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Copper(I) complexes with 3,3′-iminodipropanenitrile and 3-(diallylamino)propanenitrile: synthesis and crystal structure of σ-[{(NH(H^+)(C_2H_4CN)$_2$}Cu_3Cl_4] and π-,σ-[Cu((C_3H_5)$_2NC_2H_4CN$)ClO_4] compounds

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Starting from ethanolic or water-propanolic solutions of 3,3′-iminodipropionitrile (*L1*), 3-(diallylamino)propanenitrile (*L2*), and $CuCl_2\cdot 2H_2O$ or $Cu(ClO_4)_2\cdot 6H_2O$, respectively, two complexes, [(NH(H^+)(C_2H_4CN)$_2Cu_3Cl_4$] (I) and [Cu((C_3H_5)$_2NC_2H_4CN$)ClO_4] (II), were obtained by the alternating current electrochemical technique and investigated by single crystal X-ray diffraction. The crystal structures of I and II are monoclinic, for I: space group $P2_1/n$, a = 8.9700(2), b = 14.3951(4), c = 10.0156(3) Å, β = 94.056(1)°, V = 1290.02(6) Å^3, Z = 4; for II: space group *Cm*, a = 10.0916(8), b = 8.1061(7), c = 8.4207(7) Å, β = 116.581(5)°, V = 616.03(5) Å^3, Z = 2. The coordination of the Cu(I) atoms in complex I includes three Cl atoms and the N atom of a cyanogroup. Cations H^+*L1* connect separate corrugated layers $(Cu_3Cl_4^-)_n$ into a framework.

The coordination environment of the copper(I) atom in complex II is formed by two C=C bonds of the allyl groups of one molecule *L2*, the nitrile N atom of another molecule *L2*, and the apical O atom of a ClO_4 anion. The inorganic anions ClO_4^- also interconnect the metalorganic ribbons via O...H-C hydrogen bonds.

Copper(I) / π- and σ-Complexes / Crystal structure / 3-Aminopropanenitriles / *ac*-Electrochemical technique

Introduction

Aminonitriles belong to a well-known class of organic compounds [1] that possesses a large number of interesting properties (antibiotic, pharmacological, *etc.* [2-4]) and potential biological activity [5]. Polyfunctionally substituted aminonitriles are versatile reagents, which are utilized as precursors to substituted heterocyclic compounds [6,7]. Much less is known about Cu(I) coordination complexes with aminopropanenitriles and their allyl derivatives [8], all the more they show their usefulness as intermediates in the preparation of desired organic compounds.

Since copper(I) π,σ-complexes with β-aminonitriles derivatives are very particular and interesting, we decided to synthesize two π,σ-complexes of copper(I) chloride and perchlorate with 3,3′-iminodipropanenitrile and 3-(diallylamino)-propanenitrile, [(NH(H^+)(C_2H_4CN)$_2Cu_3Cl_4$] (**I**) and [Cu((C_3H_5)$_2NC_2H_4CN$)ClO_4] (**II**), and investigate their crystal structure.

Experimental section

Synthesis of 3,3′-iminodipropanenitrile (NH(C_2H_4CN)$_2$, L1)

3,3′-Iminodipropionitrile was obtained from acrylonitrile (8.16 mL, 0.12 mol) and a 25% aqueous solution of NH_3 (5.6 mL, 0.06 mol). The mixture of reagents was continuously stirred and cooled (5 h, 20°C) preventing the temperature from rising higher than 30°C [9], then it was heated for 1 h in a water bath with a reflux condenser at 60°C. The product (dark orange liquid) was purified by distillation in vacuum produced by a water-jet pump (85°C, 40 mm Hg). The yield of *L1* was 80% (11 mL).

Synthesis of 3-(diallylamino)propanenitrile ((C_3H_5)$_2NC_2H_4CN$, L2)

To obtain 3-(diallylamino)propanenitrile a mixture of acrylonitrile (7 mL, 0.11 mol) and diallylamine

(16 mL, 0.13 mol) was heated with a reflux condenser in a water bath at 50-60°C for 8 h and then kept at room temperature for 24 h [10]. A small amount of unreacted initial substances was distilled off in vacuum produced by a water-jet pump; the red-orange liquid was distilled at 130°C (20 mm Hg). The yield of *L2* was 75% (13 mL).

