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1-Allyl Derivatives: Synthesis and Crystal Structures for $[(NH_2C_5H_4N(C_3H_5))_2Cu_3Cl_3(NO_3)_2]$ and $[C_9H_7N(C_3H_5)Cu(NO_3)_2]$

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Abstract—1-Allyl-4-aminopyridinium chloride reacts with $Cu(NO_3)_2 \cdot 3H_2O$ in an ethanolic solution under the conditions of ac electrochemical synthesis at copper electrodes to form crystals of compound $[(NH_2C_5H_4N(C_3H_5))_2Cu_3Cl_3(NO_3)_2]$ (**I**). The crystals of compound I are monoclinic: space group $P2_1/c$, $Z = 4$, $a = 25.770(7)$, $b = 7.230(4)$, $c = 12.505(5)$ Å, $\beta = 92.58(3)°$, $V = 2328(2)$ Å^3. The direct interaction of 1-allylquinolinium nitrate with $Cu(NO_3)_2 \cdot 3H_2O$ in a methanolic solution in the presence of metallic copper yields crystals of compound $[C_9H_7N(C_3H_5)Cu(NO_3)_2]$ (**II**). The crystals of compound II are triclinic: space group $P\bar{1}$, $a = 6.756(3)$, $b = 8.391(4)$, $c = 12.489(5)$ Å, $\alpha = 77.18(3)°$, $\beta = 89.48(4)°$, $\gamma = 73.32(3)°$, $V = 662.0(5)$ Å^3. The structure of compound I is built of infinite linear anions: polymeric fragments $\{(NH_2C_5H_4N(C_3H_5))_2Cu_3Cl_3(NO_3)_2\}_n$. Each of two copper atoms (Cu(1) and Cu(2)) π-coordinates the C=C bonds of the allyl groups of the 1-allyl-4-aminopyridinium cations, the oxygen atom of the nitrate ions, and two chlorine atoms. The third copper atom Cu(3) is linearly linked with two chlorine atoms. Particular polymeric fragments are additionally joined by the N–H···O, C–H···O, C–H···Cl hydrogen bonds. The crystal structure of compound II is built-up of the isolated $L_2Cu_2(NO_3)_4$ fragments (L is the 1-allylquinolinium cation). The metal atom is localized in the trigonal pyramidal coordination environment of three oxygen atoms of the nitrate ions and of the C=C bond of the allyl group of the cation. The particular $L_2Cu_2(NO_3)_4$ fragments are additionally joined by the C–H···O hydrogen bonds.

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INTRODUCTION

Earlier studies of the crystal structures of the cuprohalide complexes of the quinoline and isoquinoline N-allyl derivatives showed the different behavior of the C=C bond of the allyl group of the corresponding cation relative to the metal atom. The studied compounds of copper(I) halides with the N-allylquinolinium cation, namely, $[C_9H_7N(C_3H_5)]Cu_2Cl_3$ [1], and $[C_9H_7N(C_3H_5)]_2CuBr_3 \cdot H_2O$ [2], contain no π interaction Cu(I)–(C = C), whereas the N-allylisoquinolinium cation with Cu(I) halides rather easily forms the π complexes $[C_9H_7N(C_3H_5)CuX_2] \cdot H_2O$ (X = Cl/Br) [3] and $[C_9H_7N(C_3H_5)CuBr_2]$ [4]. No formation of any cyanide complexes was observed for the interaction of 1-allylquinolinium halides with pseudohalide Cu(CN), but the obtained compounds contain the $[C_{24}H_{21}N_2]^+$ cation, which is the result of the catalytic dimerization of the N-allylquinolinium cations [5].

In the light of the aforesaid, it is interesting to study the behavior of the 1-allyl-4-aminopyridinium and 1-allylisoquinolinium cations in complex formation with copper nitrate.

EXPERIMENTAL

Synthesis. 1-Allyl-4-aminopyridinium chloride and 1-allylquinolinium bromide were synthesized by the heating with a reflux condenser of a solution of the corresponding allyl halide and 4-aminopyridine (or quinoline) in chloroform [6]. The crystalline salts were filtered off and thoroughly washed in the Büchner funnel with a benzene–hexane mixture.

