Practical Exam

Vilnius 2014

- Write your name and code on each page of **answer sheets**.
- This examination has **2** practical problems.
- You have 5 hours to work on the exam problems. **Begin** only when the **START** command is given.
- You must **stop** working when the **STOP** command is given.
- All results must be written in the appropriate boxes. Anything written elsewhere will not be graded.
- You are expected to follow **safety rules** given in the IChO regulations. While you are in the laboratory, you must wear **safety glasses** or your own prescription safety glasses if they have been approved. You may use **gloves** when handling chemicals.
- You will receive only **ONE WARNING** from the laboratory supervisor if you break safety rules. On the second occasion you will be dismissed from the laboratory with a resultant zero score for the entire practical examination.
- Do not hesitate to ask your assistant if you have any questions concerning safety issues or if you need to leave the room.
- The official English version of this examination is available on request only for clarification.

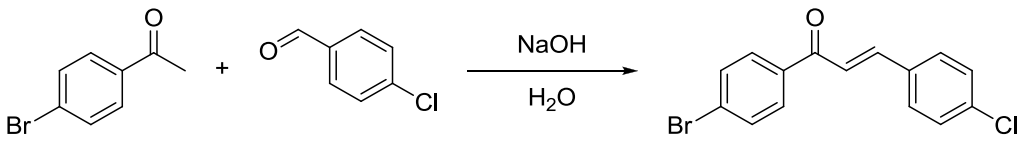
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**1** 1.00794 **H** 0.28																	**2** 4.00260 **He** 1.40
2	**3** 6.941 **Li**	**4** 9.01218 **Be**											**5** 10.811 **B** 0.89	**6** 12.011 **C** 0.77	**7** 14.0067 **N** 0.70	**8** 15.9994 **O** 0.66	**9** 18.9984 **F** 0.64	**10** 20.1797 **Ne** 1.50
3	**11** 22.9898 **Na**	**12** 24.3050 **Mg**											**13** 26.9815 **Al**	**14** 28.0855 **Si** 1.17	**15** 30.9738 **P** 1.10	**16** 32.066 **S** 1.04	**17** 35.4527 **Cl** 0.99	**18** 39.948 **Ar** 1.80
4	**19** 39.0983 **K**	**20** 40.078 **Ca**	**21** 44.9559 **Sc**	**22** 47.867 **Ti** 1.46	**23** 50.9415 **V** 1.33	**24** 51.9961 **Cr** 1.25	**25** 54.9381 **Mn** 1.37	**26** 55.845 **Fe** 1.24	**27** 58.9332 **Co** 1.25	**28** 58.6934 **Ni** 1.24	**29** 63.546 **Cu** 1.28	**30** 65.39 **Zn** 1.33	**31** 69.723 **Ga** 1.35	**32** 72.61 **Ge** 1.22	**33** 74.9216 **As** 1.20	**34** 78.96 **Se** 1.18	**35** 79.904 **Br** 1.14	**36** 83.80 **Kr** 1.90
5	**37** 85.4678 **Rb**	**38** 87.62 **Sr**	**39** 88.9059 **Y**	**40** 91.224 **Zr** 1.60	**41** 92.9064 **Nb** 1.43	**42** 95.94 **Mo** 1.37	**43** (97.905) **Tc** 1.36	**44** 101.07 **Ru** 1.34	**45** 102.906 **Rh** 1.34	**46** 106.42 **Pd** 1.37	**47** 107.868 **Ag** 1.44	**48** 112.41 **Cd** 1.49	**49** 114.818 **In** 1.67	**50** 118.710 **Sn** 1.40	**51** 121.760 **Sb** 1.45	**52** 127.60 **Te** 1.37	**53** 126.904 **I** 1.33	**54** 131.29 **Xe** 2.10
6	**55** 132.905 **Cs**	**56** 137.327 **Ba**	**57-71** **La-Lu**	**72** 178.49 **Hf** 1.59	**73** 180.948 **Ta** 1.43	**74** 183.84 **W** 1.37	**75** 186.207 **Re** 1.37	**76** 190.23 **Os** 1.35	**77** 192.217 **Ir** 1.36	**78** 195.08 **Pt** 1.38	**79** 196.967 **Au** 1.44	**80** 200.59 **Hg** 1.50	**81** 204.383 **Tl** 1.70	**82** 207.2 **Pb** 1.76	**83** 208.980 **Bi** 1.55	**84** (208.98) **Po** 1.67	**85** (210) **At**	**86** (222.02) **Rn** 2.20
7	**87** (223) **Fr**	**88** (226.03) **Ra** 2.25	**89-103** **Ac-Lr**	**104** (261.11) **Rf**	**105** (262.11) **Db**	**106** (263.12) **Sg**	**107** (262.12) **Bh**	**108** (265) **Hs**	**109** (266) **Mt**	**110** (271) **Ds**	**111** (272) **Rg**	**112** (285) **Cn**	**113** (284) **Uut**	**114** (289) **Fl**	**115** (288) **Uup**	**116** (292) **Lv**	**117** (294) **Uus**	**118** (294) **UUo**

