

Structure of Complexes Formed in the $\text{CuX}_2\text{-Cu-N-Allylisoquinolinium}$ Chloride System ($\text{X} = \text{Cl, Br}$)

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Received November 21, 2003

Abstract—The crystals of *N*-allylisoquinolinium chlorides of the compositions $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]_2\text{Cu}^{\text{II}}\text{Cl}_4$ (**I**), $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]\text{Cu}^{\text{I}}\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**II**), and $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]\text{Cu}^{\text{I}}\text{Cl}_{1.43}\text{Br}_{0.57} \cdot \text{H}_2\text{O}$ (**III**) were prepared by alternating-current electrosynthesis. X-ray diffraction analysis (using diffractometer models DARCH1 for **I**, STOE for **II**, and KUMA/CCD for **III**, MoK_α radiation) showed that the crystals of **I** are monoclinic, space group $P2_1/n$, $a = 14.91(1)$ Å, $b = 10.41(1)$ Å, $c = 16.90(1)$ Å, $\gamma = 109.73(8)^\circ$, $V = 2470(8)$ Å³, $Z = 4$. The crystals of isostructural compounds **II** and **III** are triclinic, space group $P\bar{1}$, $Z = 2$; crystals **II**: $a = 7.2446(6)$ Å, $b = 7.4379(6)$ Å, $c = 12.110(1)$ Å, $\alpha = 80.95(1)^\circ$, $\beta = 85.55(1)^\circ$, $\gamma = 86.60(1)^\circ$, $V = 641.8(2)$ Å³; crystals **III**: $a = 7.253(2)$ Å, $b = 7.459(4)$ Å, $c = 12.151(5)$ Å, $\alpha = 80.82(4)^\circ$, $\beta = 83.73(3)^\circ$, $\gamma = 86.81(4)^\circ$, $V = 644.6(9)$ Å³. The structure of **I** is composed of $\text{Cu}^{\text{II}}\text{Cl}_4^{2-}$ tetrahedra and *N*-allylisoquinolinium cations united by $\text{C-H}\cdots\text{Cl}$ hydrogen bonds in corrugated layers. The crystal structures of π -complexes **II** and **III** are built of $[\text{C}_9\text{H}_7(\text{C}_3\text{H}_5)]_2\text{Cu}_2^{\text{I}}\text{X}_4$ dimers, which form layers along the c axis due to the $\text{C-H}\cdots\text{X}$ hydrogen bonds. An important role in the structure formation is played by water molecules, which crosslink the organometallic layers to form a three-dimensional framework through the $\text{O-H}\cdots\text{X}$ contacts.

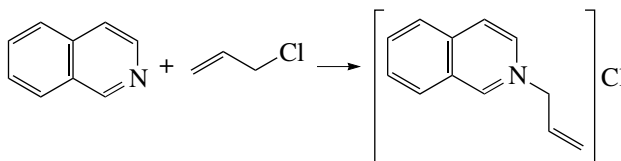
The previous studies of complexation of copper(I) halides with 1,3-diallylbenzotriazolium and 1,3-diallylbenzimidazolium halides demonstrated the possibility of Cu(I)-C=C π -interaction involving either one (CuCl complex with *N,N'*-diallylbenzimidazolium bromide $[\text{C}_7\text{H}_5\text{N}_2(\text{C}_3\text{H}_5)_2]\text{Cu}_2\text{Cl}_{0.67}\text{Br}_{2.33}$ [1]) or two allyl groups (copper(I) complexes with *N,N'*-diallylbenzotriazolium and *N,N'*-diallylbenzimidazolium cations $[\text{C}_6\text{H}_9\text{N}_3(\text{C}_3\text{H}_5)_2]\text{Cu}_2\text{Br}_3$ [2] and $[\text{C}_7\text{H}_5\text{N}_2(\text{C}_3\text{H}_5)_2]\text{Cu}_2\text{Cl}_3$ [3]).

Meanwhile, the study of copper(I) complexes with *N*-allylquinolinium halides revealed no π -interaction in the case of both the chloride complex $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]\text{Cu}_2\text{Cl}_3$ [4] and the purely bromide complex $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]\text{Cu}_2\text{Br}_3$ [5].

In continuation of these studies, it was of interest to elucidate the behavior of the allyl C=C bond of the *N*-allylisoquinolinium cation with respect to the copper(I) atom in the presence of halide ions. The purpose of this study was to prepare the complexes as high-quality single crystals in the $\text{CuX}_2\text{-Cu-N-allylisoquinolinium}$ chloride system ($\text{X} = \text{Cl, Br}$) and to study them by the X-ray diffraction method.

EXPERIMENTAL

Synthesis. *N*-Allylisoquinolinium chloride was prepared by refluxing (40 h) a chloroform solution of isoquinoline (Fluka) with allyl chloride (preliminarily dried with CaCl_2 and distilled)



The crystalline salt was thoroughly washed on a Buchner funnel with benzene and hexane.

