Problems of the 2024/25 National Chemistry Olympiad
11th and 12th grade

1. How Cool is the Atmosphere... (10 p)

During the daytime, the most important oxidant in the atmosphere is radical **A**, which cleanses the air of both natural and human-made pollutants. **A** forms in two stages. In the first stage, molecule **B**, which is an important UV absorber in the stratosphere, decomposes under sunlight into its allotrope **C** and radical **D**. In the second stage, **D** immediately reacts with water vapour, producing **A** as the only product. Radical **A** also forms in the atmosphere when **E** reacts with radical **F** (w_O = 53.3%) in a 1 : 1 molar ratio, producing compound **G** (w_O = 69.6%) as a by-product. At night, the most important oxidant in the atmosphere is radical **H**, which forms through the reaction between **G** and **B**, producing **C** as a by-product.

a) Identify the formulas of particles **A**–**H**. (4)

Radical **A** reacts with compound **I** (2,6,6-trimethyloct-2-ene) in a 1 : 1 molar ratio, producing water and **J**. **A** can also undergo an addition reaction with **I**, forming **K**.

b) Draw the structural formula of the most stable form of compound **J**. (1)

c) Draw the thermodynamically preferred structural formula of **K**. (1)

Molecule **C** is most stable in its triplet state, where it contains unpaired electrons.

d) Draw a Lewis structure representing the triplet state of molecule **C**. (1)

The concentration of stratospheric **B** is threatened by freons (chlorofluorocarbons), which break down under solar radiation to form a reactive radical **L**, which acts as a catalyst in the two-step decomposition of **B** (**reactions 1–2**).

e) Explain, based on the stability trend of radicals, why fluorocarbons in the atmosphere do not significantly affect the concentration of **B** in the stratosphere. (1)

f) Write balanced equations for **reactions 1–2**, assuming that molecule **C** is produced in both reactions. (2)

2. Chemical Volcano (10 p)

When the orange-colored solid $(NH_4)_2Cr_2O_7$ is heated in an open flame, it undergoes spontaneous decomposition, resembling a volcanic eruption. The decomposition reaction produces a dark green solid chromium oxide **A** (w_O = 31.58%) and releases various gases.

a) Determine the formula of chromium oxide **A** using calculations. (1)

b) Write a balanced equation of $(NH_4)_2Cr_2O_7$ decomposition. (1)

... $(NH_4)_2Cr_2O_7$ → ... **A** + ... N_2 + ... H_2O

It is known that the decomposition of $(NH_4)_2Cr_2O_7$ could actually occur in multiple steps. Upon gradual increase in temperature, intermediate compounds **B** and then **C** are formed, both of which are crystalline substances. When 18.61 g of $(NH_4)_2Cr_2O_7$ is heated to 235 °C, 14.83 g of compound **B** is produced. The gases released during heating are passed through a potassium hydroxide column, increasing its mass by 2.66 g. When the remaining gases are passed through a sulfuric acid solution, the total gas volume decreases in half.

c) Determine the formula of compound **B** using calculations. (3)

d) Write a balanced equation for decomposition of $(NH_4)_2Cr_2O_7$ into compound **B**. (1)

When compound **B** is heated to 260 °C, 12.40 g of unstable **C** is formed. The reaction gases once again increase the mass of the potassium hydroxide column, and the volume of the remaining gases decreases in half after being absorbed by sulfuric acid.

e) Determine the formula of compound **C** using calculations. (1)

f) Write a balanced equation for decomposition of **B** into **C**. (1)

g) Write a balanced equation for the overall decomposition of $(NH_4)_2Cr_2O_7$. (2)

... $(NH_4)_2Cr_2O_7$ → ... **A** + ... N_2 + ... H_2O + ... ________ + ... ________

3. pHenomenal Absorption (10 p)