Preparation of $[(NH(H^+)(C_2H_4CN)_2Cu_3Cl_4]$ (I)

Brown prismatic crystals of compound **I** appeared from an ethanol (3 mL) solution of $CuCl_2·2H_2O$ (0.65 g, 3.8 mmol) and *L1* (0.56 mL, 4.2 mmol titrated with 36% aqueous solution of HCl to pH = 4-4.5) under conditions of the alternating current electrochemical technique [11]. The initial solution was placed into a small test-tube and copper-wire electrodes in cork were inserted. After applying 0.5 V of alternating current (frequency 50 Hz) tension for 2 days crystals of **I** had formed on the copper electrodes. The yield of complex **I** was 65%.

Preparation of $[Cu((C_3H_5)_2NC_2H_4CN)ClO_4]$ (II)

Crystals of π-complex **II** were obtained in a similar way (alternating current, U = 0.45 V, I_{init} = 0.4 mA, time of synthesis 24 h) starting from a propanol-water (3:1) solution of 0.7 mL (4.3 mmol) of *L2* and 0.68 g (4 mmol) of $Cu(ClO_4)_2$ $6H_2O$. The yield of complex **II** was 60%.

X-ray crystal structure determination

Single crystals of **I** and **II** were preliminarily studied by photographic methods and then diffraction data were collected on a Rigaku AFC7R diffractometer equipped with a Mercury CCD area detector using graphite monochromated Mo-*K*α radiation. The intensities were corrected for Lorentz and polarization factors.

The diffraction data were treated using the Rigaku CrystalClear software suite package [12]. Both structures were solved by direct methods using the SIR-92 [13] program (teXan crystallographic software package of Molecular Structure Corporation [14]) and refined on F^2 with SHELXL-97 [15] software implemented in the program package WinGX [16]. An absorption correction was applied by the analytical method [17].

The hydrogen atoms were in part found on a difference Fourier map. The thermal parameters of all the hydrogen atoms were fixed to 1.2 times U_{eq} of the C or N atoms. The positions of the hydrogen atoms were refined with geometrical restrictions.

The crystallographic parameters and summaries of the data collections for compounds **I** and **II** are presented in Table 1. Atomic positional and displacement parameters for **I** and **II** are given in Tables 2 and 3. The figures were prepared using DIAMOND 3.1 software [18].

Results and discussion

Compound **I** $[(H^+L1)Cu_3Cl_4]$ is one more representative of halide complexes of Cu(I) with derivatives of aminonitriles.

The coordination environment of the three crystallographically independent Cu(I) atoms is a distorted tetrahedron (Fig. 1). Each polyhedron is formed by three Cl atoms and one N atom of CN-group, interconnected through edges or a single apex. The coordination geometry of the metal atoms is given in Table 4.

