Week 41

A-Level Chemistry

Homework bundle for this week

本周作业合集

exercises.lol

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A-Level Chemistry Name: _____ Score: _____

1. A transition element is a d-block element that:
   - ☐ forms one or more stable ions with incomplete d orbitals
   - ☐ has a full d sub-shell in all its ions
   - ☐ is in the s-block
   - ☐ never forms ions
2. A ligand bonds to a metal ion by:
   - ☐ donating a lone pair in a dative covalent bond
   - ☐ transferring an electron
   - ☐ sharing one electron each
   - ☐ forming an ionic bond
3. Ligand exchange is when:
   - ☐ one ligand replaces another on the metal ion (often a colour change)
   - ☐ the metal ion changes oxidation state
   - ☐ electrons are transferred
   - ☐ the complex is destroyed
4. In a free transition-metal ion, the five d orbitals are:
   - ☐ degenerate (the same energy)
   - ☐ all different energies
   - ☐ split into two sets
   - ☐ empty
5. Geometrical (cis/trans) isomerism in $[Pt(NH_3)_2Cl_2]$ means the two identical ligands are:
   - ☐ adjacent (cis) or opposite (trans)
   - ☐ always opposite
   - ☐ mirror images
   - ☐ removed
6. Transition-metal complexes can show both geometrical and optical isomerism.

   ☐ True ☐ False

7. The equilibrium constant for the formation of a complex from its aqua ion is the _____ constant.

_____

8. A transition element forms at least one ion with an incomplete _____ subshell.

_____

9. A molecule or ion that donates a lone pair to a central metal ion is a _____.

_____

10. In ligand exchange, one ligand is replaced by another around the central metal ion.

☐ True ☐ False

28. Chemistry of transition elements

Answers · 答案

A-Level Chemistry

1. **forms one or more stable ions with incomplete d orbitals**

   The incomplete d orbitals (in a stable ion) define a transition element.

2. **donating a lone pair in a dative covalent bond**

   A ligand donates a lone pair to the metal's vacant orbital — a dative (coordinate) bond.

3. **one ligand replaces another on the metal ion (often a colour change)**

   Swapping a ligand for another changes the complex and usually its colour.

4. **degenerate (the same energy)**

   They are degenerate until ligands approach and split them into two sets.

5. **adjacent (cis) or opposite (trans)**

   In a square planar complex the matching ligands sit next to each other (cis) or across (trans).

6. **True**

   Square planar/octahedral complexes show cis/trans; octahedral ones with bidentate ligands show optical isomerism.

7. **stability**

   A larger value means a more stable complex.

8. **d**

   This gives variable oxidation states and colour.

9. **ligand**

   It forms a coordinate bond to the metal.

10. **True**

    It can change the complex's colour.

A-LEVEL CHEMISTRY • EXERCISE SHEET

28.1 General properties of the transition elements

Name: _____ Class: _____ Date: _____ **Total: 32 marks**

KEY WORDS transition element 过渡元素 • complex 配合物 • complex ion 配离子 • oxidation state 氧化态 • catalyst 催化剂

Objective

Build the skills to answer exam questions on **transition elements** 过渡元素 — the definition and the four characteristic properties.

You must be able to:

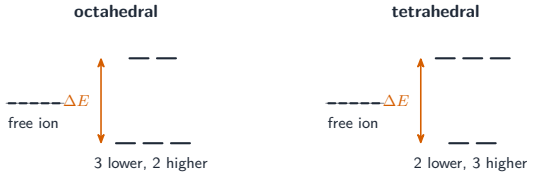
- define a transition element and explain why Sc and Zn are excluded
- state the four key properties (variable oxidation state, catalysis, complexes, colour) and why

1 Worked examples

What a transition element is

A **transition element** is a d-block element that forms one or more stable ions with **incomplete d orbitals**. (Sc and Zn are excluded: their stable ions have empty or full d orbitals.)

Coloured compounds are one of the four characteristic properties of transition elements



the complex absorbs light of energy ΔE, so we see the **complementary colour**

d-orbital splitting explains colour and variable oxidation states

property	reason
variable **oxidation state**	the 3d and 4s sub-shells are close in energy
act as a **catalyst**	more than one oxidation state; vacant d orbitals form dative bonds
form **complex ions**	vacant d orbitals accept lone pairs
coloured compounds	electrons move between split d orbitals

The definition, and the four properties that follow from it

A **transition element** 过渡元素 is a d-block element that forms **one or more stable ions with a partially filled d sub-shell**. The definition matters because it is what excludes **scandium** (its only stable ion, Sc^{3+}, is $3d^0$) and **zinc** (its only stable ion, Zn^{2+}, is $3d^{10}$) — both are d-block, neither is a transition element.

The electronic configurations, with the two exceptions the exam always asks for:

- Fill 4s before 3d: Fe is $[Ar]\,3d^6 4s^2$.
- **Chromium** is $[Ar]\,3d^5 4s^1$ and **copper** is $[Ar]\,3d^{10} 4s^1$ — a half-filled or filled d sub-shell is more stable than the expected arrangement.
- △ When an ion forms, the **4s electrons are lost FIRST**: Fe^{2+} is $3d^6$, not $3d^4 4s^2$.

The four characteristic properties, each with its reason — the reason is always the mark:

Property	Why
variable oxidation states	the 4s and 3d sub-shells are close in energy, so different numbers of electrons can be lost for a similar energy cost
coloured compounds	ligands split the d orbitals into two energy levels; an electron absorbs a photon of visible light to jump the gap, and the colour seen is the complement of the light absorbed
catalytic activity	variable oxidation states let the metal accept and donate electrons in a redox cycle (homogeneous), or its d orbitals adsorb reactants onto a surface at the right strength (heterogeneous)
complex ion formation	the ion is small and highly charged with vacant d orbitals, so it accepts lone pairs from ligands into dative bonds

Worked example. Explain why a solution of $[Cu(H_2O)_6]^{2+}$ is blue but $[Zn(H_2O)_6]^{2+}$ is colourless. In the copper complex the ligands split the 3d orbitals and the Cu^{2+} ion has a partially filled d sub-shell ($3d^9$), so an electron can be promoted across the gap by absorbing visible light; the complementary colour is transmitted, and the solution looks blue. Zn^{2+} is $3d^{10}$ — the sub-shell is full, there is no vacancy to promote an electron into, no visible light is absorbed, and the solution is colourless.

2 Practice

2.1 Define a **transition element**. [2]

2.2 State the four characteristic properties of transition elements. [2]

2.3 Give the electronic configuration of a Cr atom and of a Fe^{3+} ion. [2]

2.4 Iron forms stable Fe^{2+} and Fe^{3+} ions, but calcium forms only Ca^{2+}. Explain this difference in terms of the sub-shells involved. [2]

2.5 State why scandium is not classed as a transition element. [2]

3 Exam-style questions

3.1 Why is zinc **not** classed as a transition element? [1]

- **A** it is not in the d-block
- **B** its stable ion (Zn^{2+}) has a full d sub-shell ($3d^{10}$)
- **C** it is colourless
- **D** it has no electrons

3.2 Transition elements show variable oxidation states because: [1]

- **A** their atoms are large
- **B** the 3d and 4s sub-shells are close in energy
- **C** they are coloured
- **D** they are catalysts

3.3 Explain why transition metals can act as catalysts. [2]

3.4 Explain why scandium is not classed as a transition element, with reference to its ion. [2]

3.5 Copper and zinc are adjacent in the d block, but only copper is a transition element.

(a) Define the term transition element. [2]

(b) Complete the table of electronic configurations. [4]

Species	Configuration
Cu atom	
Cu^{2+} ion	
Zn atom	
Zn^{2+} ion	

(c) Use your answers to (b) to explain why zinc is not a transition element. [2]

(d) Explain, in terms of d orbitals, why aqueous copper(II) sulfate is blue while aqueous zinc sulfate is colourless. [4]

(e) State two other characteristic properties of transition elements, and give the reason for each. [4]

Solutions

2.1 a d-block element that forms one or more stable ions with incomplete (partly filled) d orbitals.

2.2 variable oxidation state; catalytic behaviour; form complex ions; form coloured compounds.

2.3 Cr: $[Ar]\,3d^5 4s^1$; Fe^{3+}: $[Ar]\,3d^5$.

2.4 In iron the 4s and 3d sub-shells are very close in energy, so electrons can be removed from either for a similar energy cost, giving more than one stable ion; calcium has only 4s electrons available above a noble-gas core, and removing a third electron would break into that core, which costs far too much energy.

2.5 Its only stable ion is Sc^{3+}, which has an empty d sub-shell ($3d^0$) rather than a partially filled one.

3.1 B. Zn^{2+} is $3d^{10}$ (a full d sub-shell), so it is not a transition element.

3.2 B. The close energies of 3d and 4s allow different numbers of electrons to be removed.

3.3 they have more than one stable oxidation state; and vacant d orbitals that can form dative bonds with reactants, providing a surface/intermediate.

3.4 scandium's only stable ion is Sc^{3+}, which has an empty d sub-shell ($3d^0$), so it has no incomplete d orbitals.