The Lambert-Beer Law describes the absorption of a solution:

$$A_\lambda = \varepsilon_\lambda \cdot c \cdot l$$

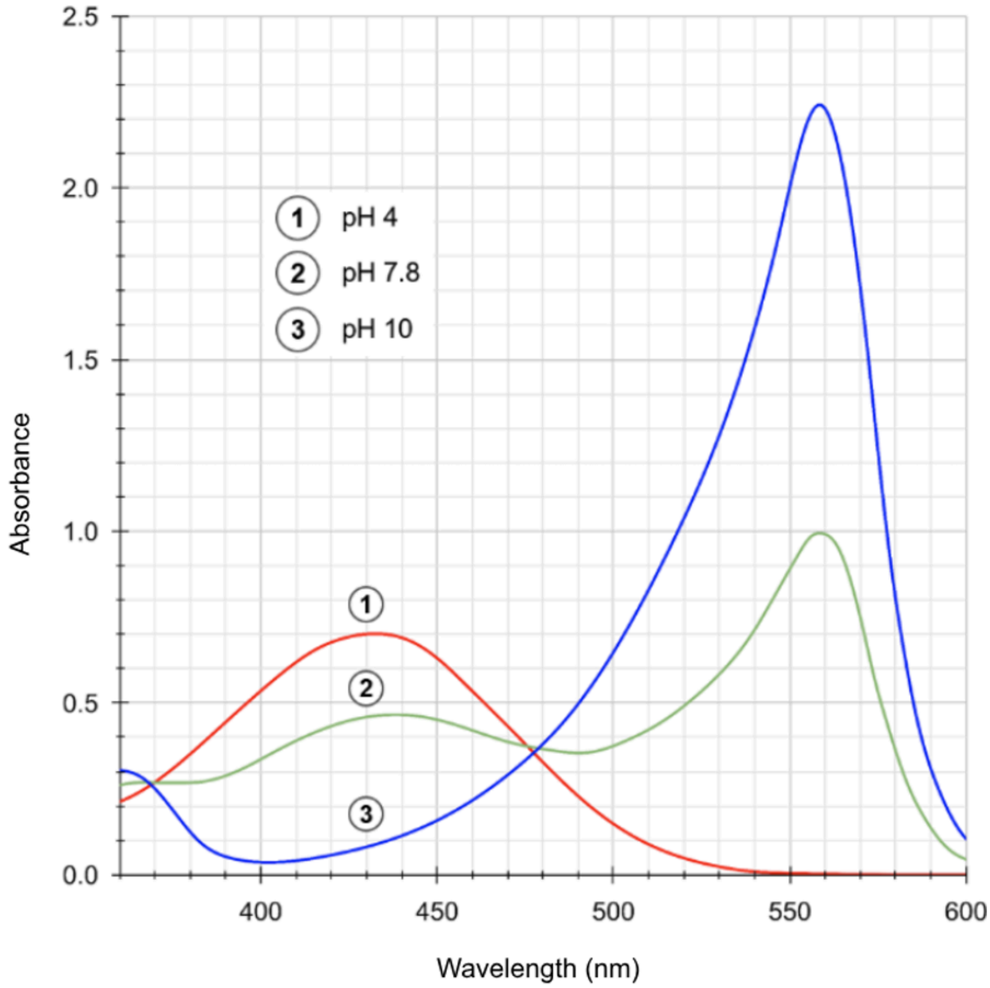
A_λ is the absorbance of the solution at wavelength λ (nm), ε_λ molar absorption coefficient ($M^{-1} \cdot cm^{-1}$) at wavelength λ, c concentration of solution (M) and l is the optical path length (cm), which is the thickness of the solution layer that the light passes through.

