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Copper(I) π-complexes with 5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole. Synthesis and crystal structure of $[Cu_2(C_{10}H_9ClN_4S)_2(H_2O)_2](NO_3)_2 \cdot C_2H_5OH$ and $[Cu_3(C_{10}H_9ClN_4S)Cl_3]$ π-compounds

Yuriy SLYVKA[1]*, Nazariy POKHODYLO[2], Roman SAVKA[2], Evgeny GORESHNIK[3], Zoran MAZEJ[3],
Maryan MYS'KIV[1]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv,*
Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
[2] *Department of Organic Chemistry, Ivan Franko National University of Lviv,*
Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
[3] *Department of Inorganic Chemistry and Technology, Jožef Stefan Institute,*
Jamova 39, SI-1000 Ljubljana, Slovenia
* *Corresponding author. Tel.: +380-32-2394-506; e-mail: yura_slyvka@ukr.net*

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Two crystalline copper(I), $[Cu_2(C_{10}H_9ClN_4S)_2(H_2O)_2](NO_3)_2 \cdot C_2H_5OH$ (1) and $[Cu_3(C_{10}H_9ClN_4S)Cl_3]$ (2), π-complexes with 5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole ($C_{10}H_9ClN_4S$) have been synthesized by the alternating-current electrochemical technique and X-ray studied. The crystals are triclinic, space group $P\bar{1}$, for 1: a = 10.760(4), b = 1.663(4), c = 15.040(4) Å, α = 101.51(4), β = 94.12(4), γ = 116.37(4) °, V = 1629.1(9) Å^3, Z = 2; for 2: a = 7.709(5), b = 10.938(6), c = 11.632(6) Å, α = 104.70(8), β = 108.20(8), γ = 104.50(8) °, V = 841.3(8) Å^3, Z = 1. The structure of 1 is built of discrete $[Cu_2(C_{10}H_9ClN_4S)_2(H_2O)_2]^{2+}$ π-complex cations, in which the Cu(I) atoms possess a trigonal pyramidal coordination environment formed by two N atoms of the tetrazole rings of adjacent $C_{10}H_9ClN_4S$ molecules, a C=C bond of an S-allyl group and an apical water molecule. Replacement of NO_3^- by Cl^- leads to the formation of endless $[Cu_2Cl_3]_\infty$ anionic chains, besides $[Cu_2(C_{10}H_9ClN_4S)_2(H_2O)_2]^{2+}$ π-complex cations, in the structure of 2. The infinite anions are bonded to the complex cations through bridging Cl atoms, so that two-dimensional layers are formed. In the structure of 2, a variety of hydrogen contacts ((Ow···O(N) 2.70-2.79 Å) unite neighboring $[Cu_2(C_{10}H_9ClN_4S)_2Cl_2]^{2+}$ cations and NO_3^- anions into a 3D-framework.

Tetrazole / Copper / Electrochemical technique / π-Complex / Crystal structure

Introduction

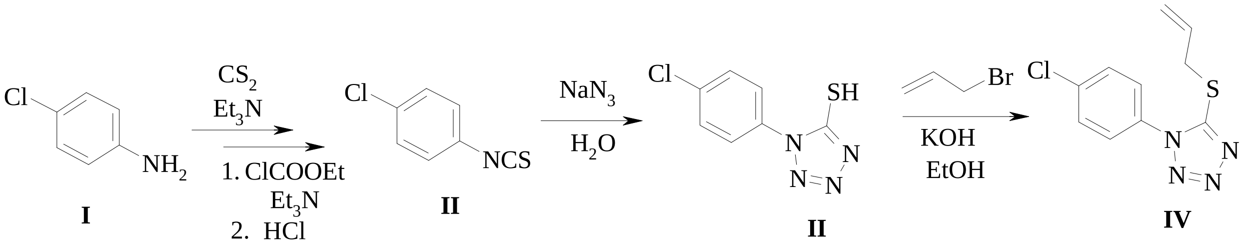
Metal tetrazole derivatives have a potential use in photo- and biological processes, medicine, for corrosion protection of metals, gas generation, biological activity and display a key application in organic syntheses [1]. In particular, metal 5-mercaptotetrazolates play an important role in the synthesis of biologically active compounds and 5-mercapto-1-phenyltetrazole, indebted to form stable complexes with various metals, is the most effective metal corrosion inhibitor. Substantial understanding of their specific ability can be achieved by systematic single crystal structure analysis.

Use of copper(I) atoms in the formation of 5-mercaptotetrazole derivatives would enhance the biological and catalytic activity of the resulting products. Most X-ray structurally investigated copper complexes with 1*R*-tetrazole derivatives are Cu(II) σ-compounds [2-5], while Cu(I) π-complexes of such type appear to be unknown. To analyze the influence of the olefin C=C bond on the 5-mercaptotetrazole core coordination ability we first synthesized 5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole ($C_{10}H_9ClN_4S$), and then obtained two π-complexes, $[Cu_2(C_{10}H_9ClN_4S)_2(H_2O)_2](NO_3)_2 \cdot C_2H_5OH$ (**1**) and $[Cu_3(C_{10}H_9ClN_4S)Cl_3]$ (**2**) and performed their structure characterization.