3.5 (a) A d-block element that forms at least one stable ion with a partially filled d sub-shell.
(b) Cu atom $[Ar]\,3d^{10}4s^1$; Cu^{2+} $[Ar]\,3d^9$; Zn atom $[Ar]\,3d^{10}4s^2$; Zn^{2+} $[Ar]\,3d^{10}$.
(c) The only stable zinc ion, Zn^{2+}, has a FULL d sub-shell; the definition requires a partially filled one, so zinc is excluded.
(d) In the copper complex the ligands split the 3d orbitals into two energy levels; Cu^{2+} is $3d^9$, so there is a vacancy and an electron can absorb a photon of visible light to jump the gap; the transmitted light is the complementary colour, which is blue. Zn^{2+} is $3d^{10}$, so the sub-shell is full, no electron can be promoted, no visible light is absorbed and the solution is colourless.
(e) Any two, each with its reason: catalytic activity, because variable oxidation states allow electrons to be accepted and donated in a redox cycle; complex ion formation, because the small, highly charged ion has vacant d orbitals that accept lone pairs from ligands.

3 **(a)** A bottle labelled **FA 5** is thought to contain hydrated zinc sulfate. It would therefore contain zinc ions and sulfate ions as well as water of crystallisation.

(i) Devise and carry out tests to investigate whether zinc ions, sulfate ions and water of crystallisation are present.

Record the tests you carry out and the observations you see in the space provided.

[5]

(ii) Use your observations in **(a)(i)** to complete Table 3.1 to show whether each species is present in **FA 5**.

Use a tick (✓) if the species is present.

Use a cross (✗) if the species is **not** present.

Table 3.1

Zn^{2+}	
SO_4^{2-}	
H_2O	

[1]

(b) You are provided with solid **FA 6**.

(i) Heat a few crystals of **FA 6** in a hard-glass test-tube until no further gas is evolved. Record all your observations.

Leave the test-tube until it is cool.

Keep the cooled residue for use in (b)(ii).

.....

.....

..... [2]

(ii) To the cooled residue from **(b)(i)**, add approximately 3 cm depth of distilled water and stir. Filter the solution formed into a test-tube.

The colour of the solution is ..... . [1]

(c) You are provided with aqueous solutions **FA 7** and **FA 8** and with solid **FA 9**.

FA 7 is an aqueous solution of **FA 6**.
FA 7, **FA 8** and **FA 9** contain compounds which all have one metal that is the same but which may be in different oxidation states.

(i) Carry out the following tests on **FA 7**, **FA 8** and **FA 9** and record your observations in Table 3.2. For each test use a 1 cm depth of a solution or a spatula measure of solid.

Table 3.2

test	*observations*		
	FA 7	**FA 8**	**FA 9**
Test 1 Add hydrogen peroxide.			
Test 2 Add aqueous sodium hydroxide, then			
leave to stand.			
Test 3 Add aqueous iron(II) sulfate.			

[4]

(ii) Suggest the identity of the metal in **FA 6**/**FA 7**, **FA 8** and **FA 9**.

The metal is ..... . [1]

(iii) Complete Table 3.3 to suggest the oxidation state of the metal in **FA 6**/**FA 7** and **FA 8**.

Table 3.3

	FA 6/**FA 7**	**FA 8**
oxidation state		

[1]

[Total: 15]

Qualitative analysis notes

1 Reactions of cations

cation	reaction with	
	NaOH(aq)	**NH_3(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	no ppt. ammonia produced on warming	–
barium, Ba^{2+}(aq)	faint white ppt. is observed unless $[Ba^{2+}(aq)]$ is very low	no ppt.
calcium, Ca^{2+}(aq)	white ppt. unless $[Ca^{2+}(aq)]$ is very low	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	pale blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

2 Reactions of anions

anion	reaction
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives cream / off-white ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives pale yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; decolourises acidified aqueous $KMnO_4$
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids); gives white ppt. with high $[Ca^{2+}(aq)]$
sulfite, SO_3^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (soluble in excess dilute strong acids); decolourises acidified ous $KMnO_4$
thiosulfate, $S_2O_3^{2-}$(aq)	gives off-white / pale yellow ppt. slowly with H^+

3 Tests for gases

gas	test and test result
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater
hydrogen, H_2	‘pops’ with a lighted splint
oxygen, O_2	relights a glowing splint

2 **(a)** Iron can form stable ions in the +2 and +3 oxidation states.

Explain why transition elements have variable oxidation states.

.....

..... [1]

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

Define complex ion.

.....

..... [1]

(c) $[Fe(H_2O)_6]^{2+}$ can be converted into $[Fe(H_2O)_4(OH)_2]$.

(i) Suggest a suitable reagent for this conversion. State the type of reaction.

reagent .....

type of reaction .....
[1]

(ii) $[Fe(H_2O)_4(OH)_2]$ is a green precipitate that turns brown on standing in air.

Table 2.1 shows electrode potentials for some electrode reactions.

Table 2.1

electrode reaction	$E^{\ominus}$ / V
$Fe(H_2O)_3(OH)_3 + H_2O + e^- \rightleftharpoons Fe(H_2O)_4(OH)_2 + OH^-$	–0.56
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40

Use the information in Table 2.1 to explain why $[Fe(H_2O)_4(OH)_2]$ turns brown on standing in air.
Include an equation for this reaction.

.....

.....

.....

.....

.....

..... [3]

(d) The complex $[Co(NH_3)_6]^{2+}$ reacts with hydrogen peroxide as shown.

reaction 1 $2[Co(NH_3)_6]^{2+} + H_2O_2 \rightarrow 2[Co(NH_3)_6]^{3+} + 2OH^-$ $E^{\ominus}_{cell} = +1.67\,V$

Calculate $\Delta G^{\ominus}$, in $kJ\,mol^{-1}$, for reaction 1.

$\Delta G^{\ominus}$ = ... $kJ\,mol^{-1}$ [2]

[Total: 8]

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.

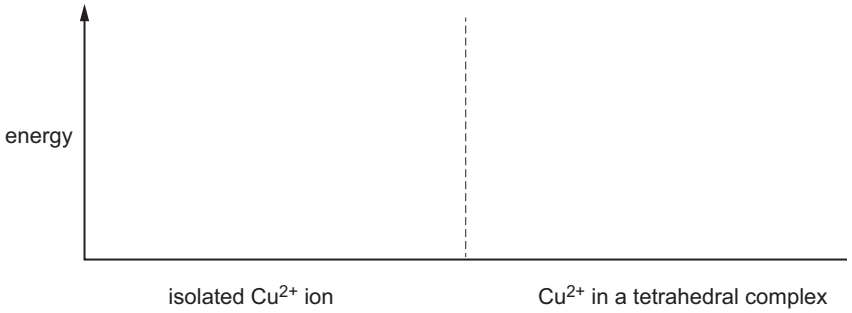
Table 5.1

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 $[Au(CN)_2Br_2]^-$ displays geometrical (cis / trans) isomerism.

Draw the structure of *trans*-$[Au(CN)_2Br_2]^-$. 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 mol dm^{-3} MnO_4^- is added.

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

$$3MnO_4^- + 5V^{2+} + 3H_2O \rightarrow 3Mn^{2+} + 5VO_3^- + 6H^+$$

(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.

..... VO_3^- + ... Zn + ... → ..... V^{2+} + ... Zn^{2+} + ...

[2]

[Total: 14]

5 Cobalt is a transition element which forms compounds containing Co^{2+} and Co^{3+} ions. Cobalt(II) sulfate dissolves in water to form a solution containing the $[Co(H_2O)_6]^{2+}$ complex ion.

(a) (i) Complete the electronic configurations of a Co^{2+} ion and a Co^{3+} ion.

Co^{2+} = [Ar] .....

Co^{3+} = [Ar] .....

[1]

(ii) Explain why transition elements can form complex ions.

.....

..... [1]

(iii) An excess of concentrated HCl is added to a solution containing $[Co(H_2O)_6]^{2+}$.

Describe the colour change observed and the state of the cobalt-containing product.

The colour changes from ..... to ..... .

The state of the cobalt-containing product is ..... .

[2]

(iv) Write an equation for the reaction occurring in **(a)(iii)**.

..... [1]

(v) Name the type of reaction occurring in **(a)(iii)**.

..... [1]

(vi) Write an equation for the reaction that occurs when an excess of NaOH(aq) is added to a solution containing $[Co(H_2O)_6]^{2+}$.

..... [1]

(b) Cobalt metal can be oxidised by acidified $K_2Cr_2O_7$. The relevant half-equations, and their $E^\ominus$ values, are shown.

$$Co^{2+} + 2e^- \rightleftharpoons Co \qquad E^\ominus = -0.28\,V$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E^\ominus = +1.33\,V$$

(i) A Co^{2+}/Co electrode is constructed in which $[Co^{2+}]$ is $0.020\,mol\,dm^{-3}$ at 298 K.

Use the Nernst equation to show that the E value for this Co^{2+}/Co electrode is –0.33 V.

[2]

(ii) An electrochemical cell is constructed using the Co^{2+}/Co electrode described in **(b)(i)** and a $Cr_2O_7^{2-}/Cr^{3+}$ electrode in which all conditions are standard.

Calculate the value of E_{cell}.

E_{cell} = ... [1]

(iii) A current is drawn from the electrochemical cell described in **(b)(ii)**.

Write an equation for the reaction taking place in the cell.

..... [1]

(iv) Complete the sentences to identify the negative electrode and the direction of electron flow when a current is drawn from the cell described in **(b)(ii)**.