If a solution contains multiple components absorbing at a given wavelength (for example **E**, **F** and **G**), the total absorbance at wavelength λ is given by the sum of the individual absorbances:

$$A_\lambda = \varepsilon_\lambda(\mathbf{E}) \cdot c(\mathbf{E}) \cdot l + \varepsilon_\lambda(\mathbf{F}) \cdot c(\mathbf{F}) \cdot l + \varepsilon_\lambda(\mathbf{G}) \cdot c(\mathbf{G}) \cdot l$$

The graph below shows the UV-Vis absorption spectra of aqueous solutions of XH at three different pH values. The analytical concentration c(XH) and the optical path length l are the same for all three spectra. XH is an acid that dissociates in aqueous solution as follows: $XH \rightleftharpoons X^- + H^+$.

- At pH = 10, XH is completely deprotonated, meaning $c(XH) = [X^-]$.
- At pH = 4, XH is completely protonated, meaning $c(XH) = [XH]$.
- At pH = 7.8 (pH of tap water in Tartu) XH is partially deprotonated, meaning the solution contains a mixture of neutral molecules and anions: $c(XH) = [X^-] + [XH]$.



a) Write the wavelengths of the absorption maxima (λ_{max1} and λ_{max2}) corresponding to the neutral form XH and anion X^-. (2)

Isosbestic point is a specific wavelength at which the absorbance of a sample does not change during a chemical reaction or a physical change of the sample.

b) Determine **i)** the number of isosbestic points on the graph and **ii)** their corresponding wavelengths. (2)

c) Calculate:

i) $\varepsilon_{\lambda max1}$(XH) and $\varepsilon_{\lambda max2}$($X^-$), given that the optical path length is l = 1.0 cm and c(XH) = 0.2025 M. (2)

ii) [X^-] and [XH] in the solution at pH = 7.8. (2)

d) i) Derive the formula for calculating the acid dissociation constant pK_a in terms of pH, [X^-] ja [XH]. (1)

ii) Calculate the pK_a value of XH in water. Give the answer with two significant figures. (1)

4. Chemical Calibration (10 p)

In analytical chemistry, a primary standard is a chemically stable solid that does not react with oxygen, CO_2, or water vapour in the air. Primary standards are used to verify the purity of various reagents.

The concentration of an iodine solution can be determined using arsenic(III) oxide. However, the hydroiodic acid formed during the reaction with arsenic(III) oxide interferes with the process and is removed using a Na_2HPO_4–NaH_2PO_4 buffer solution.

Percentages (%) of some particles in H_3PO_4 solution			
pH	**H_3PO_4**	**$H_2PO_4^-$**	**PO_4^{3-}**
5.9	0.02	95.22	0.00
6.8	0.00	71.55	0.00
7.0	0.00	61.35	0.00
7.2	0.00	50.04	0.00
7.4	0.00	38.72	0.00
8.5	0.00	4.78	0.01

a) Calculate the pH of the Na_2HPO_4–NaH_2PO_4 buffer system, given that the concentration of NaH_2PO_4 is twice that of Na_2HPO_4. (1)

In practice, a 0.12 M $NaHCO_3$ solution saturated with carbon dioxide (pH ≈ 7) is used instead of a buffer solution. $NaHCO_3$ solution is added to a 500 cm^3 volumetric flask containing an As_2O_3 (m = 0.77 g) solution, and the volume is adjusted to the mark with water. A 30 cm^3 sample of the iodine solution is titrated with 15.03 cm^3 of As_2O_3 solution.

b) Write down the color of the iodine solution **i)** after the addition of a starch solution and **ii)** at the end of the titration, at the stoichiometric point. (1)

c) i) Complete and balance the reaction equation happening in solution: (1)

… ________ + … ________ + … H_2O → … As_2O_5 + … ________

ii) Calculate the molar concentration (mol·dm^{-3}) of iodine in the solution. (1)

Solid $Na_2S_2O_3 \cdot 5H_2O$ is not suitable as a primary standard since one cannot always be sure that it is a pentahydrate. To determine its exact concentration, 55 cm^3 of sodium thiosulfate solution was titrated dropwise with bromine until a light brownish-yellow color remained. Adding excess $BaBr_2$ solution resulted in a white precipitate, which was filtered and dissolved in 20 cm^3 of 0.05 M EDTA and concentrated ammonia solution. Finally, eriochrome black (indicator) was added, and the titration required 29.18 cm^3 0.0150 M $MgCl_2$ solution to reach a red color change. EDTA reacts with metal cations in a 1 : 1 molar ratio.

