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Syntheses and crystal structures of copper(I) complexes with alkyl-thioallophanate derivatives

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Abstract—The reaction of $CuCl_2 \cdot 2H_2O$ with N-(*p*-nitrophenyl)-N′-butoxycarbonyl)-thiourea (H_2nbt) and N-(*o*-nitrophenyl)-N′-(ethoxycarbonyl)-thiourea (H_2net) gave two copper(I) complexes, $[Cu(H_2nbt)_2Cl]_2$, **1**, and $Cu(H_2net)_2Cl$, **2**, respectively. In complex **1**, the ligand H_2nbt is S,S-bonded to two Cu atoms, and the two ligand molecules exchange "long" Cu—S interactions (Cu—S = 2.700 Å) forming a dimer, in which the Cu atom has a distorted tetrahedral coordination [Cl—Cu—S(1) = 119.9(1), Cl—Cu—S(2) = 122.9(1) and S(1)—Cu—S(2) = 108.4(1)°] and is 0.387(2) Å from th basal S, S, Cl with unequal Cu—S [2.253(3), 2.244(3) Å] and Cu—Cl [2.247(3) Å] bonds. In complex **2**, the copper (I) atom is in a trigonal planar geometry [Cl—Cu—S(1) = 120.53(5), Cl—Cu—S(2) = 118.43(5) and S(1)—Cu—S(2) = 119.16(5)°] with two unequal Cu—S [2.228(1), 2.232(1) Å] and Cu—Cl [2.251(1) Å] bonds. © 1997 Elsevier Science Ltd

Keywords: Cu^I complexes; thioureas; syntheses; X-ray structures; ^1H NMR; ^{13}C NMR.

The biological activities of the complexes with thiourea derivatives have been well documented and thiourea derivatives, in this respect, have been successfully screened for various biological actions [1]. Some transition metal complexes with N-substituted thioallophanate compounds have been reported in the literature [2], and the existence of copper(II)/copper(I) redox systems has been chemically and electrochemically proved in solution [3]. In fact, in view of the copper(I) involvement in certain biochemical redox reactions [4], the investigation of the structural preferences of copper(I) compounds is an ever growing field of research. Up to now, the literature has witnessed many reports on the reduction of Cu^{II} in the presence of thione derivatives [5]. A kind of thiourea derivative, N-(*o*-nitrophenyl)-N′-(ethoxycarbonyl)-thiourea (H_2net) was recently isolated from the leaves of resistant *Pyricuiria oryzae cav.* rice variety [6], and the preliminary pharmacological tests showed that it could exhibit distinct antibacterial activity even at the low concentration of 5×10^{-5} M, and it could also repress extremely the production of root cancer and the gene expression of toxic area, as well as the entrance into the rice cell for the external gene introduced by the conversion system of the root cancer. Thus, inspired by the aforementioned biological importance, we have synthesized a series of thiourea derivatives with a basic structure similar to H_2net and their copper complexes. It is found that the copper(I) complexes were obtained from the copper(II) salts by *in situ* reduction in the presence of these thiourea derivatives in solution. In this paper, we report the synthetic and structural results of the two copper(I) complexes with N-(*p*-nitrophenyl)-N′-(butoxy-

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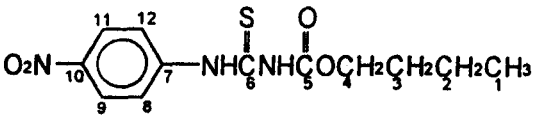
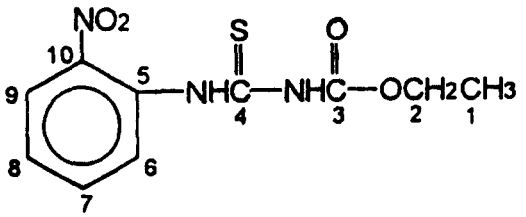
carbonyl)-thiourea (H_2nbt) and N-(*o*-nitrophenyl)-N′-(ethoxycarbonyl)-thiourea (H_2net).