The yellow plates of the complex $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]_2\text{CuCl}_4$ (**I**) were prepared as high-quality single crystals by ac electrosynthesis at copper electrodes (voltage 0.4 V, initial current 1 mA, frequency 50 Hz) [6] from an alcohol solution of *N*-allylisoquinolinium chloride and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Under the same conditions, the crystals of $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]\text{CuCl}_2 \cdot \text{H}_2\text{O}$ (**II**) were formed after 7 h as transparent plates. Using alcohol solutions of *N*-allylisoquinolinium chloride and CuBr_2 , the transparent rhombic plates of

Table 1. Crystal data and X-ray single-crystal experiment details for compounds $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]_2\text{CuCl}_4$ (**I**), $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]\text{CuCl}_2 \cdot \text{H}_2\text{O}$ (**II**), and $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]\text{CuCl}_{1.43}\text{Br}_{0.57} \cdot \text{H}_2\text{O}$ (**III**)

Parameter	Value		
	I	II	III
<i>M</i>	543.8	322.7	348.0
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
<i>a</i> , Å	14.91(1)	7.2446(6)	7.253(2)
<i>b</i> , Å	10.41(1)	7.4379(6)	7.459(4)
<i>c</i> , Å	16.90(1)	12.110(1)	12.151(5)
α , deg	90	80.95(1)	80.82(4)
β , deg	90	85.55(1)	83.73(3)
γ , deg	109.73(8)	86.60(1)	86.81(4)
<i>V</i> , Å ³	2470(8)	641.8(2)	644.6(9)
<i>Z</i>	4	2	2
$\rho(\text{exp})$, g/cm ³	1.46	1.60	1.80
$\rho(\text{calcd})$, g/cm ³	1.468	1.659	1.793
<i>F</i> (000)	1116	324	390
The number of reflections	1157	2506	2012
The number of independent reflections with $F \geq 4\sigma(F)^*$	954	1653	1925
$2\theta_{\text{max}}$, deg	43	56	54
Weighing scheme	$(\sigma(F_o^2) + 0.0017F_o^2)$	$(\sigma(F_o^2) + 0.025F_o^2)$	$(\sigma(F_o^2) + 0.0030F_o^2)$
<i>R</i>	0.0432	0.0867	0.0491
<i>R</i> _w	0.0431	0.1102	0.0542
GOOF	1.10	1.07	1.05

* A correction for the Lorentz and polarization factors was applied; for compound **II**, the reflections with $(F \geq 10\sigma(F))$ were used for structure solution.

$[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]\text{CuCl}_{1.43}\text{Br}_{0.57} \cdot \text{H}_2\text{O}$ (**III**) were obtained by the same procedure over a period of 3 days.

The densities of crystals **I**, **II**, and **III** (1.46, 1.60, 1.80 g/cm³, respectively) were determined by the flotation method in a chloroform–bromoform mixture.

X-ray diffraction analysis. After preliminary study by the photo method, the structures were solved using the diffraction arrays obtained on single-crystal diffractometers (for **I**, DARCH1, MoK α radiation, Zr- β -filter, $\theta/2\theta$ scan mode); for **II**, STOE, MoK α radiation, graphite monochromator, $\theta/2\theta$ scan mode; for **III**, KUMA/OXFORD, CCD detector, MoK α radiation. The reflection intensities were corrected for the Lorentz and polarization factors. The structures were solved by the direct method; light atoms were located using the difference Fourier syntheses. The absorption correction for structures **II** and **III** was applied analytically; those for **I** was applied by the DIFABS program. The structures were solved by the CSD [7] and SHELX97 [8] program packages. The hydrogen atoms in structure **II** found geometrically were not refined, but they were used to calculate the reliability factor. In structures **I**

and **III**, the hydrogen atoms found from difference Fourier syntheses were included in the refinement. Since the crystal of complex **II** is a polysynthetic twin, the reliability factors *R* and *R*_w were somewhat overestimated even when reflections with $(F \geq 10\sigma(F))$ were used.

The crystal data and X-ray experiment details for structures **I–III** are summarized in Table 1, atomic coordinates are listed in Table 2, and selected interatomic distances and bond and torsion angles are given in Table 3.

RESULTS AND DISCUSSION

The crystal structure of compound **I** is composed of *N*-allylisoquinolinium cations and CuCl_4^{2-} anions (Fig. 1). The copper(II) atom has a distorted tetrahedral environment of four chlorine atoms. Both crystallographically independent *N*-allylisoquinolinium cations form hydrogen bonds with the CuCl_4^{2-} anions [9], $\text{H}\cdots\text{Cl}$ 2.67(8)–2.74(8) Å (Table 4), giving rise to a lay-