Experimental section

Synthesis of $C_{10}H_9ClN_4S$

The target ligand **IV** was synthesized from commercially available 4-chloroaniline **I** in several



Scheme 1

steps (Scheme 1). 4-Chloroaniline was converted into 1-chloro-4-isothiocyanatobenzene **II** by the reaction with dithioxomethane and subsequent treatment with ethyl chlorocarbonate and HCl according to the modified Kaluza method [6]. By 1,3-dipolar cycloaddition reaction of the obtained 4-isothiocyanatobenzene **II** with azide ion, 1-(4-chlorophenyl)-1*H*-tetrazole-5-thiol **III** [7] was formed and readily reacted with 3-bromoprop-1-ene in the presence of KOH, yielding the ligand **IV** [8].

Preparation of $[Cu_2(C_{10}H_9ClN_4S)_2(H_2O)_2](NO_3)_2{\cdot}C_2H_5OH$

Crystals of **1** were obtained under the conditions of alternating-current electrochemical synthesis [9] starting from a 2-butanol–ethanol (0.5 ml butanol and 3.5 ml ethanol) solution of $Cu(NO_3)_2{\cdot}3H_2O$ (2 mmol) and $C_{10}H_9ClN_4S$ (4 mmol). The solution was placed into a small test-tube and copper-wire electrodes in cork were inserted. After applying 0.60 V of alternating current (frequency 50 Hz) tension for 48 h the green colored solution was discolored and good quality colorless crystals of **1** appeared on the copper electrodes. Yield 64 %.

Preparation of $[Cu_3(C_{10}H_9ClN_4S)Cl_3]$

Crystals of **2** were obtained in the same manner starting from a 2-butanol–ethanol (0.5 ml butanol and 3.5 ml ethanol) solution containing $Cu(Cl_3COO)_2{\cdot}xH_2O$ (2 mmol) and $C_{10}H_9ClN_4S$ (4 mmol). After applying 0.50 V of alternating current (frequency 50 Hz) tension for 72 h unstable CCl_3COOCu (appearing *in statu nascendi*) produced CuCl, which formed, in turn, colorless crystals of the $[Cu_3(C_{10}H_9ClN_4S)Cl_3]$ complex on the copper-wire electrodes in the presence of the ligand. Yield 70 %.

It should be noted that when using $CuCl_2{\cdot}2H_2O$ (instead of $Cu(Cl_3COO)_2{\cdot}xH_2O$) under the conditions mentioned above no copper(I) chloride complex was obtained.

X–ray crystal structure determination

The crystallographic parameters and summaries of the data collection for **1** and **2** are presented in Table 1. The diffraction data were collected on a CAD-4 (graphite monochromated MoK_α radiation) diffractometer. The structure was solved and refined using SHELXS-97 and SHELXL-97 [10] software, implemented in the program package WinGX [11]. In both structures the nonhydrogen atoms were found by direct methods and the hydrogen atoms geometrically.

Full-matrix least-squares refinements based on F^2 were carried out for the positional and thermal parameters of all nonhydrogen atoms. The positions of the H atoms were treated as riding atoms and refined with fixed C–H distances and with U_{iso}(H) equal to $1.2U_{eq}$(C). Atomic positional and displacement parameters for **1** and **2** are given in Tables 2 and 3.

The figures were prepared using DIAMOND 3.1 software [12]. Selected bond lengths and angles are listed in Tables 4 and 5.

Results and discussion

A fragment of the crystal structure of $[Cu_2(C_{10}H_9ClN_4S)_2(H_2O)_2](NO_3)_2{\cdot}C_2H_5OH$ (**1**) is shown in Fig. 1. The structure is built of two crystallographically independent $[Cu_2(C_{10}H_9ClN_4S)_2(H_2O)_2]^{2+}$ π-complex cations, nitrate anions and alcohol molecules. Both Cu(I) atoms possess trigonal pyramidal coordination formed by two N (N3 and N4) atoms (Cu(1)–N(3) 1.974(7), Cu(1)–N(4) 1.992(7), Cu(2)–N(7) 1.986(7), Cu(2)–N(8) 2.035(7) Å) of the tetrazole ring, a C=C bond of the S-allyl group (Cu(1)–C(1) 2.058(9), Cu(2)–C(11) 2.055 Å) of the ligand, and a water molecule, occupying the apical position of the copper(I) coordination polyhedron (Cu(1)–Ow(1) 2.058(9), Cu(2)–Ow(2) 2.188(7) Å). Selected bond lengths and angles are listed in Table 4.

5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole acts as a tridentate N,N,($S–C_3H_5$)-bridging ligand binding two copper atoms into centrosymmetric dimers containing one six-membered $\{Cu_2N_4\}$ and two seven-membered $\{CuNC_4S\}$ rings. One can notice a similar picture in the structures of $[Cu_2(C_2H_3N_4)_2]_n$ and $[Cu_3(C_2H_3N_4)_3]_n{\cdot}0.5nH_2O$ [13] ($C_2H_3N_4$ – 5-methyltetrazole), where four N atoms of the tetrazole ring participate in the Cu(I) coordination, forming the same six-membered cycle topology. The two independent π-complex cations in the structure of **1** are mutually twisted by 30 degrees and stacked in the [100] direction (Fig. 2).

