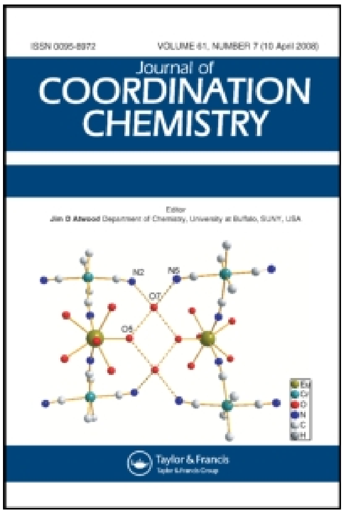

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Xu Shen[a]; Bei-Sheng Kang[b]; Yu Liu[b]; Lian-Quan Gu[b]; Xiao-Ying Huang[a]; Jie Sun[c]; Qiu-Tian Liu[a]
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COPPER(I) COMPLEXES WITH *N*-(*p*-NITROPHENYL)-*N*′-ALKOXYCARBONYLTHIOUREA: SYNTHESES AND CRYSTAL STRUCTURES OF $[Cu(H_2net)_2Cl]\cdot CH_2Cl_2$ AND $[Cu(H_2nmt)_2Cl]_2\cdot(CHCl_3)_2$

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Two copper(I) complexes, $[Cu(H_2net)_2Cl]\cdot CH_2Cl_2$ (**1**) and $[Cu(H_2nmt)_2Cl]_2\cdot(CHCl_3)_2$ (**2**), were synthesized by the reaction of $CuCl_2\cdot 2H_2O$ with *N*-(*p*-nitrophenyl)-*N*′-(ethoxycarbonyl)-thiourea (H_2net) and *N*-(*p*-nitrophenyl)-*N*′-(methoxycarbonyl)-thiourea(H_2nmt), respectively. Both complexes crystallize in the monoclinic space group *C*2/*c*. For complex **1**, $a = 29.52(2)$, $b = 13.920(6)$, $c = 14.873(3)$ Å; $\beta = 101.75(2)°$, $V = 5984(4)$ Å^3, $Z = 8$ and $R = 0.053$; for complex **2**, $a = 30.68(1)$, $b = 13.369(4)$, $c = 14.226(7)$ Å, $\beta = 99.52(4)°$, $V = 5754(4)$ Å^3, $Z = 4$ and $R = 0.063$. In complex **1**, two H_2net molecules are bonded to Cu(I) atom through two S atoms forming a mononuclear complex with trigonal geometry for the Cu(I) ion [Cl(1)–Cu–S(1) = 118.54(7), Cl(1)–Cu–S(2) = 119.70(7), S(1)–Cu–S(2) = 112.17(8)°, Cu–S(1) = 2.251(2), Cu–S(2) = 2.255(2), Cu–Cl(1) = 2.263(2) Å]. Complex **2** is a dimer formed by long Cu–S interactions [Cu–S* = 2.607(3) Å] from adjacent two H_2nmt molecules; the Cu(I) ion has distorted tetrahedral coordination [Cl(1)–Cu–S(1) = 119.8(1), Cl(1)–Cu–S(2) = 120.0(1), S(1)–Cu–S(2) = 108.85(9)°] with unequal Cu–S [2.268(2), 2.247(2) Å] and Cu–Cl(1) [2.255(2) Å] bonds.

Keywords: Cu(I); syntheses; crystal structure; *N*-(*p*-nitrophenyl)-*N*′-alkoxycarbonylthiourea; NMR

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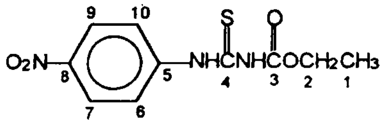
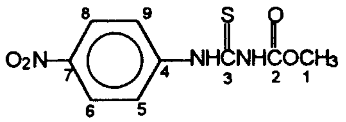
[*] Corresponding authors.