N-(*p*-nitrophenyl)-N′-(butoxycarbonyl)-thiourea (H_2nbt). (**m.f.** $C_{12}H_{15}N_3O_4S$)



N-(*o*-nitrophenyl)-N′-(ethoxycarbonyl)-thiourea (H_2net). (**m.f.** $C_{10}H_{11}N_3O_4S$)

EXPERIMENTAL

Preparation of the ligands

The ligand H_2nbt. The ligand H_2nbt was prepared by a procedure similar to that reported in the literature [3,7]. To the 20 cm^3 of acetone containing ammonium thiocyanate (1.5 g, 20 mmol) was added a solution of *n*-butylchloroformate (2.7 g, 20 mmol) in 20 cm^3 of acetone over 20 min. After the resulting mixture was stirred at 40°C for a further 30 min, it was cooled to room temperature. Then, *p*-nitrophenylamine (2.8 g, 20 mmol) in acetone (20 cm^3) was added dropwise followed by stirring for two more hours. The pale yellowish precipitate was filtered, washed with cold water and extracted with CH_2Cl_2. The organic phase was evaporated to dryness and the crude product was recrystallized from ethanol-chloroform (2 : 1, v/v). Found: C, 48.7; H, 5.4; N, 14.0. Yield, 2.9 g (42%). Calc. for $C_{12}H_{15}O_4N_3S$: C, 48.5; H, 5.1; N, 14.1%.

The ligand H_2net. This ligand was synthesized based on the above method for the preparation of the ligand H_2nbt. Yield, 58%. Found: C, 44.4; H, 4.3; N, 15.6. Calc. for $C_{10}H_{11}N_3O_4S$: C, 44.6; H, 4.1; N, 15.6%.

Syntheses of the Cu^I complexes

Complex **1,** $[Cu(H_2nbt)Cl]_2$. To the 30 cm^3 of mixed solvent THF-toluene (1 : 1, v/v) containing 0.9 g (3.0 mmol) of H_2nbt was added 0.5 g (3.0 mmol) of copper(II) chloride dihydrate. After this reaction mixture was stirred at room temperature for 3 ~ 4 h, it was kept in a refrigerator (3°C). Several days later, beautiful orange crystals were deposited, which were filtered and dried in air. Yield, 0.35 g (25%). Found: C, 41.7; H, 4.3; N, 12.3. Calc. for $C_{24}H_{30}ClCuN_6O_8S_2$: C, 41.5; H, 4.3. N, 12.1%.

Complex **2,** $Cu(H_2net)_2Cl$. To 25 cm^3 of anhydrous ethanol solution containing H_2net (0.81 g, 3.0 mmol) was added $CuCl_2 \cdot 2H_2O$ (0.51 g, 3.0 mmol). After this resulting mixture was stirred at room temperature for 2 ~ 3 h, the yellow solid precipitate was filtered, washed repeatedly with anhydrous ethanol and dried *in vacuo*. Yield, 0.8 g (60%). Found: C, 37.6; H, 3.2; N, 13.4. Calc. for $C_{20}H_{22}ClCuN_6O_8S_2$: C, 37.6; H, 3.5; N, 13.2%.

The crystals of complex **2** were obtained by the slow evaporation of the chloroform solution of complex **2** at room temperature for three weeks.

Measurements

Elemental analyses (C, H and N) were performed on a Carlo Erba 1106 elemental analyzer. NMR (^1H and ^{13}C) spectra were recorded on a Bruker AM 500 spectrometer in $CDCl_3$ solution with TMS as standard interval.

X-ray structure determination of the complex

The crystals of the complexes were mounted on an Enraf-Nonius CAD4 diffractometer for data collection using graphite-monochromated Mo-K_α radiation at 23°C. The crystallographic data are summarized in Table 1. Both the structures were solved by direct methods and the hydrogen atoms were located and added to the structure factor calculations. In complex **1,** the positions of the hydrogen atoms were not refined, while in complex **2,** their positions were refined. Both structures were refined by the full-matrix least-squares method with anisotropic temperature factors for all the non-hydrogen atoms but O(8) atom in complex **2,** which disordered with the occupancy of N(8A) at 62% and N(8B) at 38%.

RESULTS AND DISCUSSION

NMR spectra

The ^1N NMR and ^{13}C NMR spectra of the compounds obtained in $CDCl_3$ solution are summarized in Tables 2 and 3, respectively.