d) i) Complete and balance the ionic equation of the reaction between the thiosulfate and bromine: (1)

… ________ + … ________ + … H_2O → … SO_4^{2-} + … Br^- + … ________

ii) Calculate the molar concentration (mol·dm^{-3}) of sodium thiosulfate in the solution. (1)

The oxygen content of water can be determined using Winkler's method. First, a water sample is treated with Mn^{2+} ions, which are oxidised by dissolved oxygen into Mn^{3+} in the alkaline medium. The solution is then acidified, and iodide ions are added, reducing Mn^{3+} back to Mn^{2+} while releasing iodine into the solution.

750 cm^3 water sample was treated with 0.43 g $MnCl_2$ and 0.57 g KI in an alkaline environment. 85% phosphoric acid was then pipetted into the reaction mixture. Finally, a 120 cm^3 sample was titrated with the previously prepared thiosulfate solution. The titration required 26.71 cm^3 of the thiosulfate solution to reach the endpoint.

e) Calculate the oxygen content of the water sample (mg·dm^{-3}) using the sodium thiosulfate concentration found in question **d)**. *If you were unable to determine the concentration of $Na_2S_2O_3$ in question* ***d)****, assume that c($Na_2S_2O_3$) = 0.02025 M.* (2)

f) Draw the Lewis structure of the ion formed when thiosulfate is oxidised during iodometric titration. (1)

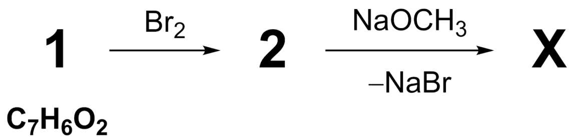
Nitrite ions interfere with oxygen content determination. To remove them, sodium azide (NaN_3) is added to the acidified iodide solution.

g) Complete and balance the ionic equation for this reaction: (1)

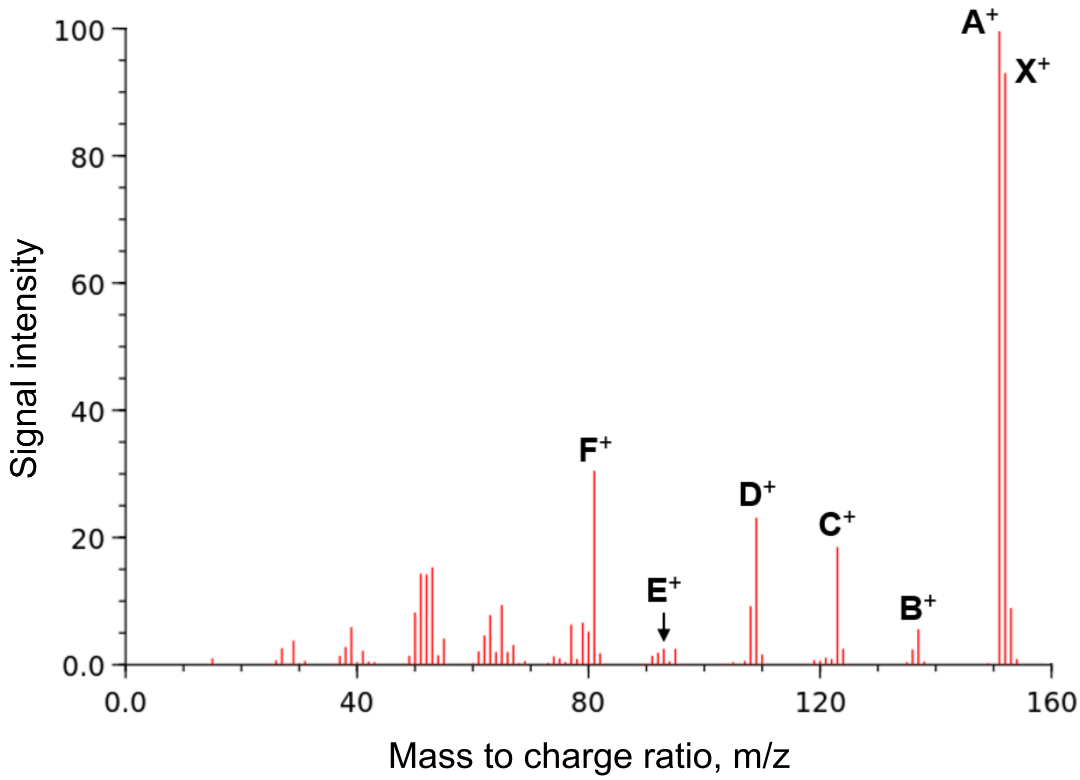
… ________ + … ________ + … H^+ → … N_2 + … H_2O + … ________