INTRODUCTION

The biological activities of complexes with thiourea derivatives have been well documented and thiourea derivatives, in this respect, have been successfully screened for various biological action.[1] Some *N*-substituted-*N*′-alkoxycarbonyl thiourea derivatives have been used in commercial fungicides. Recently, transition metal complexes with *N*-substituted thioallophanate derivatives have been reported,[2] and the existence of unusual copper(II)/copper(I) redox systems has been proved in solution.[3] In previous work,[4] we reported two Cu(I) compounds derived from *N*-(*o*-nitrophenyl)-*N*′-(ethoxycarbonyl)thiourea (H_2onet) and *N*-(*p*-nitrophenyl)-*N*′-(butoxycarbonyl)thiourea (H_2nbt) by the *in situ* reaction of $CuCl_2 \cdot 2H_2O$ with the corresponding ligand, and found that the complex with H_2onet is mononuclear, [Cu(H_2onet)$_2$Cl], whereas the complex with H_2nbt is a coordination dimer, [{Cu(H_2nbt)$_2$Cl}$_2$]. Because of our interest in studies of the coordination of copper(I) complexes of *N*-nitrophenyl-*N*′-alkoxycarbonylthiourea derivatives reference to plants,[5] we have prepared two new ligands, *N*-(*p*-nitrophenyl)-*N*′-ethoxycarbonylthiourea (H_2net) and *N*-(*p*-nitrophenyl)-*N*′-methoxycarbonylthiourea (H_2nmt), as well as two copper(I) complexes.



N-(*p*-nitrophenyl)-*N*′-ethoxycarbonylthiourea (H_2net)



N-(*p*-nitrophenyl)-*N*′-methoxycarbonylthiourea (H_2nmt)

EXPERIMENTAL

Preparation of the Ligands

H_2net

H_2net was prepared by a procedure similar to that reported in the literature.[2,3] To 35 cm^3 of acetone containing ammonium thiocyanate (3.0 g, 40 mmol) was added a solution of ethylchloroformate (4.3 g, 40 mmol) in 35 cm^3 of acetone over 30 min. After the resulting mixture was stirred at 40°C for a further 30 min, it was cooled to room temperature. To this, *p*-nitrophenylamine (5.5 g, 40 mmol) in acetone (30 cm^3) was added dropwise followed by stirring for two hours. The yellowish clear solution was evaporated *in vacuo* to dryness to give a crude yellowish product, which was recrystallized from ethanol-THF and dried *in vacuo*. Yield, 3.4 g (37%). *Anal.* Calcd. for $C_{10}H_{11}O_4N_3S$ (%): C, 44.6; H, 4.1; N, 15.6. Found: C, 44.4; H, 4.3; N, 15.7.

H_2nmt

This ligand was prepared based on the aforementioned method by the reaction of methylchloroformate, ammonium thiocyanate and *p*-nitrophenylamine. Yield, 55%. *Anal.* Calcd. for $C_9H_9O_4N_3S$ (%): C, 42.4; H, 3.5; N, 16.5. Found: C, 42.3; H, 3.7; N, 16.6.

Cu(I) Complexes

Complex 1, [Cu(H_2net)$_2$Cl]·CH_2Cl_2

To 30 cm^3 of mixed solvent CH_3OH-THF (3 : 1, v/v) containing 0.8 g (3.0 mmol) of H_2net was added 0.5 g (3.0 mmol) of copper(II) chloride dihydrate. After the reaction mixture was stirred at room temperature for 2–3 h the precipitate formed was isolated by filtration, washed with methanol and THF and dried *in vacuo*. Yield, 0.5 g (35%). Crystals of **1** were obtained by dissolving 0.3 g of the product in CH_2Cl_2 (15 cm^3) to give a yellowish clear solution, which was evaporated slowly at 17–20°C for about three weeks to deposit beautiful yellow crystals. Yield, 10%. *Anal.* Calcd. for $C_{21}H_{24}O_8N_6Cl_3S_2Cu$ (%): C, 34.9; H, 3.3; N, 11.6. Found: C, 34.7; H, 3.1; N, 11.6.

