UNEXPECTED OXIDATIVE C-H ALCOHOL FUNCTIONALIZATION OF 2-THIOHYDANTOINE DERIVITIVE DURING ELECTROCHEMICALLY ASSISTED CuCl π-COMPLEX FORMATION WITH Fe(III)/Cu(0) SOURCE OF Cu(I)

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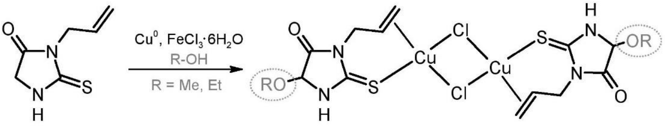
In the present work, we present a synthesis and crystal structures of two new CuCl π-complexes $[Cu_2(me\text{-}ath)_2Cl_2]$ (**1**), $[Cu_2(et\text{-}ath)_2Cl_2]$ (**2**) with 5-alkoxy-3-allyl-2-thiohydantoins, which were formed *in situ* from 3-allyl-2-thiohydantoin during electrochemically assisted synthesis in corresponding alcohol solutions (Scheme 1). As far as authors are concerned, similar reactions have not been previously submitted for this class of compounds and as a result, mechanism of this reaction is currently unstudied. Nevertheless, it is reasonable to suggest, that a crucial role in it is caused by the Fe ions used in a Fe(III)/Cu(0) source of Cu(I) ions, since, in similar systems with Cu(II)/Cu(0) source, such reaction hasn't been observed.



Scheme 1. Scheme of the π-complexes formation

Both complexes crystalize in the centrosymmetric $P2_1/c$ space group in a form of dimeric $[Cu_2L_2Cl_2]$ fragments in which both *R*- and *S*- isomers of the new-formed ligand are presented. In these compounds, Cu(I) atoms have a trigonal-pyramidal coordination environment formed with two bridge Cl atoms (one in basal and one in apical position) and two coordination sites of ligand molecules – namely – thiogroup S atom and C=C double bond of the allyl group. The main difference between these two compounds is in the Cu–Cl$_{apical}$ distance, which is equal to 2.7454(8) Å in **1** and 3.057(2) Å in **2**, which can be explained by the larger sterical hindrances for crystal packing in the case of ethoxy derivative compared to the methoxy one.

Table 1. Table 1. Selected crystal data of **1** & **2**

	Composition	V, Å^3	Cu–Cl1$_{apical}$ distance, Å	C7=C8 distance, Å
1	$[Cu_2(me\text{-}ath)_2Cl_2]$	1051.03(9)	2.7454(8)	1.365(4)
2	$[Cu_2(et\text{-}ath)_2Cl_2]$	1127.38(14)	3.057(2)	1.361(4)

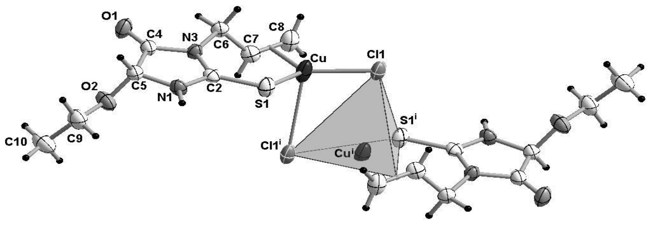


Fig. 1. Fragment of crystal structure **2**. Symmetry code: (*i*) 1-*x* 1-*y*, -*z*