As shown in Table 2, it is found that all the ligand proton signals but the ones in the aromatic ring of the free ligands are observed to shift to lower fields upon binding to the Cu^I ions. The proton signals of the aromatic ring are found to be shifted up-field. It is noticeable that the large down-field shifted effects for δ(NH)(NHC(O)) are mainly ascribed to the hydrogen bonds contributed by NH ··· Cl in the two complexes, which is consistent with the X-ray crystallographic result.

In view of the ^{13}C NMR spectra of the compounds as shown in Table 3, the chemical shifts of the carbon

Table 1. Summary of crystal data, intensity collection and structure refinement parameters for the complexes **1** and **2**

Compound	**1**	**2**
Formula	$C_{48}H_{60}Cl_2Cu_2N_{12}O_{16}S_4$	$C_{20}H_{22}ClCuN_6O_8S_2$
F.W	1387.33	637.55
Crystal size (mm)	0.25 × 0.20 × 0.18	0.50 × 0.20 × 0.15
Crystal shape/colour	Prism/orange	Prism/orange
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
(C)		
a(Å)	8.770(5)	7.939(3)
b(Å)	14.132(3)	11.107(3)
c(Å	14.453(4)	15.607(3)
α	118.51(2)	97.06(2)
β	91.09(3)	100.36(2)
γ	102.60(3)	77.47(2)
V(Å^3)	1520(1)	1316(1)
Z	1	2
Dc (g cm^{-3})	1.52	1.61
μ(Mo-K_α)(cm^{-1})	9.93	11.39
F(000)	716	652
2θ max.(°)	50.0	49.9
Scan width(°)	0.45 + 0.35tanθ	0.45 + 0.35tanθ
Scan speed(min^{-1})	< 5.49 (in ω)	< 6.8 (in ω)
No. of reflections measured	5338	4642
No. of reflections with $I > 3\sigma(I)$	2499	3536
No. of variables	379	440
R	0.069	0.056
R_w	0.073	0.066
GOF	1.53	1.93
Max. shift in final cycle	0.27	0.25
$\Delta\rho$ max, min (eÅ^{-3})	0.65, −0.70	0.83, −1.04

Table 2. ^{1}H NMR spectra data of the compounds (in ppm)

	Assignment[a]					
Compound	NH PhNHC(S)	NH NHC(O)	Aromatic ring	CH [OCH_2]	CH [$2CH_2$]	CH [CH_3]
H_2nbt	11.93 (s, 1H)	8.30 (s, 1H)	7.99 ~ 8.28 (q, 4H)	4.25 ~ 4.28 (t, 2H)	1.41 ~ 1.73 (m, 4H)	0.96 ~ 0.99 (t, 3H)
1	12.02 (s, 1H)	11.18 (s, 1H)	7.75 ~ 8.27 (q, 4H)	4.30 ~ 4.33 (t, 2H)	1.48 ~ 1.77 (m, 4H)	0.97 ~ 1.00 (t, 3H)
H_2net	12.54 (s, 1H)	8.25 (s, 1H)	7.27 ~ 8.47 (m, 4H)	4.32 ~ 4.37 (q, 2H)	-	1.34 ~ 1.38 (t, 3H)
2	12.66 (s, 1H)	10.96 (s, 1H)	7.45 ~ 8.11 (m, 4H)	4.37 ~ 4.42 (q, 2H)	-	1.40 ~ 1.43 (t, 3H)

[a] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

atoms of the free ligands are found to be down or up-field shifted compared with those of the complexes.

Description of the structures

The molecular structures and the packing in the unit cells of the complexes **1** and **2** are depicted in Figs. 1, 2, 3, and 4, respectively. Selected bond lengths and angles of the complexes are presented in Table 4.

