InkChemistry

ANSWER BOOK

Ligands, the shapes of complexes, isomerism and ligand substitution

Transition metals · Unit C14

AQA 3.2.5.2, 3.2.5.3 · OCR A 5.3.1

19 questions · 61 marks

NAVY EDITION

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SECTION A · Short, 1 to 2 marks

A1 LSC-Q14

B1 the platinum complex is square planar, so the two chloride ligands can be adjacent (90°) or opposite (180°). **B1** the zinc complex is tetrahedral, where every position is adjacent to every other, so only one arrangement exists. [2]

A2 LSC-Q16

B1 $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$ is an equilibrium. **B1** adding water lowers the chloride concentration and raises the water concentration, so the position moves left and blue $[Cu(H_2O)_6]^{2+}$ forms. [2]

A3 LSC-Q20

B1 the trans isomer cannot bind to two neighbouring guanine bases, so it has no anticancer effect. **B1** it can still bind to other molecules in the body and cause side effects, so a mixture adds toxicity with no benefit. [2]

SECTION B · Standard, 3 to 5 marks

B1 LSC-Q1

B1 $[Cu(H_2O)_6]^{2+}$ is octahedral, with bond angles of 90°. **B1** $[CuCl_4]^{2-}$ is tetrahedral, with Cl–Cu–Cl bond angles of 109.5°; allow 109°. **B1** cisplatin is square planar, with bond angles of 90°. **B1** $[Ag(NH_3)_2]^+$ is linear, with an N–Ag–N bond angle of 180°. [4]

B2 LSC-Q6

B1 four particles (one complex and three diamine molecules) become seven (one complex and six ammonia molecules). **B1** the number of particles increases, so the entropy increases and ΔS is positive. **B1** ΔH is close to zero, because six Co–N bonds are broken and six similar Co–N bonds are formed. **B1** so $\Delta G = \Delta H - T\Delta S$ is negative and the substitution is feasible. [4]

B3 LSC-Q11

B1 inside the cell, where the chloride concentration is low, the two chloride ligands are replaced by water. **B1** the platinum bonds to nitrogen atoms on guanine bases in DNA. **B1** it bonds to two guanine bases next to each other on the same strand, so the DNA bends. **B1** the DNA cannot be copied (replication is prevented), so the cell cannot divide and dies. [4]

B4 LSC-Q12

B1 benefit: it is highly effective against some cancers, with survival from testicular cancer above 90%. **B1** drawback: it also acts on healthy rapidly dividing cells, causing hair loss and damage to the lining of the gut. **B1** drawback: it can damage the kidneys, so the dose must be limited. **B1** judgement: its use is justified where the benefit outweighs the risk, with the lowest effective dose and the patient's informed consent. [4]

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B5 LSC-Q3 **B1** $[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$. **B1** the pink solution becomes a pale straw-coloured solution, which darkens on standing in air. **B1** the coordination number stays at 6 and the complex stays octahedral, because NH_3 and H_2O are similar in size and both uncharged. [3]

B6 LSC-Q7 **M1** $T\Delta S = 298 \times 0.210 = 62.6$ kJ mol^{-1}, with ΔS converted to kJ K^{-1} mol^{-1}. **M1** $\Delta G = \Delta H - T\Delta S = -4.0 - 62.6$. **A1** $\Delta G = -67$ kJ mol^{-1}, to two significant figures. [3]

B7 LSC-Q8 **M1** Mr = 195.1 + 2(17.0) + 2(35.5) = 300.1. **M1** percentage = 195.1 ÷ 300.1 × 100. **A1** 65.0%, to three significant figures. [3]

B8 LSC-Q9 **B1** both are octahedral, with four ammonia and two chloride ligands round a cobalt(III) ion. **B1** in the cis isomer the two chloride ligands are on adjacent positions, 90° apart. **B1** in the trans isomer the two chloride ligands are on opposite positions, 180° apart. [3]

B9 LSC-Q10 **B1** three bidentate ligands occupy the six positions of an octahedral complex. **B1** the ligands can be arranged in two ways that are mirror images of each other. **B1** the mirror images are non-superimposable, so they are optical isomers that rotate plane-polarised light in opposite directions. [3]

B10 LSC-Q13 **B1** the blue form is the tetrahedral $[CoCl_4]^{2-}$ complex, with chloride ligands. **B1** absorbed water replaces the chloride ligands to give the pink octahedral $[Co(H_2O)_6]^{2+}$. **B1** the change to $[CoCl_4]^{2-}$ is endothermic, so heating, which also drives off water, moves the equilibrium back to the blue complex. [3]

B11 LSC-Q17 **B1** the complex is $[Fe(C_2O_4)_3]^{3-}$. **B1** it is octahedral with coordination number 6, each ethanedioate forming two coordinate bonds. **B1** four particles become seven, so the entropy increases and the substitution is favoured (chelate effect). [3]

B12 LSC-Q18 **B1** the Pt–Cl and Pt–N bonds are polar, each with a bond dipole. **B1** in the trans isomer identical bonds are opposite each other, 180° apart, so the dipoles cancel and there is no overall dipole. **B1** in the cis isomer both chlorine atoms are on the same side, so the dipoles do not cancel and the molecule is polar. [3]

B13 LSC-Q19 **M1** Kstab = antilog 18.3 = 2.0×10^{18} dm^9 mol^{-3}. **M1** ratio = Kstab × $[en]^3 = 2.0 \times 10^{18} \times (0.010)^3$. **A1** ratio = 2.0×10^{12}, to two significant figures. [3]

B14 LSC-Q21 **B1** $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow [Co(H_2O)_4(OH)_2] + 2H_2O$; allow $Co(OH)_2$ as the product. **B1** the pink solution gives a blue precipitate, which does not dissolve in excess sodium hydroxide. **B1** on standing in air the precipitate turns pink and then darkens to brown as cobalt(II) is oxidised to cobalt(III). [3]

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B15 LSC-Q23 **B1** the complex salt is much less soluble in ethanol than in water, so adding ethanol makes it crystallise out of the solution. **B1** water would dissolve some of the crystals; cold ethanol removes the remaining solution without dissolving the product. **B1** some complex stays dissolved in the water and ethanol, and some is lost on the filter paper and in transfer; ignore 'human error'. [3]

SECTION C · Long, 6 marks or more

C1 LSC-Q4 **Indicative content** [6]

B1 $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$, with only four of the six water ligands replaced. **B1** the blue solution becomes a deep blue solution; a pale blue precipitate may form first, before the ammonia is in excess. **B1** ammonia and water are similar in size and both uncharged, so the coordination number stays at 6 and the complex stays octahedral. **B1** $[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$, with all six water ligands replaced by four chloride ions. **B1** the blue solution turns yellow-green (accept green, then yellow), and adding water reverses the change, so it is an equilibrium. **B1** chloride ions are larger than water molecules and repel one another, so only four fit round Cu^{2+}: coordination number 4, tetrahedral.

Levels

Level 3 (5–6 marks) both equations are correct with the right number of ligands replaced, both observations are given, and the two shapes are explained from the size and charge of the ligands: ammonia replacing water without changing the coordination number, and the larger chloride ions fitting only four round the copper.

Level 2 (3–4 marks) both observations and one equation are right and the shapes are named; the second equation has the wrong number of ligands or does not balance, or the shapes are not tied to ligand size.

Level 1 (1–2 marks) one colour change or one complex is given; six ammonia ligands are often shown replacing all six waters, and the change of shape is not explained.

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