AUSTRALIAN CHEMISTRY OLYMPIAD
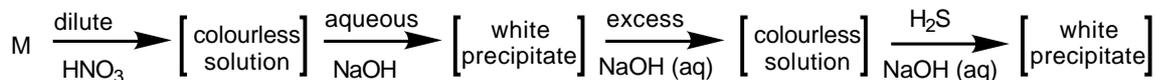
QUALIFYING EXAMINATION

1989

General Instructions

(1)   This paper is in **two** sections and candidates must answer each section according to the instructions. *ie.* Answer **ALL** questions in section A and **any three** (3) in section B.

(2)   All answers must be written in the space provided in the answer book.

(3)   Rough working must be done on left-hand pages of the answer book.

(4)   You are not permitted to refer to books or periodic tables and the only permitted aid is an electronic calculator.

(5)   **Make sure your NAME, HOME ADDRESS and HOME TELEPHONE NUMBER are written on the cover sheet**. Your teacher will fill in the other information.

(6)   You are permitted **10 minutes** to read the paper followed by **120 minutes** to work the questions.

(7)   Data relevant to a question will be found at the end of the question.

SECTION A

It is intended that candidates devote not more than **30 minutes to this section.** Answer **ALL** fifteen (15) questions in this section. Only one choice is allowed per question and this should be made by clearly ticking the chosen answer box in **the answer book.** If you make a mistake, **correct it clearly** so that the examiners can read your answer.

Q1   A metal **M** and its compounds can give the following observable changes in a sequence of reactions
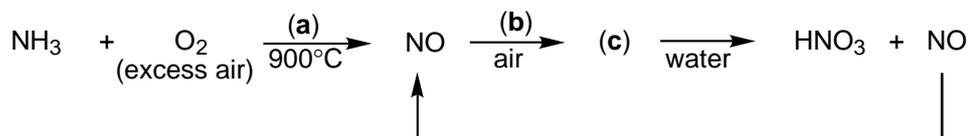
$$M \xrightarrow[\text{HNO}_3]{\text{dilute}} \left[\begin{array}{c}\text{colourless}\\\text{solution}\end{array}\right] \xrightarrow[\text{NaOH}]{\text{aqueous}} \left[\begin{array}{c}\text{white}\\\text{precipitate}\end{array}\right] \xrightarrow[\text{NaOH (aq)}]{\text{excess}} \left[\begin{array}{c}\text{colourless}\\\text{solution}\end{array}\right] \xrightarrow[\text{NaOH (aq)}]{\text{H}_2\text{S}} \left[\begin{array}{c}\text{white}\\\text{precipitate}\end{array}\right]$$

Which of the following metals corresponds to M?

   A. Magnesium.
   B. Zinc.
   C. Aluminium.
   D. Lead.
   E. Tin.

Q2   A student prepared a sample of silicon chloride by passing chlorine over heated silicon and collecting the condensed silicon chloride in a small specimen tube. He analysed the chloride by dissolving a known mass of it in water, and titrating the solution with standard silver nitrate solution. The formula of the silicon chloride as obtained by this method was $SiCl_{2.6}$ as against a 'true' formula of $SiCl_4$. Which of the following possible errors could have resulted in this wrong formula?

   A. The silicon chloride contained excess, dissolved chlorine.
   B. The 'standard' silver nitrate solution was less concentrated than was stated on the label.
   C. More silicon chloride than the student supposed was actually used owing to inaccurate weighing.
   D. The small specimen tube was not dry.
   E. The reaction between the silicon and the chlorine stopped prematurely, leaving some unreacted silicon in the reaction tube.

Q3   The following flow diagram represents the industrial preparation of nitric acid from ammonia.

$$NH_3 \quad + \quad \underset{\text{(excess air)}}{O_2} \quad \xrightarrow[\text{900°C}]{\text{(a)}} \quad NO \quad \xrightarrow[\text{air}]{\text{(b)}} \quad \text{(c)} \quad \xrightarrow[\text{water}]{} \quad HNO_3 \quad + \quad NO$$

Which line of entry describes the undefined reagents, products and reaction conditions?