The Cu(1) and Cu(2) atoms deviate only by 0.32 and 0.39 Å, respectively, from the base of the trigonal pyramid, and the distances Cu–*m* (*m* – middle

Table 1 Crystal data and structure refinement for compounds **1** and **2.**

	1	**2**
Empirical formula	$C_{22}H_{24}Cl_2Cu_2N_{10}O_9S_2$	$C_{10}H_9Cl_4Cu_3N_4S$
Formula weight	834.61 g mol^{-1}	339.67 g mol^{-1}
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
Unit cell dimensions	a = 10.760(4) Å	a = 7.709(5) Å
	b = 11.663(4) Å	b = 10.938(6) Å
	c = 15.040(4) Å	c = 11.632(6) Å
	α = 101.51(4) °	α = 104.70(8) °
	β = 94.12(4) °	β = 108.20(8) °
	γ = 116.37(4) °	γ = 104.50(8) °
Volume	1629.1(9) Å^3	841.3(8) Å^3
Z	2	1
Calculated density	1.70 g cm^{-3}	2.17 g cm^{-3}
Absorption coefficient	1.66 mm^{-1}	4.51 mm^{-1}
$F(000)$	844	536
Crystal size	0.29 × 0.24 × 0.16 mm	0.26 × 0.18 × 0.16 mm
Colour, shape	colorless, unspecified	colorless, unspecified
Theta range for data collection	2.02 to 26.00 deg	2.06 to 30.95 deg
Limiting indices	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $0 \leq l \leq 18$	$-10 \leq h \leq 10$, $-15 \leq k \leq 15$, $-4 \leq l \leq 11$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Measured reflections	6778	4667
Unique reflections	6412	4359
Observed reflect. [$I > 2\sigma(I)$]	3901	2397
Free parameters	426	199
Goodness-of-fit on F^2	1.061	1.069
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0888, wR_2 = 0.2336	R_1 = 0.0898, wR_2 = 0.2513
R indices (all data)	R_1 = 0.1550, wR_2 = 0.2786	R_1 = 0.1465, wR_2 = 0.2804
Largest diff. peak and hole	1.806 and -1.290 e Å^{-3}	2.007 and -2.334 e Å^{-3}

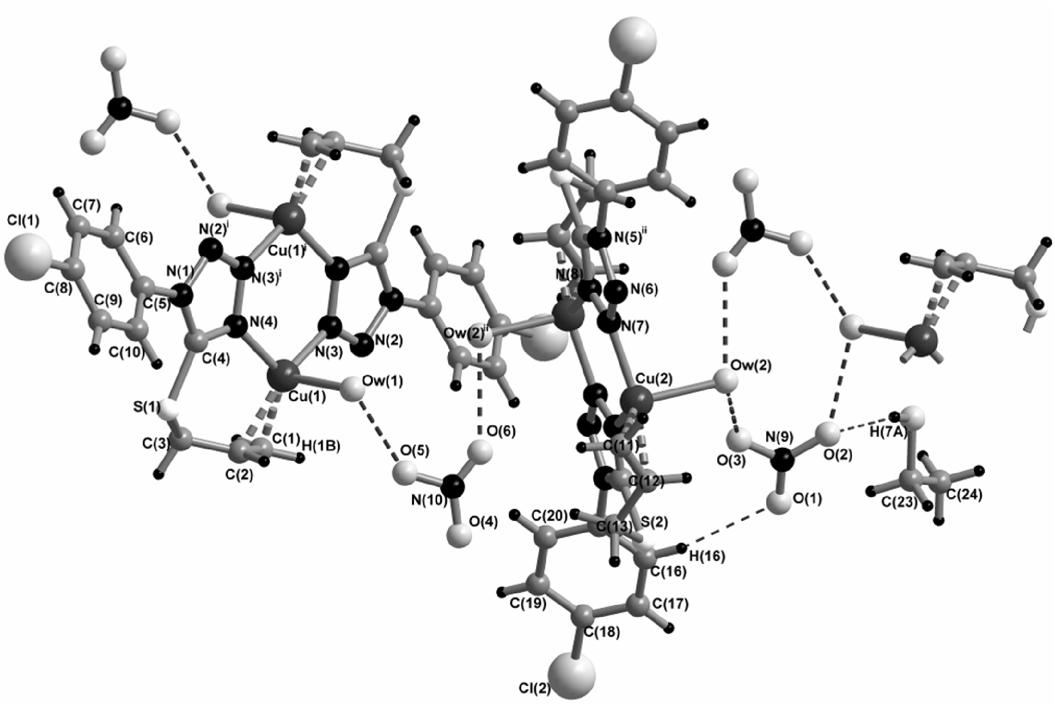


Fig. 1 Fragment of **1**. Hydrogen bonds (and Ow – O(N) contacts) are depicted as dashed lines. Symmetry codes: (*i*) –*x*, –*y*, 2–*z*; (*ii*) 2–*x*, –*y*, 1–*z*.

Table 2 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **1**.