Atomic number → **1** / 1.00794 / **H** / 0.28 ← Atomic weight; **Atomic symbol**; Covalent radius, Å

57 138.906 **La** 1.87	**58** 140.115 **Ce** 1.83	**59** 140.908 **Pr** 1.82	**60** 144.24 **Nd** 1.81	**61** (144.91) **Pm** 1.83	**62** 150.36 **Sm** 1.80	**63** 151.965 **Eu** 2.04	**64** 157.25 **Gd** 1.79	**65** 158.925 **Tb** 1.76	**66** 162.50 **Dy** 1.75	**67** 164.930 **Ho** 1.74	**68** 167.26 **Er** 1.73	**69** 168.934 **Tm** 1.72	**70** 173.04 **Yb** 1.94	**71** 174.04 **Lu** 1.72
89 (227.03) **Ac** 1.88	**90** 232.038 **Th** 1.80	**91** 231.036 **Pa** 1.56	**92** 238.029 **U** 1.38	**93** (237.05) **Np** 1.55	**94** (244) **Pu** 1.59	**95** (243.06) **Am** 1.73	**96** (247.07) **Cm** 1.74	**97** (247.07) **Bk** 1.72	**98** (251.08) **Cf** 1.99	**99** (252.08) **Es** 2.03	**100** (257.10) **Fm**	**101** (258.10) **Md**	**102** (259.1) **No**	**103** (260.1) **Lr**

Practical Task #1 part A

Synthesis of a disubstituted chalcone



Chalcones are chemical compounds bearing both aromatic ketone and enone functional groups. They are conveniently prepared in an aldol condensation reaction between acetophenones and aromatic aldehydes. Some chalcones show biological activity while others are useful intermediates in organic synthesis. In this task you will prepare 1-(4-bromophenyl)-3-(4-chlorophenyl)-2-propen-1-one (4'-bromo-4-chlorochalcone) which precipitates from the reaction mixture and is separated by simple filtration.

Chemicals at your workplace:

4'-Bromoacetophenone	Approx. 400 mg in a glass bottle (**Acetophenone**)
10 M NaOH solution	Approx. 1 ml in a glass bottle (**NaOH**)

Chemicals for general use:

4-Chlorobenzaldehyde	At the nearest balance (**Chlorobenzaldehyde**)
Methanol	In a fume hood with a 25 ml graduated cylinder (**MeOH**)
2-Propanol	Near the vacuum filtration system (**2-Propanolis**)

Personal equipment:

1	Erlenmeyer flask with cork, 25 ml
1	Pre-weighed Petri dish (**Product**)
1	Magnetic stirrer
1	Magnetic stirring bar, 10 mm
1	Graduated pipette, 1 ml
1	Vacuum filtration equipment
1	Rubber bulb
1	"**Synthesis waste**" container
1	Spatula

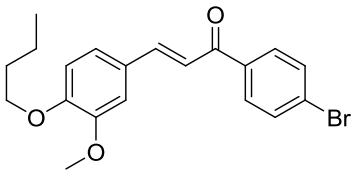
Vacuum aspirators and balances are for general use.

1. Weigh approx. 310 mg of 4-chlorobenzaldehyde directly into the 25 ml Erlenmeyer flask. To the same flask add the pre-weighed 4'-bromoacetophenone (approx. 400 mg) and 10 ml of methanol.
2. Put the flask onto the magnetic stirrer, insert the stirring bar (10 mm) and begin to mix the contents of the reaction flask. Wait for the reagents to dissolve.
3. Using a graduated pipette add 0,30 ml of 10 M NaOH solution into the reaction mixture.
4. Stir the solution for 15 minutes. Product should start to precipitate.
5. Remove the flask from the magnetic stirrer and set it aside for at least 2 hours. It is advised to occasionally swirl the reaction mixture by hand. You should use this time to perform the remaining practical tasks.
6. Using the vacuum filtration equipment filter out the precipitate and thoroughly wash it with 2-propanol.
7. Transfer the product from the Buchner funnel into the pre-weighed Petri dish. Discard the filter paper, but include the stirring bar. Pour the contents of the Bunsen flask into the waste container labeled "Synthesis waste".