Table 2. Atomic coordinates and thermal parameters ($B_{\text{iso}}/B_{\text{eq}}$)* in structures **I**, **II**, and **III**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}/B_{\text{eq}}, \text{\AA}^2$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}/B_{\text{eq}}, \text{\AA}^2$
I					II				
Cu	0.2292(1)	0.4696(2)	0.65548(9)	3.77(6)	Cu	0.0719(2)	0.2001(2)	0.5360(1)	3.21(4)
Cl(1)	0.3396(3)	0.5639(4)	0.5639(2)	5.3(1)	Cl(1)	0.0730(5)	0.1823(4)	0.7240(2)	3.56(7)
Cl(2)	0.2696(2)	0.2881(3)	0.6905(2)	4.7(1)	Cl(2)	-0.2207(4)	0.1383(4)	0.4897(2)	3.34(7)
Cl(3)	0.0712(2)	0.3676(4)	0.6391(2)	5.6(1)	O	0.533(2)	0.199(2)	0.7271(10)	5.2(3)
Cl(4)	0.2298(3)	0.6577(4)	0.7176(2)	6.5(2)	N	0.204(1)	0.321(11)	0.1830(7)	2.6(2)
N(1)	0.0647(7)	0.181(1)	0.8566(5)	3.7(4)	C(1)	0.288(2)	0.363(2)	0.460(1)	3.8(3)
N(2)	0.6357(7)	0.198(1)	0.0396(5)	4.4(4)	C(2)	0.161(2)	0.357(1)	0.3849(9)	3.7(3)
C(1)	0.051(1)	-0.142(2)	0.7884(9)	5.9(7)	C(3)	0.181(2)	0.223(2)	0.300(1)	3.7(3)
C(2)	0.085(1)	-0.014(2)	0.7822(8)	4.8(6)	C(4)	0.259(1)	0.489(1)	0.1583(8)	2.7(2)
C(3)	0.0298(9)	0.081(1)	0.7934(8)	4.2(5)	C(5)	0.161(2)	0.219(1)	0.102(9)	2.9(2)
C(4)	0.0675(9)	0.307(1)	0.850(1)	5.8(6)	C(6)	0.176(1)	0.286(1)	-0.0092(8)	2.5(2)
C(5)	0.0869(9)	0.135(1)	0.9256(8)	4.4(5)	C(7)	0.334(2)	0.755(2)	0.0148(9)	3.3(3)
C(6)	0.1118(9)	0.216(2)	0.9904(8)	3.8(5)	C(8)	0.350(2)	0.829(2)	-0.0915(9)	3.1(2)
C(7)	0.0944(9)	0.534(2)	0.9014(8)	4.2(6)	C(9)	0.310(2)	0.733(2)	-0.180(1)	3.3(3)
C(8)	0.115(1)	0.622(1)	0.964(1)	4.6(6)	C(10)	0.256(2)	0.557(2)	-0.154(1)	3.5(3)
C(9)	0.1406(9)	0.582(2)	1.037(1)	5.0(6)	C(11)	0.236(1)	0.470(1)	-0.0397(8)	2.6(2)
C(10)	0.1374(8)	0.451(2)	1.0487(8)	4.1(6)	C(12)	0.275(1)	0.569(2)	0.0445(9)	2.9(2)
C(11)	0.0932(9)	0.397(1)	0.910(1)	4.0(6)	H(1a)	0.400	0.278	0.461	} 6.0
C(12)	0.1151(8)	0.355(2)	0.9868(9)	3.2(5)	H(1b)	0.268	0.451	0.514	
C(13)	0.636(2)	-0.015(2)	0.201(1)	11(1)	H(2)	0.047	0.440	0.385	
C(14)	0.671(1)	0.042(2)	0.140(1)	7.3(8)	H(31)	0.068	0.149	0.307	
C(15)	0.630(1)	0.053(2)	0.0615(9)	7.1(7)	H(32)	0.291	0.138	0.315	
C(16)	0.6464(8)	0.294(1)	0.0917(6)	2.8(4)	H(4)	0.289	0.557	0.218	
C(17)	0.619(1)	0.217(2)	-0.0407(9)	5.3(6)	H(5)	0.118	0.093	0.125	
C(18)	0.6126(10)	0.335(2)	-0.0641(8)	5.5(7)	H(6)	0.149	0.212	-0.065	
C(19)	0.6564(8)	0.525(2)	0.1248(8)	4.3(6)	H(7)	0.366	0.824	0.074	
C(20)	0.651(1)	0.645(2)	0.104(1)	5.4(7)	H(8)	0.388	0.958	-0.111	
C(21)	0.633(1)	0.670(1)	0.026(1)	5.3(6)	H(9)	0.325	0.794	-0.260	
C(22)	0.620(1)	0.570(2)	-0.0305(8)	4.7(6)	H(10)	0.228	0.489	-0.214	
C(23)	0.6417(9)	0.420(2)	0.0680(9)	3.6(5)	H(w1)	0.433	0.259	0.681	
C(24)	0.6233(8)	0.439(2)	-0.0115(9)	4.0(6)	H(w2)	0.621	0.131	0.677	
III									
H(1a)	-0.007(6)	-0.197(9)	0.800(5)	} 4.0	Cu	-0.9273(1)	-0.3010(1)	-0.46455(7)	3.20(2)
H(1b)	0.115(6)	-0.163(9)	0.765(5)		X(1)**	-0.9286(2)	-0.3143(2)	-0.2746(1)	3.39(3)
H(2)	0.146(6)	0.036(9)	0.783(5)		X(2)	1.2262(2)	-0.3608(2)	-0.5126(1)	3.27(3)
H(31)	0.003(6)	0.104(9)	0.739(5)		O	-0.4636(8)	-0.2991(8)	-0.2746(5)	5.2(1)
H(32)	-0.036(6)	0.011(9)	0.815(5)		N	-0.7981(7)	-0.1814(7)	-0.8172(4)	2.5(1)
H(4)	0.042(6)	0.345(9)	0.811(5)		C(1)	-0.711(1)	-0.139(1)	-0.5407(6)	3.5(2)
H(5)	0.093(6)	0.045(9)	0.929(5)		C(2)	-0.8365(9)	-0.1490(9)	-0.6140(5)	2.9(2)
H(6)	0.115(6)	0.176(9)	1.039(5)		C(3)	-0.818(1)	-0.2759(9)	-0.6980(6)	3.2(2)
H(7)	0.087(6)	0.559(9)	0.842(5)		C(4)	-0.7425(8)	-0.0139(8)	-0.8434(5)	2.2(2)
H(8)	0.135(6)	0.718(9)	0.972(5)		C(5)	-0.8393(8)	-0.2792(8)	-0.8980(5)	2.6(2)
H(9)	0.162(6)	0.615(9)	1.067(5)		C(6)	-0.8202(9)	-0.2070(9)	1.0066(5)	2.7(2)
H(10)	0.156(6)	0.409(9)	1.097(5)		C(7)	-0.6676(9)	-0.2517(9)	-0.9822(6)	2.8(2)
H(13a)	0.557(6)	-0.044(9)	0.188(5)		C(8)	-0.6521(9)	-0.332(1)	1.0917(6)	2.9(2)
H(13b)	0.691(6)	-0.006(9)	0.235(5)		C(9)	-0.691(1)	-0.236(1)	1.1766(6)	3.3(2)
H(14)	0.737(6)	0.108(9)	0.140(5)		C(10)	-0.7427(9)	-0.058(1)	1.1521(6)	3.1(2)
H(151)	0.691(6)	0.067(9)	0.047(5)		C(11)	-0.7645(8)	-0.0286(8)	1.0387(5)	2.3(1)
H(152)	0.565(6)	-0.002(9)	0.084(5)		C(12)	-0.7237(8)	-0.0706(8)	-0.9551(5)	2.4(2)
H(16)	0.670(6)	0.271(9)	0.144(5)		H(1a)	-0.722(8)	-0.027(8)	-0.501(5)	2(1)
H(17)	0.633(6)	0.150(9)	-0.060(5)		H(1b)	-0.591(9)	-0.230(9)	-0.534(6)	4(7)
H(18)	0.595(6)	0.327(9)	-0.124(5)		H(2)	-0.927(9)	-0.061(9)	-0.620(6)	6(2)
H(19)	0.662(6)	0.495(9)	0.182(5)		H(31)	-0.700(9)	-0.341(8)	-0.693(7)	5(2)
H(20)	0.653(6)	0.714(9)	0.144(5)		H(32)	-0.891(9)	-0.342(9)	-0.691(5)	3(1)
H(21)	0.649(6)	0.777(9)	0.005(5)	H(4)	-0.710(8)	-0.030(8)	-0.790(5)	1(1)	
H(22)	0.624(6)	0.608(9)	-0.082(5)						

