

- 5 (a) Copper shows typical properties of transition elements, including its behaviour as a catalyst.

Complete Table 5.1 to show the total number of **unpaired** electrons in the 3d and 4s orbitals of an isolated gaseous Cu atom and a Cu^{2+} ion.

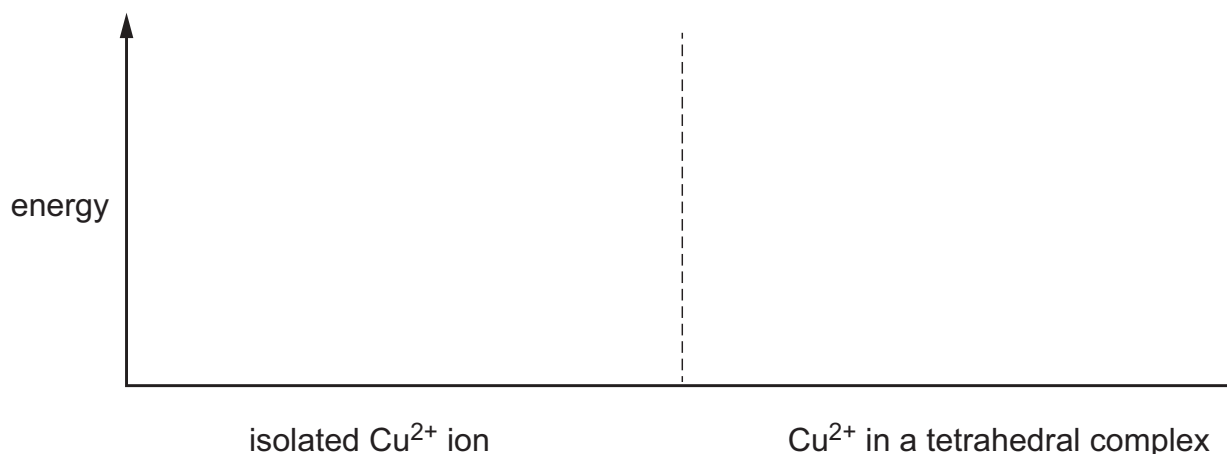
Table 5.1

species	number of unpaired electrons	
	3d	4s
Cu		
Cu^{2+}		

[1]

- (b) The 3d orbitals in an isolated Cu^{2+} ion are degenerate.

Complete the diagram to show the relative energies of the 3d orbitals in an isolated Cu^{2+} ion and in Cu^{2+} in a tetrahedral complex.



[2]

- (c) Explain why transition elements behave as catalysts.

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

(d) CN^- is a monodentate ligand.

Table 5.2 shows information about two complex ions that contain only CN^- ions as ligands.

Complete Table 5.2.

Table 5.2

metal ion	coordination number	formula of complex ion	charge of complex ion
Ag^+	2		
Fe^{2+}			4-

[2]

(e) The complex ion $[\text{Au}(\text{CN})_2\text{Br}_2]^-$ displays geometrical (cis/trans) isomerism.

Draw the structure of *trans*- $[\text{Au}(\text{CN})_2\text{Br}_2]^-$. State its shape and the Br-Au-Br bond angle.

shape

Br-Au-Br bond angle =

[2]

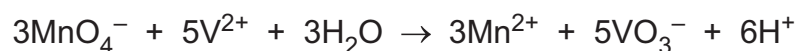
- (f) An impure sample of a vanadium(V) compound of mass 0.250 g is dissolved in aqueous acid. This solution contains VO_3^- ions.

An excess of zinc is added to this solution. All the VO_3^- ions are reduced to V^{2+} ions and Zn atoms are oxidised to Zn^{2+} ions.

The unreacted zinc is removed and the resulting solution is titrated with acidified MnO_4^- .

The end-point is reached when 22.5 cm^3 of $0.0750 \text{ mol dm}^{-3} \text{ MnO}_4^-$ is added.

A redox reaction takes place and all the V^{2+} reacts forming VO_3^- .



- (i) Calculate the percentage by mass of vanadium in the 0.250 g of impure sample.

Assume the impurities do not contain any vanadium ions.

Show your working.

percentage of vanadium = [3]

- (ii) Complete the equation for the reaction between acidified VO_3^- ions and Zn metal.



[2]

[Total: 14]

6 (a) Nickel forms complexes.

- (i) Give the formula and charge of the tetrahedral complex formed by Ni atoms with carbon monoxide molecules. Carbon monoxide is a monodentate ligand. This is complex **E**.

E = [1]

- (ii) Give the formula and charge of the octahedral complex formed by Ni^{2+} ions with ethanedioate ions. This is complex **F**.

F = [2]

- (iii) Identify which complex, **E** or **F**, exists as a mixture of two stereoisomers and the type of stereoisomerism involved.

The complex which exists as a mixture of two stereoisomers is

The type of stereoisomerism involved is

[1]

- (b) Cadmium forms complexes with methylamine, CH_3NH_2 , and 1,2-diaminoethane, *en*. The values of the stability constants, K_{stab} , of these complex ions are given in Table 6.1.

Table 6.1

complex	K_{stab}
$[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$	3.5×10^6
$[\text{Cd}(\text{en})_2]^{2+}$	4.0×10^{10}

- (i) Explain, by reference to its structure, why CH_3NH_2 acts as a monodentate ligand.

..... [1]

- (ii) Some $\text{Cd}^{2+}(\text{aq})$ is added to a solution containing equal concentrations of CH_3NH_2 and *en*.