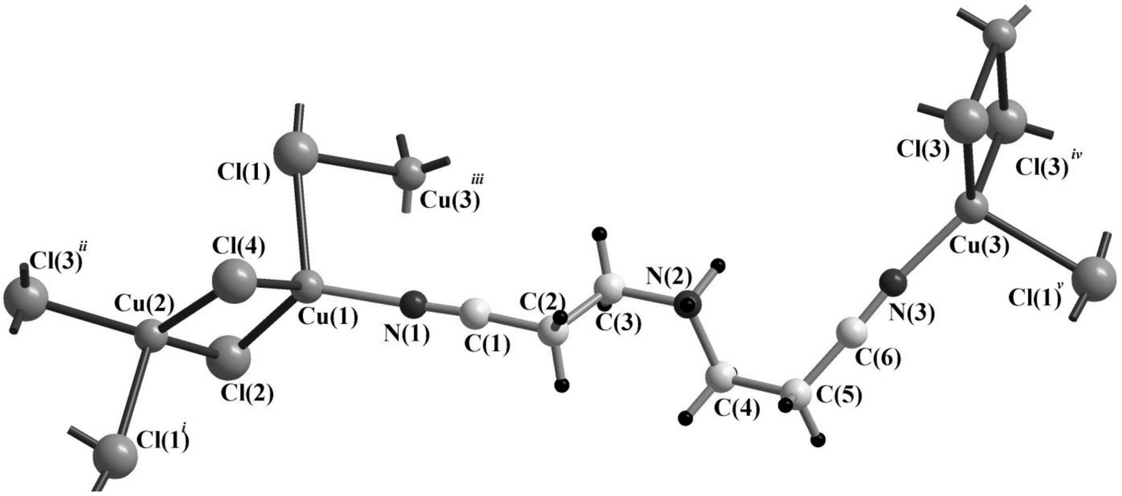

Fig. 1 Fragment of the crystal structure of $[\{NH^+(C_2H_4CN)_2\}Cu_3Cl_4]$ (**I**).
Symmetry codes: (*i*) −1/2+*x*, 1.5−*y*, −1/2+*z*; (*ii*) 1−*x*, 1−*y*, 2−*z*; (*iii*) 1/2+*x*, 1/2−*y*, −1/2−*z*; (*iv*) 1−*x*, −*y*, 3−*z*; (*v*) −1/2+*x*, 1/2−*y*,1/2+*z*.

Table 1 Crystallographic data and experimental details for **I** and **II**.

Parameter	**I**	**II**
Empirical formula	$C_6H_{10}Cl_4Cu_3N_3$	$C_9H_{14}ClCuN_2O_4$
Formula weight	456.62	313.22
Temperature, K	200	200
Wavelength, Å	0.71069	0.71069
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, Cm
Unit cell dimensions		
a, Å	8.9700(2)	10.0916(8)
b, Å	14.3951(4)	8.1061(7)
c, Å	10.0156(3)	8.4207(7)
β, °	94.056(1)	116.581(5)
Volume, $Å^3$	1290.02(6)	616.03(9)
Z	4	2
Calculated density, $g \cdot cm^{-3}$	2.351	1.689
Absorption coefficient, mm^{-1}	5.70	1.99
$F(000)$	888	320
Crystal size, mm	0.15 × 0.10 × 0.10	0.12 × 0.10 × 0.08
Color, shape	Brown, prism	Colourless, chunk
Theta range for data collection, °	1.4-29.0	2.7-27.1
Limiting indices	$-12 \le h \le 12$, $-19 \le k \le 19$, $-13 \le l \le 13$	$0 \le h \le 12$, $-10 \le k \le 10$, $-10 \le l \le 9$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Measured reflections	10967	1232
Independent reflections	3000	711
Observed reflections $[I > 2\sigma(I)]$	2494	698
Free parameters	146	92
Weight scheme [a]	$[\sigma^2(F_o^2) + (0.1515P)^2+1.3183P]^{-1}$	$[\sigma^2(F_o^2) + (0.0707P)^2+2.108P]^{-1}$
Goodness-of-fit on F^2	1.24	1.2
Final R indices $[I > 2\sigma(I)]$	$R = 0.078$, $wR = 0.266$	$R = 0.056$, $wR = 0.134$
Residual electron density, $e \cdot Å^{-3}$	2.07 and –1.34	0.66 and –0.61

[a] $P = (F_o^2 + 2F_c^2)/3$.