Table 2. (Contd.)

Atom	x	y	z	$B_{\text{iso}}/B_{\text{eq}}, \text{\AA}^2$	Atom	x	y	z	$B_{\text{iso}}/B_{\text{eq}}, \text{\AA}^2$
H(5)	-0.871(9)	-0.378(9)	-0.880(5)	3(2)	H(9)	-0.681(9)	-0.301(9)	1.257(6)	4(2)
H(6)	-0.847(9)	-0.257(9)	1.055(6)	4(2)	H(10)	-0.769(9)	-0.008(9)	1.210(6)	3(1)
H(7)	-0.630(9)	-0.307(9)	-0.926(6)	3(2)	H(w1)	-0.527(9)	-0.371(9)	-0.277(6)	3(1)
H(8)	-0.606(9)	-0.444(9)	1.109(6)	3(2)	H(w2)	-0.381(9)	-0.290(9)	-0.333(9)	13(1)

* For non-hydrogen atoms, $B_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (\hat{a}_i \hat{a}_j)$; for hydrogen atoms, B_{iso} .

** X(1) = 0.75(1) Cl + 0.25(1) Br, X(2) = 0.68(1) Cl + 0.32(1) Br.

ered structure in which corrugated layers are oriented along [001]. The crystal-chemical nonequivalence of the cations corresponds to differences between the respective torsion angles, which describe the position of the allyl group relative to the plane of the aromatic ring. In the absence of significant hydrogen bonds or coordination to a metal atom, the allyl groups of the cations are disordered, which shows as an apparent shortening of the C=C bonds (1.21(3) and 1.26(3) Å).

In the crystal structure of **II**, the $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]_2\text{Cu}_2\text{Cl}_4$ dimers are connected by C–H...Cl hydrogen bonds (H...Cl 2.69–2.90 Å) to form layers along the y axis (Fig. 2). An important structure-forming role belongs to water molecules, which cross-

link the layers to give a three-dimensional framework through O–H...Cl hydrogen bonds (H...Cl 2.45–2.70 Å) (Table 4). The copper(I) atom has a trigonal-bipyramidal environment formed by three Cl atoms and an allyl C=C bond of the *N*-allylisoquinolinium cation (the bond length is 1.35(2) Å).

