

# Copper(I) $\pi$ -Complexes with *N*-Allylazomethines: Synthesis and Crystal Structure of the $2\text{CuCl} \cdot \text{R}-\text{CH}=\text{N}-\text{C}_3\text{H}_5$ (**R** = 2-Furyl or Phenyl) Compounds

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**Abstract**—The  $2\text{CuCl} \cdot \text{C}_4\text{H}_3(\text{O})-\text{CH}=\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$  (**I**) and  $2\text{CuCl} \cdot \text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$  (**II**) complexes were prepared by an electrochemical synthesis from the ethanol solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and *N*-allyl-2-furylaldimine or *N*-allylbenzaldimine, and their crystal structures were determined [DARCh diffractometer,  $\text{MoK}_\alpha$  radiation, 1453 ( $F \geq 4\sigma F$ ) and 1890 ( $F \geq 6\sigma F$ ) reflections,  $R = 0.028$  and  $0.030$  for **I** and **II**, respectively]. Both compounds crystallize in the monoclinic system; space group  $P2_1/n$ ,  $Z = 4$ . Unit cell parameters are:  $a = 15.716(3)$ ,  $b = 8.764(2)$ ,  $c = 8.426(2)$  Å, and  $\alpha = 111.27(2)^\circ$  for **I** and  $a = 16.175(3)$ ,  $b = 8.827(3)$ ,  $c = 8.757(4)$  Å, and  $\alpha = 110.37(3)^\circ$  for **II**. In both structures, copper(I) is coordinated separately in the  $\pi$  and  $\sigma$  modes to form plane triangles, excepting  $\sigma$ -coordinated Cu(I) atom in **I**, where weakly bonded apical O atom appears [Cu–O 2.788(4) Å]. The lengths of the coordinated C=C bonds are equal to 1.366(7) (**I**) and 1.351(8) Å (**II**), respectively.

Our previous studies on the  $\pi$ -complexation of allyl- and diallylamine with copper(I) salts have shown that both C=C bonds and N atoms of amino groups are capable of coordinating to the same copper(I) atoms because of the formation of the N–H $\cdots$ X (X = Cl, Br, O, or F) contacts and ensuing weakening of the donating properties of nitrogen atom [1]. It is of interest to study the coordination abilities of the C=C bond and the nitrogen atom of azomethine –CH=N– grouping for a series of aldimines, in particular, for  $\text{C}_4\text{H}_3(\text{O})-\text{CH}=\text{N}-\text{C}_3\text{H}_5$  and  $\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{C}_3\text{H}_5$ , prepared from furfural (or benzaldehyde) and allylamine. For this purpose, the copper(I) chloride  $\pi$ -complexes  $2\text{CuCl} \cdot \text{L}$  with *N*-allyl-2-furylaldimine and *N*-allylbenzaldimine were prepared, and their crystal structures were studied.

## EXPERIMENTAL

The ligands were prepared by the condensation of allylamine with furfural or benzaldehyde [2]. High-grade single crystals of  $2\text{CuCl} \cdot \text{C}_4\text{H}_3(\text{O})-\text{CH}=\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$  (**I**) and  $2\text{CuCl} \cdot \text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$  (**II**) were synthesized by an ( $U = 0.3$  V) electrochemical reduction of Cu(II) to Cu(I) in ethanol solutions containing  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and corresponding ligand. The monoclinic prism-shaped crystals were grown by cooling the solution to  $-3^\circ\text{C}$  for several days after electrolysis.

The crystallographic data and experimental parameters are listed in Table 1.

The structures were solved by direct method; light atoms and H atoms were located from difference Fourier syntheses. All non-hydrogen atoms were refined by

full-matrix anisotropic method using CSD program package [3].

Atomic coordinates and thermal parameters for **I** and **II** are listed in Table 2, and interatomic distances, bond angles, and torsion angles are summarized in Table 3.