Predict which of the two complexes in Table 6.1 forms at the higher concentration.

Explain your answer.

complex that forms at the higher concentration

explanation

..... [1]

- (iii) Complete the expression for the K_{stab} of $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$.

$K_{\text{stab}} =$

[1]

1 (a) Define a transition element.

.....

 [1]

(b) The 3d orbitals in an isolated gaseous Cu^{2+} ion are degenerate.

(i) Define the term degenerate.

.....
 [1]

(ii) Complete the electronic configuration of Cu^{2+} .

$1s^2$ [1]

(c) (i) State the colours of the aqueous solutions for the **two** copper(II) complex ions shown.

- $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$
- $[\text{CuCl}_4]^{2-}(\text{aq})$ [1]

(ii) Explain why aqueous complex ions of transition elements are usually coloured.

.....

 [3]

(d) (i) When an excess of $\text{NH}_3(\text{aq})$ is added to a solution of $[\text{CuCl}_4]^{2-}(\text{aq})$, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$ is formed.

State the type of reaction.

Complete the equation for this reaction. State symbols are **not** required.

type of reaction

equation

$[\text{CuCl}_4]^{2-} + \dots\dots\dots \rightarrow [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + \dots\dots\dots$

- (ii) The $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ complex ion shows stereoisomerism.

Complete the three-dimensional diagrams in Fig. 1.1 to show the **two** different stereoisomers of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

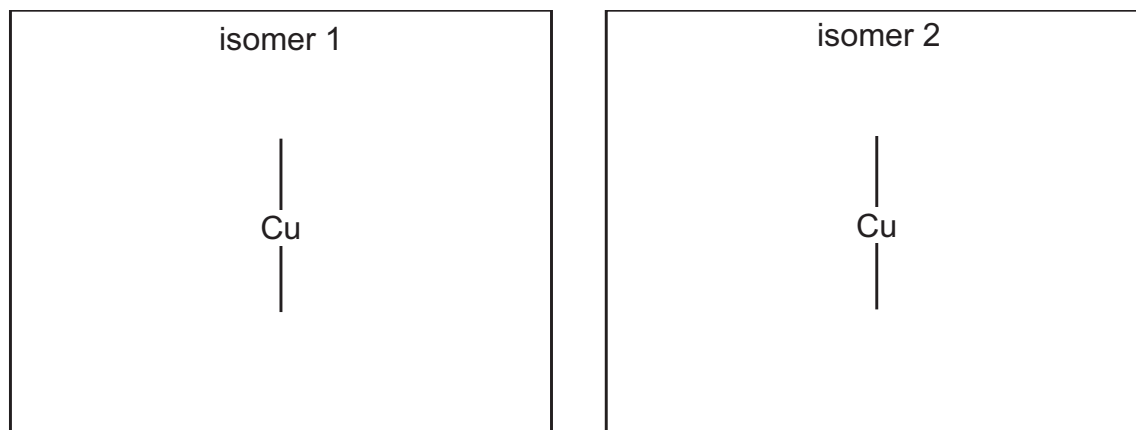


Fig. 1.1

[2]

- (iii) Deduce which stereoisomer in (d)(ii) is polar.

Explain your answer.

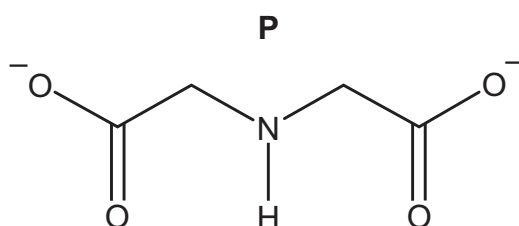
polar isomer

explanation

.....

[1]

- (e) The dianion **P** can act as a tridentate ligand.



- (i) Suggest how **P** can form **three** dative covalent bonds.

.....

.....

..... [1]

- (ii) 2 moles of dianion **P**, $\text{C}_4\text{H}_5\text{NO}_4^{2-}$, react with 1 mole of aqueous cobalt(III) ions, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ to form 1 mole of complex ion **Q**.

Deduce the formula and charge of **Q**.

..... [1]

- (f) Table 1.1 shows values for the stability constants, K_{stab} , of some silver(I) complexes.

Table 1.1

complex	value of K_{stab}
$[\text{Ag}(\text{CN})_2]^{-}(\text{aq})$	1.1×10^{18}
$[\text{Ag}(\text{NH}_3)_2]^{+}(\text{aq})$	1.2×10^7
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}(\text{aq})$	2.9×10^{13}

- (i) Define the stability constant of a complex.

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

- (ii) Use the information in Table 1.1 to identify the most stable silver(I) complex.

Explain your answer.

most stable

explanation

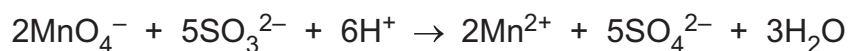
..... [1]

(g) Sodium sulfite, Na_2SO_3 , is used as a food preservative.

A 3.75 g sample of impure Na_2SO_3 is dissolved in distilled water and made up to 250 cm^3 in a volumetric flask.

10.0 cm^3 of this solution requires 18.70 cm^3 of acidified $0.0150\text{ mol dm}^{-3}$ MnO_4^- (aq) to reach the end-point.

The equation for the reaction is shown.



Calculate the percentage by mass of Na_2SO_3 in the sample.

percentage by mass of Na_2SO_3 = [3]

[Total: 19]