A similar structure is characteristic of compound **III** consisting of centrosymmetric dimers $[\text{C}_9\text{H}_7(\text{C}_3\text{H}_5)]_2\text{Cu}_2(\text{Cl}_{1.43}\text{Br}_{0.57})_2$ united through C–H...X hydrogen bonds (H...Cl 2.89(7) Å) into layers parallel to the z axis (Fig. 3). As in structure **II**, water molecules form O–H...X hydrogen bonds (H...X 2.5(1)–2.92(7) Å), which crosslink adjacent organometallic dimers to form a three-dimensional cage. The

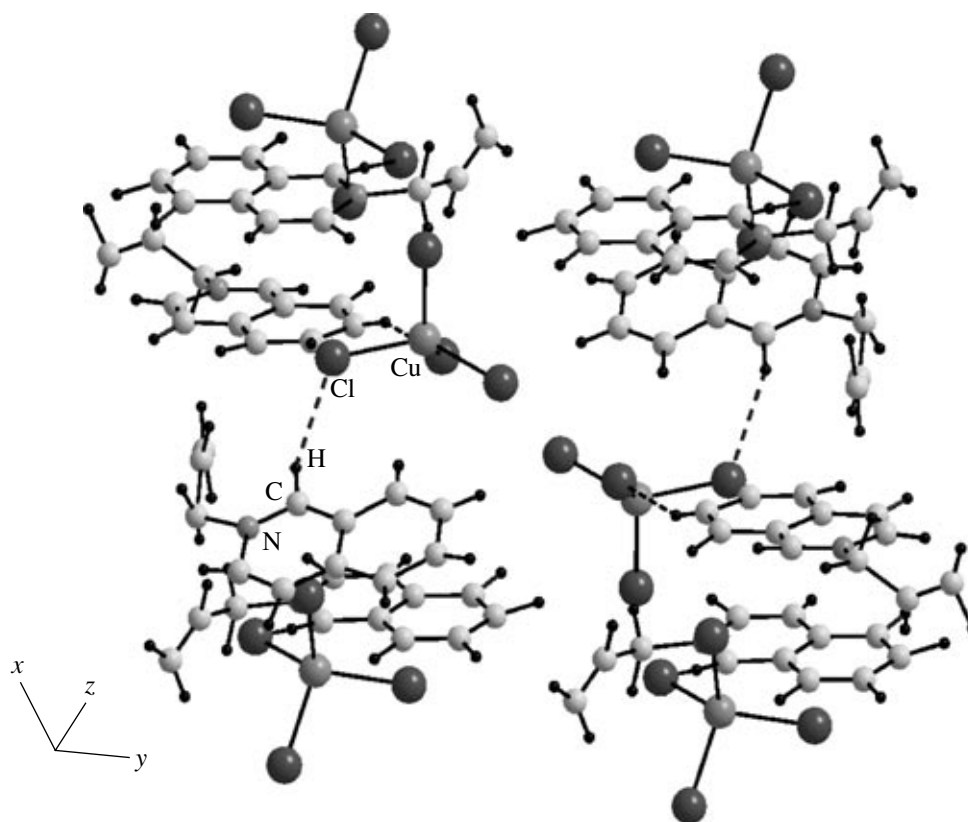


Fig. 1. Crystal structure of $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]_2\text{CuCl}_4$ (**I**).

Table 3. Bond lengths (*d*) and bond (ω) and torsion (τ) angles in structures **I**, **II**, and **III***