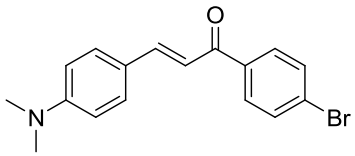
Practical Task #1 part B

Purification of a trisubstituted chalcone

It is fortunate when purification by crystallization or distillation is possible but organic chemists often have to rely on chromatographic methods. Chromatography is based on different interaction between various compounds and a stationary phase (usually silica gel). Polar compounds tend to have higher affinities to silica gel than less polar compounds. Because of that it is more difficult for the mobile phase (eluent) to elute the polar compounds through the column and **less polar compounds get washed out first**. Same effect is seen on TLC plates – eluent carries less polar compounds further than the polar compounds. In this task you will purify a mixture of reaction products – separate the **non-polar target compound chalcone A** from its relatively **polar contaminant chalcone B**. Since your goal is to purify chalcone A you may have to sacrifice some of the yield.



Target compound
Chalcone A



Contaminant
Chalcone B

Chemicals at your workplace:

Eluent	8:2 PE:EtOAc in a plastic bottle, 75 ml (**Eluent**)
Ethyl acetate	20 ml in a plastic bottle (**EtOAc**)
Product mixture solution	In a small glass bottle (**PM**)

Personal equipment:

4	Pasteur pipettes
2	Rubber teats for Pasteur pipettes
1	Pre filled chromatographic column in a laboratory stand
1	Test tube stand
8	Test tubes
1	TLC set: covered beaker, silica gel plates 4×2 cm, glass capillaries (3 pcs. in a test tube), tweezers
1	"**Chromatographically purified product**" bottle
1	"**Chromatography waste**" bottle

UV lamp is for general use.
You may ask for a single refill of eluent and ethyl acetate.

1. Chromatographic column is pre-filled with silica gel. Place the "chromatography waste" container under the column and use the stopcock to equalize the solvent layer with the sand layer.

2. Using a Pasteur pipette **carefully** add the Product mixture solution (labeled PM) to the top of the sand layer. Do not disturb the sand/silica gel.
3. Open the stopcock and allow the solution to soak. Close the stopcock immediately after the solution has fully soaked.
4. Using a Pasteur pipette carefully pour small amount of eluent into the chromatographic column to wash down any remaining sample on the walls.
5. Repeat step 3.
6. Trying not to disturb the stationary phase fill the column with eluent to the top.
7. Position the first test tube below the column and open the stopcock. Observe the separation of the mixture while periodically refilling the column with fresh eluent. IT IS ESSENTIAL NOT TO LET THE STATIONARY PHASE TO DRY OUT.
8. Change the test tube when it fills up or when a compound starts to come out of the column. Collect as much of the target compound as possible while ensuring its separation from the contaminant. It is up to you to choose the best size of the fractions. Don't forget to wash the tip of the column with ethyl acetate before moving to the next test tube.
9. Continue collecting the solution until all of the target compound has left the column. Close the stopcock when finished.
10. Perform TLC analysis of every fraction collected. You should analyze all fractions on a single TLC plate by placing a separate dot for every fraction and then developing the plate in eluent. You may use the UV lamp (366 nm) to better visualize the spots.
11. Choose the fractions containing only the target compound and transfer them to the "Chromatographically purified product" bottle. Transfer the remaining fractions to the "Chromatography waste" bottle.

Practical Task #2

Kinetics of cobalt (III) complex

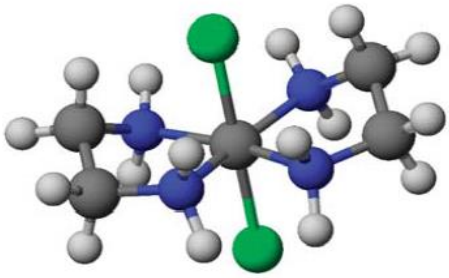
List of materials and equipment/glassware

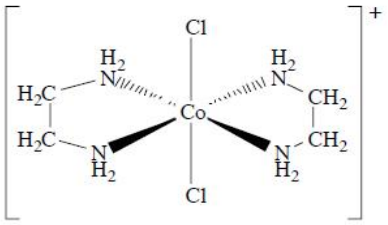
trans-$[Co(en)_2Cl_2]Cl$ in a bottle (with formula on it)	1g
400 mL to 600 mL chemical beaker	2
250ml chemical beaker filled with distilled H_2O	1
Crystallizator	1
10 mL graduated cylinder	1
Test tube	3
5ml graduated pipette	2
Electric stirrer with heating	1
Stir bar	1
3-5 mL glass Pasteur pipette	2
Thermometer	1
100 mL Erlenmeyer flask	1
50 mL Erlenmeyer flask	1
Stand with two holders	1
Distilled water	0.25 L
Ice	15 cubes
Glass rod	1
Balance (+-0.01g)	For common use
A4 sheet of white paper	1
A4 sheet of graph paper	1
Ruler	1
Stopwatch	1
Weighing pan	1
Rubber bulb	1
Spatula	1
Pipette stand	1
Waste container (“INORGANIC WASTE”)	1

