

Grand Prix Chimique
Zagreb, Croatia
25th-30th August 2007

PREPARATIVE TASK

EXPERIMENTAL PROCEDURE

**Reaction of bis(pentane-2,4-dionato)copper(II) with
nicotinamide and 4,4'-bipyridine**

Metal complexes of β -diketones have been studied intensively for many years and have proved useful in a wide range of applications. However, these compounds have not been extensively studied in terms of supramolecular chemistry and solid-state self-assembly involving weak interactions. In this context, copper(II) β -diketonate molecules, being planar and coordinatively unsaturated, are suitable for the exploration of weak interactions that steer the self-assembly of molecules in solids. In particular, the ability of such molecules to form adducts by binding additional ligands provides a way to construct extended metal-containing motifs in which the assembly and organization of molecules is regulated by weak interactions (e.g. hydrogen bonds). Consequently, different choices of addend molecules are expected to result in different solid-state architectures.

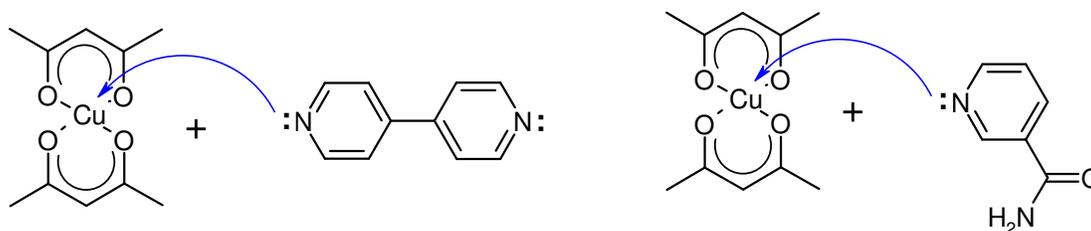
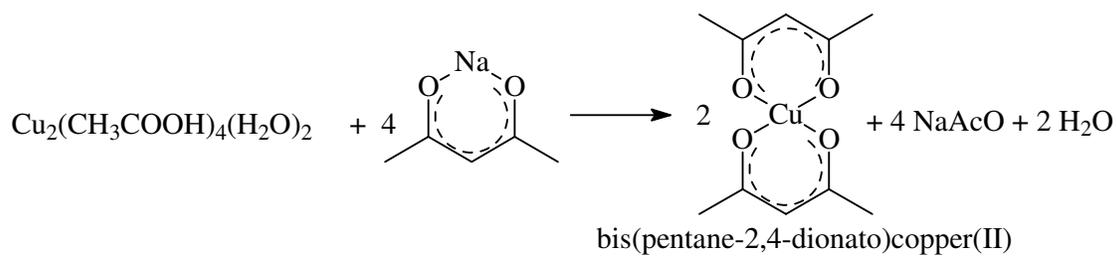
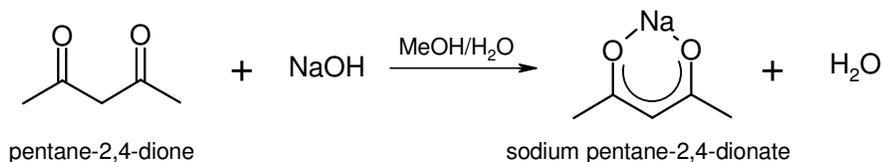
The goal of this experiment is the preparation of the adduct complexes of bis(pentane-2,4-dionato)copper(II) with nicotinamide and 4,4'-bipyridine.

Before the preparation of the adduct complexes, it is necessary to prepare the starting copper(II) β -diketonato compound: bis(pentane-2,4-dionato)copper(II)

This compound is prepared by reacting copper(II) diacetate monohydrate and sodium pentane-2,4-dionate.

The sodium salt is prepared by the reaction of sodium hydroxide and pentane-2,4-dione.

Reaction scheme



Final reaction steps

List of equipment (to be shared and found on the desks and central desk)

Every desk is equipped with: filter paper, silicon grease, scissors, capillaries for determination of the melting point, two ceramic plates, two mortar shells with pestles and paper towels. All of this equipment is meant to be shared by four competitors.

There is also one electric heater for obtaining hot water. It is also meant to be shared by four competitors.