Previous structural studies of halide complexes of aminonitrile indicate that the formation of metal-halide fragments of different complexity, from separate (Cu_2Cl_2) units to polymer anionic chains $(Cu_2Hal_3^{-})_n$ for $C_3H_5NHC_2H_4CN$ (3-(allylamino)-propanenitrile), or polymer anionic chains of $(CuHal_2^{-})_n$ for $(C_3H_5)_2NC_2H_4CN$ (3-(diallylamino)propanenitrile), $(HOC_2H_4)NHC_2H_4CN$ (3-[2-hydroxyethyl)amino]-propanenitrile), $(C_3H_5)(HOC_2H_4)NC_2H_4CN$ (3-[2-hydroxyethyl)(allyl)amino]propanenitrile) [8,19], depends directly on the nature of the ligand. The use of 3,3'-iminodipropanenitrile $(NH(C_2H_4CN)_2$, *L1*) (in the molecule of which there are two closely situated propanenitrile groups) as a ligand allowed obtaining a complex with anion nets $(Cu_3Cl_4^{-})_n$ (Fig. 2), which could not be achieved in the structure of CuCl with the 1,4-bis(2-cyanoethyl)piperazinediium cation $(NCC_2H_4)(H^+)NC_4H_8N(H^+)(C_2H_4CN)$ (polyanionic chains $(CuHal_2^{-})_n$) [20].

Hydrogen bonds [21] additionally connect the organic and inorganic (C/N−H…Cl) parts of the structure of **I** into a single whole. Their role is also substantial in the strengthening of the structures of complexes **I-II**, which is especially noticeable in the π-complex **II** (Table 5).

As we can see, 3,3'-iminodipropanenitrile in complex **I** serves only as bridging ligand. However, the presence of two equidistant cyanogroups theoretically gives it the opportunity to be a chelate ligand, *i.e.* it can be coordinated by two CN-groups to one atom of Cu(I). Chelating-bridging mode of coordination *L* is realized for the metal atom in complex **II**. The molecule of 3-(diallylamino)-propanenitrile connects neighboring Cu(I) atoms into an infinite coordination polymer by binding to one atom with two olefinic bonds, and to the second atom with a CN-group.

The π-complex $[Cu\{(C_3H_5)_2NC_2H_4CN\}ClO_4]$ (**II**) is isostructural to the previously studied copper(I) tetrafluoroborate complex $[Cu\{(C_3H_5)_2NC_2H_4CN\}BF_4]$ [20]. A trigonal pyramidal coordination of the copper(I) atom in complex **II** is formed by two C=C bonds of the allyl groups from one molecule *L2*, the N atom from a CN-group of the neighboring *L2* molecule and the oxygen atom of the ClO_4 anion at the apical position.

Table 2 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **I**.

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq} [a]
Cu(1)	0.61802(11)	0.63760(6)	0.69152(9)	0.0578(4)
Cu(2)	0.56025(12)	0.79713(7)	0.51388(11)	0.0690(4)
Cu(3)	0.42309(13)	−0.02120(8)	1.36260(10)	0.0709(4)
Cl(1)	0.83069(18)	0.68517(12)	0.84994(15)	0.0539(4)
Cl(2)	0.6995(2)	0.66141(12)	0.48154(16)	0.0560(4)
Cl(3)	0.33240(18)	0.06218(11)	1.54280(17)	0.0536(5)
Cl(4)	0.44387(19)	0.76541(11)	0.70894(16)	0.0528(4)
N(1)	0.5334(7)	0.5247(4)	0.7618(6)	0.0566(13)
N(2)	0.4286(7)	0.2379(4)	0.9885(5)	0.0500(12)
N(3)	0.3878(7)	0.0277(4)	1.1843(6)	0.0558(13)
C(1)	0.4784(8)	0.4618(5)	0.8069(7)	0.0545(15)
C(2)	0.4039(8)	0.3799(5)	0.8555(8)	0.0612(17)
C(3)	0.5100(8)	0.3177(4)	0.9351(7)	0.0539(14)
C(4)	0.3967(8)	0.1605(4)	0.8924(6)	0.0501(13)
C(5)	0.2917(9)	0.0890(5)	0.9489(7)	0.0585(16)
C(6)	0.3428(8)	0.0531(4)	1.0810(7)	0.0524(14)
H(1N)	0.3413	0.2586	1.0163	0.060*
H(2N)	0.4825	0.2154	1.0605	0.060*
H(2A)	0.3582	0.3457	0.7798	0.073*
H(2B)	0.3250	0.3993	0.9108	0.073*
H(3A)	0.5859	0.2952	0.8787	0.065*
H(3B)	0.5594	0.3523	1.0086	0.065*
H(4A)	0.4897	0.1304	0.8735	0.060*
H(4B)	0.3513	0.1851	0.8090	0.060*
H(5A)	0.1942	0.1173	0.9546	0.070*
H(5B)	0.2800	0.0373	0.8869	0.070*

[a] For non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor $U_{\mathrm{eq}} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j)$, for hydrogen U_{iso} was set equal to 1.2U_{eq}(C or N).