	(a)	(b)	(c)
A	catalyst	cool (~25°C)	NO_2
B	catalyst	cool (~25°C)	N_2O
C	catalyst	high pressure	NO_2
D	high pressure	catalyst	N_2O_3
E	high pressure	catalyst	NO_2

Q4   In the reaction below which has reached equilibrium, which of the following would cause precipitation of more silver?

$$Ag^+ \text{ (aq)} \quad + \quad Fe^{2+} \text{ (aq)} \quad \rightleftharpoons \quad Ag \text{ (s)} \quad + \quad Fe^{3+} \text{ (aq)} \quad \Delta H < 0$$

   A. Warming.
   B. Removing some of the solid silver.
   C. Increasing the concentration of Fe^{2+} ions.
   D. Increasing the concentration of Fe^{3+} ions.
   E. Decreasing the concentration of Fe^{2+} ions.

Q5 When ammonia is heated in a 0.50 litre vessel at 430°C and 100 atm pressure it decomposes into nitrogen and hydrogen.

$$2NH_3 \text{ (g)} \rightleftharpoons N_2 \text{ (g)} + 3H_2 \text{ (g)}$$

If, after heating a pure sample of ammonia, the equilibrium mixture is found to contain 0.30 moles of NH_3(g), 0.90 moles H_2(g) and 0.30 moles of N_2(g), which of the following pair of values is correct?

	Initial moles of NH_3	K_c at 430° C for ammonia formation
A	0.80	0.37
B	0.90	0.92
C	0.80	0.92
D	0.90	3.70
E	0.90	0.10

Q6 The three elements **X, Y** and **Z** with the electronic configurations shown below all form hydrides

Element	Electronic configuration.
X	$1s^2,2s^2,2p^2$
Y	$1s^2,2s^2,2p^6,3s^1$
Z	$1s^2,2s^2,2p^6,3s^2,3p^6,3d^{10},4s^2,4p^5$

Which line of properties (A, B, C, D or E) correctly lists properties of the hydrides of these elements ?

	Hydride of **X**	Hydride of **Y**	Hydride of **Z**
A	Colourless gas insoluble in H_2O.	Silver/grey solid, reacts with H_2O to form an alkali.	Colourless gas forms a strong acid in H_2O.
B	Colourless liquid, no reaction with H_2O.	Silver/grey solid, forms H_2 with H_2O.	Ionic solid with formula ZH.
C	Colourless gas found naturally.	Does not conduct electricity in the molten state.	Colourless gas, reacts with Cl_2.
D	Non-polar compound reacts with Cl_2 in light	Silver/grey ionic solid with formula YH_2.	Forms when water is added to phosphorus and elemental Z.
E	Colourless gas which burns with air.	Silver/grey solid which reacts violently with acids.	Colourless, corrosive liquid at STP.

Q7 Arsine (AsH_3) is a molecular hydride of a group 5 element. The most likely structure for the arsine molecule in the vapour phase is?
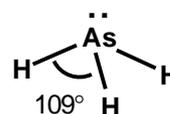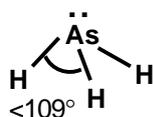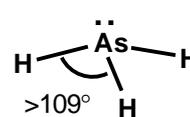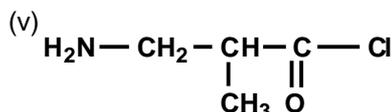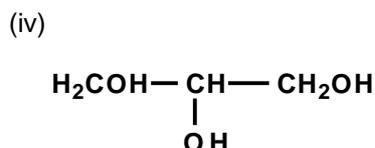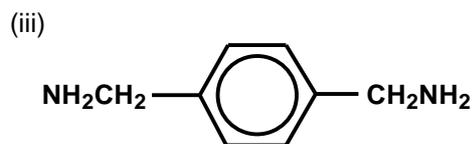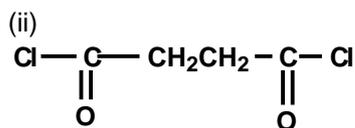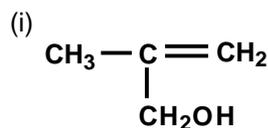
A.
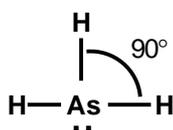
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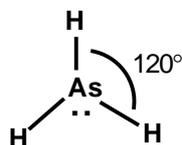
C.