Every desk is equipped with two apparatuses for vacuum filtration. Each of them is meant to be shared by two competitors. It is your obligation to clean the glassware and the Büchner funnel immediately after the use (it will be sufficient to wash it with water and rinse it with rinsing ethanol and disconnect the apparatus from the vacuum).

There are two canisters per desk (each at one sink) equipped with large funnels. You are obliged to wash your equipment over the funnel and collect all the washings in the canisters.

There are three canisters in the fumehoods each intended for one of your waste mother liquors. You are obliged to collect your mother liquors in those canisters.

There are four ballances on the central desk. There is one set of chemicals per a pair of opposite ballances.

There is one oven on the central desk meant to be shared by sixteen competitors. You are obliged to be careful while working with the oven.

There is one binocular magnifier on the central desk of the laboratory ONE meant to be shared by all competitors.

List of equipment (on the bench)

Item	Quantity
Erlenmeyer flask 100 mL	2
Beaker 400 mL	1
Beaker 600 mL	1
Two-neck round-bottomed flask 100 mL	1
Liebig condenser	1
Dropping funnel	1
Petri dish	3
Graduated cylinder 25 mL	1
Glass rod	1
Spatula	1
Chemical spoon	1
Thiele apparatus for determination of melting point	1
Thermometer with a cuted rubber stopper	1
Dropper	1
Glass tube	1
Test-tube	6
Test-tube stand	1
Magnetic stirbar	1
Magnetic stirer	1
Plastic bottle for sodium pentane-2,4-dionate	1
Small glass bottle for bis(pentane-2,4-dionato)copper(II)	1
Crystallizing dish (water bath for round-bottomed flask)	1
Support stand and clamps	

List of chemicals (R- and S-codes)

Chemical	Aggregation	R-codes	S-codes
Distilled water	(l)		
Sodium hydroxide	(s)	35	26/37/39/45
Pentane-2,4-dione	(l)	10/20/22/36/37/38	26/36
Methanol	(l)	11/23/24/25/39	7/16/24/36/37/45
Ethanol	(l)	11/20/21/22/36/37/38/40	7/16/24/25/36/37/39/45
Acetone	(l)	11/36/66/67	9/16/26
<i>N,N'</i> -dimethylformamide	(l)	20/21/36/61	45/53
Copper(II) diacetate monohydrate	(s)	20/22/36/37/38	22/26/28/36/37/39
Nicotinamide	(s)	36/37/38	26/36
4,4'-Bipyridine	(s)	20/21/22/36/37/38	26/27/28/36/37/39/45

4,4'-bipyridine is also a toxic compound.

List of chemicals (quantities and position)

Chemical	Quantity	Position
Distilled water	500 mL	bench
Methanol	250 mL	bench; shared by four competitors
Ethanol	250 mL	bench; shared by four competitors
Acetone	250 mL	bench; shared by four competitors
<i>N,N'</i> -dimethylformamide	250 mL	central desk; shared by two weighing places
Copper(II) diacetate monohydrate	100 g	central desk; shared by two weighing places
Nicotinamide	20 g	central desk; shared by two weighing places
Sodium hydroxide	100 g	central desk; shared by two weighing places
Pentane-2,4-dione	100 mL	central desk; shared by two weighing places
4,4'-Bipyridine	65 mg	test-tube E

$$A_r(\text{C}) = 12.011 \quad A_r(\text{H}) = 1.008 \quad A_r(\text{O}) = 15.999$$

$$A_r(\text{N}) = 14.007 \quad A_r(\text{Cu}) = 63.546 \quad A_r(\text{Na}) = 22.999$$

List of common abbreviations

Pentane-2,4-dione (acetylacetone)	Hacac
Sodium pentane-2,4-dionate	Na(acac)
Copper(II) diacetate monohydrate	Cu(AcO)₂(H₂O) (AcO = acetate ion)
Bis(pentane-2,4-dionato)copper(II)	Cu(acac)₂
Nicotinamide	na
4,4'-bipyridine	44bpy
Methanol	MeOH
Ethanol	EtOH
N,N'-dimethylformamide	dmf

STEP I

Assemble the apparatus needed for **PART II**.