Table 3 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **II**.

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq} [a]	Occ. (<1)
Cu(1)	0.97069(10)	0	0.63150(9)	0.0288(4)	
Cl(1)	0.5654(4)	½	0.2327(4)	0.0320(7)	
O(1)	0.4923(13)	½	0.0400(12)	0.042(2)	
O(2)	0.6580(12)	0.3579(10)	0.2978(12)	0.063(2)	
O(3)	0.4546(16)	½	0.2949(17)	0.077(5)	
N(1)	0.7545(13)	0	0.5056(14)	0.034(2)	
N(2)	0.3449(13)	0	−0.0831(13)	0.025(2)	
C(1)	0.6345(15)	0	0.4008(16)	0.027(3)	
C(2)	0.4844(15)	0	0.2551(16)	0.031(3)	
C(3)	0.4904(15)	0	0.0738(17)	0.032(3)	
C(4)	0.2609(9)	0.1514(10)	−0.0969(10)	0.0274(17)	
C(5)	0.1459(9)	0.1833(11)	−0.2841(10)	0.0273(16)	
C(6)	0.0114(11)	0.2573(11)	−0.3297(12)	0.0342(19)	
H(2A)	0.4315	0.0969	0.2635	0.038*	0.5
H(2B)	0.4315	−0.0969	0.2635	0.038*	0.5
H(3A)	0.5451	0.0965	0.0685	0.038*	0.5
H(3B)	0.5451	−0.0965	0.0685	0.038*	0.5
H(4A)	0.3287	0.2441	−0.0562	0.033*	
H(4B)	0.2127	0.1425	−0.0202	0.033*	
H(5)	0.1675	0.1504	−0.3757	0.033*	
H(6A)	−0.0141	0.2919	−0.2416	0.041*	
H(6B)	−0.0543	0.273	−0.4487	0.041*	

[a] For non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor $U_{\mathrm{eq}} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j)$, for hydrogen U_{iso} was set equal to 1.2U_{eq}(C or N).