As shown in Fig. 1, the Cu^I atom of the complex **1** is bonded to the S(1), S(2) and Cl atoms at a distance of 0.387(2) Å below the S(1)S(2)Cl plane. The fourth site of the tetrahedral coordination is occupied by the S(1)* atom from a centrosymmetrically related CuS_2Cl group at a long distance of 2.700(3) Å, giving a coordination dimer. The atoms in the Cu_2S_2 core are coplanar and the two *trans* positional chlorine atoms stabilize the complex with intramolecular hydrogen bonds. The S(1)* atom lies approximately on the line

Table 3. ^{13}C NMR spectral data of the compounds (in ppm)

	Assignment									
Cpd[a]	C_1[b]	C_2	C_3	C_4	C_5	C_6	C_7	C_8 (C_{12})[c]	C_9 (C_{11})[c]	C_{10}
H_2nbt	13.54	18.85	30.45	67.26	177.53	152.95	145.13	123.14	124.51	139.23
1	13.39	18.70	30.32	67.52	178.93	153.92	146.16	124.44	125.13	141.72
H_2net	14.18	63.37	179.02	152.10	142.45	125.13	133.41	126.67	128.26	132.72
2	14.16	63.71	179.92	153.10	143.38	125.24	133.37	127.70	129.34	131.52

[a] Cpd = compound,
[b] The positions of the carbon atoms are denoted in the structures of the free ligands,
[c] For H_2nbt and complex **1**, the carbon atoms of C_8 and C_{12}, and C_9 and C_{10} appear as one signal due to overlapping.

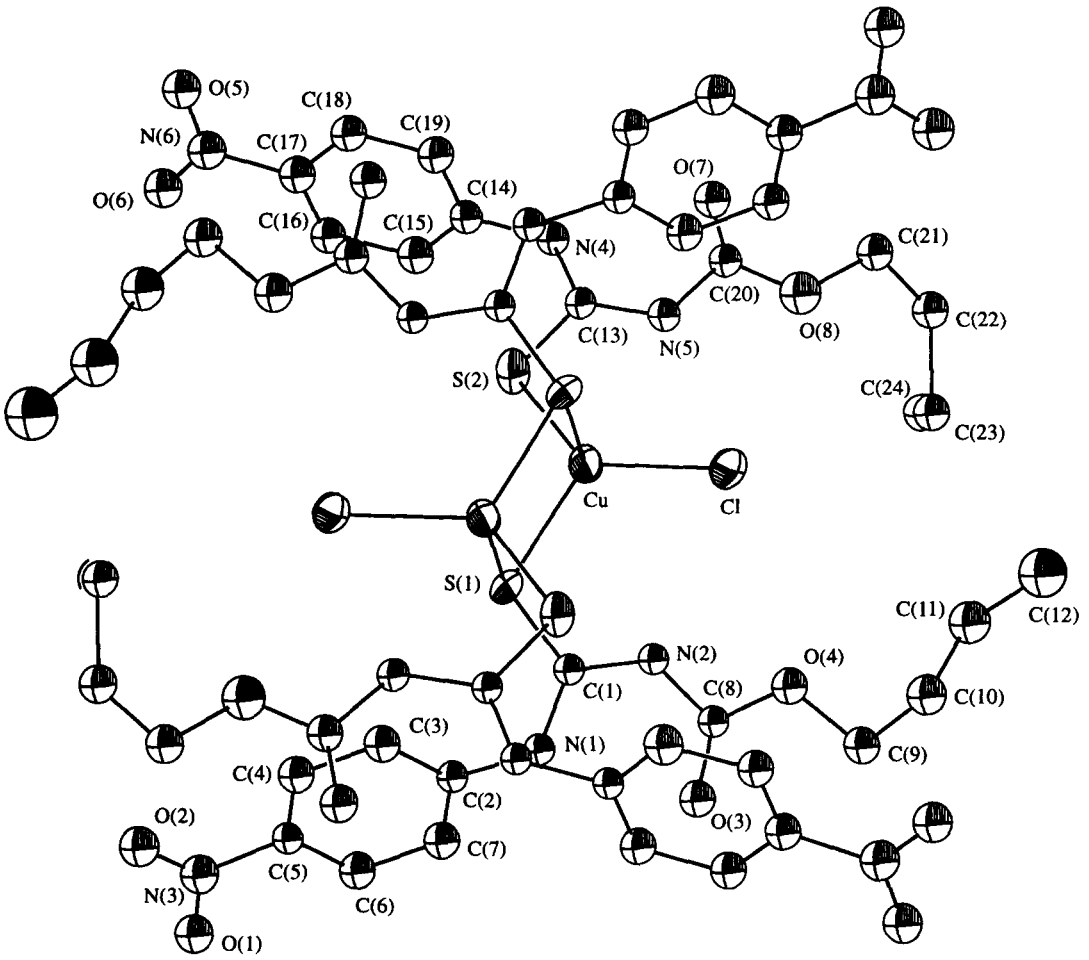


Fig. 1. The structure of complex **1** with the hydrogen atoms omitted for clarity.