5. What substance is this? **(10 p)**

Compound **X** (M = 152 g·mol^{-1}) is a well-known aromatic flavoring compound widely used in sweets. It is known that compound **1** is a para-substituted aromatic compound that reacts with 2,4-dinitrophenylhydrazine (2,4-DNPH).



The mass spectrum of compound **X**, obtained using electrospray ionization, shows the most intense peaks at m/z values: 152 (**X**$^+$), 151 (**A**$^+$), 137 (**B**$^+$), 123 (**C**$^+$), 109 (**D**$^+$), 93 (**E**$^+$) ja 81 (**F**$^+$).



a) Identify the molecular formula of compound **X**. (0.5)

b) Draw the structural formulas of compounds **1**, **2**, and **X**. (3)

c) What is the name of the ion in the mass spectrum of **X** that has a m/z value of 152? (0.5)

- ☐ Zwitterion
- ☐ Molecular ion
- ☐ Carbanion
- ☐ Fragment ion

d) What is the general name for the ions in the mass spectrum of **X** at *m/z* values 151, 137, 123, 109, 93, and 81? (0.5)

- ☐ Zwitterion
- ☐ Molecular ion
- ☐ Carbanion
- ☐ Fragment ion

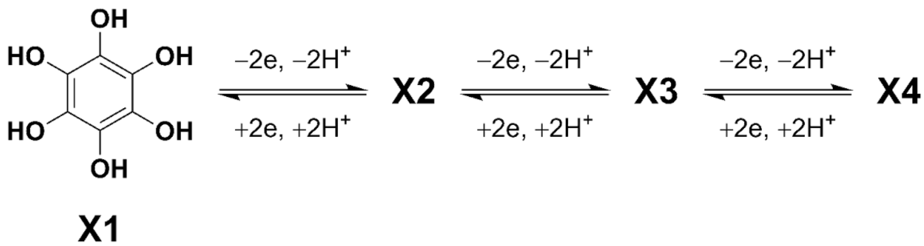
e) The mass spectrum also shows an ion at *m/z* = 153. Briefly explain the possible reasoning why this ion could have a *m/z* value that is higher by one unit. (0.5)

f) Draw the possible structural formulas of the ions corresponding to *m/z* values 151, 137, 123, 109, and 93. (5)

6. Isomers and Frameworks (18 p)

Part 1

In recent years, benzenehexol (**X1**) has been used in the production of metal-organic frameworks (MOFs). The synthesis of these frameworks will be explored in the second part of this problem. Benzenehexol can exist in various oxidised forms **X1–X4**. It is known that compound **X2** has one more mirror plane compared to **X3**, and the final oxidation product is a binary compound **X4**.



a) Draw the structural formulas of compounds **X2–X4**. (1.5)

The binary compound **X4** is extremely unstable, so for further handling it is converted into an octahydrate, which is stable under standard conditions.

b) Draw ***six*** different isomers of the binary compound **X4**: (3)