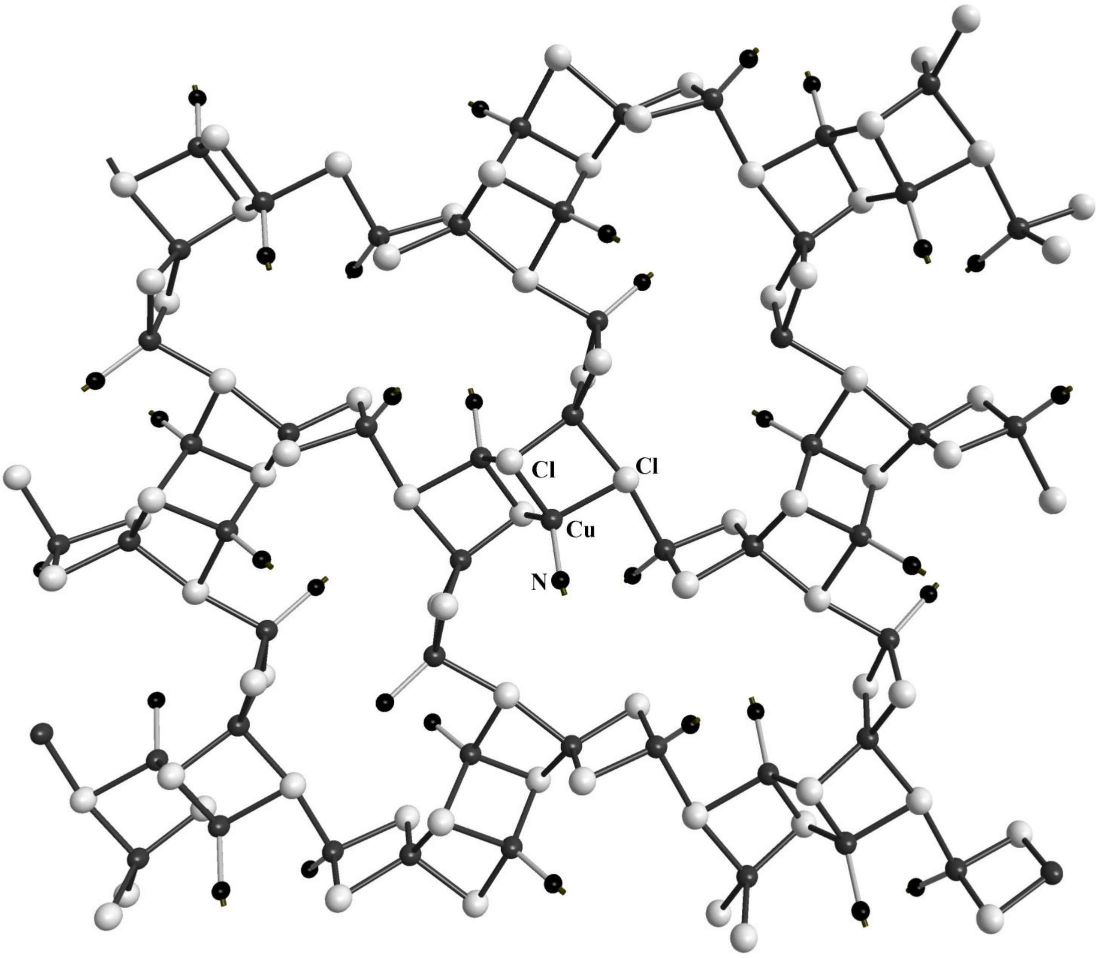

Fig. 2 Fragment of the crystal structure of $[\{NH^+(C_2H_4CN)_2\}Cu_3Cl_4]$ (**I**).

Table 4 Selected bond lengths and angles in the structure of **I**.

Bond	*d*, Å	Angle	*ω*, deg
Cu(1)−N(1)	1.946(6)	N(1)−Cu(1)−Cl(2)	127.8(8)
Cu(1)−Cl(2)	2.301(9)	N(1)−Cu(1)−Cl(4)	109.7(9)
Cu(1)−Cl(4)	2.428(9)	Cl(2)−Cu(1)−Cl(4)	101.6(7)
Cu(1)−Cl(1)	2.489(9)	N(1)−Cu(1)−Cl(1)	107.5(9)
Cu(2)−Cl(4)	2.325(8)	Cl(2)−Cu(1)−Cl(1)	105.3(4)
Cu(2)−Cl(3)^{i,a}	2.330(9)	Cl(4)−Cu(1)−Cl(1)	102.34(6)
Cu(2)−Cl(2)	2.354(8)	Cl(4)−Cu(2)−Cl(3)^{i}	126.40(8)
Cu(2)−Cl(1)^{ii}	2.554(9)	Cl(4)−Cu(2)−Cl(2)	103.11(7)
Cu(3)−N(3)	1.924(6)	Cl(3)^{i}−Cu(2)−Cl(2)	117.10(7)
Cu(3)−Cl(3)	2.360(9)	Cl(4)−Cu(2)−Cl(1)^{ii}	99.81(7)
Cu(3)−Cl(3)^{iii}	2.400(2)	Cl(3)^{i}−Cu(2)−Cl(1)^{ii}	94.87(7)
Cu(3)−Cl(1)^{iv}	2.502(2)	Cl(2)−Cu(2)−Cl(1)^{ii}	113.95(7)
Cl(1)−Cu(3)^{v}	2.502(2)	N(3)−Cu(3)−Cl(3)	118.7(8)
Cl(1)−Cu(2)^{vi}	2.554(8)	N(3)−Cu(3)−Cl(3)^{iii}	122.8(2)
Cl(3)−Cu(2)^{i}	2.330(9)	Cl(3)−Cu(3)−Cl(3)^{iii}	100.25(6)
Cl(3)−Cu(3)^{iii}	2.400(2)	N(3)−Cu(3)−Cl(1)^{iv}	105.4(7)
N(3)−C(6)	1.144(9)	Cl(3)−Cu(3)−Cl(1)^{iv}	112.82(7)
Cu(1)−Cu(2)	2.929(6)	Cl(3)^{iii}−Cu(3)−Cl(1)^{iv}	94.49(6)
Cu(3)−Cu(3)^{iii}	3.052(2)	C(6)−N(3)−Cu(3)	168.7(6)