D.

E.

Q8 Equal volumes of two solutions of hydrochloric acid are mixed. One solution has a pH 1 while the other pH 5. The pH of the solution obtained is?

    A. Less than 1.
    B. Between 1 and 2.
    C. 3.
   **D.** Between 4 and 5.
    E. More than 5.

Q9 Suppose that the following five substances were under consideration for the preparation of a polymer of relatively high molecular mass.

(i)

$$CH_3 - C = CH_2$$
$$\quad\quad\;\; | $$
$$\quad\quad CH_2OH$$

(ii)

$$Cl - C - CH_2CH_2 - C - Cl$$
$$\quad\quad \| \quad\quad\quad\quad\quad \|$$
$$\quad\quad O \quad\quad\quad\quad\quad O$$

(iii)

$$NH_2CH_2 - \bigcirc - CH_2NH_2$$

(iv)

$$H_2COH - CH - CH_2OH$$
$$\quad\quad\quad\quad\; | $$
$$\quad\quad\quad\quad OH$$

(v)

$$H_2N - CH_2 - CH - C - Cl$$
$$\quad\quad\quad\quad\quad | \quad \|$$
$$\quad\quad\quad\quad CH_3 \; O$$

In which of the following cases is a polymer of high relative molecular mass **least** likely to be formed?

    A. (i) alone with a catalyst.
    B. (v) alone.
    C. (ii) alone with or without a catalyst.
    D. (ii) and (iv) reacting together.
    E. (ii) and (iii) reacting together.

Q10 How many isomers of 2-naphthol are generated by moving the OH group around the rings? **DO NOT** count 2-naphthol itself.
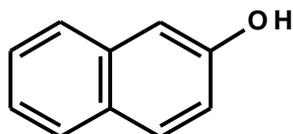

2-naphthol

    A. 0
    B. 7
    C. 3
    D. 2
    E. 1

Q11 Chromium(III) chloride, $CrCl_3.6H_2O$, dissolves in water to form a complex species. If a solution prepared by dissolving 0.1 mole of chromium(III) chloride in water is treated with excess silver nitrate solution, 0.2 mole of silver chloride is precipitated.

The most probable formula of the complex species present in the solution is?

    A. $[Cr(H_2O)_6]^{3+}$
    B. $[Cr(H_2O)_5 \, Cl]^{2+}$
    C. $[Cr(H_2O)_4 \, Cl_2]^{+}$
    D. $[Cr(H_2O)_3 \, Cl]^{2+}$
    E. $[Cr(H_2O)_2 \, Cl_2 \,]^{+}$

Q12 The following diagram shows an electrochemical cell in which the respective half cells contain aqueous 1.0 M solutions of the salts XCl_2 and YCl_3. Given that

$$3X(s) \quad + \quad 2Y^{3+}(aq) \quad \longrightarrow \quad 3X^{2+}(aq) \quad + \quad 2Y(s) \qquad \mathcal{E}_{cell} > 0$$
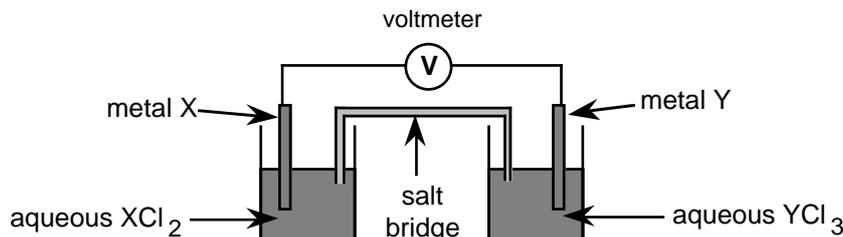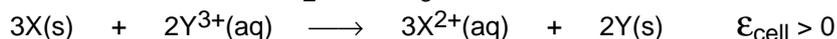
Which one of the following statements is correct?