PART I - Preparation of sodium pentane-2,4-dionate

Prepare a solution by dissolving 4.0 g (0.10 mol) of sodium hydroxide in 5.0 mL of water and then adding 20.0 mL of methanol to the obtained aqueous solution. Add the prepared solution slowly, with agitation, to 10.0 g (0.10 mol) of pentane-2,4-dione contained in a 100 mL Erlenmeyer flask. The fine creamy-white crystals of the salt should immediately begin to separate from the solution. Stopper the flask and cool it on an ice/water bath for 30 minutes. Collect the sodium salt on a Büchner funnel using vacuum filtration and dry it for 1 hour in an oven at 120 °C. The weight of the anhydrous product is expected to be 9-10 g (yield 70-80 %). The product is stable and can be stored indefinitely in a stoppered jar.

PART II - Preparation of bis(pentane-2,4-dionato)copper(II)

Prepare a solution of 1.95 g (16.0 mmol) of sodium pentane-2,4-dionate in 15 mL of ethanol. Pour the solution into a two-necked 100 mL round-bottomed flask. Use a hot water bath to facilitate the dissolution of the sodium compound. Connect the flask to a reflux condenser and a dropping funnel. Heat the contents of the flask, with efficient stirring, on a hot water bath.

Prepare a solution by dissolving $\frac{1}{4}$ of the stoichiometric amount of copper(II) diacetate monohydrate in 20 mL of ethanol. Use a hot water bath to facilitate the dissolution of the copper(II) compound.

Add the hot ethanolic solution of copper(II) diacetate monohydrate to the stirred hot solution of sodium pentane-2,4-dionate over a period of 2-3 minutes, with the help of a dropping funnel (if necessary, filter the hot ethanolic solution of copper(II) diacetate monohydrate into the dropping funnel).

Stir the obtained reaction mixture for 20 minutes on the hot water bath and then transfer the contents of the reaction flask into a 100 mL Erlenmeyer flask. Cool the flask on an ice/water bath for 30 minutes.

Collect the resulting blue precipitate of bis(pentane-2,4-dionato)copper(II) by vacuum filtration over a Büchner funnel and dry it for 15 minutes in an oven set at 120 °C.

PART III - Reaction of the bis(pentane-2,4-dionato)copper(II) with either nicotinamide and 4,4'-bipyridine respectively

Weigh 40-42 mg of bis(pentane-2,4-dionato)copper(II) into each of the three test test-tubes **A**, **B** and **C**. Add 3.5 mL of *N,N*-dimethylformamide solvent into each test-tube and then stopper them.

Weigh a four-fold stoichiometric amount [with respect to the copper(II) compound] of nicotinamide into the test-tube **D**.

Warm the test-tubes **A**, **B** and **C** on a boiling water bath until all bis(pentane-2,4-dionato)copper(II) is dissolved. After dissolving bis(pentane-2,4-dionato)copper(II), transfer the contents of the test-tube **B** into the test-tube **D** that was also pre-heated on a boiling water bath. Place the test-tube **D** back into the boiling water bath.

After bis(pentane-2,4-dionato)copper(II) has been dissolved, transfer the contents of the test-tube **C** into the test-tube **E** that was also pre-heated on a boiling water bath for a couple of minutes. Place the test-tube **E** back into the boiling water bath.

Keep the test-tubes **A**, **D** and **E** in the boiling water bath for a couple of minutes and then transfer them into an ice/water bath to allow precipitation. Observe briefly the contents of the test-tubes under a binocular magnifier.

PART IV - Nicotinamide

Nicotinamide must be purified by recrystallisation before the reaction with bis(pentane-2,4-dionato)copper(II). The purity of recrystallised nicotinamide is assessed by measuring its melting point in a Thiele melting point tube. Sufficiently pure nicotinamide will have a melting point in the range 130-135 °C.

Recrystallize 1.50 g of nicotinamide from a mixture of 18 mL of acetone and 2 mL of ethanol:

weigh 1.50 g of nicotinamide and add to it 20 mL of the solvent mixture. Heat the suspension on a hot water bath until the solid dissolves. After brief boiling, filter the hot solution and place it to cool in an ice/water bath.