[a] Symmetry codes: (*i*) –*x*+1, –*y*+1, –*z*+2; (*ii*) *x*–½, –*y*+3/2, *z*–½; (*iii*) –*x*+1, –*y*, –*z*+3; (*iv*) *x*–½, –*y*+½, *z*+½; (*v*) *x*+½, –*y*+½, *z*–½; (*vi*) *x*+½, –*y*+3/2, *z*+½.

Bonds lengths: Cu(1)–*m* 2.035(4) (*m* – middle point of the C=C-bond), Cu(1)−N(1) 1.953(12), Cu(1)−O(3) 2.766(6) Å (Table 6).

Due to the chelate-bridging function of the *L2* molecule, the structure of **II** consists of polymer metalorganic chains, in which the neighboring copper atoms are related by a symmetry plane *n* (Fig. 3). ClO_4-tetrahedra play a bridging role between separate $(CuL^+)_n$-ribbons with the help of C-H…O contacts (Table 5) forming a 3D-framework.

The replacement of the tetrafluoroborate Cu(II) salt by its perchlorate analogue leads in general to the formation of isostructural complexes. The cationic status of *L2* favors the appearance of $[Cu(H^+L)ClO_4]H_2O\cdot ClO_4$ and $[Cu(H^+L)BF_4]H_2O\cdot BF_4$ π-complexes [22], which crystallize in the monoclinic space group $P2_1/n$. The coordination behavior of *L* and co-ligands in these compounds is practically the same: up to now there is only one example of a non-isomorphic pair, $[Cu(DAF)H_2O]BF_4$ and $[Cu(DAF)ClO_4]$ (DAF N,N-diallylformamid) [23].

Table 5 Geometry of selected H-contacts in the structures of **I** and **II**.

No	Contact D–H…A	Bond length, Å			Angle D–H…A, deg	Atom coordinates of A
		D–H	H…A	D…A		
I	C(2)−H(2A)···Cl(2)	0.97	2.63	3.488(9)	147	$-x+1, -y+1, -z+1$
	C(2)−H(2B)···Cl(3)	0.97	2.79	3.566(8)	137	$-x+\frac{1}{2}, y+\frac{1}{2}, -z+5/2$
	C(3)−H(3B)···Cl(3)	0.97	2.74	3.475(7)	133	$x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$
	C(4)−H(4A)···N(3)	0.97	2.61	3.446(9)	145	$-x+1, -y, -z+2$
	N(2)−H(1N)···Cl(1)	0.90	2.26	3.128(5)	161	$-x+1, -y+1, -z+2$
	N(2)−H(2N)···Cl(4)	0.90	2.37	3.163(6)	147	$-x+1, -y+1, -z+2$
II	C(4)−H(4A)···O(1)	0.97	2.55	3.516(8)	176	$-\frac{1}{2}+x, \frac{1}{2}-y, -1+z$
	C(4)−H(4B)···O(1)	0.97	2.75	3.603(8)	147	$-\frac{1}{2}+x, -\frac{1}{2}+y, z$
	C(5)−H(5)···O(2)	0.93	2.70	3.593(4)	159	$-\frac{1}{2}+x, \frac{1}{2}-y, -1+z$

Table 6 Selected bond lengths and angles in the structure of **II**.