Complex 2, [Cu(H_2nmt)$_2$Cl]$_2$·($CHCl_3$)$_2$

To 30 cm^3 of methanol containing H_2nmt (0.8 g, 3.0 mmol) was added $CuCl_2 \cdot 2H_2O$ (0.5 g, 3.0 mmol) and the mixture stirred at room temperature for 3 h. The precipitate formed was filtered off, washed with methanol and dried *in vacuo*. Yield, 0.5 g (10%). Crystals of complex **2** were obtained by dissolving the above product (0.4 g) in chloroform (85 cm^3) at room temperature (23°C) to give an orange clear solution, which was evaporated slowly at 17–20°C for about four weeks to give orange crystals.

Anal. Calcd. for $C_{19}H_{19}O_8N_6Cl_4S_2Cu$ (%): C, 31.3; H, 2.6; N, 11.5. Found: C, 31.1; H, 2.4; N, 11.3.

Measurements

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

X-ray Structure Determination

Crystallographic data are summarized in Table I. Both structures were solved by direct methods (SHELXL-93), and refined by full-matrix least-squares methods with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were located and added to the structure factor calculations, but were not refined. Final atomic parameters are listed in Tables II and III, respectively.

TABLE I Summary of crystal data, intensity collection and structure refinement parameters for complexes **1** and **2**

Compound	**1**	**2**
Formula	$C_{21}H_{24}O_8N_6Cl_3S_2Cu$	$C_{38}H_{38}O_{16}N_{12}Cl_8S_4Cu_2$
Formula weight	722.48	1457.74
Crystal size/mm	0.20 × 0.20 × 0.30	0.50 × 0.10 × 0.09
Crystal shape/colour	prism/yellow	prism/orange
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*/2/*c*
Cell constants		
a/Å	29.52(2)	30.68(1)
b/Å	13.920(6)	13.369(4)
c/Å	14.873(3)	14.226(7)
β/°	101.75(2)	99.52(4)
V/Å^3	5984(4)	5754(4)
Z	8	4
Dc/g cm^{-3}	1.604	1.683
Diffractometer	Rigaku AFC7R	Enraf-nonius CAD4
μ(MoKα)cm^{-1}	11.91	13.26
F(000)	2944.00	2944.00
$2\theta_{max.}$/°	45.0	50.0
Scan width/°	$1.57+0.30\tan\theta$	$0.65 + 0.35\tan\theta$
Scan speed/min.$^{-1}$	16.0 (in ω) – up to 4 scans	<4.09 (in ω)
No. of reflections with $I > 3\sigma(I)$	2667 ($R_{int}=0.009$)	2723 ($R_{int}=0.051$)
No. of variables	371	361
R	0.053	0.063
R_w	0.066	0.069
GOF	2.40	1.58

TABLE II Final atomic coordinates and equivalent isotropic thermal parameters for complex **1**