The ..... electrode is the negative electrode.

Electrons flow from the ..... electrode to the ..... electrode. [1]

(c) A molten Co^{2+} salt is electrolysed using a current of 0.500 A.

0.547 g of cobalt metal forms at the cathode. Under the conditions used no other reduction reaction occurs at the cathode.

Calculate the time in minutes for which the current flows to produce this mass of cobalt.

Give your answer to **three** significant figures.

time = ... min [3]

[Total: 15]

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}
$[Cd(CH_3NH_2)_4]^{2+}$	3.5×10^6
$[Cd(en)_2]^{2+}$	4.0×10^{10}

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

..... [1]

(ii) Some $Cd^{2+}(aq)$ 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 $[Cd(CH_3NH_2)_4]^{2+}$.

K_{stab} =

[1]

[Total: 7]

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.

- $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ .....
- $[CuCl_4]^{2-}(aq)$ .....

[1]

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

.....

.....

.....

.....

.....

..... [3]

(d) **(i)** When an excess of $NH_3(aq)$ is added to a solution of $[CuCl_4]^{2-}(aq)$, $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is formed.

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

type of reaction .....

equation

$[CuCl_4]^{2-}$ + ... $[Cu(NH_3)_4(H_2O)_2]^{2+}$ + ...

[2]

(ii) The $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion shows stereoisomerism.

Complete the three-dimensional diagrams in Fig. 1.1 to show the **two** different stereoisomers of $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

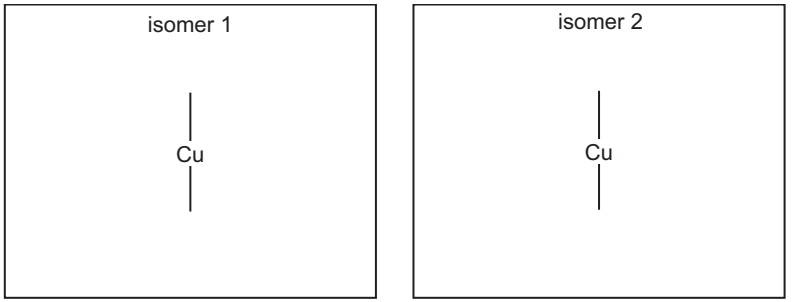


Fig. 1.1

[2]

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

Explain your answer.

polar isomer .....

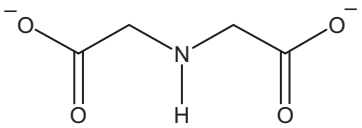
explanation .....

.....

[1]

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

P



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

.....

.....

..... [1]

(ii) 2 moles of dianion **P**, $C_4H_5NO_4^{2-}$, react with 1 mole of aqueous cobalt(III) ions, $[Co(H_2O)_6]^{3+}$ 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}
$[Ag(CN)_2]^-(aq)$	1.1×10^{18}
$[Ag(NH_3)_2]^+(aq)$	1.2×10^{7}
$[Ag(S_2O_3)_2]^{3-}(aq)$	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 mol dm^{-3} $MnO_4^-(aq)$ to reach the end-point.

The equation for the reaction is shown.

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Calculate the percentage by mass of Na_2SO_3 in the sample.

percentage by mass of Na_2SO_3 = ... [3]

[Total: 19]

A-LEVEL CHEMISTRY • EXERCISE SHEET

28.2 Ligands and complexes

Name: _____ Class: _____ Date: _____ **Total: 33 marks**

KEY WORDS ligand 配体 • coordination number 配位数 • monodentate 单齿 • octahedral 八面体形 • tetrahedral 四面体形

Objective

Build the skills to answer exam questions on **ligands and complexes** 配体和配合物 — **denticity** 齿数, complex shapes, **coordination number** 配位数, and **ligand exchange** 配体交换.

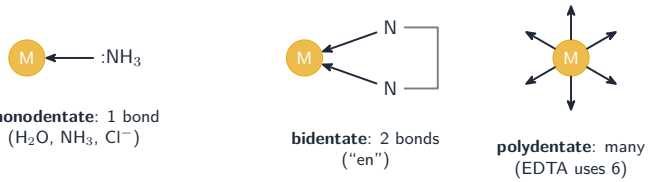
You must be able to:

- define a ligand and classify ligands as mono-, bi- or polydentate
- describe complex shapes and deduce coordination number and charge
- describe the ligand-exchange reactions of copper(II) and cobalt(II)

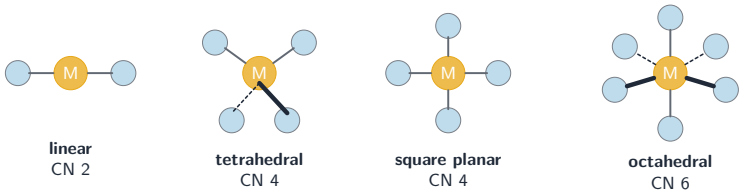
1 Worked examples

Ligands and complexes

A **ligand** has a lone pair that forms a **dative covalent bond** to the central metal ion.

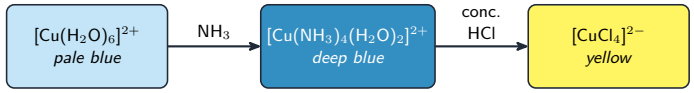


Monodentate (1 bond: H_2O, NH_3, Cl^-, CN^-); bidentate (2: en, $C_2O_4{}^{2-}$); polydentate ($EDTA^{4-}$, 6)



Coordination number → shape: 2 linear, 4 tetrahedral or square planar, 6 octahedral

Ligand exchange



Ligand exchange changes colour: $[Cu(H_2O)_6]^{2+}$ (pale blue) → $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (deep blue) → $[CuCl_4]^{2-}$ (yellow)

Ligands, denticity and the charge on a complex

A **ligand** 配体 is a molecule or ion with a **lone pair** that it donates into a vacant orbital of a metal ion, forming a **dative (coordinate) bond** 配位键. The metal ion is the electron-pair **acceptor**, the ligand the **donor** — a Lewis acid and a Lewis base.

Denticity 齿数 is how many dative bonds one ligand forms:

Denticity	Examples	Bonds per ligand
monodentate 单齿	H_2O, NH_3, Cl^-, CN^-, OH^-	1
bidentate 双齿	1,2-diaminoethane ("en"), ethanedioate $C_2O_4^{2-}$	2
polydentate 多齿	$EDTA^{4-}$	6

Coordination number 配位数 is the number of **dative bonds**, not the number of ligands — three bidentate ligands give a coordination number of 6, not 3. Coordination number decides the shape: **6 → octahedral** (90° bond angles), **4 → tetrahedral** (109.5°) or **square planar** (90°), **2 → linear** (180°).

Working out the overall charge, which is a mark in almost every question on this topic:

$$\text{charge on complex} = \text{oxidation number of metal} + \sum(\text{charges on ligands})$$

Worked example. Give the coordination number, shape and overall charge of the complex formed when Cr^{3+} bonds to four water molecules and two chloride ions.

1. Bonds: $4 + 2 = 6$, so the coordination number is 6 and the shape is **octahedral**.
2. Charges: $+3$ from chromium, 0 from each water, -1 from each chloride, giving $+3 + 0 - 2 = +1$.
3. Formula: $[Cr(H_2O)_4Cl_2]^+$.

Ligand exchange replaces one ligand with another, often with a **colour change** — the exam's evidence that a reaction happened. Adding concentrated HCl to pink $[Co(H_2O)_6]^{2+}$ gives blue $[CoCl_4]^{2-}$: both the colour and the coordination number change, from 6 (octahedral) to 4 (tetrahedral), because chloride is the larger ligand and fewer fit around the ion.

2 Practice

2.1 Define a **ligand**. [2]

2.2 State the coordination number and shape of $[Cu(H_2O)_6]^{2+}$. [2]

2.3 Define a ligand, and state the type of bond it forms with the metal ion. [2]

2.4 Give the coordination number and shape of $[Ni(en)_3]^{2+}$, where en is bidentate. [2]

2.5 Deduce the overall charge on the complex formed by Fe^{3+} with six cyanide ions. [2]

3 Exam-style questions

3.1 Which is a **bidentate** ligand? [1]

- **A** H_2O
- **B** Cl^-
- **C** 1,2-diaminoethane (en)
- **D** NH_3

3.2 The overall charge on $[CuCl_4]^{2-}$ shows copper is in oxidation state: [1]

- **A** +1
- **B** +2
- **C** +3
- **D** +4

3.3 (a) Write the formula and state the colour of the complex formed when excess ammonia is added to $[Cu(H_2O)_6]^{2+}$. [2]

(b) State what is meant by **ligand exchange**. [2]

3.4 Deduce the coordination number and shape of $[CuCl_4]^{2-}$. [2]

3.5 Cobalt(II) forms a range of complexes.

(a) Define the term ligand, and explain why a ligand must have a lone pair. [3]

(b) Complete the table for three cobalt complexes. [6]

Complex	Coordination number	Shape	Overall charge
$[Co(H_2O)_6]^?$ from Co^{2+}			
$[CoCl_4]^?$ from Co^{2+}			
$[Co(en)_3]^?$ from Co^{3+}			

(c) Concentrated hydrochloric acid is added to a pink solution of $[Co(H_2O)_6]^{2+}$ and the solution turns blue. Explain what has happened, including the change in coordination number. [4]

(d) Explain why 1,2-diaminoethane is described as bidentate while ammonia is monodentate. [2]

Solutions

2.1 a species with a lone pair of electrons that forms a dative (coordinate) bond to a central metal ion.