Atom	*x*	*y*	*z*	U_{eq}/U_{iso} [a]	Atom	*x*	*y*	*z*	U_{eq}/U_{iso} [a]
Cu(1)	0.17714(10)	0.01794(12)	0.99339(8)	0.0414(3)	C(11)	0.9562(10)	0.293(1)	0.6064(8)	0.050(2)
Cu(2)	0.97885(10)	0.12422(10)	0.58686(8)	0.0362(3)	C(12)	0.8489(9)	0.2022(10)	0.6332(7)	0.043(2)
Cl(1)	-0.3224(3)	-0.7457(3)	1.2506(2)	0.0583(7)	C(13)	0.7021(8)	0.1217(9)	0.5756(7)	0.046(2)
Cl(2)	1.9741(2)	0.6152(3)	0.6163(2)	0.0659(8)	C(14)	0.6944(8)	-0.1178(9)	0.5273(6)	0.0350(19)
S(1)	0.1916(2)	-0.2104(3)	1.11811(19)	0.0495(7)	C(15)	1.5148(8)	0.3408(8)	0.5448(6)	0.0363(19)
S(2)	0.6056(2)	-0.0458(2)	0.58792(19)	0.0475(6)	C(16)	1.5818(9)	0.3778(11)	0.4753(7)	0.051(3)
O(1)	0.3741(8)	0.3019(10)	0.2634(7)	0.090(3)	C(17)	1.7262(10)	0.4645(10)	0.4962(7)	0.052(3)
O(2)	0.1692(10)	0.2169(11)	0.1826(6)	0.098(3)	C(18)	1.7932(8)	0.5072(9)	0.5878(7)	0.043(2)
O(3)	0.2009(11)	0.1791(11)	0.3114(8)	0.107(4)	C(19)	1.7249(10)	0.4692(10)	0.6555(7)	0.053(3)
O(4)	1.4866(15)	0.1053(15)	0.7104(11)	0.144(6)	C(20)	1.5811(10)	0.3807(10)	0.6339(7)	0.052(3)
O(5)	1.3491(17)	0.0485(14)	0.7938(11)	0.159(6)	C(23)	0.641(2)	0.508(2)	0.8964(14)	0.131(7)
O(6)	1.286(2)	0.075(3)	0.6874(18)	0.318(18)	C(24)	0.595(2)	0.392(2)	0.9176(17)	0.143(8)
O(7)	0.8007(11)	0.5692(10)	0.9003(7)	0.094(3)	H(1A)	0.412	0.190	1.089	0.073
N(1)	-0.0872(7)	-0.2744(7)	1.1056(5)	0.0330(15)	H(1B)	0.404	0.143	0.980	0.073
N(2)	0.1773(7)	0.2316(7)	0.9228(5)	0.0348(16)	H(3A)	0.304	0.020	1.168	0.063
N(3)	0.1061(7)	0.1333(7)	0.9547(5)	0.0333(15)	H(3B)	0.417	-0.030	1.158	0.063
N(4)	0.0324(7)	-0.1072(7)	1.0506(5)	0.0353(16)	H(2)	0.328	-0.070	0.989	0.063
N(5)	1.3667(6)	0.2426(7)	0.5235(5)	0.0346(16)	H(6)	-0.277	-0.343	1.207	0.051
N(6)	1.2704(7)	0.2674(7)	0.5637(5)	0.0401(17)	H(7)	-0.375	-0.533	1.260	0.055
N(7)	1.1541(7)	0.1579(7)	0.5367(5)	0.0360(16)	H(9)	-0.108	-0.648	1.151	0.053
N(8)	0.8295(6)	-0.0630(6)	0.5196(5)	0.0307(15)	H(10)	-0.018	-0.464	1.091	0.053
N(9)	0.2492(9)	0.2317(9)	0.2513(7)	0.055(2)	H(11A)	0.943	0.310	0.549	0.060
N(10)	1.3711(11)	0.0758(11)	0.7235(8)	0.064(3)	H(11B)	1.044	0.340	0.645	0.060
Ow(1)	0.1134(8)	-0.1218(7)	0.8549(5)	0.0563(18)	H(12)	0.865	0.187	0.691	0.052
Ow(2)	1.0324(7)	0.0665(7)	0.7080(5)	0.0537(18)	H(13A)	0.709	0.117	0.511	0.055
C(1)	0.3926(9)	0.1231(12)	1.0363(9)	0.061(3)	H(13B)	0.648	0.168	0.592	0.055
C(2)	0.3468(9)	-0.0048(12)	1.0423(8)	0.052(3)	H(16)	1.533	0.346	0.415	0.061
C(3)	0.3275(9)	-0.0409(11)	1.1281(8)	0.053(3)	H(17)	1.776	0.493	0.450	0.063
C(4)	0.0401(8)	-0.1969(9)	1.0899(6)	0.0340(18)	H(19)	1.772	0.501	0.716	0.063
C(5)	-0.1388(9)	-0.3863(8)	1.1426(6)	0.0337(18)	H(20)	1.532	0.350	0.680	0.063
C(6)	-0.2448(9)	-0.4056(9)	1.1943(7)	0.042(2)	H(7A)	0.829	0.641	0.887	0.142
C(7)	-0.3025(9)	-0.5178(10)	1.2266(7)	0.046(2)	H(23A)	0.619	0.567	0.940	0.157
C(8)	-0.2506(9)	-0.6051(9)	1.2086(6)	0.040(2)	H(23B)	0.594	0.495	0.835	0.157
C(9)	-0.1432(10)	-0.5879(9)	1.1605(7)	0.044(2)	H(24A)	0.495	0.354	0.915	0.214
C(10)	-0.089(1)	-0.4773(10)	1.1258(6)	0.044(2)	H(24B)	0.641	0.406	0.979	0.214
C(11)	0.9562(10)	0.293(1)	0.6064(8)	0.050(2)	H(24C)	0.616	0.334	0.874	0.214

[a] For non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, for hydrogen U_{iso} was set equal to $1.2U_{eq}$(C).

point of the C=C bond) are equal to 1.944(9) and 1.953(9) Å (the angle C–Cu–C equals 38.9(4) °), which proves a sufficient efficiency of the Cu(I)–(C=C) interaction.