N-Allylquinolinium nitrate was synthesized by the interaction of hot solutions of equimolar amounts of 1-allylquinolinium bromide and silver nitrate in methanol. A precipitate of silver bromide was filtered off, and the filtrate was evaporated. The crystalline salt was washed with a small amount of cold methanol.

Yellow crystals of the compound $[(para\text{-}NH_2C_5H_4N(C_3H_5))_2Cu_3Cl_3(NO_3)_2]$ (**I**) were obtained at the copper electrodes using the ac electrochemical synthesis from an ethanolic solution of 1-allyl-4-aminopyridinium chloride and $Cu(NO_3)_2 \cdot 3H_2O$.

Yellow prismatic crystals of the $[C_9H_7N(C_3H_5)Cu(NO_3)_2]$ complex (**II**) were obtained from a methanolic solution of 1-allylquinolinium

Table 1. Crystallographic data and selected parameters of X-ray experiment for single crystals of compounds **I** and **II**

Parameter	Value	
	I	**II**
FW	691.4	715.6
Space group	$P2_1/c$	$P\bar{1}$
a, Å	25.770(7)	6.756(3)
b, Å	7.230(4)	8.391(4)
c, Å	12.505(5)	12.489(5)
α, deg	90	77.83(3)
β, deg	92.58(3)	89.48(4)
γ, deg	90	73.32(3)
V, Å^3	2328(2)	662.0(5)
Z	4	2
ρ(calcd), g/cm^3	1.973	1.795
Crystal size	0.14 × 0.16 × 0.38	0.16 × 0.25 × 0.28
μ_{Mo}, mm^{-1}	3.1	1.7
T, K	110	110
Number of measured reflections	19519	10462
Number of independent reflections with $F \geq 2\sigma F$*	5530	3754
$2\theta_{max}$, deg	60	60
Number of refined parameters	307	199
Weight scheme, w**	$1/[\sigma^2(F^2_{изм}) + (0.032P)^2 + 15.8P]$	$1/[\sigma^2(F^2_{изм}) + (0.042P)^2 + 0.151P]$
R	0.051	0.032
wR	0.113	0.076
Goodness-of-fit	1.02	1.04

Notes: * The correction to the Lorentz and polarization factors was applied.

** $P = (F^2_{meas} + 2F^2_{calcd})/3$.

nitrate chloride and $Cu(NO_3)_2 \cdot 3H_2O$ in the presence of metallic copper.

X-Ray diffraction analysis. After preliminary studies by the photomethod, diffraction sets obtained on a KUMA-KM4/CCD single-crystal diffractometer (CCD detector, MoK_α radiation, graphite monochromator, ω scan mode; OXFORD-Cryosystem low-temperature attachment) were used for structure determination of compounds **I** and **II**. Corrections to the Lorentz and polarization factors were applied to reflection intensities. The X-ray diffraction data were processed using the CrysAlis RED program [8]. Structures **I** and **II** were solved by direct methods, and light atoms were revealed from the difference Fourier syntheses. An absorption correction was applied by the analytical method [9] using the linear sizes and habit of the crystals. The structures were solved using the SHELX program package [10]. The hydrogen atoms found in the difference Fourier syntheses were refined in the riding model along with the non-hydrogen atoms.

The figures were drawn using the DIAMOND program [11]. The crystallographic data and details of X-ray experiment are collected in Table 1. The coordinates and temperature factors of atoms are deposited with the Cambridge Structural Database (nos. 690361 and 690362; http://www.ccdc.cam.ac.uk/conts/retrieving.html).