2.2 coordination number 6; octahedral.

2.3 A ligand is a molecule or ion that donates a lone pair of electrons to a metal ion; the bond formed is a dative, or coordinate, bond.

2.4 Three bidentate ligands form six dative bonds, so the coordination number is 6; the shape is octahedral.

2.5 $+3 + 6(-1) = -3$; the complex is $[Fe(CN)_6]^{3-}$.

3.1 C. 1,2-diaminoethane (en) forms two dative bonds — bidentate.

3.2 B. $x + 4(-1) = -2 \Rightarrow x = +2$.

3.3 (a) $[Cu(NH_3)_4(H_2O)_2]^{2+}$; deep blue.
(b) one ligand is replaced by another ligand around the central metal ion, often with a colour change.

3.4 coordination number 4; tetrahedral.

3.5 (a) A ligand is a molecule or ion that donates a lone pair of electrons to a metal ion, forming a dative bond; it must have a lone pair because the metal ion supplies no electrons to the bond — both electrons come from the ligand.
(b) $[Co(H_2O)_6]^{2+}$: 6, octahedral, 2+. $[CoCl_4]^{2-}$: 4, tetrahedral, 2−. $[Co(en)_3]^{3+}$: 6, octahedral, 3+.
(c) Ligand exchange has occurred: chloride ions have replaced the water ligands; the coordination number falls from 6 to 4 because chloride is a larger ligand and fewer fit around the ion; the shape changes from octahedral to tetrahedral, which is what changes the colour from pink to blue.
(d) 1,2-diaminoethane has two nitrogen atoms, each with a lone pair, so one molecule forms two dative bonds to the same metal ion; ammonia has only one nitrogen with one lone pair, so it forms one bond.

3 **(a)** A bottle labelled **FA 5** is thought to contain hydrated zinc sulfate. It would therefore contain zinc ions and sulfate ions as well as water of crystallisation.

(i) Devise and carry out tests to investigate whether zinc ions, sulfate ions and water of crystallisation are present.

Record the tests you carry out and the observations you see in the space provided.

[5]

(ii) Use your observations in **(a)(i)** to complete Table 3.1 to show whether each species is present in **FA 5**.

Use a tick (✓) if the species is present.

Use a cross (✗) if the species is **not** present.

Table 3.1

Zn^{2+}	
SO_4^{2-}	
H_2O	

[1]

(b) You are provided with solid **FA 6**.

(i) Heat a few crystals of **FA 6** in a hard-glass test-tube until no further gas is evolved. Record all your observations.

Leave the test-tube until it is cool.

Keep the cooled residue for use in (b)(ii).

.....

.....

..... [2]

(ii) To the cooled residue from **(b)(i)**, add approximately 3 cm depth of distilled water and stir. Filter the solution formed into a test-tube.

The colour of the solution is ..... . [1]

(c) You are provided with aqueous solutions **FA 7** and **FA 8** and with solid **FA 9**.

FA 7 is an aqueous solution of **FA 6**.
FA 7, **FA 8** and **FA 9** contain compounds which all have one metal that is the same but which may be in different oxidation states.

(i) Carry out the following tests on **FA 7**, **FA 8** and **FA 9** and record your observations in Table 3.2. For each test use a 1 cm depth of a solution or a spatula measure of solid.

Table 3.2

test	*observations*		
	FA 7	**FA 8**	**FA 9**
Test 1 Add hydrogen peroxide.			
Test 2 Add aqueous sodium hydroxide, then			
leave to stand.			
Test 3 Add aqueous iron(II) sulfate.			

[4]

(ii) Suggest the identity of the metal in **FA 6**/**FA 7**, **FA 8** and **FA 9**.

The metal is ..... . [1]

(iii) Complete Table 3.3 to suggest the oxidation state of the metal in **FA 6**/**FA 7** and **FA 8**.

Table 3.3

	FA 6/**FA 7**	**FA 8**
oxidation state		

[1]

[Total: 15]

Qualitative analysis notes

1 Reactions of cations

cation	**reaction with**	
	NaOH(aq)	**NH_3(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	no ppt. ammonia produced on warming	–
barium, Ba^{2+}(aq)	faint white ppt. is observed unless $[Ba^{2+}(aq)]$ is very low	no ppt.
calcium, Ca^{2+}(aq)	white ppt. unless $[Ca^{2+}(aq)]$ is very low	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	pale blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

2 Reactions of anions

anion	**reaction**
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives cream/off-white ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives pale yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; decolourises acidified aqueous $KMnO_4$
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids); gives white ppt. with high $[Ca^{2+}(aq)]$
sulfite, SO_3^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (soluble in excess dilute strong acids); decolourises acidified ous $KMnO_4$
thiosulfate, $S_2O_3^{2-}$(aq)	gives off-white/pale yellow ppt. slowly with H^+

3 Tests for gases

gas	test and test result
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater
hydrogen, H_2	'pops' with a lighted splint
oxygen, O_2	relights a glowing splint

3 Half-fill the 250 cm^3 beaker with water and place it on a tripod and gauze. Heat the water until boiling then switch off your Bunsen burner. This will be your hot water bath for use in **(b)(i)**. Start **(a)(i)** while the water is heating.

(a) **FA 4** is an aqueous solution containing three ions. One ion is **not** listed in the Qualitative analysis notes. **FA 5** is an aqueous solution containing two ions. The cation in **FA 5** is listed in the Qualitative analysis notes. The anions in both **FA 4** and **FA 5** contain sulfur.

(i) Carry out the following tests using a 1 cm depth of either **FA 4** or **FA 5** in a test-tube. Record your observations in Table 3.1.

Table 3.1

test	*observations*	
	FA 4	**FA 5**
Test 1 Add aqueous sodium hydroxide.		
Test 2 Add aqueous ammonia.		
Test 3 Add aqueous sodium carbonate.		
Test 4 Add aqueous barium chloride or aqueous barium nitrate.		
Test 5 Add acidified aqueous potassium manganate(VII).		

[5]

(ii) From your observations in **(a)(i)**, deduce the identities of the ions present in **FA 4** and **FA 5**. Give the formula of each ion in Table 3.2. If you are unable to identify an ion write 'unknown'.

Table 3.2

ions present	**FA 4**	**FA 5**
cations		
anions		

[3]

(b) (i) Both **FA 6** and **FA 7** are one of propan-1-ol, propan-2-ol, methanoic acid or ethanoic acid. You will carry out tests to investigate the identities of **FA 6** and **FA 7**. For each test use a 1 cm depth of **FA 6** or **FA 7** in a test-tube. Record your observations in Table 3.3.

Table 3.3

test	*observations*	
	FA 6	**FA 7**
Test 1 Add a few drops of acidified aqueous potassium manganate(VII), then		
place the test-tube in the hot water bath.		
Test 2 Add a 2 cm depth of aqueous iodine followed by drops of aqueous sodium hydroxide until the colour just disappears.		
If no reaction is visible, place the test-tube in the hot water bath.		
Test 3 Add aqueous sodium carbonate.		

[3]

(ii) From your observations in **(b)(i)** deduce the identities of **FA 6** and **FA 7**. Give reasons for your answers.

FA 6 is .....

reasons .....

.....

FA 7 is .....

reasons .....

.....

[2]

(c) A student carrying out a similar set of tests identifies two unknown compounds to be ethanol and propanoic acid.

Write an equation for the reaction between these two compounds.

..... [1]

[Total: 14]

Qualitative analysis notes

1 Reactions of cations

cation	reaction with	
	NaOH(aq)	**NH_3(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	no ppt. ammonia produced on warming	–
barium, Ba^{2+}(aq)	faint white ppt. is observed unless [Ba^{2+}(aq)] is very low	no ppt.
calcium, Ca^{2+}(aq)	white ppt. unless [Ca^{2+}(aq)] is very low	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	pale blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

2 Reactions of anions

anion	reaction
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives cream / off-white ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives pale yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; decolourises acidified aqueous $KMnO_4$
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids); gives white ppt. with high [Ca^{2+}(aq)]
sulfite, SO_3^{2-}(aq)	gives white ppt. with B q) (soluble in excess dilute strong acids); decolourises acidified aqueous $KMnO_4$
thiosulfate, $S_2O_3^{2-}$(aq)	gives off-white/pale yellow ppt. slowly with H^+

3 Tests for gases

gas	test and test result
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater
hydrogen, H_2	'pops' with a lighted splint
oxygen, O_2	relights a glowing splint

3 (a) (i) To a 1 cm depth of **FB 4** in a boiling tube, slowly add a 1 cm depth of dilute nitric acid. Stir gently until the reaction is complete. Use this solution for your tests.
Select reagents to identify which sodium halide is present.
Record details of the reagents used and your observations.
Identify the sodium halide that is present as an impurity in **FB 4**.

The formula of the impurity is .....

[2]

(ii) Suggest why it is necessary to add the nitric acid to **FB 4** before carrying out your tests in **(a)(i)**.

.....

..... [1]

(b) **FB 7** contains a metal cation which is listed in the Qualitative analysis notes.