perpendicular to the basal S(1)S(2)Cl plane as shown by the angles made by the S(1)*—Cu bond with the Cu—S(1), Cu—S(2) and Cu—Cl bonds. [S(1)*—Cu—S(1) = 101.0(1), S(1)*—Cu—Cl = 97.5(1), S(1)—Cu—S(2) = 101.6(1)°].

The Cu^I environment (Fig. 2) for complex **2** is trigonal planar [Cl—Cu—S(1) = 120.53(5), Cl—Cu—S(2) = 118.43(5) and S(1)—Cu—S(2) = 119.16(5)°] contributed by two S and one Cl atoms. As in complex 1, the chlorine atom forms intramolecular hydrogen bonds to stabilize the complex; other hydrogen bonds are listed in Table 4.

The Cu—S bond distances [2.253(3) and 2.244(3) Å] of complex **1** lie within the range of those found in the Cu^I complexes with tetrahedral or flattened tetrahedral geometry, $[Cu(2,4\text{-dithiobiuret})Cl]_n \cdot n$DMF [8] [flattened tetrahedral, 2.258(2), 2.245(2) Å], $[Cu(1,4\text{-oxathiane})_3(OClO_3)]$ [9] (tetrahedral, 2.23, 2.27, 2.29 Å) and [Cu(pma)](BPh_4) [10] (flattened tetrahedral, 2.230, 2.275 Å), and the Cu—S

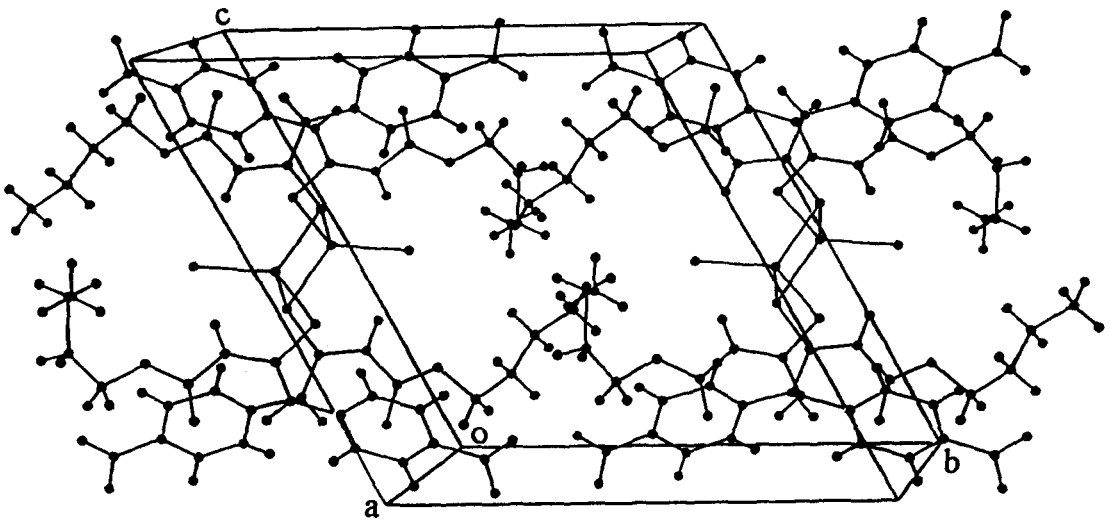


Fig. 2. The molecular packing in the unit cell for complex **1**.