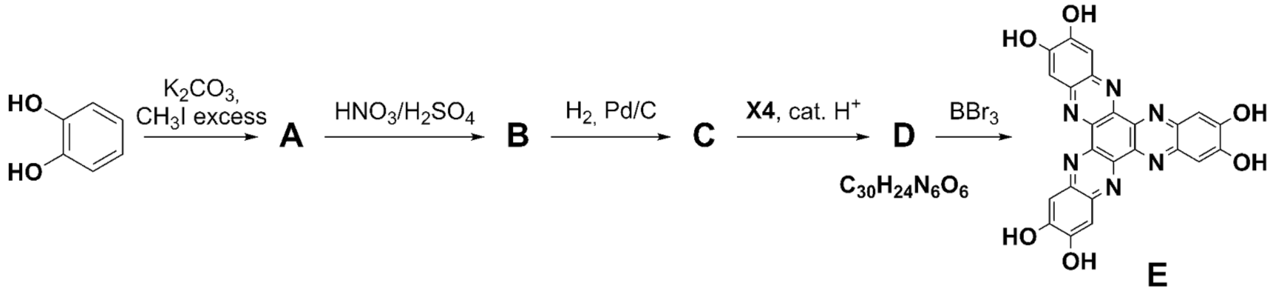
- **i)** ***two*** isomers containing a *six*-membered ring;
- **ii)** ***two*** isomers containing *five*-membered rings;
- **iii)** ***two*** isomers containing *three*-membered rings.

Upon complete hydrogenation of compounds **X1–X4**, a symmetric alcohol **X5** is obtained, which has multiple stereoisomers.

c) Draw all possible stereoisomers of compound **X5** and circle the chiral stereoisomers among the drawn structures. (5.5)

Part 2

The following synthesis scheme depicts the laboratory synthesis of compound **E**, which can be viewed as a derivative of **X1**.