(i) Place half the sample of **FB 7** in a hard-glass test-tube. Heat gently at first and then more strongly.
Record your observations.

.....

.....

..... [2]

(ii) Use the 25 cm^3 measuring cylinder to measure 20 cm^3 of **FB 1**.
Place the remaining sample of **FB 7** in a boiling tube and add portions of **FB 1** from the measuring cylinder until all the **FB 7** has reacted. Stir until the reaction is complete.
Record your observations.

Keep this solution for use in (b)(iii).

.....

.....

.....

..... [2]

(iii) Carry out the following tests. For each test use a 1 cm depth of the solution from **(b)(ii)** in a test-tube.
Record your observations in Table 3.1.
Identify the metal ion present in **FB 7**.

Table 3.1

test	*observations*
Test 1 Add aqueous sodium hydroxide.	
Test 2 Add aqueous ammonia.	
Test 3 Add a piece of aluminium foil.	

The formula of the metal ion in **FB 7** is .....

[4]

(c) **FB 8** is an acidified aqueous solution containing a metal cation which is listed in the Qualitative analysis notes.

(i) Carry out the following tests. For each test use a 1 cm depth of **FB 8** in a test-tube.
Record your observations in Table 3.2.
Identify the metal ion present in **FB 8**.

Table 3.2

test	*observations*
Test 1 Add aqueous sodium hydroxide.	
Test 2 Add a 1 cm depth of acidified aqueous potassium manganate(VII).	

The formula of the metal ion in **FB 8** is .....

[3]

(ii) State the type of reaction between the metal ion in **FB 8** and acidified aqueous potassium manganate(VII).
Explain how your observations support your answer.

.....

.....

..... [1]

[Total: 15]

Qualitative analysis notes

1 Reactions of cations

cation	reaction with	
	NaOH(aq)	**NH_3(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	no ppt. ammonia produced on warming	–
barium, Ba^{2+}(aq)	faint white ppt. is observed unless [Ba^{2+}(aq)] is very low	no ppt.
calcium, Ca^{2+}(aq)	white ppt. unless [Ca^{2+}(aq)] is very low	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	pale blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

2 Reactions of anions

anion	reaction
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives cream / off-white ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives pale yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; decolourises acidified aqueous $KMnO_4$
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids); gives white ppt. with high [Ca^{2+}(aq)]
sulfite, SO_3^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (soluble in excess dilute strong acids); decolourises acidified aqueous $KMnO_4$
thiosulfate, $S_2O_3^{2-}$(aq)	gives off-white / pale yellow ppt. slowly with H^+

3 Tests for gases

gas	test and test result
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater
hydrogen, H_2	'pops' with a lighted splint
oxygen, O_2	relights a glowing splint

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.

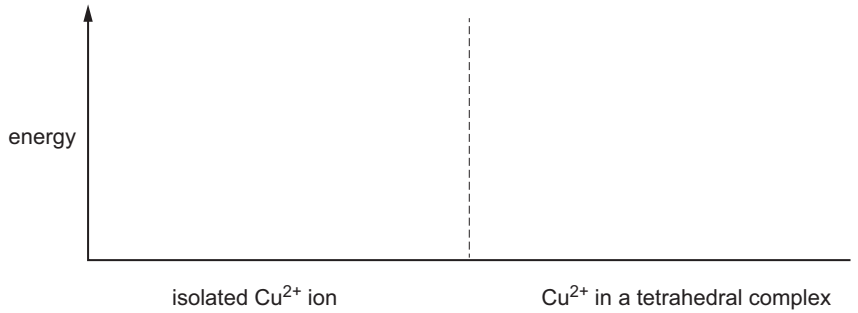
Table 5.1

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 $[Au(CN)_2Br_2]^-$ displays geometrical (cis / trans) isomerism.

Draw the structure of *trans*-$[Au(CN)_2Br_2]^-$. 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 mol dm^{-3} MnO_4^- is added.

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

$$3MnO_4^- + 5V^{2+} + 3H_2O \rightarrow 3Mn^{2+} + 5VO_3^- + 6H^+$$

(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.

..... VO_3^- + ... Zn + ... → ..... V^{2+} + ... Zn^{2+} + ...

[2]

[Total: 14]

5 Cobalt is a transition element which forms compounds containing Co^{2+} and Co^{3+} ions. Cobalt(II) sulfate dissolves in water to form a solution containing the $[Co(H_2O)_6]^{2+}$ complex ion.

(a) (i) Complete the electronic configurations of a Co^{2+} ion and a Co^{3+} ion.

Co^{2+} = [Ar] .....

Co^{3+} = [Ar] .....

[1]

(ii) Explain why transition elements can form complex ions.

.....

..... [1]

(iii) An excess of concentrated HC*l* is added to a solution containing $[Co(H_2O)_6]^{2+}$.

Describe the colour change observed and the state of the cobalt-containing product.

The colour changes from ..... to ..... .

The state of the cobalt-containing product is ..... .

[2]

(iv) Write an equation for the reaction occurring in **(a)(iii)**.

..... [1]

(v) Name the type of reaction occurring in **(a)(iii)**.

..... [1]

(vi) Write an equation for the reaction that occurs when an excess of NaOH(aq) is added to a solution containing $[Co(H_2O)_6]^{2+}$.

..... [1]

(b) Cobalt metal can be oxidised by acidified $K_2Cr_2O_7$. The relevant half-equations, and their $E^\ominus$ values, are shown.

$Co^{2+} + 2e^- \rightleftharpoons Co$ $\quad E^\ominus = -0.28\,V$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $\quad E^\ominus = +1.33\,V$

(i) A Co^{2+}/Co electrode is constructed in which $[Co^{2+}]$ is $0.020\,mol\,dm^{-3}$ at 298 K.

Use the Nernst equation to show that the E value for this Co^{2+}/Co electrode is –0.33 V.

[2]

(ii) An electrochemical cell is constructed using the Co^{2+}/Co electrode described in **(b)(i)** and a $Cr_2O_7^{2-}/Cr^{3+}$ electrode in which all conditions are standard.

Calculate the value of E_{cell}.

E_{cell} = ... [1]

(iii) A current is drawn from the electrochemical cell described in **(b)(ii)**.

Write an equation for the reaction taking place in the cell.

..... [1]

(iv) Complete the sentences to identify the negative electrode and the direction of electron flow when a current is drawn from the cell described in **(b)(ii)**.

The ..... electrode is the negative electrode.

Electrons flow from the ..... electrode to the ..... electrode.

[1]

(c) A molten Co^{2+} salt is electrolysed using a current of 0.500 A.

0.547 g of cobalt metal forms at the cathode. Under the conditions used no other reduction reaction occurs at the cathode.

Calculate the time in minutes for which the current flows to produce this mass of cobalt.

Give your answer to **three** significant figures.

time = ... min [3]

[Total: 15]

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.

- $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ .....
- $[CuCl_4]^{2-}(aq)$ .....

[1]

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

.....

.....

.....

.....

.....

..... [3]

(d) **(i)** When an excess of $NH_3(aq)$ is added to a solution of $[CuCl_4]^{2-}(aq)$, $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is formed.

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

type of reaction .....

equation

$[CuCl_4]^{2-}$ + ... $[Cu(NH_3)_4(H_2O)_2]^{2+}$ + ...

[2]

(ii) The $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion shows stereoisomerism.

Complete the three-dimensional diagrams in Fig. 1.1 to show the **two** different stereoisomers of $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

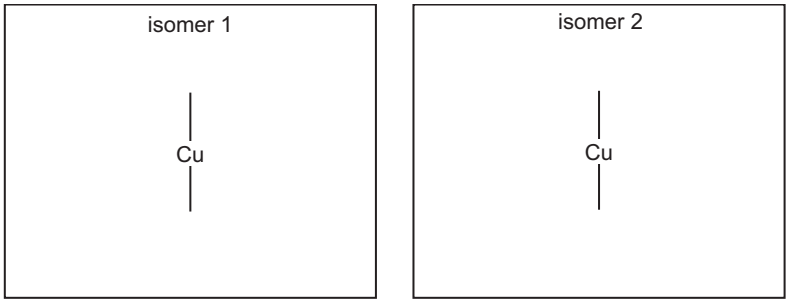


Fig. 1.1

[2]

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

Explain your answer.

polar isomer .....

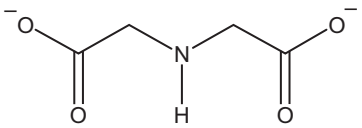
explanation .....

.....

[1]

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

P



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

.....

.....

..... [1]

(ii) 2 moles of dianion **P**, $C_4H_5NO_4^{2-}$, react with 1 mole of aqueous cobalt(III) ions, $[Co(H_2O)_6]^{3+}$ 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}
$[Ag(CN)_2]^-(aq)$	1.1×10^{18}
$[Ag(NH_3)_2]^+(aq)$	1.2×10^{7}
$[Ag(S_2O_3)_2]^{3-}(aq)$	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 mol dm^{-3} $MnO_4^-(aq)$ to reach the end-point.

The equation for the reaction is shown.