RESULTS AND DISCUSSION

The crystal structure of π complex **I** is built of the infinite polymeric fragments $\{(NH_2C_5H_4N(C_3H_5))_2Cu_3Cl_3(NO_3)_2\}_n$ oriented along the z axis of the unit cell (Fig. 1). The coordination polyhedron of each of the two π-coordinated copper atoms (Cu(1) and Cu(2)) is a trigonal pyramid, whose base contains the C=C double bond of the allyl group of one of the two 1-allyl-4-aminopyridinium cations, the oxygen atom of the nitrate ion, and the chlorine atom. In the both cases, the apical positions are occupied by the chlorine atoms. Nearly the same parameters of both the coordination sites and N-allylquinolinium cations (the metal atom shifts from the plane of the base by 0.30 and 0.29 Å, the Cu–m distance is 1.95 and 1.94 Å, the C=C bond length is 1.371(6) and 1.360(6) Å, the CCuC angle is 38.7(2)° and 38.6(2)°, and the dihedral angle between the base of the coordination polyhedron and C=C bond of the allyl group of the cation is 10° and 13°, respectively) indicate the absence of a noticeable difference between the efficiency of the Cu(I)–(C=C) π interaction for the Cu(1) and Cu(2) atoms. The third metal atom Cu(3) exists in an almost linear coordination environment, which is not characteristic for univalent copper (angle Cl(2)Cu(3)Cl(3) 175.38°). The binding of the particular $\{LCuCl_2(NO_3)\}$ pyramids between each other (due to the bidentate function of the Cl(1) atom) and to nearly linear $\{CuCl_2\}$ results in the formation of a unique zigzag-like fragment $\{(LCuCl_2(NO_3))_2CuCl_2\}_n$. A comparison of the structure of complex **I** with that for the [(1-allyl-4-aminopyridinium)$CuCl_2$] π complex con-

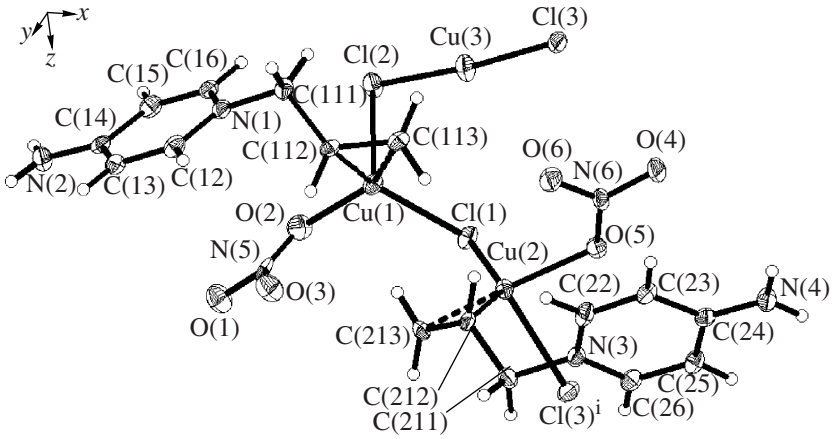

Fig. 1. Projection of the asymmetric unit in structure **I**. The 50% probability ellipsoids and numeration scheme are shown. Bond lengths: Cu(1)–Cl(1) 2.293(1), Cu(1)–Cl(2) 2.620(2), Cu(1)–O(2) 2.034(3), Cu(1)–C(113) 2.066(4), Cu(1)–C(112) 2.075(4), Cu(2)–Cl(1) 2.298(1), Cu(2)–Cl(3)^{i} 2.651(2), Cu(2)–O(5) 2.029(3), Cu(2)–C(213) 2.037(4), Cu(2)–C(212) 2.078(5), Cu(3)–Cl(3) 2.130(1), and Cu(3)–Cl(2) 2.134(1) Å; bond angles: O(2)Cu(1)m_1 127.3°, Cl(1)Cu(1)m_1 123.2°, O(2)Cu(1)Cl(1) 102.8(1)°, Cl(2)Cu(1)m_1 107.5°, O(2)Cu(1)Cl(2) 87.7(1)°, Cl(1)Cu(1)Cl(2) 98.4(1)°, O(5)Cu(2)m_2 147.6(2)°, O(5)Cu(2)Cl(1) 102.5(1)°, Cl(1)Cu(2)m_2 123.2°, O(5)Cu(2)Cl(3)^{i} 86.3(1)°, Cl(3)Cu(2)m_2 107.7°, Cl(1)Cu(2)Cl(3)^{i} 98.2(1)°, and Cl(3)Cu(3)Cl(2) 175.4(1)°. Symmetry transformations:^{i} $x - 1$, $y - 1.5$, $z + 0.5$.