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Cu	0.54310(3)	0.02826(6)	0.57351(7)	5.06(2)
Cl(1)	0.54810(6)	0.1867(1)	0.6080(1)	5.14(5)
Cl(2)	0.4992(2)	0.3782(5)	0.1144(5)	22.7(3)
Cl(3)	0.5853(2)	0.3488(5)	0.0666(4)	19.7(2)
S(1)	0.48554(6)	−0.0578(1)	0.6128(1)	3.87(4)
S(2)	0.60827(6)	−0.0590(1)	0.5828(1)	4.01(4)
O(1)	0.4392(2)	0.2645(3)	0.6649(4)	5.8(1)
O(2)	0.3803(2)	0.1621(3)	0.6681(4)	5.4(1)
O(3)	0.2973(2)	−0.3941(4)	0.7222(5)	7.9(2)
O(4)	0.3503(4)	−0.4546(6)	0.683(1)	24.7(6)
O(5)	0.6593(2)	0.2665(3)	0.5705(4)	6.5(2)
O(6)	0.7196(2)	0.1671(3)	0.5676(4)	5.9(1)
O(7)	0.7568(2)	−0.4524(4)	0.5985(5)	7.7(2)
O(8)	0.7986(2)	−0.4007(4)	0.7267(4)	6.1(2)
N(1)	0.4518(2)	0.1106(4)	0.6489(4)	3.8(1)
N(2)	0.4061(2)	−0.0187(4)	0.6669(4)	4.1(1)
N(3)	0.3318(3)	−0.3851(5)	0.7020(6)	7.8(2)
N(4)	0.6462(2)	0.1103(3)	0.5720(4)	4.2(1)
N(5)	0.6967(2)	−0.0160(4)	0.5852(4)	4.2(1)
N(6)	0.7707(2)	−0.3893(4)	0.6556(6)	5.2(2)
C(1)	0.4198(3)	0.1780(5)	0.6617(5)	4.4(2)
C(2)	0.4453(2)	0.0129(4)	0.6454(4)	3.4(2)
C(3)	0.3899(2)	−0.1138(5)	0.6722(5)	4.3(2)
C(4)	0.3452(2)	−0.1252(5)	0.6748(6)	5.1(2)
C(5)	0.3262(2)	−0.2142(5)	0.6854(5)	5.0(2)
C(6)	0.3524(3)	−0.2903(5)	0.6918(6)	5.5(2)
C(7)	0.3981(4)	−0.2815(7)	0.695(1)	16.3(5)
C(8)	0.4169(3)	−0.1923(8)	0.685(1)	15.1(5)
C(9)	0.4109(3)	0.3448(7)	0.6877(9)	9.2(3)
C(10)	0.4409(7)	0.415(1)	0.732(2)	18.0(9)
C(11)	0.6793(3)	0.1815(5)	0.5695(5)	5.1(2)
C(12)	0.6534(2)	0.0143(4)	0.5796(4)	3.6(2)
C(13)	0.7139(2)	−0.1119(5)	0.6011(5)	3.9(2)
C(14)	0.6915(2)	−0.1895(5)	0.5528(5)	4.7(2)
C(15)	0.7107(2)	−0.2811(5)	0.5698(5)	4.8(2)
C(16)	0.7510(2)	−0.2905(5)	0.6345(5)	4.2(2)
C(17)	0.7746(2)	−0.2143(5)	0.6811(5)	4.6(2)
C(18)	0.7552(2)	−0.1236(5)	0.6626(5)	4.7(2)
C(19)	0.6881(3)	0.3501(6)	0.5618(7)	7.3(3)
C(20)	0.6561(4)	0.4335(7)	0.555(1)	13.4(5)
C(21)	0.5334(6)	0.314(1)	0.054(1)	22.0(9)

RESULTS AND DISCUSSION

Description of the Structures

Molecular structures and packing in the unit cell of complexes **1** and **2** are depicted in Figures 1 to 4. Selected bond lengths and angles in the complexes are presented in Table IV.

TABLE III Final atomic coordinates and equivalent isotropic thermal parameters for complex **2**