How to use the stopwatch:

- press „mode“ button once and you will be in the chronograph mode
- press „reset“ button once to start from zero
- press „ST./STP.“ button once to start
- press „ST./STP.“ button once more to stop
- press „reset“ button to start from zero again

This experiment is a study of the rate of a chemical reaction and the dependence of that rate on the temperature. You will first determine the order of the reaction in the reactant of interest and then you will study the temperature dependence of the rate. This latter study will enable you to calculate the activation energy, E_a, for the reaction. The compound to be studied is the beautiful green, cobalt-based complex called *trans*-dichlorobis(ethylenediamine)cobalt(+) ion.





The ethylenediamine molecule and the chloride ions are called "ligands."

The nitrogen atoms of the ethylenediamine molecule all lie in a plane surrounding the Co^{3+} ion. The line connecting the two Cl^- ions is perpendicular to this plane and passes through the Co^{3+} ion. The prefix *trans* indicates that Cl^- ions are in opposite positions in the complex ion.

The reaction you will study is the aquation of the green complex ion *trans*-$[Co(en)_2Cl_2]^+$ to form the red complex ion $[Co(en)_2(H_2O)Cl]^{2+}$.

trans-$[Co(en)_2Cl_2]^+$ (aq) + H_2O(l) → $[Co(en)_2(H_2O)Cl]^{2+}$(aq) + Cl^- (aq)
green **red**

In this reaction Cl^- ion is replaced by a water molecule in complex ion. Reactions such as this have been studied extensively, and experiments suggest that the initial step in the reaction is the breaking of the Co–Cl bond to give a five-coordinate intermediate.

trans–$[Co(en)_2Cl_2]^+$ (aq) → $[Co(en)_2Cl]^{2+}$(aq) + Cl^-(aq)

$[Co(en)_2Cl]^{2+}$(aq) + H_2O(l) → $[Co(en)_2(H_2O)Cl]^{2+}$(aq)

Experimental Procedure

Begin by preparing an ice-bath in which you cool a 10 mL graduated cylinder, two test tubes, empty 50 mL Erlenmeyer flask and a 100 mL Erlenmeyer flask containing about 100 mL of distilled water. You should use two 400-600 mL beakers as ice baths for water, cylinder and test tubes. One more ice bath is the crystallizator. You will use it for cooling 50 mL flask. The test tubes and graduated cylinder must be dry in the inside except for some slight condensation of moisture from the air.

Fill a 250-mL beaker with water and begin heating it to approximately 80 ºC to prepare your constant temperature bath.

I part – determining the ratio that gives the gray color

- Weight out about 0.3 g of *trans*-$[Co(en)_2Cl_2]Cl$ and dissolve it in 35 mL (use 5 mL pipette) of cold water in your 50 mL flask. Mix the solution thoroughly and keep it cold in the ice bath to inhibit the aquation reaction.
- To prepare a sample of the final product (that is $[Co(en)_2(H_2O)Cl]^{2+}$) of the aquation, add about 10 mL of the green solution, which you prepared in Step 1, to a test tube and heat this in your approximately 80 ºC bath for about 3-5 minutes. The colour of the solution should now be pink to raspberry, indicating that the following reaction has occurred.
  trans-$[Co(en)_2Cl_2]^+$ (aq) + H_2O(liq) → $[Co(en)_2(H_2O)Cl]^{2+}$(aq) + Cl^-(aq)
  green **red**

Cool this pink solution in the ice bath.

Put the 10 mL graduated cylinder in an ice bath, add about 4.5-5.0 mL of the green stock solution, and record the volume to the nearest 0.1 mL. Add the pink solution dropwise with thorough stirring and observe the changes of colours from green to faintly green then to grey and finally to faintly pink (use white sheet of paper as a white background). Under TRIAL 1 on the Report Form, record the volume when the solution appears faintly green, when the appearance is gray, and when the appearance is faintly pink.

Empty the graduated cylinder and add about 2.5 mL of the green stock solution and about 4.5 mL of cold water. Add pink solution and record the data as above under TRIAL 2.