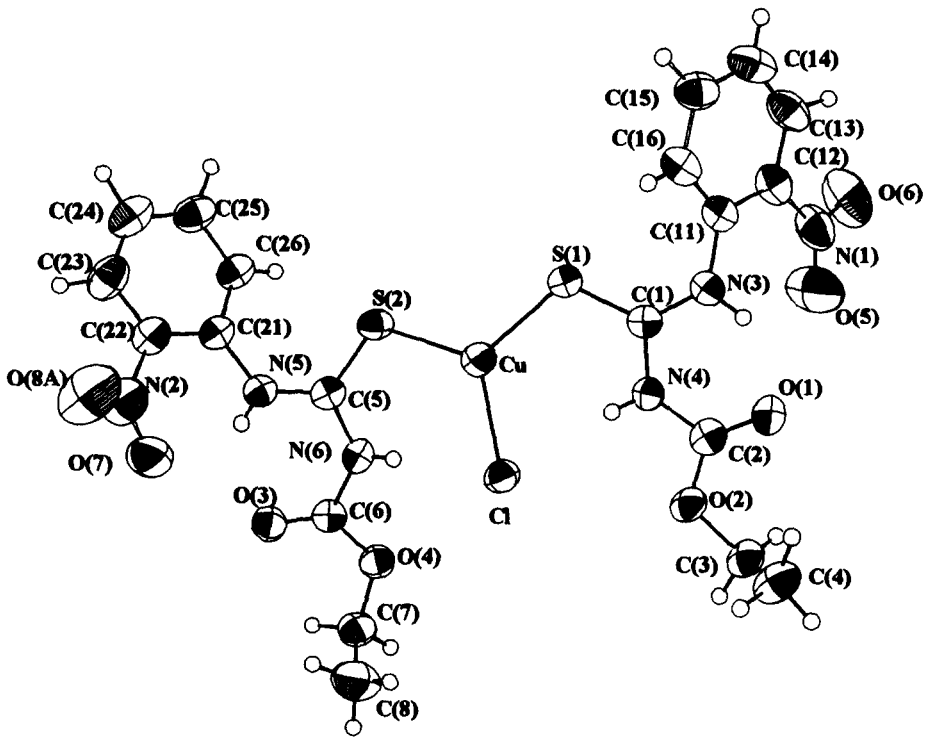


Fig. 3. The structure of complex **2**.

bond distances of 2.228(1) and 2.232(1) Å in complex **2** are shorter than those in [8–10] and complex **1**, but close to the Cu—S distances for $[Cu\{(Ph_2PS)_2CH_2\}Cl]$ [11] (2.23, 2.25 Å) with trigonal planar geometry. Therefore, as expected the Cu(I)—S bond distance is sensitive to the coordination environment of the copper(I) atom.

The Cu—Cl bond distances of 2.247(3) Å in complex **1** and 2.251(1) Å in complex **2** are shorter than those of the Cu^I complexes with heterocyclic thiones and phosphines as ligands, such as $[Cu(tptp)(pmtH)Cl]_2$ [12] [2.300(1) Å], $[Cu(tptp)(tzdtH)Cl]_2$ [13] [2.283(1) Å], $[Cu(tmtp)(bzimtH_2)Cl]_2$ [14] [2.391(2) Å] and that of [8] (2.302 Å), but larger than that of [11] (2.18 Å). Thus, this shortening of the Cu(I)—Cl may be due to the bulk of the ligands attached to the copper atom.

It is noteworthy that complex **1** is a dimer, whereas complex **2** is a monomer even though the two ligands are very similar to each other in the structure. This may be due to the fact that the crystals of complex **1** were deposited from non-polar solvents (toluene-