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Cu	0.04233(03)	0.06291(08)	0.06333(08)	4.11(5)
Cl(1)	0.04226(07)	0.23028(16)	0.08309(16)	4.5(1)
Cl(2)	0.01319(12)	0.6238(03)	0.1460(03)	10.8(2)
Cl(3)	0.08154(13)	0.7196(03)	0.0698(02)	11.2(2)
Cl(4)	0.06628(14)	0.5115(03)	0.0421(03)	11.8(3)
S(1)	−0.01015(06)	−0.03183(14)	0.11565(14)	3.06(9)
S(2)	0.10651(06)	−0.02152(15)	0.08652(16)	3.5(1)
O(1)	−0.0562(02)	0.3012(04)	0.1753(04)	4.4(3)
O(2)	−0.1114(02)	0.1945(04)	0.1864(04)	5.0(3)
O(3)	−0.1481(02)	−0.4438(05)	0.1792(08)	9.7(5)
O(4)	−0.2043(02)	−0.3693(05)	0.2067(06)	7.8(4)
O(5)	0.1552(02)	0.3175(05)	0.0784(05)	6.1(4)
O(6)	0.2132(02)	0.2140(05)	0.0793(05)	5.8(3)
O(7)	0.2965(03)	−0.3713(05)	0.2050(06)	6.9(4)
O(8)	0.2457(02)	−0.4312(05)	0.0961(06)	7.2(4)
N(1)	−0.0448(02)	0.1401(05)	0.1543(05)	3.5(3)
N(2)	−0.0888(02)	0.0046(05)	0.1677(05)	3.4(3)
N(3)	−0.1679(03)	−0.3683(06)	0.1885(06)	5.2(4)
N(4)	0.1428(02)	0.1554(05)	0.0797(05)	4.0(3)
N(5)	0.1908(02)	0.0224(05)	0.0876(05)	4.2(3)
N(6)	0.2637(03)	−0.3627(06)	0.1432(07)	5.3(4)
C(1)	−0.0507(03)	0.0398(05)	0.1471(05)	2.8(3)
C(2)	−0.0746(03)	0.2123(06)	0.1742(06)	3.5(4)
C(3)	−0.0835(04)	0.3826(07)	0.2020(08)	6.5(6)
C(4)	−0.1071(03)	−0.0917(06)	0.1660(05)	2.8(3)
C(5)	−0.0826(03)	−0.1775(06)	0.1656(08)	5.1(5)
C(6)	−0.1037(03)	−0.2679(06)	0.1700(08)	5.5(5)
C(7)	−0.1471(03)	−0.2721(06)	0.1765(06)	3.7(4)
C(8)	−0.1715(03)	−0.1866(07)	0.1766(07)	4.3(4)
C(9)	−0.1510(02)	−0.0969(06)	0.1710(07)	4.1(4)
C(10)	0.1494(03)	0.0555(06)	0.0840(05)	3.3(4)
C(11)	0.1745(03)	0.2292(07)	0.0793(07)	4.3(4)
C(12)	0.1832(04)	0.4048(08)	0.0794(10)	8.2(7)
C(13)	0.2071(03)	−0.0759(06)	0.0996(06)	3.8(4)
C(14)	0.2481(03)	−0.0892(06)	0.1556(07)	4.2(4)
C(15)	0.2671(03)	−0.1824(07)	0.1688(07)	4.4(4)
C(16)	0.2437(03)	−0.2622(06)	0.1273(06)	4.0(4)
C(17)	0.2045(03)	−0.2502(07)	0.0676(07)	4.7(5)
C(18)	0.1860(03)	−0.1588(07)	0.0527(07)	4.6(4)
C(19)	0.0424(04)	0.6270(07)	0.0493(07)	6.2(5)

As shown in Figure 1, Cu(I) in **1** has trigonal geometry [Cl(1)–Cu–S(1) = 118.54(1), Cl(1)–Cu–S(2) = 119.70(7), S(1)–Cu–S(2) = 112.17(8)°] made up of two S atoms from two ligands (H_2net) and one Cl. Cu(I) atom is 0.4075(3) Å above the S(1)S(2)Cl(1) plane. The chlorine atoms forms intramolecular hydrogen bonds to stabilize the complex (Table IV).

As seen in Figure 3, Cu(I) of complex **2** is bonded to S(1), S(2) and Cl(1) atoms at a distance of 0.442(1) Å above the S(1)S(2)Cl(1) plane. The fourth