**Table 1.** Summary of crystal data, data collection and refinement for **I** and **II**

Parameter	<b>I</b>	<b>II</b>
<i>M</i>	333.2	331.2
Space group	$P2_1/n$	$P2_1/n$
<i>a</i> , Å	15.716(3)	16.175(3)
<i>b</i> , Å	8.764(2)	8.827(3)
<i>c</i> , Å	8.426(2)	8.757(4)
$\alpha$ , deg	111.27(2)	110.37(3)
<i>V</i> , Å <sup>3</sup>	1081.5(8)	1172(1)
<i>Z</i>	4	4
$\rho$ (calcd), g/cm <sup>3</sup>	2.046(2)	1.945(2)
$\mu_{\text{Mo}}$ , cm <sup>-1</sup>	45.29	41.76
Radiation	$\text{MoK}_\alpha$	$\text{MoK}_\alpha$
Diffractometer	DARCh	DARCh
Scan mode	$\theta/2\theta$	$\theta/2\theta$
Number of reflections:		
measured	1453	1890
unique	1445	1870
( $F \geq n\sigma F$ )	$n = 4$	$n = 6$
$2\theta_{\text{max}}$ , deg.	60	65
Number of refined parameters	163	184
<i>R</i>	0.028	0.030
<i>R<sub>w</sub></i>	0.031	0.030

**Table 2.** Positional and thermal\* parameters for atoms in **I** and **II**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å <sup>2</sup>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å <sup>2</sup>
<b>I</b>					<b>II</b>				
Cu(1)	0.08071(4)	0.10961(7)	-0.14396(7)	3.84(2)	Cu(1)	-0.08514(4)	0.13776(7)	-0.10912(8)	3.68(2)
Cu(2)	0.04790(4)	0.17704(8)	0.26177(7)	4.35(2)	Cu(2)	0.04180(4)	0.24716(7)	0.16241(9)	4.29(2)
Cl(1)	0.12440(8)	0.2911(2)	0.1115(1)	4.74(4)	Cl(1)	-0.12377(9)	-0.1114(1)	-0.2775(2)	4.66(4)
Cl(2)	-0.06228(7)	0.1074(1)	-0.1414(2)	4.86(4)	Cl(2)	0.05374(8)	0.1430(2)	-0.1170(2)	5.46(4)
O	0.1450(2)	0.3584(4)	0.5442(4)	4.4(1)	N	-0.0272(2)	0.4370(4)	0.2559(4)	3.1(1)
N	-0.0253(2)	0.2600(4)	0.4590(4)	3.4(1)	C(1)	-0.1931(3)	0.2605(6)	-0.0423(6)	4.0(1)
C(1)	0.1916(3)	0.0504(6)	-0.2764(6)	4.2(2)	C(2)	-0.1318(3)	0.3616(5)	0.0363(6)	3.3(1)
C(2)	0.1283(3)	-0.0338(5)	-0.3837(5)	3.5(1)	C(3)	-0.1155(3)	0.4046(6)	0.2151(6)	3.6(1)
C(3)	-0.1154(3)	0.2139(6)	0.4324(6)	4.1(1)	C(4)	-0.0082(3)	0.5823(5)	0.3405(5)	3.3(1)
C(4)	-0.0040(3)	0.3521(5)	0.6107(5)	3.6(1)	C(5)	0.0747(3)	0.6450(5)	0.3922(5)	3.0(1)
C(5)	0.0811(3)	0.4059(5)	0.6620(5)	3.6(1)	C(6)	0.0832(3)	0.8101(5)	0.4798(6)	4.0(1)
C(6)	0.1130(4)	0.5010(6)	0.8148(6)	5.0(2)	C(7)	0.1591(4)	0.8780(6)	0.5278(7)	4.4(2)
C(7)	0.2004(4)	0.5132(7)	0.7905(8)	5.7(2)	C(8)	0.2288(3)	0.7819(6)	0.4945(7)	4.1(2)
C(8)	0.2176(4)	0.4268(7)	0.6277(8)	5.3(2)	C(9)	0.2217(3)	0.6175(6)	0.4116(6)	3.8(1)
H(1.1)	0.208(3)	0.155(6)	-0.274(7)	7(1)	C(10)	0.1460(3)	0.5506(5)	0.3613(6)	3.6(1)
H(1.2)	0.226(3)	-0.009(5)	-0.233(5)	3.9(9)	H(1.1)	-0.222(2)	0.207(4)	0.012(5)	2.6(9)
H(2)	0.107(3)	0.021(5)	-0.450(6)	5(1)	H(1.2)	-0.208(3)	0.264(5)	-0.138(6)	4(1)
H(3.1)	-0.141(3)	0.265(5)	0.531(5)	5(1)	H(2)	-0.107(2)	0.431(4)	-0.011(5)	2.2(8)
H(3.2)	-0.138(2)	0.242(4)	0.345(4)	2.6(7)	H(3.1)	-0.145(3)	0.493(5)	0.262(6)	5(1)
H(4)	-0.044(3)	0.388(5)	0.699(5)	5(1)	H(3.2)	-0.130(2)	0.326(4)	0.255(5)	2.6(8)
H(6)	0.079(3)	0.546(5)	0.907(6)	4(1)	H(4)	-0.049(3)	0.660(5)	0.366(5)	4(1)
H(7)	0.237(4)	0.566(8)	0.871(8)	8(2)	H(6)	0.034(2)	0.869(4)	0.500(5)	2.7(9)
H(8)	0.267(4)	0.403(7)	0.562(8)	7(2)	H(7)	0.162(3)	0.995(6)	0.585(6)	5(1)
					H(8)	0.283(3)	0.834(6)	0.524(6)	5(1)
					H(9)	0.268(3)	0.549(5)	0.389(5)	4(1)
					H(10)	0.143(3)	0.448(5)	0.306(6)	4(1)