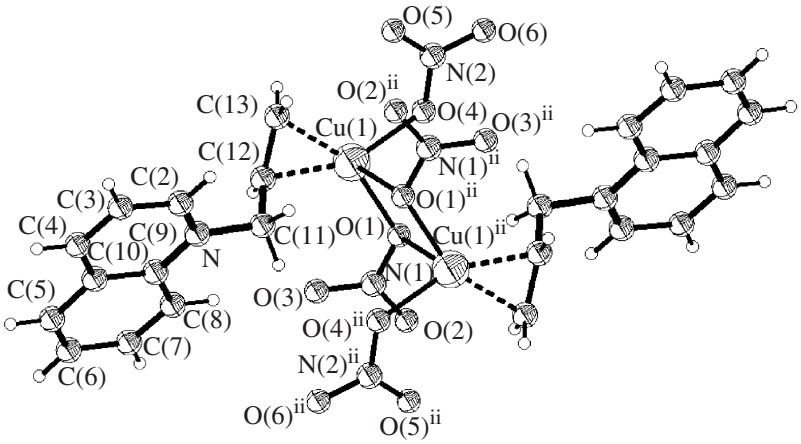

Fig. 2. Projection of the topological unit in structure **II**. The 50% probability ellipsoids and numeration scheme are shown. Bond lengths: Cu(1)–O(4) 1.979(2), Cu(1)–O(1) 1.995(2), Cu(1)–C(12) 2.006(2), and Cu(1)–C(13) 2.019(2) Å; bond angles: O(4)Cu(1)O(1) 87.0(1)°, O(4)Cu(1)m 136.7°, O(1)Cu(1)m 136.1°, O(1)^{ii}Cu(1)m 136.1°, and O(4)Cu(1)O(1)^{ii} 92.3(1)°. Symmetry transformations: ^{ii} $-x + 1$, $-y + 1$, $-z + 1$.

taining the simplest $CuCl_2^-$ inorganic fragment [12, 13] shows that the presence of the NO_3^- ions in the first case substantially complicates the structure.

The coordination polyhedron of the metal atom in structure **II** is a trigonal pyramide (the Cu atom shifts from the base plane by 0.06 Å). The base of the coordination polyhedron contains the C=C double bond of the allyl group of the N-allylquinolinium cation and two oxygen atoms of the nitrate ions. Isolated topological units of the $L_2Cu_2(NO_3)_4$ composition (L is the N-allylquinolinium cation) are formed due to the bidentate nature of the O(1) oxygen atom, which is simultaneously situated in the base of one polyhedron and in the apical position of the second polyhedron (Fig. 2). In structure **II**, the presence of only oxygen atoms (no chlorine atoms) in the coordination sphere of the metal atom results in somewhat higher efficiency of the Cu(I)–(C=C) π interaction compared to complex **I** (the Cu–m distance is 1.89 Å, the C=C bond length is

