, $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$.

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
$[\text{Cd}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$		
$[\text{Cd}(\text{OH})_4]^{2-}(\text{aq})$		
$[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}(\text{aq})$		
$[\text{CdCl}_4]^{2-}(\text{aq})$		

explanation

 [2]