Bond	<i>d</i> , Å	Angle	ω , τ deg	Bond	<i>d</i> , Å	Angle	ω , τ deg
I				Cu–C(1)	2.10(1)	Cl(2)CuCl(2)'	93.8(1)
Cu–Cl(1)	2.231(4)	Cl(1)CuCl(2)	100.7(2)	Cu–C(2)	2.09(1)		
Cu–Cl(2)	2.248(4)	Cl(1)CuCl(4)	99.1(2)	Cu– <i>m</i> **	1.98(1)		
Cu–Cl(3)	2.251(4)	Cl(2)CuCl(4)	134.0(2)	C(1)–C(2)	1.35(2)	C(1)C(2)C(3)	123(1)
Cu–Cl(4)	2.218(4)	Cl(1)CuCl(3)	128.4(6)	C(2)–C(3)	1.54(2)	C(2)C(3)N	111(1)
		Cl(2)CuCl(3)	99.8(1)	C(3)–N	1.49(1)	C(3)NC(5)	114.1(9)
		Cl(3)CuCl(4)	99.6(2)	N–C(4)	1.32(1)	NC(5)C(6)	122(2)
C(1)–C(2)	1.26(3)	C(1)C(2)C(3)	125(2)	N–C(5)	1.39(1)	C(5)C(6)C(11)	116.9(9)
C(2)–C(3)	1.49(3)	C(2)C(3)N(1)	115(1)	C(5)–C(6)	1.35(2)	C(6)C(11)C(10)	122(1)
C(3)–N(1)	1.46(2)	C(3)N(1)C(5)	122(1)	C(6)–C(11)	1.44(2)	C(6)C(11)C(12)	119.5(9)
N(1)–C(4)	1.30(2)	C(5)N(1)C(4)	120(1)	C(11)–C(12)	1.40(2)	C(11)C(10)C(9)	121(1)
N(1)–C(5)	1.34(2)	N(1)C(4)C(11)	123(1)	C(11)–C(10)	1.43(2)	C(10)C(9)C(8)	119(1)
C(5)–C(6)	1.36(2)	C(7)C(4)C(11)	123(2)	C(9)–C(10)	1.37(2)	C(9)C(8)C(7)	122(1)
C(6)–C(12)	1.43(2)	C(4)C(11)C(12)	120(1)	C(8)–C(9)	1.44(2)	C(8)C(7)C(12)	120(1)
C(12)–C(11)	1.44(2)	C(11)C(7)C(8)	121(1)	C(8)–C(7)	1.32(2)	C(7)C(12)C(4)	120(1)
C(8)–C(9)	1.39(3)	C(7)C(8)C(9)	121(1)	C(7)–C(12)	1.45(2)	C(12)C(4)N	118.2(9)
C(9)–C(10)	1.36(3)	C(8)C(9)C(10)	121(1)	C(12)–C(4)	1.41(2)		
C(7)–C(8)	1.36(2)	C(10)C(12)C(6)	127(1)	O–H(<i>w</i> 1)	0.99	H(<i>w</i> 1)OH(<i>w</i> 2)	107
C(11)–C(7)	1.43(2)	C(10)C(12)C(11)	119(1)	O–H(<i>w</i> 2)	1.02		
C(4)–C(11)	1.35(2)	C(12)C(6)C(5)	120(1)	III			
C(10)–C(12)	1.41(2)	C(6)C(5)N(1)	123(1)	Cu–X(1)	2.293(5)	C(1)CuC(2)	38.3(3)
		C(1)C(2)C(3)N(1)	–120	Cu–X(2)	2.389(3)	X(1)CuX(2)	111.1(2)
		C(2)C(3)N(1)C(4)	141	Cu–X(2)'	2.743(4)	X(1)CuX(2)'	99.6(2)
C(13)–C(14)	1.21(3)	C(13)C(14)C(15)	133(2)	Cu–C(1)	2.076(8)	X(2)CuX(2)'	95.3(1)
C(14)–C(15)	1.48(3)	C(14)C(15)N(2)	114(1)	Cu–C(2)	2.045(8)		
C(15)–N(2)	1.53(2)	C(15)N(2)C(17)	116(1)	Cu– <i>m</i>	1.950(8)		
N(2)–C(16)	1.30(2)	C(15)N(2)C(16)	123(1)	C(1)–C(2)	1.35(1)	C(1)C(2)C(3)	124.5(7)
N(2)–C(17)	1.41(2)	N(2)C(16)C(23)	120(1)	C(2)–C(3)	1.49(1)	C(2)C(3)N	113.6(6)
C(16)–C(23)	1.39(2)	N(2)C(17)C(18)	120(1)	C(3)–N	1.50(1)	C(3)NC(4)	121.6(6)
C(23)–C(19)	1.42(2)	C(16)C(23)C(19)	119(1)	N–C(4)	1.313(9)	NC(5)C(6)	120.7(6)
C(19)–C(20)	1.33(2)	C(16)C(23)C(24)	119(1)	N–C(5)	1.380(9)	C(5)C(6)C(11)	120.0(7)
C(20)–C(21)	1.39(3)	C(23)C(19)C(20)	120(1)	C(5)–C(6)	1.34(1)	C(6)C(11)C(10)	123.3(6)
C(21)–C(22)	1.36(2)	C(19)C(20)C(21)	120(2)	C(6)–C(11)	1.40(1)	C(6)C(11)C(12)	118.7(6)
C(22)–C(24)	1.42(2)	C(20)C(21)C(22)	121(1)	C(11)–C(12)	1.41(1)	C(11)C(10)C(9)	119.7(7)
C(24)–C(18)	1.37(2)	C(21)C(22)C(24)	122(1)	C(11)–C(10)	1.42(1)	C(10)C(9)C(8)	120.4(7)
C(24)–C(23)	1.40(2)	C(22)C(24)C(18)	126(1)	C(9)–C(10)	1.38(1)	C(9)C(8)C(7)	120.4(7)
C(18)–C(17)	1.32(3)	C(24)C(18)C(17)	121(1)	C(8)–C(9)	1.41(1)	C(8)C(7)C(12)	119.1(7)
		C(1)C(2)C(3)N(1)	116	C(8)–C(7)	1.37(1)	C(7)C(12)C(4)	120.1(6)
		C(2)C(3)N(1)C(4)	–21	C(7)–C(12)	1.41(1)	C(12)C(4)N	120.5(6)
		II		C(12)–C(4)	1.40(1)		
Cu–Cl(1)	2.261(3)	C(1)CuC(2)	37.7(5)	O–H(<i>w</i> 1)	0.73(8)	H(<i>w</i> 1)OH(<i>w</i> 2)	110(9)
Cu–Cl(2)	2.323(3)	Cl(1)CuCl(2)	109.4(1)	O–H(<i>w</i> 2)	0.88(9)		
Cu–Cl(2)'	2.733(3)	Cl(1)CuCl(2)'	100.1(1)				

