

**COPPER(I)  $\pi$ -COMPLEXES**  
**WITH ALLYL[(4,6-DIMETHYLPYRIMIDIN-2-YL)SULFANIL]ACETATE:**  
**SYNTHESIS, CRYSTAL STRUCTURE AND NLO PROPERTIES**

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Derivatives of pyrimidine have been a field of intensive studies in pharmaceuticals, biochemistry and synthetic organic chemistry over the last decades. But complexes of allyl derivatives of pyrimidine with copper(I) are not well researched, even though complexes with ligands containing conformationally rigid heterocyclic fragments and flexible allyl groups in recent years have become a field of interest in crystal engineering. In our work we investigated structural behavior of copper(I)  $\pi$ -complexes with allyl[(4,6-dimethylpyrimidin-2-yl)sulfanil]acetate (**L**) (Fig. 1).

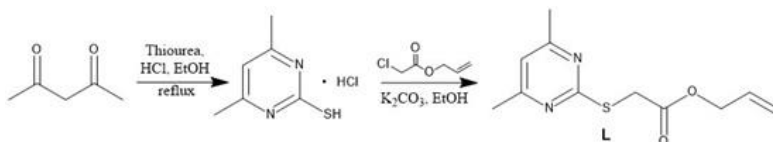


Fig. 1. Synthesis of **L**

**L** was obtained as shown in the Fig. 1. Allyl chloroacetate used in second step was prepared via esterification from monochloroacetic acid and allyl alcohol. Crystals of four complexes (**1–4**, Table 1) were prepared by means of *ac* electrochemical synthesis from ethanolic solutions of **L** and corresponding copper(II) halides. Compounds **1** and **2** were synthesised using excess of copper(II) salt, for obtaining **3** and **4** excessive amounts of **L** were used.

Table 1. Selected crystal data of **1–4**

	Composition	Space group	$V, \text{\AA}^3$	$Z$	Coordination type
<b>1</b>	$[\text{Cu}_2\text{LCl}_2]$	$C2/c$	3158.0(6)	8	$\pi, \sigma$
<b>2</b>	$[\text{Cu}_3\text{LBr}_3]$	$P\bar{1}$	890.51(11)	2	$\pi, \sigma$
<b>3</b>	$[\text{CuLCl}]$	$P2_1/n$	1356.19(13)	4	$\pi, \sigma$
<b>4</b>	$[\text{CuLBr}]$	$P2_1/n$	1385.30(14)	4	$\pi, \sigma$

The polymeric structure of **1** contains two types of Cu(I) atoms, connected by bridging Cl atom. First type of Cu atoms is  $\pi$ -bonded with allylic C=C double bond of one **L** molecule, second type forms  $\sigma$ -bond with N atom of another **L** molecule.

Complex **2** crystallizes in centrosymmetric  $P\bar{1}$  space group. It is a 1D polymer, in which **L** is  $\pi$ -coordinated via allyl group and  $\sigma$ -coordinated through N and S atoms.

Complexes **3** and **4** are isostructural and also possess polymeric structure, in which each Cu(I) atom forms  $\pi$ -bond with allyl group of one molecule of ligand,  $\sigma$ -bond with N atom of second molecule of **L**, and also bond with Cl atom.

For compounds **3** and **4** nonlinear optical properties (particularly, second harmonic generation) were measured.