The crystal packing of $[Cu_2(C_{10}H_9ClN_4S)_2(H_2O)_2](NO_3)_2\cdot C_2H_5OH$ (**1**) is governed by a variety of hydrogen contacts [14,15], which occur between the water molecules and oxygen atoms (Ow···O(N) 2.70–2.79 Å), on the one hand, between hydrogen atoms and oxygen atoms of nitrate anions ((C)H···O(N) 2.56–2.71 Å), on the other hand. The latter unite adjacent $[Cu_2(C_{10}H_9ClN_4S)_2Cl_2]^{2+}$ cations and NO_3^- anions into a three-dimensional framework [16].

A quite different coordination manner of Cu(I) atoms is displayed in the structure of $[Cu_3(C_{10}H_9ClN_4S)Cl_3]$ (**2**) (Fig. 3), where the apical position of the trigonal pyramidal environment of the metal is occupied by a chlorine atom. In the structure of **2** copper(I) atoms are located in three crystallographically independent sites. The Cu(1) atom, similarly to **1,** possesses trigonal pyramidal coordination environment formed by N3 and N4 atoms of two adjacent $C_{10}H_9ClN_4S$ molecules (Cu(1)–N(3) 1.991(7) Å, Cu(1)–N(4) 2.021(8) Å) of the tetrazole ring, a C=C bond of an S-allyl group (Cu(1)–C(1) 2.079(9) Å) in the base of the polyhedron and by a Cl(2) atom at the apical position. Thus, 5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole plays a twice-bridging role connecting two Cu(1) atoms into $[Cu_2(C_{10}H_9ClN_4S)_2Cl_2]^{2+}$ dimeric cations with six-membered $\{Cu_2N_4\}$ and seven-membered $\{CuNC_4S\}$ rings topology. The efficiency of the Cu(I)–(C=C) interaction is confirmed by the fact that Cu(1) moderately deviates (by 0.36 Å) from the base of the trigonal pyramid and Cu–*m* is equal to 1.977(9) Å

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

Atom	*x*	*y*	*z*	U_{eq}/U_{iso} [a]	Atom	*x*	*y*	*z*	U_{eq}/U_{iso} [a]
Cu(1)	0.18779(16)	0.48665(11)	1.14131(11)	0.0415(4)	C(5)	-0.0644(12)	0.0554(8)	0.6931(8)	0.0325(17)
Cu(2)	0.3935(2)	0.6077(3)	0.9466(2)	0.1045(8)	C(6)	0.0958(13)	0.0232(10)	0.6981(10)	0.044(2)
Cu(3)	0.4300(3)	0.86938(19)	0.9343(2)	0.0963(7)	C(7)	0.0693(14)	-0.105(1)	0.618(1)	0.046(2)
Cl(1)	-0.1437(5)	-0.3519(3)	0.4376(3)	0.0694(9)	C(8)	-0.1147(16)	-0.1920(9)	0.5350(9)	0.047(2)
Cl(2)	0.5126(4)	0.6195(2)	1.1431(3)	0.0514(6)	C(9)	-0.2728(15)	-0.1556(10)	0.5251(10)	0.052(3)
Cl(3)	0.2539(3)	0.6629(3)	0.7881(3)	0.0566(7)	C(10)	-0.2519(14)	-0.0309(9)	0.6062(10)	0.045(2)
Cl(4)	0.4075(3)	0.95900(19)	1.1290(2)	0.0322(5)	H(1A)	0.143	0.426	1.326	0.052
S	0.1747(3)	0.1490(2)	0.9996(2)	0.0362(5)	H(1B)	0.349	0.540	1.361	0.052
N(1)	-0.0391(9)	0.1826(7)	0.7819(6)	0.0318(15)	H(2)	0.415	0.393	1.224	0.045
N(2)	-0.1225(10)	0.2679(7)	0.7473(7)	0.0371(16)	H(3A)	0.027	0.214	1.137	0.042
N(3)	-0.0740(9)	0.3683(7)	0.8509(7)	0.0378(17)	H(3B)	0.189	0.163	1.204	0.042
N(4)	0.0418(9)	0.3522(7)	0.9572(7)	0.0347(16)	H(6)	0.221	0.085	0.754	0.053
C(1)	0.2590(14)	0.4523(9)	1.3151(9)	0.044(2)	H(7)	0.177	-0.131	0.621	0.056
C(2)	0.2974(12)	0.3638(9)	1.2329(9)	0.038(2)	H(9)	-0.396	-0.215	0.464	0.062
C(3)	0.1601(12)	0.2185(8)	1.1534(9)	0.0354(19)	H(10)	-0.360	-0.006	0.603	0.054
C(4)	0.0595(11)	0.2327(7)	0.9143(9)	0.0334(18)					

[a] For non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, for hydrogen U_{iso} was set equal to $1.2U_{eq}$(C).