* For structures **II** and **III**, the coordinates of symmetrically transformed atoms, Cl(2)' and X(2)', respectively: 1 – *x*, –*y*, 1 – *z*.** *m* is the midpoint of the C=C bond.

trigonal-pyramidal environment of the copper(I) atom includes three X atoms (a random mix of Cl and Br atoms) and the allyl C=C bond of the *N*-allylisoquinolinium cation. The length of the coordinated C=C bond is 1.35(1) Å.

Thus, unlike *N*-allylquinolinium halides [4], *N*-allylisoquinolinium chloride forms zwitterion π -complexes with copper(I) halides. Apparently, these different types of behavior of Cu(I) with respect to the C=C bond of the allyl group that quaternizes either the quinoline or isoquinoline nitrogen atom are explained by different electronic structures of the corresponding heteroatomic nuclei. This shows itself indirectly in the different pK_a values of the bases, i.e., quinoline (4.90) and isoquinoline (5.40) [10]. For comparison, the pK_a value of the dinitrogen base, benzimidazole, is 5.53; its onium 1,3-diallyl derivative forms the π -complexes mentioned above with copper(I) chloride (or bromide) [1, 3]. The interaction of Cu(I) with the C=C bond of 1-allyl-4-aminopyridinium and 1-allyl-2-aminopyridinium chloride (or bromide) occurs in a similar way.

The interaction of the C=C bond of the 1-allyl-4-aminopyridinium and 1-allyl-2-aminopyridinium chloride (or bromide) with the Cu(I) atom is also found in the π -complexes $[n\text{-H}_2\text{NC}_5\text{H}_4\text{NC}_3\text{H}_5]\text{CuCl}_2 \cdot \text{H}_2\text{O}$, $[p\text{-H}_2\text{NC}_5\text{H}_4\text{NC}_3\text{H}_5][\text{CuCl}_{2-x}\text{Br}_x] \cdot \text{H}_2\text{O}$ ($x = 0.65$), and $[p\text{-H}_2\text{NC}_5\text{H}_4\text{NC}_3\text{H}_5]\text{CuBr}_2 \cdot \text{H}_2\text{O}$ [11], as well as in $[o\text{-H}_2\text{NC}_5\text{H}_4\text{NC}_3\text{H}_5]\text{CuCl}_2$ and $[o\text{-H}_2\text{NC}_5\text{H}_4\text{NC}_3\text{H}_5]\text{CuCl}_{2-x}\text{Br}_x$ ($x = 1.10$) [12]. The pK_a values of the bases, 2-aminopyridine and 4-aminopyridine, are equal to 6.86 and 9.25, respectively [13]. It is evident that the electronic structure of 2- and 4-substi-

Table 4. Selected hydrogen bonds in the structures of compounds **I**, **II**, and **III**

The D–H...A bond	Distance, Å		The DHA angle, deg	Coordinates of the A atom
	H...A	D...A		
I				
C(8)–H(8)...Cl(1)	2.67(8)	3.54(2)	152	x, y, z
C(16)–H(16)...Cl(4)	2.74(8)	3.66(1)	153	x, y, z
II				
C(6)–H(6)...Cl(1)	2.69	3.58(1)	153	x, y, z
C(9)–H(9)...Cl(2)	2.90	3.82(1)	152	$1 + x, y, z$
O–H(w2)...Cl(2)	2.45	3.34(1)	147	$1 + x, y, z$
O–H(w1)...Cl(1)	2.70	3.34(1)	123	x, y, z
III				
C(6)–H(6)...X(1)	2.89(7)	3.524(9)	160	x, y, z
C(9)–H(9)...X(2)	2.91(4)	3.767(9)	154	$1 + x, y, z$
O–H(w1)...X(1)	2.92(7)	3.381(7)	124	$1 + x, y, z$
O–H(w2)...X(2)	2.5(1)	3.285(8)	157	x, y, z

tuted pyridines is also favorable for the π -interaction between the C=C bond of the allyl group of the pyridinium cations and Cu(I). This explains the reason for the formation of the polysynthetic twin crystals (due to the too fast growth) in the case of complex **II**, while the replacement of some of the Cl atoms by Br atoms (in compound **III**) decreases (due to steric hindrance) the rate of the crystal growth for π -complex **III** and, as a