Table 2. Hydrogen bonding geometry in structures **I** and **II**

Contact D–H···A	Distance, Å			Angle DHA, deg	Coordinates of A atom
	H–A	H···A	D···A		
			I		
N(2)–H(2*A*)···O(2)	0.88	2.16	3.021(5)	166	–*x*, *y* + 1/2, –*z* + 1/2
N(2)–H(2*B*)···O(3)	0.88	2.26	3.111(5)	162	–*x*, *y* – 1/2, –*z* + 1/2
N(4)–H(4*A*)···O(5)	0.88	2.15	3.020(5)	169	–*x* + 1, –y + 2, –*z* + 1
N(4)–H(4*B*)···O(4)	0.88	2.06	2.902(5)	159	–*x* + 1, y + 1/2, –*z* + 1/2
C(13)–H(13)···O(1)	0.95	2.46	3.283(6)	145	–*x*, *y* + 1/2, –*z* + 1/2
C(15)–H(15)···O(1)	0.95	2.43	3.289(6)	150	–*x*, *y* – 1/2, –*z* + 1/2
C(25)–H(25)···O(4)	0.95	2.38	3.230(5)	150	–*x* + 1, –y + 2, –*z* + 1
C(22)–H(22)···Cl(3)	0.95	2.79	3.684(5)	157	*x*, *y* + 1, *z*
C(113)–H(11*A*)···Cl(1)	0.95	2.82	3.685(5)	151	*x*, –*y* + 3/2, *z* –1/2
			II		
C(2)–H(2)···O(2)	0.95	2.50	3.298(3)	141	*x*, *y* –1, *z*
C(4)–H(4)···O(6)	0.95	2.25	3.199(3)	175	*x*, *y* –1, *z* + 1
C(8)–H(8)···O(3)	0.95	2.46	3.410(3)	177	*x*, *y*, *z*

1.382(3) Å, the CCuC angle is 40.2(1)°, and dihedral angle between the base of the coordination polyhedron and the C=C bond of the allyl group of the cation is 6°).

The structure-forming role of hydrogen bonding in the crystals of compounds **I** and **II** is interesting. Both the stronger N–H···O hydrogen bonds [14] in structure **I** (Table 2, Fig. 3) and weaker C–H···O and C–H···Cl bonds in compounds **I** and **II** additionally stabilize the structure, connecting particular topological units into a three-dimensional framework. In addition, in structure

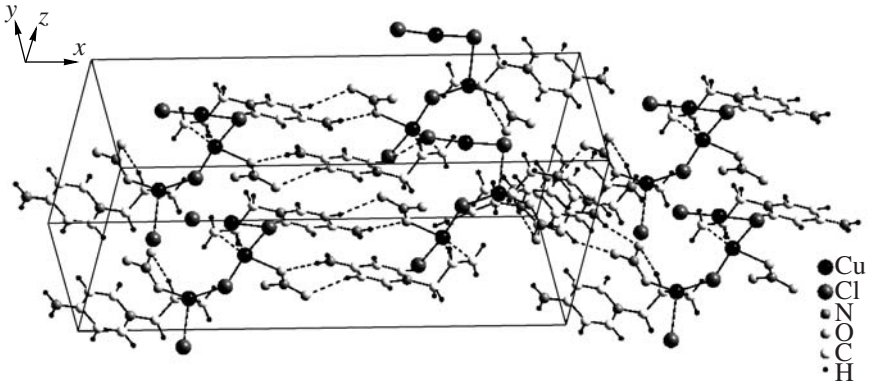

Fig. 3. Spatial network of hydrogen contacts in the structure of compound **I**.

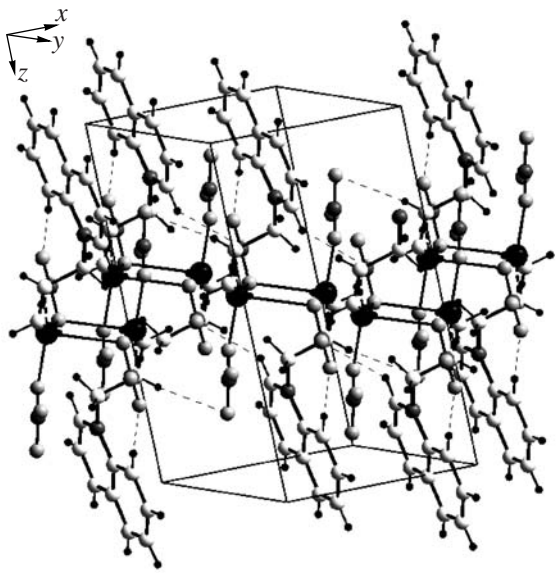

Fig. 4. Hydrogen bonding in the structure of complex **II**.

II the hydrogen bonds additionally stabilize the conformation of the $\{L_2Cu_2(NO_3)_4\}$ dimeric fragment (Fig. 4).

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