A. The electrode made from metal X has positive polarity.
B. Electrode Y is the anode.
C. The flow of electrons is from Y to X.
D. The reaction at electrode X is an oxidation.
E. The salt bridge would most likely contain silver nitrate.

Q13 The unstable isotope $^{212}_{82}Pb$ decays with the emission of a β^- particle to form ?

A. An atom with a mass number of 211.
B. An atom with an atomic number of 81.
C. The atom $^{213}_{82}X$.
D. An ion with a charge of +1.
E. An atom with an atomic number of 83.

Q14 Which one of the following reactions is accompanied by an enthalpy change which is equal to the bond energy for H–I?

A. $HI(g) \quad \longrightarrow \quad H(g) \quad + \quad I(g)$
B. $HI(g) \quad \longrightarrow \quad 1/2H_2(g) \quad +1/2I_2(g)$
C $HI(g) \quad \longrightarrow \quad 1/2H_2(g) \quad +1/2I_2(s)$
D. $2HI(g) \quad \longrightarrow \quad H_2(g) \quad + \quad I_2(g)$
E. $HI(g) \quad \longrightarrow \quad H^+(g) \quad + \quad I^-(g)$

Q15 For a series of indicators the following colours and pH range over which colour change takes place are as follows.

Indicator	Colour change over pH range
U	yellow to blue pH 0.0 to 1.6
V	red to yellow pH 2.8 to 4.1
W	red to yellow pH 4.2 to 5.8
X	yellow to blue pH 6.0 to 7.7
Y	colourless to red pH 8.2 to 10.0

Which of the following statements is correct?

A. Indicator V could be used to find the equivalence point for a 0.1M acetic acid and 0.1M ammonium hydroxide (ammonia solution) titration.
B Indicator Y could be used to distinguish between 0.1M and 0.001 M NaOH solutions in water.
C Indicator X could be used to distinguish between solutions of ammonium chloride and sodium acetate.
D Indicator W would be suitable for use in determining the concentration of acetic acid in white vinegar by base titration.
E. Indicator U could be used to distinguish between 0.1 M and 0.01M sulfuric acid.

SECTION B

Candidates should answer any **three** (3) of the four questions in this section. Be sure that **ALL** relevant working is shown in your answers to numerical questions. You should devote 90 minutes to this section.

Q16   Pyrolusite , MnO_2, is the main ore from which manganese is produced. The manganese content of the ore may be determined by reducing the MnO_2 under acidic conditions to Mn^{2+} with the oxalate ion, $C_2O_4^{2-}$, the oxalate ion being oxidised to carbon dioxide during the reaction.
The analytical determination is carried out by adding a known excess volume of oxalate solution to a suspension of the pyrolusite and digesting the mixture on a hot water bath until all the MnO_2 has been reduced. The excess, unreacted, oxalate solution is then titrated with standardised potassium permanganate, $KMnO_4$, solution, after which the manganese content of the ore can be calculated.
Potassium permanganate solution is standardised, under acidic conditions, against oxalate ion where the MnO_4^- ion is reduced to Mn^{2+} and the oxalate ion is oxidised to carbon dioxide.

(a)   A student prepared a standard solution of sodium oxalate by weighing 3.2000g of the dry, anhydrous salt, dissolving it in distilled water and making the solution up to 500.0mL. Three successive titrations, under acidic conditions, of 25.0mL aliquots of the oxalate solution required 24.80mL, 24.76 mL and 24.72mL respectively of potassium permanganate solution.