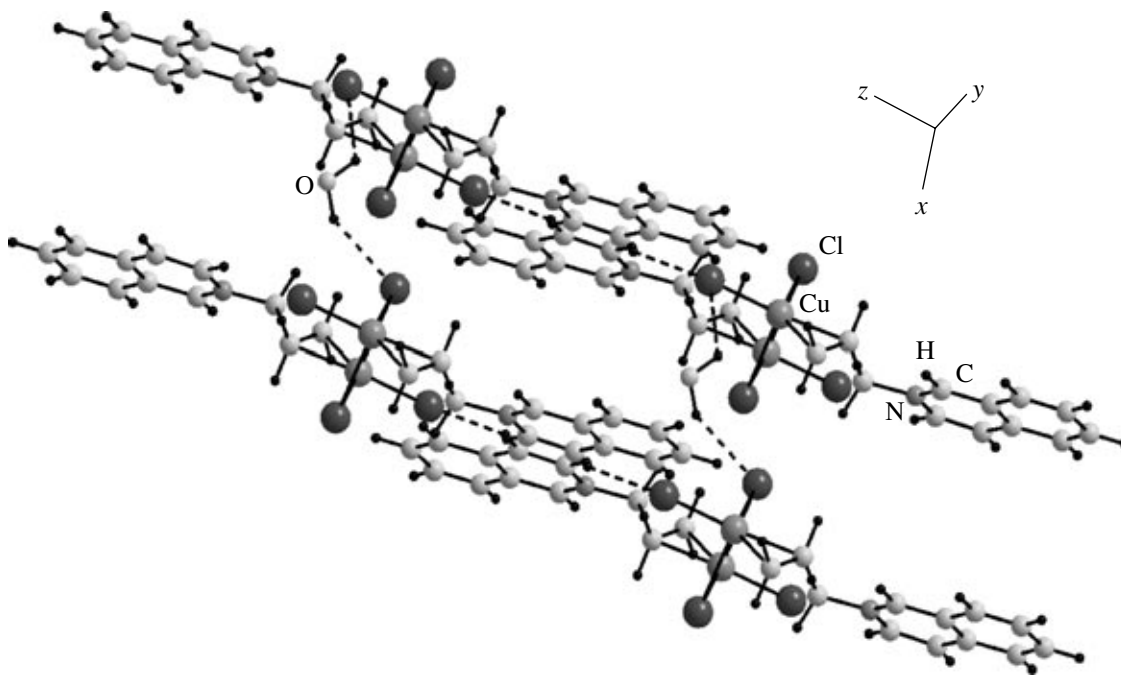


Fig. 2. Fragment of the structure of the π -complex $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]\text{CuCl}_2 \cdot \text{H}_2\text{O}$ (**III**).

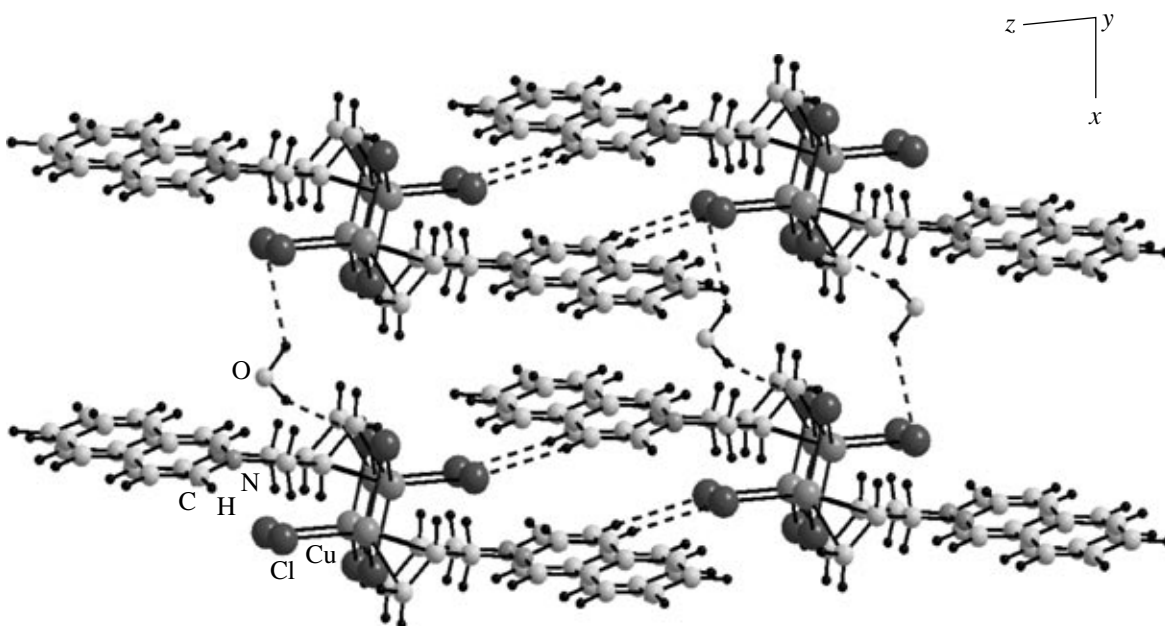


Fig. 3. Crystal structure of the π -complex $[\text{C}_9\text{H}_7\text{N}(\text{C}_3\text{H}_5)]\text{CuCl}_{1.43}\text{Br}_{0.57} \cdot \text{H}_2\text{O}$ (III).

consequence, promotes the formation of high-quality crystals of this compound, which is isostructural to **II**.

ACKNOWLEDGMENTS

This study was supported by the State Foundation for Basic Research of Ukraine (DFFD), project no. F7/557 2001.

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