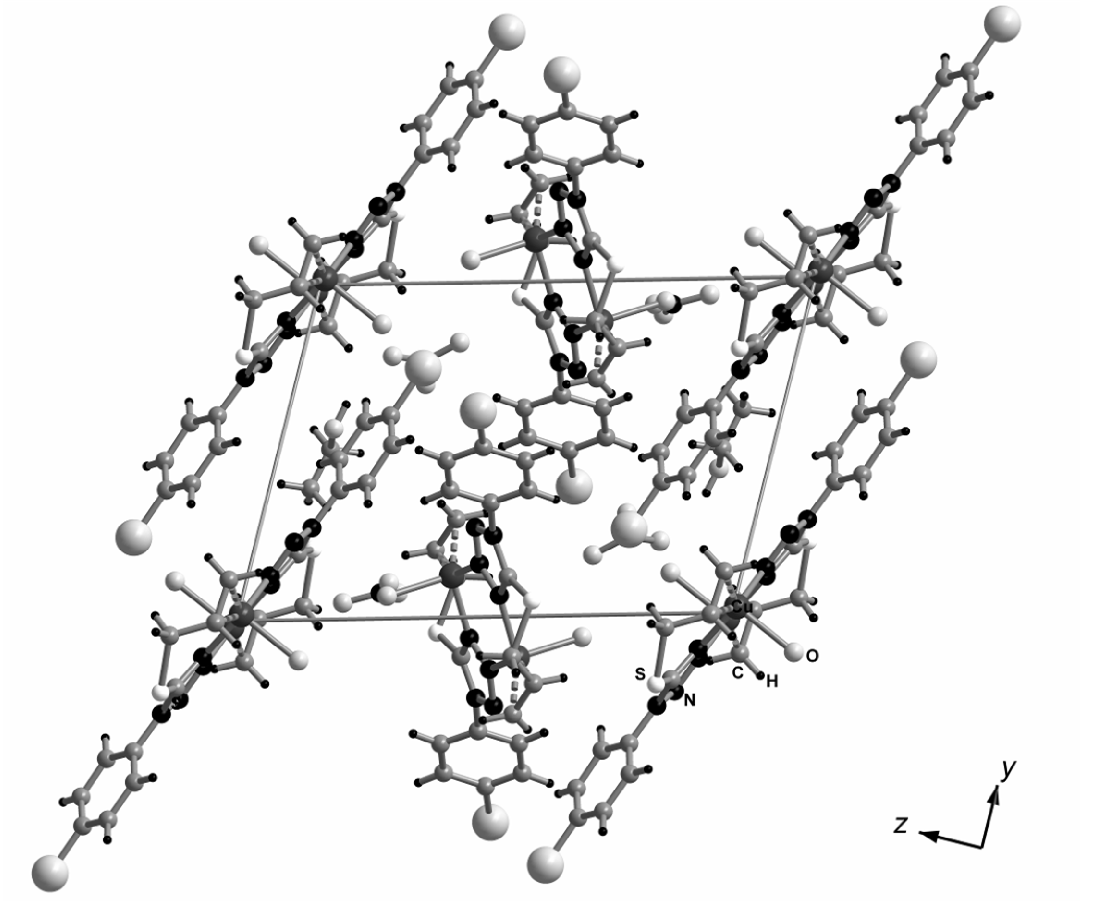


Fig. 2 Projection of the crystal structure of **2** on the *yz* plane.

Table 4 Selected bond lengths and angles in the structure of **1**.

Bond	*d*, Å	Angle	ω, deg
Cu(1)–C(1)	2.058(9)	C(1)–Cu(1)–N(3)	109.6(4)
Cu(1)–C(2)	2.064(9)	N(3)–Cu(1)–N(4)	108.6(3)
Cu(1)–*m*(1) [a]	1.944(9)	C(2)–Cu(1)–N(4)	98.3(4)
Cu(1)–N(3)	1.974(7)	C(1)–Cu(1)–C(2)	38.9(4)
Cu(1)–N(4)	1.992(7)	C(1)–Cu(1)–*m*(1)	19.47(4)
Cu(1)–Ow(1)	2.217(7)	C(1)=C(2)–C(3)	122(4)
C(1)=C(2)	1.37(5)	C(1)–Cu(1)–Ow(1)	113.0(4)
C(2)–C(3)	1.44(5)	N(3)–Cu(1)–Ow(1)	94.9(3)
N(3)–N(4)^{i} [b]	1.375(9)	Cu(1)–N(3)–N(4)^{i}	123.1(5)
N(3)–N(2)	1.27(4)	N(3)^{i}–N(4)–Cu(1)	126.6(5)
Cu(2)–C(11)	2.055(9)	C(11)–Cu(2)–N(7)	108.5(3)
Cu(2)–C(12)	2.070(9)	N(7)–Cu(2)–N(8)	107.5(3)
Cu(2)–*m*(2) [a]	1.953(9)	C(12)–Cu(2)–N(8)	99.4(3)
Cu(2)–N(7)	1.986(7)	C(11)–Cu(2)–C(12)	37.6(4)
Cu(2)–N(8)	2.035(7)	C(11)–Cu(2)–*m*(2)	18.9(4)
Cu(2)–Ow(2)	2.188(7)	C(11)=C(12)–C(13)	123.5(9)
C(11)=C(12)	1.33(4)	C(11)–Cu(2)–Ow(2)	118.7(4)
C(12)–C(13)	1.51(4)	N(7)–Cu(2)–Ow(2)	97.2(3)
N(7)–N(8)	1.339(9)	Cu(2)–N(7)–N(8)^{ii} [b]	123.2(5)
N(7)–N(6)	1.289(9)	N(7)^{ii}–N(8)–Cu(2)	128.4(5)