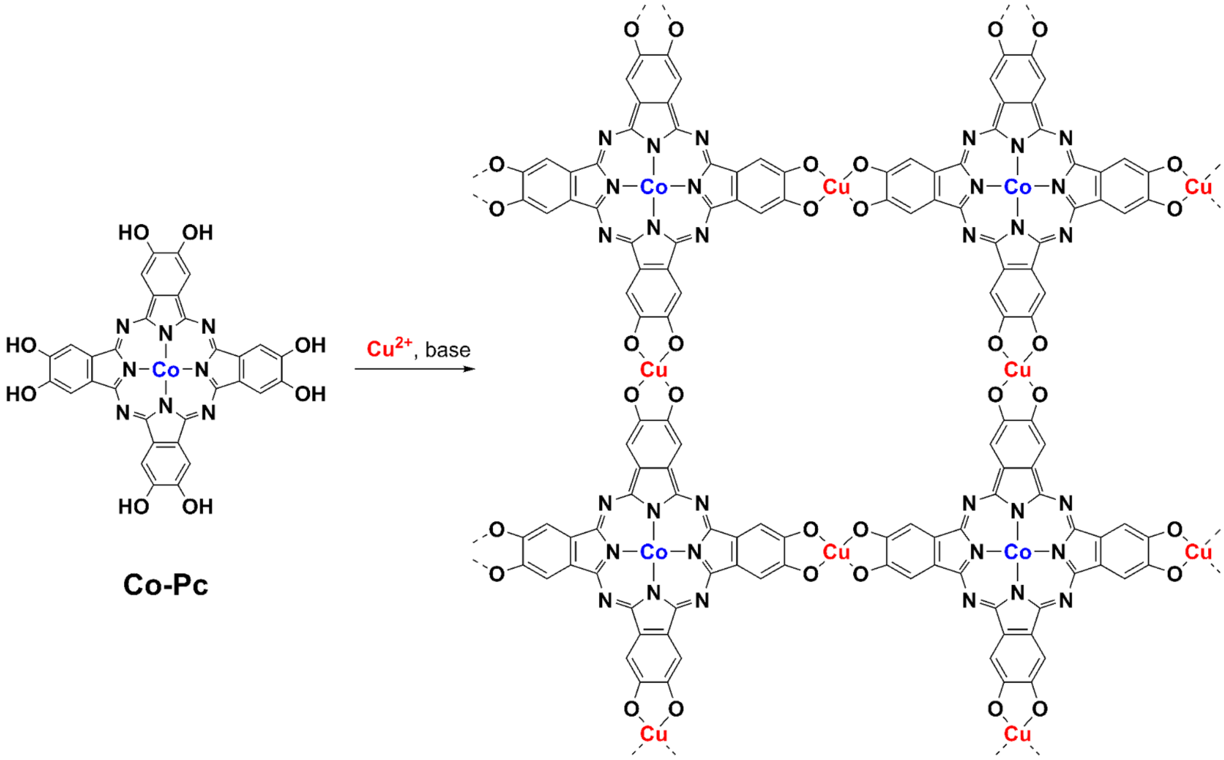


Hints:

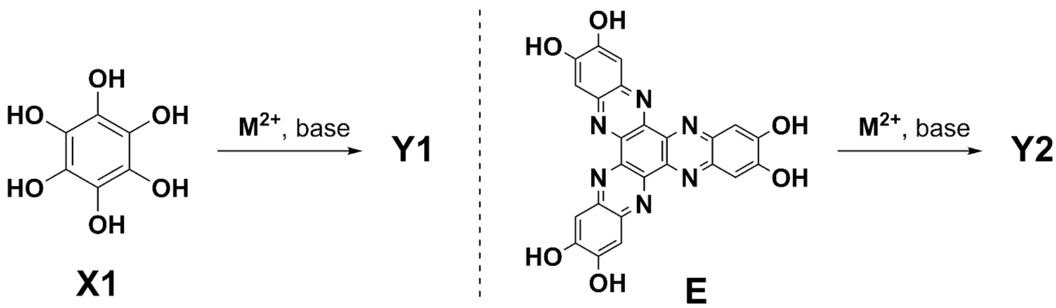
- Compound **A** is the product of a double S_N2 nucleophilic substitution reaction.
- In the step **A** → **B**, a dinitration happens.
- The step **C** → **D** produces H_2O as the only by-product.

d) Draw the structural formulas of compounds **A–D**. (4)

The following scheme describes the synthesis of a MOF based on a single phthalocyanine (Pc) unit. $\mathbf{Cu^{2+}}$ ions with planar configuration are coordinated to four oxygen atoms of the phthalocyanine molecules. These phthalocyanine molecules, upon coordination with $\mathbf{Cu^{2+}}$ ions, form a rigid framework with square-shaped cavities, which are called "pores". The given scheme shows the periodic (i.e. repeating) unit of the MOF, which contains one square-shaped pore. Due to the periodic nature of the MOF and its pore structure, the molecular formula of the MOF is **Cu$_2$(Co-Pc)**.



Compounds **X1** and **E** are used in the synthesis of planar metal-organic frameworks, which are used in electrochemistry as electrodes or electrocatalysts. When reacted with divalent metal cations $\mathbf{M^{2+}}$ (for example Cu^{2+} or Pt^{2+}), these compounds form conjugated planar periodic structures **Y1** and **Y2**, respectively, where each metal cation is coordinated to four oxygen atoms.



e) Choose the shape of the pores in **Y1** and **Y2** MOFs from the following options: (1)

- ☐ triangular
- ☐ square
- ☐ hexagonal

f) Draw the pore structures of **Y1** and **Y2** MOFs. (2)

g) Considering the periodicity of **Y1** and **Y2** MOFs, select the correct molecular formula from the list below. "L" represents the ligand, i.e. molecules of **X1** or **E**. (1)

- ☐ M_3L
- ☐ M_2L
- ☐ M_3L_2
- ☐ M_2L_3