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Calculate the percentage by mass of Na_2SO_3 in the sample.

percentage by mass of Na_2SO_3 = ... [3]

[Total: 19]

A-LEVEL CHEMISTRY • EXERCISE SHEET

28.3 Colour of complexes

Name: _____ Class: _____ Date: _____ **Total: 28 marks**

KEY WORDS degenerate 简并 • non-degenerate 非简并 • complementary colour 互补色 • colour of complexes 配合物的颜色 • complex 配合物

Objective

Build the skills to answer exam questions on the **colour of complexes** 配合物的颜色 — **d-orbital splitting** d 轨道分裂 and why transition complexes are coloured.

You must be able to:

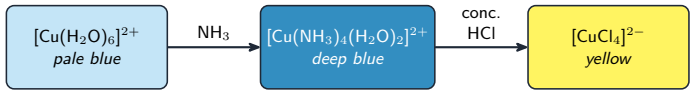
- define degenerate and non-degenerate d orbitals
- describe the splitting in octahedral and tetrahedral complexes
- explain colour in terms of the frequency of light absorbed (ΔE)

1 Worked examples

d-orbital splitting and colour

the complex absorbs light of energy ΔE, so we see the **complementary colour**

*Ligands split the five **degenerate** d orbitals into two **non-degenerate** sets separated by a gap ΔE*



Ligand exchange changes the complex colour

- **octahedral:** three lower + two higher.
- **tetrahedral:** two lower + three higher.

A complex absorbs light whose energy equals ΔE, promoting a d electron to the higher set. We **see** the **complementary colour** of the light absorbed. Different ligands give a different ΔE → different colour (why ligand exchange changes colour).

Why a complex is coloured, and what changes the colour

In a free gaseous ion the five 3d orbitals are **degenerate** — equal in energy. When **ligands** approach, their lone pairs repel the d electrons unequally: the orbitals pointing towards the ligands rise in energy and the others fall, so the set **splits** into two levels separated by ΔE.

The colour, in the order the marks are awarded:

1. The complex absorbs a photon whose energy equals ΔE.
2. That promotes an electron from the lower set to the higher — a **d–d transition**.
3. The frequency absorbed follows $\Delta E = h\nu$, so a larger ΔE means a higher frequency and a shorter wavelength absorbed.
4. The colour **seen** is the **complement** of the light absorbed: a complex absorbing red looks green; absorbing green, it looks red.

Why some ions are colourless. A d–d transition needs a **partially filled** d subshell. Sc^{3+} ($3d^0$), Cu^+ and Zn^{2+} ($3d^{10}$) have no vacancy to promote an electron into, absorb no visible light, and are colourless.

Three things change ΔE, and therefore the colour:

Change	Effect
the ligand	ligands have a fixed order of splitting power (the spectrochemical series): $I^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^-$ — a stronger-field ligand gives a larger ΔE
the oxidation state	a higher charge pulls the ligands closer, increasing the repulsion and so ΔE
the coordination number / shape	octahedral and tetrahedral fields split the orbitals differently, so a change of geometry changes the colour

Worked example. Adding concentrated ammonia to pale blue $[Cu(H_2O)_6]^{2+}$ gives a deep blue solution. Explain. Ammonia replaces four of the water ligands by ligand exchange. Ammonia is higher in the spectrochemical series than water, so the splitting ΔE increases. A larger ΔE means light of a different (higher) frequency is absorbed, so the complementary colour transmitted changes, and the solution deepens to blue.

2 Practice

2.1 Define **degenerate** d orbitals. [1]

2.2 State how the five d orbitals split in an **octahedral** complex. [1]

2.3 Explain why Zn^{2+} complexes are colourless. [2]

2.4 State the relationship between the energy gap ΔE and the frequency of light absorbed. [1]

2.5 Name three factors that change the size of ΔE. [3]

3 Exam-style questions

3.1 A transition-metal complex is coloured because an electron is promoted: [1]

- **A** out of the atom
- **B** between two non-degenerate d orbitals
- **C** into the nucleus
- **D** between s orbitals

3.2 The colour we see is: [1]

- **A** the colour of light absorbed
- **B** the complementary colour of the light absorbed
- **C** always green
- **D** white

3.3 Explain, in terms of d orbitals, why $[Cu(H_2O)_6]^{2+}$ is coloured. [3]

3.4 Explain why changing the ligand around a transition-metal ion changes the colour of the complex. [2]

3.5 Aqueous cobalt(II) chloride is pink because of the complex $[Co(H_2O)_6]^{2+}$.

(a) Explain, in terms of d orbitals, why this complex is coloured. [4]

(b) The pink solution absorbs green light. State the relationship between the colour absorbed and the colour seen. [1]

(c) Concentrated hydrochloric acid is added and the solution turns blue, forming $[CoCl_4]^{2-}$. Explain the colour change, referring to both the ligand and the shape. [4]

(d) A solution of $[Sc(H_2O)_6]^{3+}$ is colourless. Explain why. [2]

(e) Predict, with a reason, whether $[Co(CN)_6]^{4-}$ would absorb light of a higher or lower frequency than $[Co(H_2O)_6]^{2+}$. [2]

Solutions

2.1 d orbitals that have the same energy.

2.2 into a lower set of three and a higher set of two orbitals.

2.3 Zn^{2+} has a full $3d^{10}$ sub-shell; there is no vacancy to promote an electron into, so no d–d transition occurs and no visible light is absorbed.

2.4 $\Delta E = h\nu$, so a larger gap corresponds to a higher frequency absorbed.

2.5 The identity of the ligand; the oxidation state of the metal ion; the coordination number or the shape of the complex.

3.1 B. An electron is promoted between two non-degenerate d orbitals.

3.2 B. We see the complementary colour of the light absorbed.

3.3 the ligands split the d orbitals into two sets separated by ΔE; the complex absorbs light of energy equal to ΔE, promoting a d electron to the higher set; the colour seen is the complementary colour of the light absorbed.

3.4 a different ligand gives a different splitting energy ΔE; so a different frequency of light is absorbed, and a different complementary colour is seen.

3.5 (a) The ligands split the five degenerate 3d orbitals into two levels separated by ΔE; Co^{2+} has a partially filled d sub-shell, so an electron can be promoted; it absorbs a photon whose energy equals ΔE, a d–d transition; the light not absorbed is transmitted, and the complementary colour is what is seen.
(b) The colour seen is the complement of the colour absorbed.
(c) Chloride ligands replace the water by ligand exchange; chloride is lower in the spectrochemical series than water, so ΔE decreases; the coordination number also falls from 6 to 4 and the shape changes from octahedral to tetrahedral, which splits the orbitals differently; a different frequency is therefore absorbed and the complementary colour seen changes from pink to blue.
(d) Sc^{3+} has an empty $3d^0$ sub-shell; with no d electrons there can be no d–d transition, so no visible light is absorbed.
(e) A higher frequency; cyanide is higher in the spectrochemical series than water, so it produces a larger ΔE, and $\Delta E = h\nu$.

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.

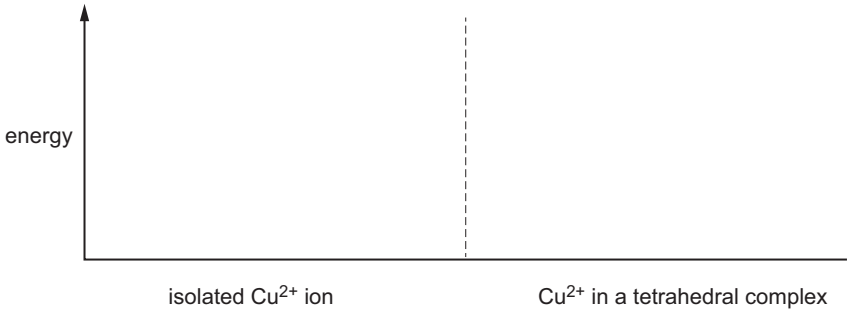
Table 5.1

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 $[Au(CN)_2Br_2]^-$ displays geometrical (cis / trans) isomerism.

Draw the structure of *trans*-$[Au(CN)_2Br_2]^-$. 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 mol dm^{-3} MnO_4^- is added.

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

$$3MnO_4^- + 5V^{2+} + 3H_2O \rightarrow 3Mn^{2+} + 5VO_3^- + 6H^+$$

(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.

..... VO_3^- + ... Zn + ... → ..... V^{2+} + ... Zn^{2+} + ...

[2]

[Total: 14]

5 Cobalt is a transition element which forms compounds containing Co^{2+} and Co^{3+} ions. Cobalt(II) sulfate dissolves in water to form a solution containing the $[Co(H_2O)_6]^{2+}$ complex ion.

(a) (i) Complete the electronic configurations of a Co^{2+} ion and a Co^{3+} ion.

Co^{2+} = [Ar] .....

Co^{3+} = [Ar] .....

[1]

(ii) Explain why transition elements can form complex ions.

.....

..... [1]

(iii) An excess of concentrated HCl is added to a solution containing $[Co(H_2O)_6]^{2+}$.

Describe the colour change observed and the state of the cobalt-containing product.

The colour changes from ..... to ..... .

The state of the cobalt-containing product is ..... .

[2]

(iv) Write an equation for the reaction occurring in **(a)(iii)**.

..... [1]

(v) Name the type of reaction occurring in **(a)(iii)**.

..... [1]

(vi) Write an equation for the reaction that occurs when an excess of NaOH(aq) is added to a solution containing $[Co(H_2O)_6]^{2+}$.