What is the molarity of the permanganate solution?

(b)   In determining the manganese in pyrolusite a student weighed 0.2123g of the ore into a 250mL conical flask, added 50mL of 2M H_2SO_4 and a 50.0mL aliquot of the standard sodium oxalate solution by pipette to the flask. The flask was carefully heated on a water bath and when all the MnO_2 had been reduced the excess oxalate ion was titrated with the standardised potassium permanganate solution where a titre of 12.87mL was required to react with the excess oxalate.

How many moles of MnO_2 were contained in the sample of pyrolusite?

(c)   What is the % purity (by mass) of the pyrolusite?

(d)   At approximately what temperature should the end point for $KMnO_4 / C_2O_4^{2-}$ titrations be determined, and why?

(e)   An alternative but less frequently used method for this analysis replaces $C_2O_4^{2-}$ with Fe^{2+}. Again the excess of reductant being determined by volumetric analysis with $KMnO_4$. However for accurate determinations of manganese this method requires some special care.

Can you suggest what this might be, assuming that the method used is basically the same as that described for the oxalate method?

DATA
Relative atomic masses: C = 12.01; O = 16.00; K = 39.10; Mn = 54.94; Na = 22.99.

Q17   Before the advent of spectroscopy chemists relied heavily on their knowledge of stoichiometry and chemical reactions to help them determine the structures of newly discovered molecules.
For example the following basic chemistry would have been available in an organic chemistry text in the year 1945

> Cyclohexane, 2-methyl-1-pentene and 2-methyl-2-pentene all have the same molecular formula C_6H_{12}, yet their chemistry is sufficiently different to enable these molecules to be distinguished. Firstly the two alkenes each react with hydrogen and a catalyst to give 2-methylpentane, where as cyclohexane is inert to this reaction. Cyclohexane does not react with oxidants such as potassium permanganate. However this reagent cleaves the double bonds in the olefins such that 2-methyl-1-pentene affords carbon dioxide and pentan-2-one whilst 2-methyl-2-pentene yields propanone and propanoic acid. Furthermore both the alkenes will add water according to Markovnikov's Rule to afford 2-methylpentan-2-ol. Again cyclohexane is unreactive to the hydration conditions.

Using this information chemists were able to ascertain the structure of the compound limonene which they could isolate from the peel of oranges, lemons and grapefruit. See if you can solve the problem given the following additional information.

(a)   Combustion analysis of limonene revealed that it contained 88.24% carbon and 11.76% hydrogen. When reacted with hydrogen in the presence of a catalyst limonene added the equivalent of two moles of hydrogen to yield a product which was shown to have a molecular weight of approximately 140.
What is the molecular formula of limonene and how many rings are likely to be present in its structure?

(b)   Limonene reacts with potassium permanganate to yield only one solid product, the structure of the compound is shown below.
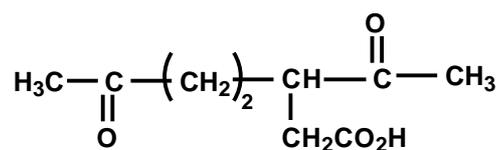
What was the other product, which the chemists failed to see, likely to have been?

(c)   What possible structures can you propose for limonene on the basis of the above information?

(d)   Many molecules isolated from natural sources may be considered as being built up from a simple 5 carbon building block known as isoprene which is linked in a head to tail fashion as shown below. This head to tail linking is so common that it may be used to help decide between possible structures based on isoprene.
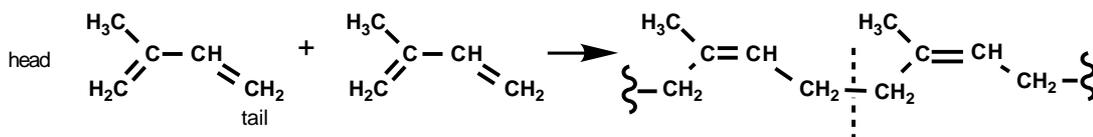
If you assume that the head to tail rule (known as the isoprene rule) applies to limonene. Which of your above structures would you favour as being the correct one to assign to limonene and its hydrogenation product?