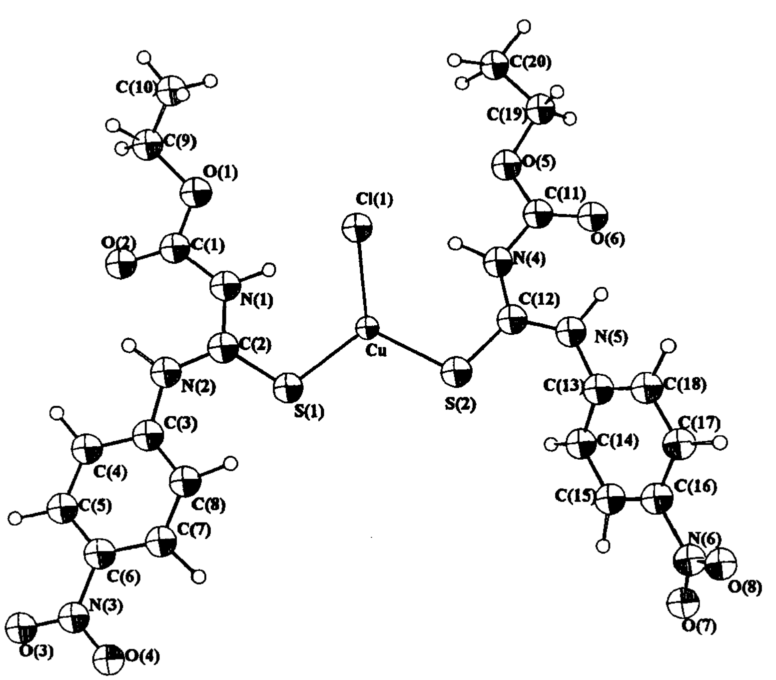


FIGURE 1 ORTEP drawing of complex **1** with ellipsoids at the 45% probability level.

site of tetrahedral coordination is occupied by the S(1)* atom from a centrosymmetrically related CuS_2Cl group at a distance of 2.607(3) Å, giving a coordination dimer. The atoms in the Cu_2S_2 core are coplanar and the two *trans* chlorine atoms stabilize the complex with intramolecular and other hydrogen bonds as listed in Table III. S(1)* atom lies approximately perpendicular to the basal S(1)S(2)Cl plane as shown by the angles made by the S(1)*–Cu bond with Cu–S(1), Cu–S(2) and Cu–Cl(1) [S(1)*–Cu–S(1) = 93.31(8), S(1)*–Cu–Cl(1) = 105.7(1), S(1)*–Cu–S(2) = 104.19(9)°].

The Cu–S bond lengths 2.251(2) and 2.255(2) Å in complex **1**, and 2.268(2) and 2.247(2) Å in complex **2** are consistent with values found for complexes with tetrahedral or trigonal-pyramidal coordination geometry, such as $[Cu(2,4\text{-dithiobiuret})Cl]_n \cdot nDMF$[6] [trigonal pyramidal, 2.258(2), 2.245(2) Å], $[Cu(1,4\text{-oxathiane})_3 \cdot (OClO_3)]$[7] (tetrahedral, 2.23, 2.27, 2.29 Å] and $[Cu(pma)](BPh_4)$[8] (trigonal pyramidal, 2.230, 2.275 Å), but are shorter than the bond lengths found for tetrahedrally coordinated copper(I) with triphenylphosphine-containing, thione-S donors,[9–12] (Cu–S = 2.302–2.382 Å). This is due to the fact that triphenylphosphine imposes greater steric bulk around the copper atom.