..... [1]

(b) Cobalt metal can be oxidised by acidified $K_2Cr_2O_7$. The relevant half-equations, and their $E^\ominus$ values, are shown.

$Co^{2+} + 2e^- \rightleftharpoons Co$ $\quad E^\ominus = -0.28\,V$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $\quad E^\ominus = +1.33\,V$

(i) A Co^{2+}/Co electrode is constructed in which $[Co^{2+}]$ is $0.020\,mol\,dm^{-3}$ at 298 K.

Use the Nernst equation to show that the E value for this Co^{2+}/Co electrode is –0.33 V.

[2]

(ii) An electrochemical cell is constructed using the Co^{2+}/Co electrode described in **(b)(i)** and a $Cr_2O_7^{2-}/Cr^{3+}$ electrode in which all conditions are standard.

Calculate the value of E_{cell}.

E_{cell} = ... [1]

(iii) A current is drawn from the electrochemical cell described in **(b)(ii)**.

Write an equation for the reaction taking place in the cell.

..... [1]

(iv) Complete the sentences to identify the negative electrode and the direction of electron flow when a current is drawn from the cell described in **(b)(ii)**.

The ..... electrode is the negative electrode.

Electrons flow from the ..... electrode to the ..... electrode. [1]

(c) A molten Co^{2+} salt is electrolysed using a current of 0.500 A.

0.547 g of cobalt metal forms at the cathode. Under the conditions used no other reduction reaction occurs at the cathode.

Calculate the time in minutes for which the current flows to produce this mass of cobalt.

Give your answer to **three** significant figures.

time = ... min [3]

[Total: 15]

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.

- $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ .....
- $[CuCl_4]^{2-}(aq)$ .....

[1]

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

.....

.....

.....

.....

.....

..... [3]

(d) **(i)** When an excess of $NH_3(aq)$ is added to a solution of $[CuCl_4]^{2-}(aq)$, $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is formed.

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

type of reaction .....

equation

$[CuCl_4]^{2-}$ + ... $\rightleftharpoons$ $[Cu(NH_3)_4(H_2O)_2]^{2+}$ + ...

[2]

(ii) The $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion shows stereoisomerism.

Complete the three-dimensional diagrams in Fig. 1.1 to show the **two** different stereoisomers of $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

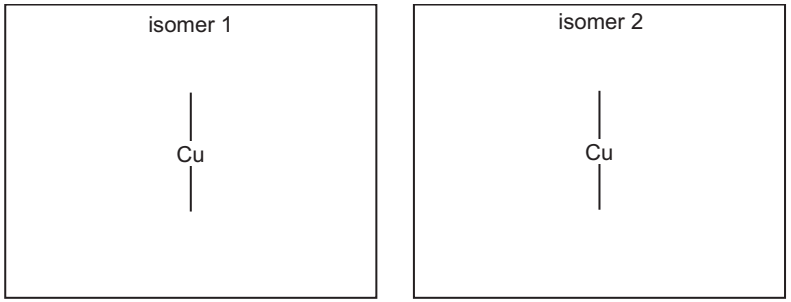


Fig. 1.1

[2]

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

Explain your answer.

polar isomer .....

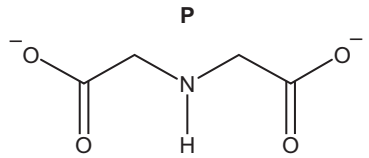
explanation .....

.....

[1]

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

P



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

.....

.....

..... [1]

(ii) 2 moles of dianion **P**, $C_4H_5NO_4^{2-}$, react with 1 mole of aqueous cobalt(III) ions, $[Co(H_2O)_6]^{3+}$ 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}
$[Ag(CN)_2]^-(aq)$	1.1×10^{18}
$[Ag(NH_3)_2]^+(aq)$	1.2×10^{7}
$[Ag(S_2O_3)_2]^{3-}(aq)$	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 mol dm^{-3} MnO_4^-(aq) to reach the end-point.

The equation for the reaction is shown.

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Calculate the percentage by mass of Na_2SO_3 in the sample.

percentage by mass of Na_2SO_3 = ... [3]

[Total: 19]

A-LEVEL CHEMISTRY • EXERCISE SHEET

28.4 Stereoisomerism in transition element complexes

Name: _____ Class: _____ Date: _____ **Total: 21 marks**

KEY WORDS stereoisomerism in complexes 配合物的立体异构 • cis 顺式 • geometrical 几何 • optical 旋光 • optical isomerism 旋光异构

Objective

Build the skills to answer exam questions on **stereoisomerism in complexes** 配合物的立体异构 — **geometrical** 几何 (cis/trans) and **optical** 旋光 isomerism, and the polarity of complexes.

You must be able to:

- describe cis/trans isomerism in square planar and octahedral complexes
- describe optical isomerism in octahedral complexes with bidentate ligands
- deduce the overall polarity of such complexes

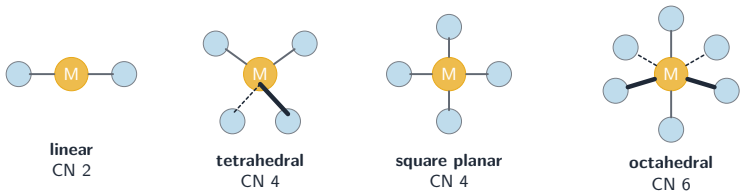
1 Worked examples

Geometrical and optical isomerism

square planar $[Pt(NH_3)_2Cl_2]$

cis (same side) **trans** (opposite)

Cis/trans in $[Pt(NH_3)_2Cl_2]$: the two identical ligands are adjacent (cis) or opposite (trans)



Complex shapes underlie their stereoisomerism

- **geometrical (cis/trans):** square planar (e.g. $[Pt(NH_3)_2Cl_2]$) and octahedral (e.g. $[Co(NH_3)_4(H_2O)_2]^{2+}$).
- **optical:** octahedral complexes with bidentate ligands (e.g. $[Ni(en)_3]^{2+}$) have two non-superimposable mirror images.

Polarity: a *cis* form may be polar (dipoles do not cancel); the matching *trans* form is often non-polar.

2 Practice

2.1 Name the type of stereoisomerism shown by $[Pt(NH_3)_2Cl_2]$. [1]

2.2 State what makes a complex show optical isomerism. [1]

3 Exam-style questions

3.1 Optical isomerism is shown by: [1]

- **A** $[CuCl_4]^{2-}$
- **B** $[Ni(en)_3]^{2+}$
- **C** $[Cu(H_2O)_6]^{2+}$
- **D** $[Ag(NH_3)_2]^{+}$

3.2 The *trans* isomer of a square planar complex is often: [1]

- **A** polar
- **B** non-polar (dipoles cancel)
- **C** optically active
- **D** coloured only

3.3 (a) Draw the cis and trans isomers of the square planar complex $[Pt(NH_3)_2Cl_2]$. [2]

(b) Explain why $[Ni(en)_3]^{2+}$ shows optical isomerism. [2]

3.4 State, with a reason, which of the cis or trans form of $[Pt(NH_3)_2Cl_2]$ is polar. [2]

3.5 The complex $[Pt(NH_3)_2Cl_2]$ is square planar; $[Co(NH_3)_4Cl_2]^+$ is octahedral; $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ is octahedral with three bidentate ligands.

(a) Draw the two geometrical isomers of $[Pt(NH_3)_2Cl_2]$ and label each cis or trans. [3]

(b) Explain which of the two is polar, and why the other is not. [2]

(c) State how many geometrical isomers $[Co(NH_3)_4Cl_2]^+$ has, and describe how they differ. [2]

(d) Explain what makes $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ **optically** active, and describe how the two forms could be told apart. [4]

Solutions

2.1 geometrical (cis/trans) isomerism.

2.2 it has two non-superimposable mirror images (e.g. an octahedral complex with bidentate ligands).

3.1 B. $[Ni(en)_3]^{2+}$ (octahedral with three bidentate ligands) shows optical isomerism.

3.2 B. In the trans form the dipoles cancel, so it is non-polar.

3.3 (a) cis — the two NH_3 (and two Cl) adjacent; trans — the two NH_3 (and two Cl) opposite.
(b) it is octahedral with three bidentate (en) ligands, giving two non-superimposable mirror images (enantiomers).

3.4 the cis form is polar; its two Pt–Cl dipoles are on the same side and do not cancel, while in the trans form they are opposite and cancel.

3.5 (a) Square planar with Pt at the centre; **cis** has the two Cl on adjacent corners, **trans** has them opposite.
(b) The **cis** isomer is polar: its two Pt–Cl bond dipoles point to the same side and add, whereas in the trans isomer they point in exactly opposite directions and cancel, so the molecule has no overall dipole.
(c) Two: in the *cis* form the two chloride ligands occupy adjacent (90°) positions, in the *trans* form they are opposite (180°).
(d) The three bidentate ligands wrap round the metal in a propeller arrangement, so the complex has no plane of symmetry; it is therefore **chiral** and exists as two non-superimposable mirror images (optical isomers / enantiomers). They rotate the plane of plane-polarised light by equal amounts in **opposite** directions, which a polarimeter detects; in every other physical and chemical property they are identical.

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.