\* For non-hydrogen atoms  $B_{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* \hat{a}_i \hat{a}_j$ .

## RESULTS AND DISCUSSION

Complexes **I** and **II** are typical molecular compounds. The  $(Cu_2Cl_2 \cdot L)_2$  dimers incorporate a  $Cu_4Cl_4$  cycle as an inorganic fragment. The copper(I) atoms in these compounds are separately coordinated in the  $\sigma$  and  $\pi$  modes. In both structures, the  $\pi$ -coordinated copper atom is located in the plane of a triangle formed by the C=C bond and two chlorine atoms, the coordinated C=C bonds being elongated to 1.366(7) and 1.351(8) Å for **I** and **II**, respectively. The second independent copper atom in structure **I** has a distorted tetrahedral environment involving the nitrogen atom, two chlorine atoms, and the axial oxygen atom. The elongated Cu(2)–O distance [2.788(4) Å] and OCu(2)N angle [70.8(1)°] in **I** indicate that the fourth vertex of the coordination polyhedron of Cu(2) is “occupied” as a

result of the packing effect. In **II**, the O atom in the L molecule is absent, so that similar copper atom has a trigonal planar environment (Figs. 1, 2).

The short Cu–N contacts [1.932(4) (**I**) and 1.941(5) Å (**II**)] are evidence for the efficient interaction. In the amino complexes, this bond is considerably longer: 2.017(2) Å in  $CuCl \cdot$  allylamine and 2.030(4) and 2.063(4) Å in  $2CuCl \cdot$  diallylamine [4, 5]. Such a behavior of the amine nitrogen atom relative to Cu(I) is due both to the presence of the N(H)⋯Cl hydrogen bonds, which draw electron density away from the nitrogen atom to the chlorine atoms, and to the steric hindrances about the N(H) atoms.

The atomic charges in  $\pi$ -complexes **I** and **II** were calculated using the ZINDO method (HYPERCHEM program package [6]). Because of the  $p-d_\pi$  Cl–Cu