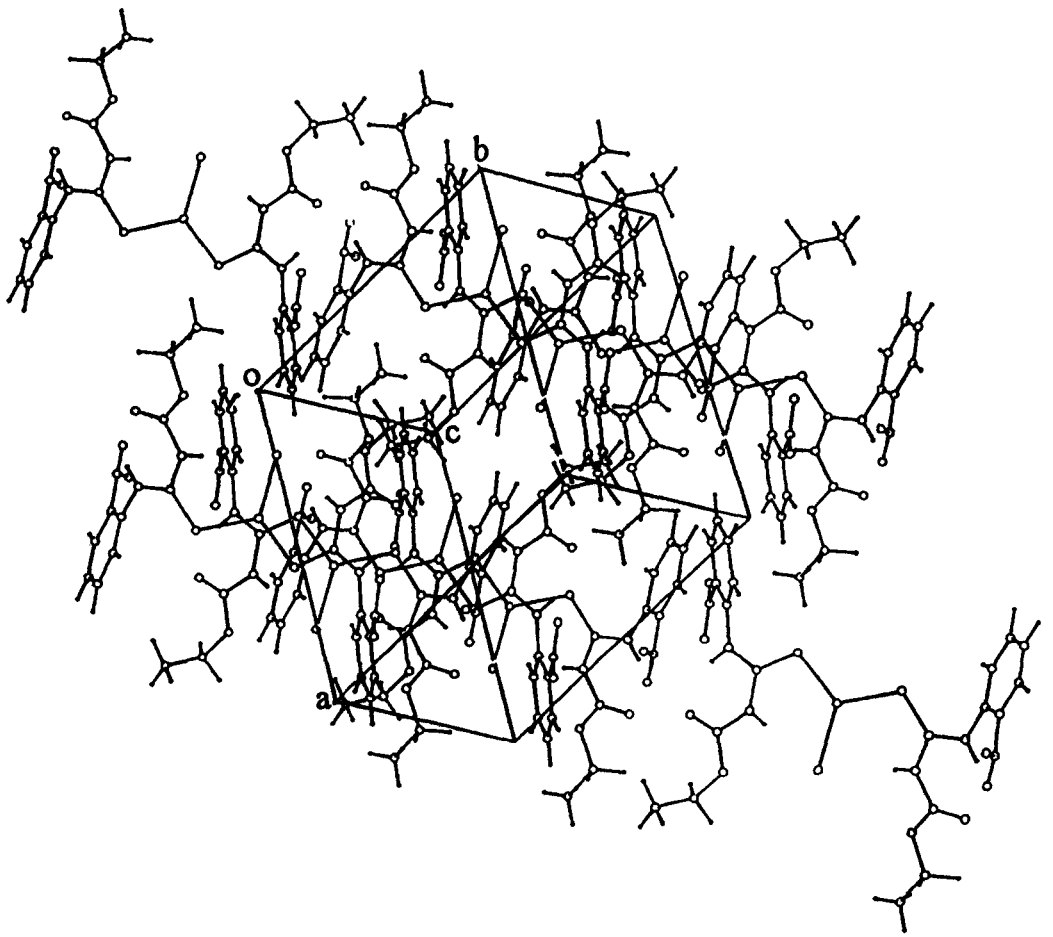


Fig. 4. The molecular packing in the unit cell for complex **2**.

Table 4. Selected bond distances (Å) and angles (°) for the complexes

1					
Cu—S(1)*	2.700(3)	Cu—S(1)	2.253(3)	Cu—S(2)	2.244(3)
Cu—Cl	2.247(3)				
Cl—Cu—S(1)	119.9(1)	S(1)—Cu—S(1)*	101.0(1)	C(1)—S(1)—Cu	111.5(3)
Cl—Cu—S(1)*	97.5(1)	S(2)—Cu—S(1)	108.4(1)	C(1)*—S(1)*—Cu	103.0(3)
Cl—Cu—S(2)	122.9(1)	S(2)—Cu—S(1)*	101.6(1)	C(13)—S(2)—Cu	110.1(3)
				Cu—S(1)—Cu*	79.0(1)
Intramolecular hydrogen bonds					
N(2)···Cl	3.250	N(5)···Cl	3.269	N(2)—H(2)···Cl	169.0
N(5)—H(4)···Cl	165.9				
2					
Cu—S(1)	2.228(1)	Cu—S(2)	2.232(1)	Cu—Cl	2.251(1)
S(1)—Cu—S(2)	119.16(5)	S(1)—Cu—Cl	120.53(5)	S(2)—Cu—Cl	118.43(5)
C(1)—S(1)—Cu	110.8(1)	C(5)—S(2)—Cu	110.9(1)		
Intramolecular hydrogen bonds					
N(3)···O(1)	2.656(5)	N(4)···Cl	3.181(4)	N(5)···O(3)	2.675(5)
N(6)···Cl	3.190(4)				
N(3)—H(1)···O(1)	142(4)	N(4)—H(2)···Cl	170(5)	N(5)—H(3)···O(3)	137(5)
N(6)—H(4)···Cl	163(4)				

Symmetry operator: *: $1-x, -y, 1-z$

THF) while the crystals of complex **2** were obtained from the polar one ($CHCl_3$).

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