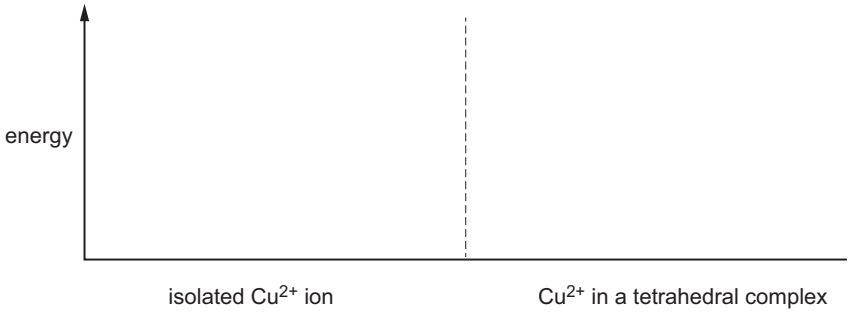
Table 5.1

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 $[Au(CN)_2Br_2]^-$ displays geometrical (cis / trans) isomerism.

Draw the structure of *trans*-$[Au(CN)_2Br_2]^-$. 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 mol dm^{-3} MnO_4^- is added.

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

$$3MnO_4^- + 5V^{2+} + 3H_2O \rightarrow 3Mn^{2+} + 5VO_3^- + 6H^+$$

(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.

..... VO_3^- + ... Zn + ... → ..... V^{2+} + ... Zn^{2+} + ...

[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}
$[Cd(CH_3NH_2)_4]^{2+}$	3.5×10^6
$[Cd(en)_2]^{2+}$	4.0×10^{10}

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

..... [1]

(ii) Some $Cd^{2+}(aq)$ 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 $[Cd(CH_3NH_2)_4]^{2+}$.

K_{stab} =

[1]

[Total: 7]

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.

- $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ .....
- $[CuCl_4]^{2-}(aq)$ .....

[1]

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

.....

.....

.....

.....

.....

..... [3]

(d) **(i)** When an excess of $NH_3(aq)$ is added to a solution of $[CuCl_4]^{2-}(aq)$, $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is formed.

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

type of reaction .....

equation

$[CuCl_4]^{2-}$ + ... ⑤ $[Cu(NH_3)_4(H_2O)_2]^{2+}$ + ...

[2]

(ii) The $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion shows stereoisomerism.

Complete the three-dimensional diagrams in Fig. 1.1 to show the **two** different stereoisomers of $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

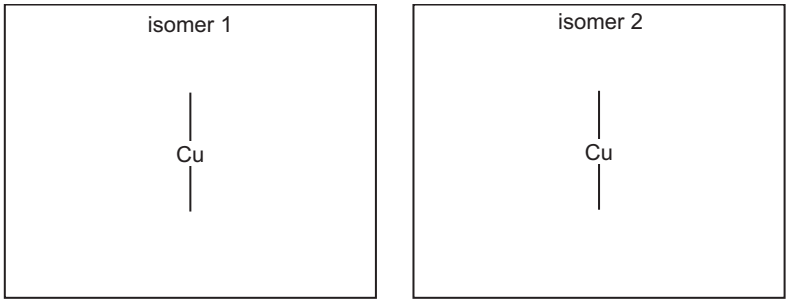


Fig. 1.1

[2]

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

Explain your answer.

polar isomer .....

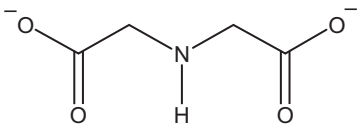
explanation .....

.....

[1]

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

P



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

.....

.....

..... [1]

(ii) 2 moles of dianion **P**, $C_4H_5NO_4^{2-}$, react with 1 mole of aqueous cobalt(III) ions, $[Co(H_2O)_6]^{3+}$ to form 1 mole of complex ion **Q**.

Deduce the formula and charge of **Q**

..... ⑧ ..... [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}
$[Ag(CN)_2]^-(aq)$	1.1×10^{18}
$[Ag(NH_3)_2]^+(aq)$	1.2×10^{7}
$[Ag(S_2O_3)_2]^{3-}(aq)$	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 mol dm^{-3} $MnO_4^-(aq)$ to reach the end-point.

The equation for the reaction is shown.

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Calculate the percentage by mass of Na_2SO_3 in the sample.

percentage by mass of Na_2SO_3 = ... [3]

[Total: 19]

A-LEVEL CHEMISTRY • EXERCISE SHEET

28.5 Stability constants

Name: _____ Class: _____ Date: _____ **Total: 10 marks**

KEY WORDS stability constant 稳定常数 • complex 配合物 • complex ion 配离子 • ligand 配体 • ligand exchange 配体交换

Objective

Build the skills to answer exam questions on **stability constants** 稳定常数 (K_{stab}) — what they are, writing the expression, and using them.

You must be able to:

- define the stability constant of a complex
- write a K_{stab} expression (leaving out water)
- use K_{stab} values to compare stability and predict ligand exchange

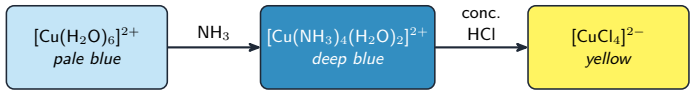
1 Worked examples

■ Stability constants

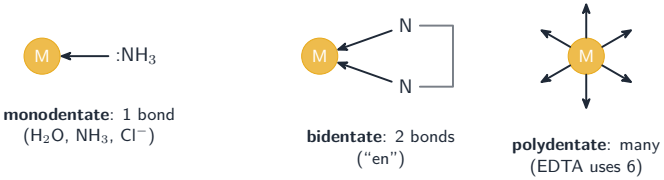
The **stability constant** K_{stab} is the equilibrium constant for forming a complex ion from the metal ion and its ligands in solution. **Water is left out** of the expression.

For $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$:

$$K_{stab} = \frac{[[Cu(NH_3)_4(H_2O)_2]^{2+}]}{[[Cu(H_2O)_6]^{2+}][NH_3]^4}$$



*A **large** K_{stab} = a very stable complex; ligand exchange moves towards the larger K_{stab}*



Ligand denticity affects stability constants

2 Practice

2.1 Define the **stability constant** of a complex. [1]

2.2 State what a large value of K_{stab} tells you about a complex. [1]

3 Exam-style questions

3.1 Which species is **omitted** from a K_{stab} expression in aqueous solution? [1]

- **A** the metal ion
- **B** the incoming ligand
- **C** water
- **D** the complex ion

3.2 In a ligand exchange, the equilibrium moves towards the complex with the: [1]

- **A** smaller K_{stab}
- **B** larger K_{stab}
- **C** smaller charge
- **D** more water ligands

3.3 For $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$:

(a) Write the expression for K_{stab}. [2]

(b) The ammonia complex has a much larger K_{stab} than the water complex. Explain what this means for the ligand-exchange reaction. [2]

3.4 Explain why adding excess ammonia to $[Cu(H_2O)_6]^{2+}$ forms the ammonia complex. [2]

Solutions

2.1 the equilibrium constant for the formation of a complex ion from the metal ion and its ligands in solution.

2.2 the complex is very stable.

3.1 C. Water is omitted from the K_{stab} expression.

3.2 B. The equilibrium moves towards the complex with the larger K_{stab}.

3.3 (a) $K_{stab} = \dfrac{[[Cu(NH_3)_4(H_2O)_2]^{2+}]}{[[Cu(H_2O)_6]^{2+}][NH_3]^4}$.
(b) the ammonia complex is more stable, so the equilibrium lies far to the right and the exchange goes almost to completion.

3.4 the ammonia complex has a much larger K_{stab} (is more stable); so excess ammonia drives the equilibrium to replace the water ligands and form the ammonia complex.

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.

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Explain your answer.

complex that forms at the higher concentration .....

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K_{stab} =

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(d) **(i)** When an excess of $NH_3(aq)$ is added to a solution of $[CuCl_4]^{2-}(aq)$, $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is formed.

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

type of reaction .....

equation

$[CuCl_4]^{2-}$ + ... (22) $[Cu(NH_3)_4(H_2O)_2]^{2+}$ + ...

[2]

(ii) The $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion shows stereoisomerism.

Complete the three-dimensional diagrams in Fig. 1.1 to show the **two** different stereoisomers of $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

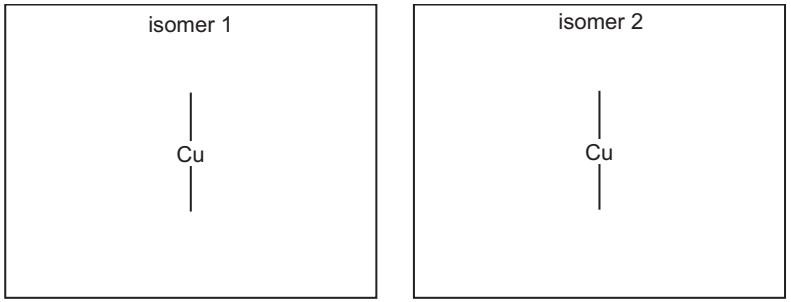


Fig. 1.1

[2]

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

Explain your answer.

polar isomer .....

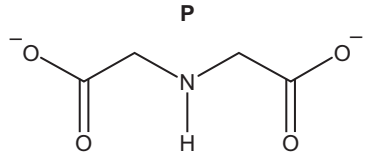
explanation .....

.....

[1]

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

P



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Calculate the percentage by mass of Na_2SO_3 in the sample.

percentage by mass of Na_2SO_3 = ... [3]

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