[a] *m*(1) and *m*(2) – middle points of the C(1)=C(2) and C(11)=C(12) bonds, respectively;

[b] symmetry codes: (*i*) –*x*, –*y*, 2–*z*; (*ii*) 2–*x*, –*y*, 1–*z*.

Table 5 Selected bond lengths and angles in the structure of **2**.

Bond	*d*, Å	Angle	ω, deg
Cu(1)–C(1)	2.079(9)	C(1)–Cu(1)–N(3)	110.7(4)
Cu(1)–C(2)	2.095(9)	N(3)–Cu(1)–N(4)	105.5(3)
Cu(1)–*m*(1) [a]	1.977(9)	C(2)–Cu(1)–N(4)	99.7(3)
Cu(1)–N(3)	1.991(7)	C(1)–Cu(1)–C(2)	37.4(3)
Cu(1)–N(4)	2.021(8)	C(1)–Cu(1)–*m*(1)	18.8(3)
Cu(1)–Cl(2)	2.552(4)	C(1)=C(2)–C(3)	123.8(9)
C(1)=C(2)	1.338(13)	C(1)–Cu(1)–Cl(2)	105.5(3)
C(2)–C(3)	1.52(4)	N(3)–Cu(1)–Cl(2)	97.6(2)
N(3)–N(4)^{i} [b]	1.363(9)	Cu(1)–N(3)–N(4)^{i}	124.2(6)
N(3)–N(2)	1.28(4)	Cl(2)–Cu(2)–Cl(2)^{ii}	92.3(5)
Cu(2)–Cl(2)	2.136(4)	Cl(2)–Cu(2)–Cl(3)	157.5(6)
Cu(2)–Cl(2)^{ii} [b]	2.801(4)	Cl(2)^{ii}–Cu(2)–Cl(3)	111.0(5)
Cu(2)–Cl(3)	2.140(4)	Cu(2)–Cl(2)–Cu(2)^{ii}	87.8(5)
Cu(3)–Cl(3)	2.215(5)	Cu(2)–Cl(3)–Cu(3)	81.8(5)
Cu(3)–Cl(4)	2.307(3)	Cl(3)–Cu(3)–Cl(4)	126.0(5)
Cu(3)–Cl(4)^{iii} [b]	2.395(3)	Cl(3)–Cu(3)–Cl(4)^{iii}	119.3(5)
Cu(2)–Cu(3)	2.850(4)	Cl(4)–Cu(3)–Cl(4)^{iii}	112.2(5)
Cu(3)–Cu(3)^{iii}	2.622(5)	Cu(3)–Cl(4)–Cu(3)^{iii}	67.8(5)

[a] *m*(1) – middle point of C(1)=C(2) bond;

[b] symmetry codes: (*i*) –*x*, 1–*y*, 2–*z*; (*ii*) 1–*x*, 1–*y*, 2–*z*; (*iii*) 1–*x*, 2–*y*, 2–*z*.