Bond	*d*, Å	Angle	*ω*, deg
Cu(1)−N(1)	1.953(12)	N(1)−Cu(1)−C(6)^i	100.1(3)
Cu(1)−*m* ^{a}	2.035(4)	C(6)^i−Cu(1)−C(6)^{ii}	158.6(5)
Cu(1)−O(3)	2.766(6)	C(5)^{ii}−Cu(1)−C(5)^i	86.3(5)
Cu(1)−C(6)$^{i,\,b}$	2.123(9)	C(6)^i−Cu(1)−C(5)^i	37.3(3)
Cu(1)−C(6)^{ii}	2.123(9)	C(1)−N(1)−Cu(1)	165.0(11)
Cu(1)−C(5)^i	2.171(8)	N(1)−C(1)−C(2)	175.4(14)
Cl(1)−O(2)	1.429(8)	C(6)−C(5)−C(4)	124.8(7)
Cl(1)−O(3)	1.432(12)		
Cl(1)−O(1)	1.451(10)		
N(1)−C(1)	1.136(17)		
C(5)=C(6)	1.373(12)		

[a] *m* – middle point of the C(5)=C(6) bond;
[b] symmetry codes: (*i*) *x*+1, –*y*, *z*+1; (*ii*) *x*+1, *y*, *z*+1; (*iii*) *x*, –*y*+1, *z*; (*iv*) *x*, –*y*, *z*; (*v*) *x*–1, *y*, *z*–1.

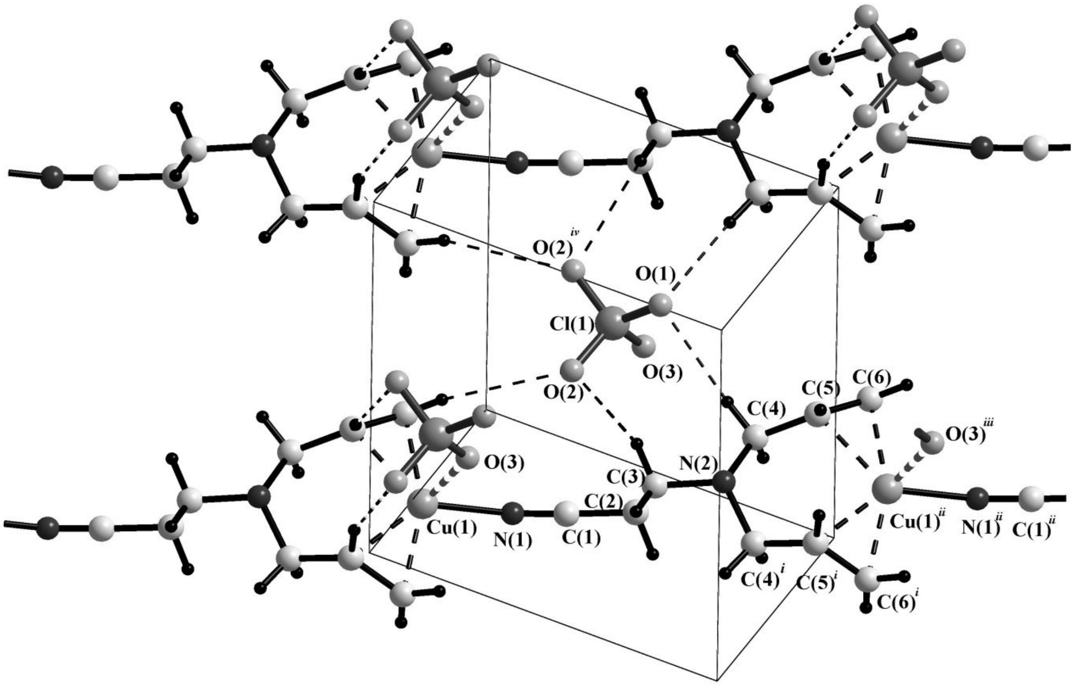

Fig. 3 Projection of the structure of [Cu((C_3H_5)$_2$NC_2H_4CN)ClO_4] (**II**).
Symmetry codes: (*i*) *x*, −*y*, *z*; (*ii*) −1+*x*, *y*, −1+*z*; (*iii*) −1/2+*x*, −1/2+*y*, −1+*z*; (*iv*) *x*, 1−*y*, *z*.

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