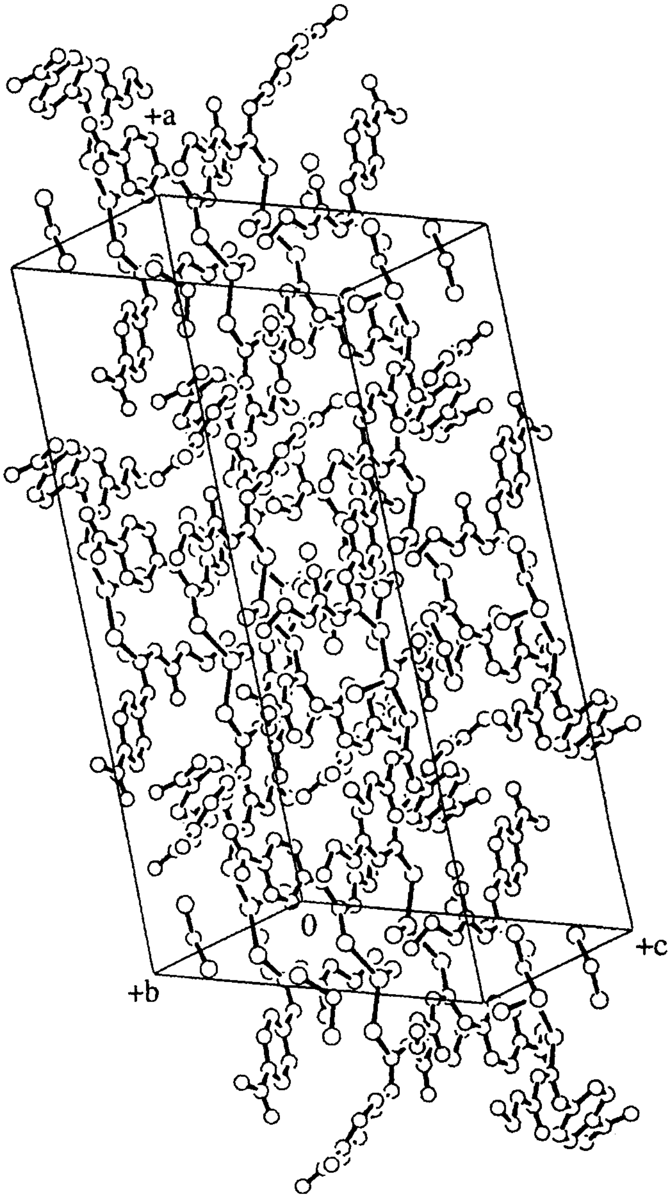


FIGURE 2 Molecular packing in the unit cell for complex 1.

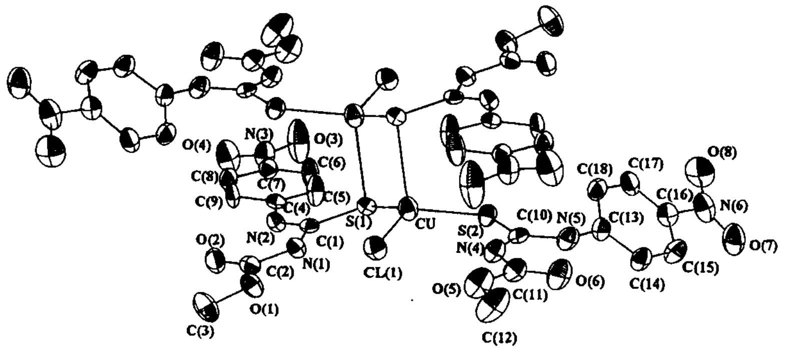


FIGURE 3 ORTEP drawing of complex **2** with ellipsoids at the 45% probability level (hydrogen atoms are omitted for clarity).

Cu–Cl bond distances (2.263(2) in **1** and 2.255(2) Å in **2**) are shorter than those of Cu(I) complexes with heterocyclic thiones and phosphines, such as $[\mathrm{Cu(tptp)(pmtH)Cl}]_2$[13] (2.300(1) Å), $[\mathrm{Cu(tptp)(tzdtHH)Cl}]_2$[14] (2.283(1) Å), $[\mathrm{Cu(tmtp)(bzimtH_2)Cl}]_2$[15] (2.391(2) Å) and $[\mathrm{Cu(PPh_3)_2(bztzdtH)Cl}]$-$\mathrm{CH_3COCH_3}$[6,12] (2.302 Å), but longer than in $[\mathrm{Cu\{(Ph_2PS)_2CH_2\}Cl}]$[16] (trigonal planar geometry, 2.18 Å). This shortening may be due to the bulk of the ligands attached to the copper atom.

It is noteworthy that the Cu–S and Cu–Cl bond lengths of **1** and **2** are longer than those of the copper(I) complexes of our previous study[3] $[\mathrm{Cu(H_2onet)_2Cl}$, Cu–S = 2.228(1), 2.232(1), Cu–Cl = 2.251(1) Å], and $[\{\mathrm{Cu(H_2onet)_2Cl}\}_2$, Cu–S = 2.253(3), 2.244(3), Cu–Cl = 2.247(3) Å]; this may be the result of steric effects imposed by the solvent contained in the two complexes in this work.