Calculate the ratio indicated on your Report Form for the two trials. The values should be identical within the limits of your ability to detect the colors. This value shows the ratio between *trans*-$[Co(en)_2Cl_2]^+$ (green) and $[Co(en)_2(H_2O)Cl]^{2+}$ (pink-raspberry) species when the grey color appears in your kinetic runs.

II part – determination of reaction order of ligand exchange

1) Add 5 mL of the green stock solution to a cold test tube. To another test tube add 2.5 mL of the green stock solution and 2.5 mL of cold water. Mix well. Immerse these test tubes in the ice bath immediately.
2) Set up a constant temperature bath and adjust the bath temperature to 55-60 °C. Simultaneously transfer the two cold test tubes made up in Step 1 to the bath and begin timing.
   - The test tubes should be immersed deep enough so the liquid level in the tubes is below the water bath level.
   - Starting at the same temperature and having the same solution volume, the temperature of both solutions will increase with the same rate. (Do not worry if the bath temperature declines slightly.)
3) Observe the immersed test tubes against a white background, and record temperature and the time when each solution turns gray.
4) In the answer sheet mark the correct answer about the order of the reaction, followed by the right reasoning.

III part – measurement of activation energy

1) Prepare a new stock solution of *trans*–$[Co(en)_2Cl_2]^+$ by dissolving about 0.3 g of the solid in 5 mL of cold water in a test tube. Store the solution in an ice bath.
2) Add 5 mL of water to a test tube. Clamp the tube so it is immersed in the warm temperature bath. From this point on do not remove the tube from the bath.
3) Hold the bath temperature steady at ±1 °C at some temperature in the 50-75 °C range.
4) When the bath temperature has been constant for a few minutes, rapidly add about 8 drops of the cold, green stock solution to the warm water in the test tube in the water bath. Stir quickly with a stirring rod and observe the time.
5) Observe the color of the reaction solution as in the I part of the experiment and record the time it takes to turn gray.
6) Repeat Steps 2)-5) at three other temperatures (at the very least) in the 50-75 °C range. (It is best to have 4-6 data points for this part of the experiment.)
7) Make a graph ln(1/t) dependence from 1/T graph (from formula

$$ln\frac{1}{t} = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + lnA - ln\left(ln\frac{c_o}{c}\right)$$

where R=8.314J/(K*mol)), A is Arrhenius constant.

8) Use the graph to calculate E_a.

Practical Exam

Answer sheets

Write your name and code on the top of each page

Practical Task #1 part A

Synthesis of a disubstituted chalcone

Upon leaving the workplace you are required to obtain a signature from any of the supervisors signifying that you have provided the Petri dish with the product.

	Supervisor signature
Petri dish with the product was left at the workplace.	

Practical Task #1 part B

Purification of a trisubstituted chalcone

Upon leaving the workplace you are required to obtain a signature from any of the supervisors signifying that you have provided the bottle with the chromatographically purified product.

	Supervisor signature
Bottle with the chromatographically purified product was left at the workplace.	

Practical Task #2

Kinetics of cobalt (III) complex

I part

m(*trans*-$[Co(en)_2Cl_2]Cl$)= _____ (mass for the preparation of the first stock solution)

	Initially green solution; V, mL	Additionally added water; V, mL	Faintly green solution; V, mL	Gray solution; V, mL	Faintly pink solution; V, mL	Ratio of V(green):V(pink) in gray solution
TRIAL 1						
TRIAL 2						
					Average	

II part

Temperature of the water bath	….....K
Time when the stock solution turns grey	….....s
Time when the diluted solution turns grey	….....s

Your experiment proves that the reaction is (tick the right answer):

- of 0 order, because diluted solution changed colour faster.
- of 0 order, because both solutions changed colour at the same time.
- of 0 order, because diluted solution changed colour slower.
- of 1st order, because diluted solution changed colour faster.
- of 1st order, because both solutions changed colour at the same time.
- of 1st order, because diluted solution changed colour slower.
- of 2nd order, because diluted solution changed colour faster.
- of 2nd order, because both solutions changed colour at the same time.
- of 2nd order, because diluted solution changed colour slower.

III part

m(*trans*-$[Co(en)_2Cl_2]Cl$)= _____(mass for the preparation of the second stock solution)

Test number	T, K	t, s	1/T, K^{-1}	1/t, s^{-1}	ln 1/t
1.					
2.					
3.					
4.					
5.					
6.					
7.					

E_a=_____

Show you calculations here:

[Graph paper will be given here by organizer.]