**Table 3.** Bond lengths, bond angles ( $\omega$ ) and torsion ( $\varphi$ ) angles for **I** and **II**

Bond*	<i>d</i> , Å		Angle*	$\omega$ , deg.	
	<b>I</b>	<b>II</b>		<b>I</b>	<b>II</b>
Cu(1)–Cl(1)	2.269(2)	2.268(4)	Cl(1)Cu(1)Cl(2)	107.4(1)	106.3(2)
Cu(1)–Cl(2)	2.247(3)	2.248(4)	Cl(1)Cu(1) <i>m</i> (12)	121.9(1)	123.9(2)
Cu(1)–C(1)	2.033(5)	2.031(6)	Cl(2)Cu(1) <i>m</i> (12)	130.1(1)	129.5(2)
Cu(1)–C(2)	2.092(5)	2.084(6)	C(1)Cu(1)C(2)	38.7(2)	38.3(2)
Cu(1)– <i>m</i> (12)	1.946(5)	1.943(6)			
Cu(2)–Cl(1)	2.229(3)	2.247(4)	Cl(1)Cu(2)Cl(2)	109.2(1)	110.4(2)
Cu(2)–Cl(2)	2.337(3)	2.303(4)	Cl(1)Cu(2)O	87.5(1)	
Cu(2)–N	1.932(4)	1.941(5)	Cl(1)Cu(2)N	134.7(2)	131.8(2)
Cu(2)–O	2.788(4)		Cl(2)Cu(2)O	120.4(1)	
			Cl(2)Cu(2)N	116.1(2)	117.6(2)
			OCu(2)N	70.8(1)	
			Cu(1)Cl(1)Cu(2)	94.1(1)	95.4(2)
			Cu(1)Cl(2)Cu(2)	84.87(9)	83.6(1)
C(1)–C(2)	1.366(7)	1.351(8)			
C(1)–H(1.1)	0.95(6)	0.91(4)			
C(1)–H(1.2)	0.92(4)	0.88(5)			
C(2)–C(3)	1.494(7)	1.501(8)	C(1)C(2)C(3)	122.9(5)	122.9(5)
C(2)–H(2)	0.93(5)	0.94(4)			
C(3)–H(3.1)	0.88(4)	0.88(5)	C(2)C(3)N	112.2(4)	112.3(5)
C(3)–H(3.2)	0.93(4)	0.91(4)			
C(3)–N	1.468(6)	1.476(7)			
N–C(4)	1.284(6)	1.275(7)	C(3)NC(4)	116.2(4)	116.4(5)
C(4)–C(5)	1.431(7)	1.461(7)	NC(4)C(5)	124.3(5)	126.6(5)
C(4)–H(4)	0.93(4)	0.93(5)			
C(5)–C(6)	1.351(7)	1.397(8)	C(4)C(5)C(6)	131.1(5)	118.0(5)
C(5)–O	1.366(6)		OC(5)C(4)	119.1(4)	
			OC(5)C(6)	109.8(5)	
C(5)–C(10)		1.394(7)	C(4)C(5)C(10)		124.3(5)
			C(6)C(5)C(10)		117.7(5)
O–C(8)	1.360(7)		C(5)OC(8)	106.3(4)	
C(6)–C(7)	1.40(1)	1.368(8)	C(5)C(6)C(7)	106.2(5)	121.2(5)
C(6)–H(6)	0.91(5)	0.93(4)			
C(7)–C(8)	1.333(9)	1.379(9)	C(6)C(7)C(8)	107.7(6)	119.9(6)
C(7)–H(7)	0.88(7)	0.98(6)			
C(8)–C(9)		1.383(9)	C(7)C(8)O	110.0(6)	
C(8)–H(8)	0.93(6)	0.98(5)	C(7)C(8)C(9)		119.9(6)
C(9)–C(10)		1.364(8)	C(8)C(9)C(10)		120.1(6)
C(9)–H(9)		0.94(5)			
C(10)–H(10)		0.87(5)	C(9)C(10)C(5)		121.2(5)
Angle	$\varphi$ , deg.		Angle	$\varphi$ , deg.	
	<b>I</b>	<b>II</b>		<b>I</b>	<b>II</b>
Cu(1)Cl(1)Cu(2)Cl(2)	44.1	46.8	C(2)C(3)NC(4)	115.7	112.5
Cu(1)Cl(2)Cu(2)Cl(1)	128.2	129.7	C(3)NC(4)C(5)	178.2	178.2
Cu(1)C(1)C(2)C(3)	106.2	106.2	NC(4)C(5)C(6)	179.7	177.7
Cu(2)NC(4)C(5)	2.3	0.7	C(4)C(5)C(6)C(7)	179.9	178.0
C(1)C(2)C(3)N	146.8	148.9			

\* *m*(12) is the midpoint of the multiple C(1)=C(2) bond.