(e)   The addition of one molecule of water to limonene affords an alcohol.
Can you suggest a structure for this compound and support you choice with a reason?

(f)   What is the most likely product from the addition of two molecule of water to limonene?

DATA
Relative atomic masses: C = 12.01; O = 16.00; H = 1.01.

Q18 (a) In industry, sodium chlorate is produced by electrolysis of sodium chloride in aqueous solution. Titanium is used as the anode and iron as the cathode. Hydrogen and chlorine are formed together with small amounts of oxygen.
Write the balanced chemical equations for the cathode and anode reactions, and also for the formation of oxygen.

(b) Why is the anode made of titanium rather than iron?

(c) The chlorine gas dissolves in the electrolyte, forming hypochlorous acid, HClO and chloride ions. Write the balanced chemical equation for the reaction between chlorine and the electrolyte.

(d) The hot electrolyte solution is pumped into the reaction vessel, where chlorate ions form by the reaction

$$2HClO \quad + \quad ClO^- \quad + \quad 2OH^- \quad \longrightarrow \quad ClO_3^- \quad + \quad 2H_2O \quad + \quad 2Cl^-$$

The correct molar ratio between HClO and ClO$^-$ is achieved by adjusting the pH value of the solution.
Calculate the pH value that should be maintained in the reaction vessel given that the pK$_a$ for HClO is 7.5.

(e) The solution is concentrated by evaporation. Solid sodium chlorate is filtered off and the solution is returned to the electrolysis cell. For different reasons (eg formation of oxygen), not all the electricity consumed is used for production of sodium chlorate. In practice 5.3 kWh are needed to produce 1kg of sodium chlorate. The voltage over the electrolysis cell is 3.2V.
Calculate the efficiency of the process (current yield) in moles per faraday.

(f) A chlorate factory produces 20,000 metric tons of sodium chlorate a year. The plant is running day and night except for a week once a year for maintenance. The cell voltage is 3.2V and the electricity is delivered at a mains voltage of 120kV
Calculate the minimum current that the factory would need from the mains if the current yield had been 100%.

(g) Sodium perchlorate is produced from sodium chlorate by further electrochemical oxidation in aqueous solution. Write a balanced equation for the formation of the perchlorate ion from the chlorate ion.

DATA
Relative atomic masses: Cl = 35.45;   O = 16.00;   H = 1.01;   Na = 22.99.
1 faraday = 96,486 coulombs.
1 coulomb = 1 amp sec.

Q19 (a) The transition metal ion Pt^{2+} is known to bind a variety of charged and neutral species, known as **Ligands (L)**, to give complex ions of the type PtL_4^{m+} in which the ligands adopt a square-planar arrangement about the metal ion. For example, consider the two complexes $[Pt(NH_3)_4]Cl_2$ and $[Pt(NH_3)_2Cl_2]$. In the first case only the four NH_3 molecules are bound, or **coordinated**, to the metal ion (as indicated by the square brackets in the formula) while in the latter case two NH_3 molecules and two Cl^- ions are coordinated to the metal ion. The second example exists in two isomeric forms, where the chlorines are *cis* or *trans* to each other, which are shown below.

Draw suitable diagrams to illustrate all the isomers that exist for each of the following square-planar complexes.

Note: py is the symbol used for the pyridine ligand. You should simply use the symbol py without recourse to further detail.