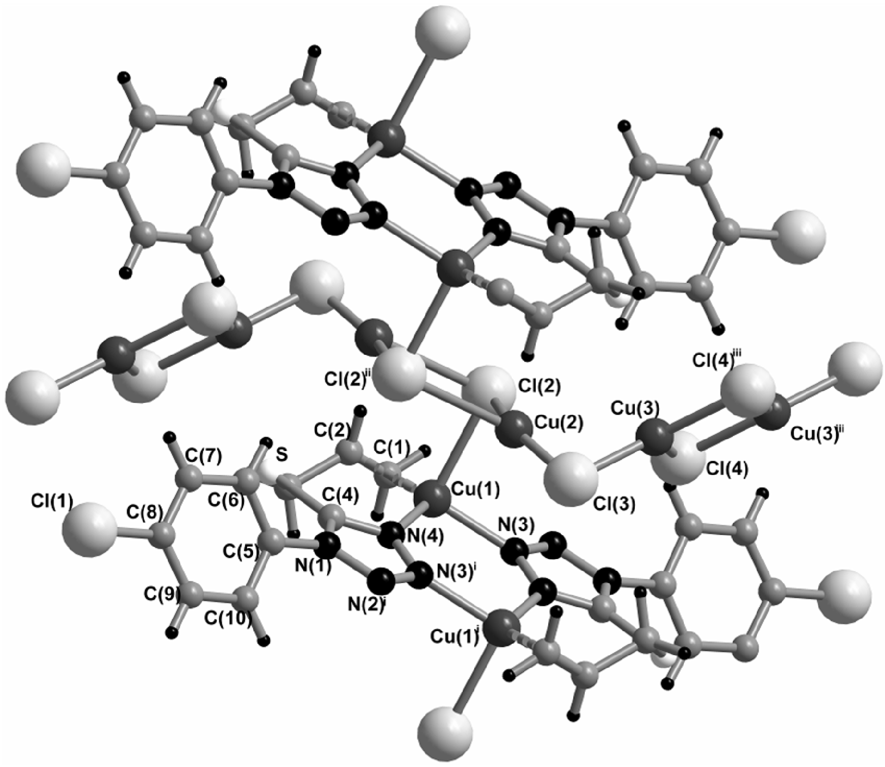


Fig. 3 Fragment of **2**. Symmetry codes: (*i*) –*x*, 1–*y*, 2–*z*; (*ii*) 1–*x*, 1–*y*, 2–*z*; (*iii*) 1–*x*, 2–*y*, 2–*z*.

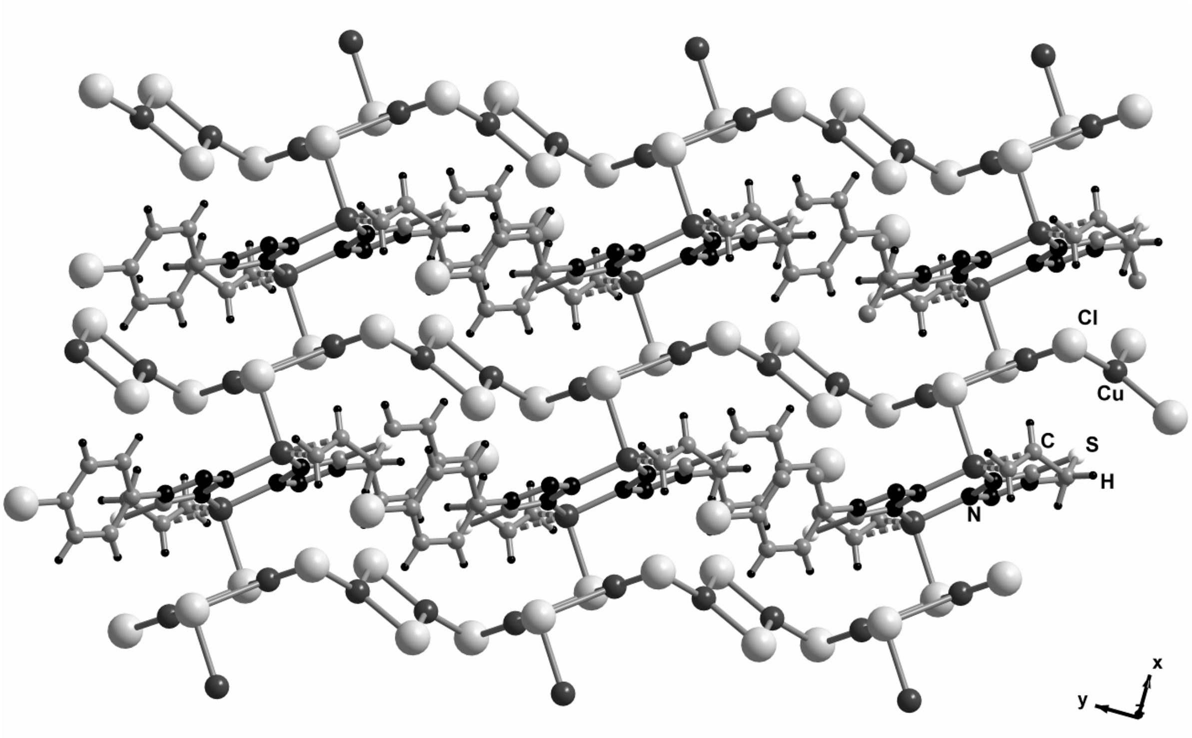


Fig. 4 A polymeric layer of **2** projected on the *xy* plane.

(the angle C–Cu–C equals 37.4(3) °). Selected bond lengths and angles in the structure of **2** are listed in Table 5. Both Cu(2) and Cu(3) atoms possess a trigonal coordination environment which consists of Cl atoms only. As one can see, Cl(2), Cl(3) and Cl(4) atoms in the structure **2** play a bridging role, connecting Cu(1) and Cu(2) coordination triangles into an infinite $[Cu_2Cl_3^-]_\infty$ inorganic chain running along the [010] direction. As a result, Cl(2) atoms bind together neighboring $[Cu_2(C_{10}H_9ClN_4S)_2Cl_2]^{2+}$ cations and infinite $[Cu_2Cl_3^-]_\infty$ chains into 2D layers (Fig. 4). A similar $Cu_2Cl_3^-$ inorganic fragment with trigonal coordination environment of Cu(I) is also present in copper(I) complexes with N,N'-bis(2-

hydroxy-formamide-6-formyl-4-methylphenolato)-1,3-diaminopropane $[Cu_6Cl_4(C_{42}H_{42}N_8O_8)]_n$ [17], bis(22-chloro-5,10,15,20-tetraphenyl-m-benziporpyrinato) $[Cu_4Cl_6(C_{92}H_{58}N_6)]\cdot 4(CH_2Cl_2)$ [18].

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