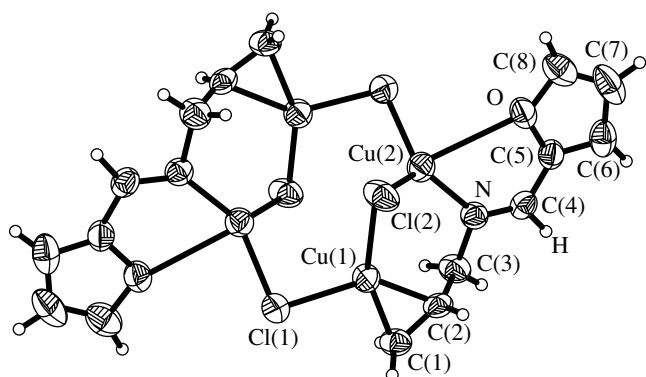


Fig. 1. Structure of the  $(\text{Cu}_2\text{Cl}_2 \cdot \text{L})_2$  dimer in **I**.

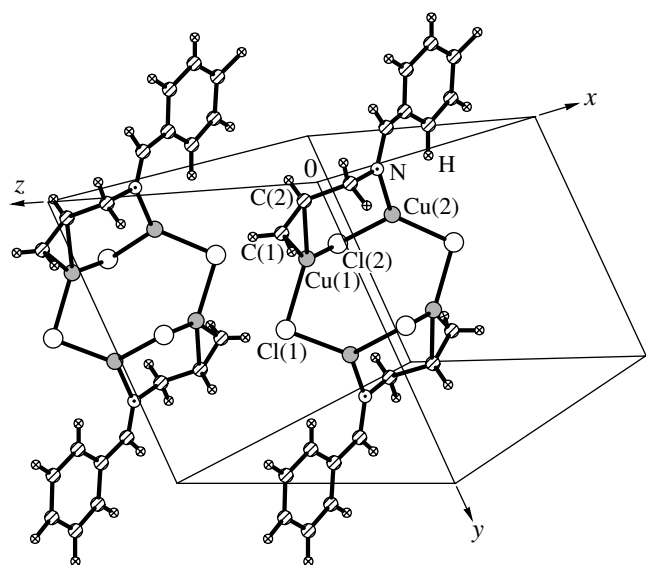


Fig. 2. Fragment of structure **II**.

interaction, the copper atoms in **I** and **II** bear insignificant effective charges:  $q_{\text{Cu}} = 0.02\bar{e}$  (**I**) and  $0.03\bar{e}$  (**II**) on the atom coordinated by the  $\text{C}=\text{C}$  bond and  $q_{\text{Cu}} = -0.01\bar{e}$  (**I**) and  $0.00\bar{e}$  (**II**) on the atom coordinated by

the nitrogen atom. The effective  $\text{Cu}-\text{N}$  interaction also leads to a decrease in the negative charge on the nitrogen atom: in the complexes, it is equal only to  $-0.04\bar{e}$ , whereas in the isolated ligand molecules,  $q_{\text{N}} = -(0.20-0.30)\bar{e}$ . The nitrogen donor atom in the coordination sphere of  $\text{Cu}(\text{I})$  suppresses contribution of the  $(\text{M} \leftarrow \text{L})\sigma$  component to the  $\text{Cu}-(\text{C}=\text{C})$  interaction, the shorter the  $\text{Cu}-\text{N}$  contact, the stronger the effect. Owing to the relatively small contribution from the  $(\text{M} \rightarrow \text{L})\pi$ -dative component of metal-olefin bond and to the efficient  $\text{Cu}-\text{N}$  interaction, the metal atoms in the complexes under study are coordinated separately in the  $\pi$  and  $\sigma$  modes. In the amino complexes, where the  $\text{N}(\text{H})\cdots\text{Cl}$  hydrogen bonds partly draw electron density away from the nitrogen atom to chlorine atoms, the  $\text{Cu}-\text{N}$  interaction is less strong, making allowance for the mixed  $\sigma$ - and  $\pi$ -coordination of copper(I).

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