  (i) $[Pt(py)_2Br_2]$
  (ii) $[Pt(NH_3)_2BrI]$
  (iii) $K[Pt(NH_3)Cl_2Br]$
  (iv) $[Pt(NH_3)(py)ClBr]$

(b) In the chemistry of Pt^{2+}, the particular isomer formed is dependent on the preparative route taken and is governed by the relative positions of ligands in the following series (known as the **trans series**):

  $CN^- > I^- > Br^- > Cl^- > py > NH_3 > OH^- > H_2O$

Thus, if a complex of the type $[PtX_3Y]$ reacts with Z to give $[PtX_2YZ]$ the relative positions of X and Y in the **trans series** governs the manner in which the reaction proceeds. If Y > X, replacement is exclusively *trans* to Y whereas if X > Y replacement is exclusively *cis* to Y. For example, $Pt(NH_3)_3Cl$ reacts with Br^- to give exclusively *trans*-$[Pt(NH_3)_2ClBr]$ because $Cl^- > NH_3$ in the **trans series**.

Draw suitable diagrams to show the stereochemistry of the complexes *1-3* in the following reaction scheme.
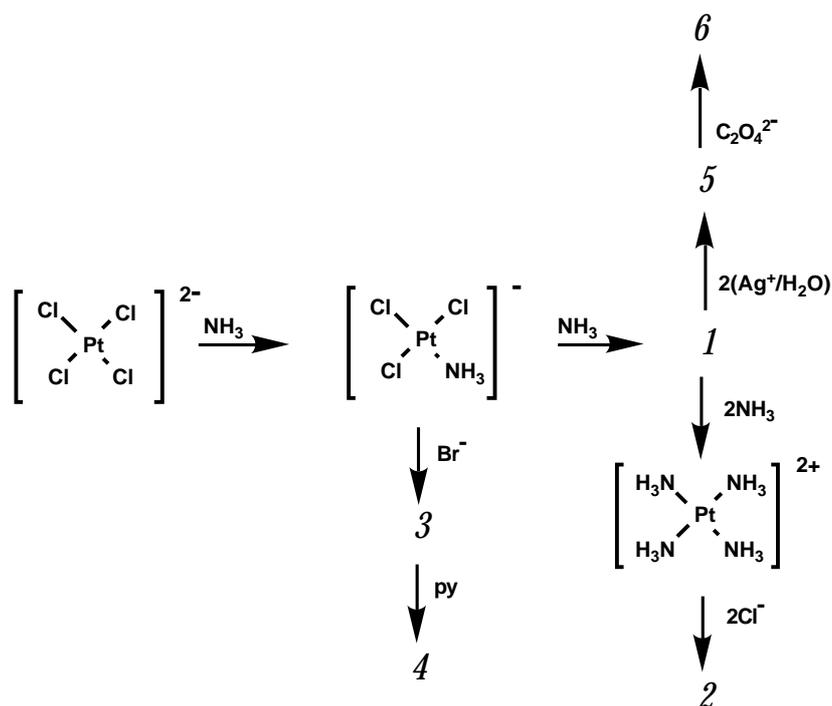
(c)   The reactivity of square-planar coordination compounds of the type [PtX$_2$YZ] with W is more complex, but in general the ligand situated *trans* to the ligand with highest priority in the **trans series** is the one which is displaced. Given this information, draw a suitable diagram to show the stereochemistry for the product, *4*, obtained by reacting *3* (in the previous reaction scheme) with 1 equivalent of pyridine (py).

(d)   The reaction of chloro complexes with silver ion and water leads to the formation of an aquo complex in which water replaces the chlorine. Draw a suitable diagram to show the stereochemistry for the product, *5*, obtained by reacting *1* (in the previous reaction scheme) with 2 equivalents of silver ion and water.

(e)   Given that the oxalate anion (shown below) is a bidentate ligand, draw a suitable diagram to show the stereochemistry for the product, *6*, derived from complex *5* (in the previous reaction scheme) when reacted with 1 equivalent of oxalate ion.

$$^-O - C - C - O^-$$
$$\quad\; \| \;\;\; \|$$
$$\quad\; O \;\;\; O$$

oxalate anion