NMR Spectra

^{1}H and ^{13}C NMR data for the compounds obtained in $\mathrm{CDCl_3}$ are summarized in Tables V and VI, respectively. It is found that all proton signals but those in the aromatic ring of the free ligands are observed to shift to lower fields upon binding to copper(I). Signals from the aromatic ring are found to be shifted upfield. Large downfield shifts for δ(NH)(NHC(O)) are ascribed to hydrogen bonds. As far as the ^{13}C NMR spectra of the compounds are concerned, the chemical shifts of the carbon atoms of the Cu(I) complexes are observed to be shifted upfield in comparison to those of the free ligands.

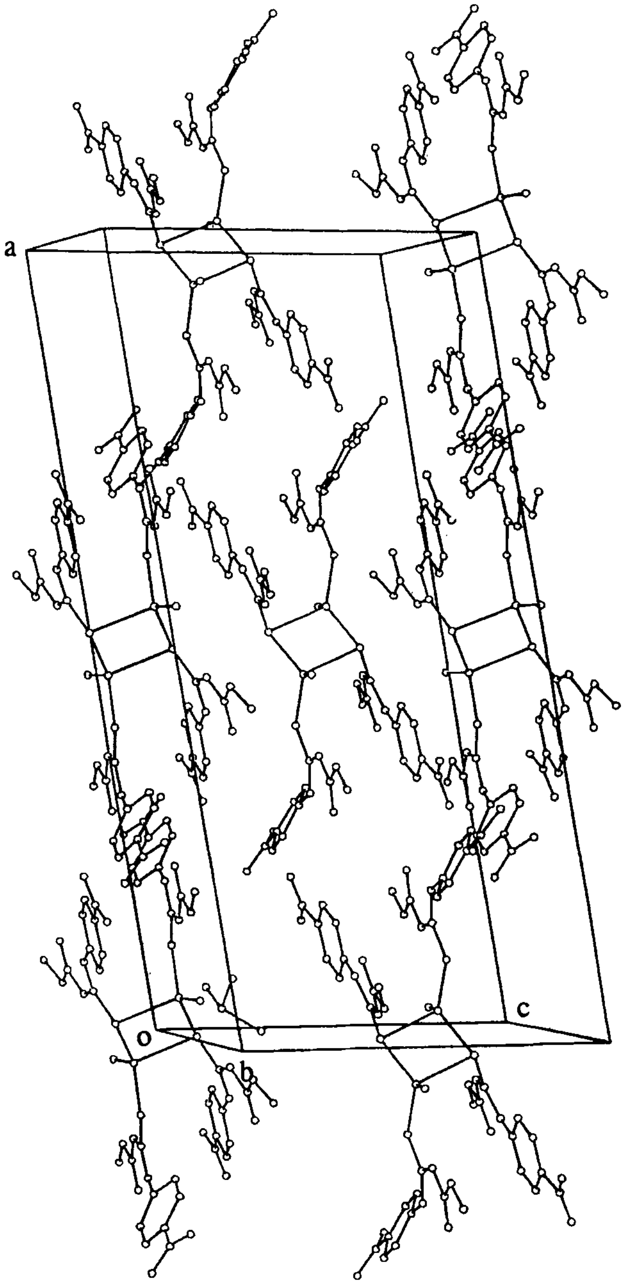


FIGURE 4 Molecular packing in the unit cell for complex **2**.

TABLE IV Selected bond distances (Å) and angles (°) for the complexes

1					
Cu–S(1)	2.251(2)	Cu–S(2)	2.255(2)	Cu–Cl(1)	2.263(2)
S(1)–Cu–S(2)	112.17(8)	S(1)–Cu–Cl(1)	118.54(7)	S(2)–Cu–Cl(1)	119.70(7)
Cu–S(1)–C(2)	112.2(2)	Cu–S(2)–C(12)	110.0(2)		
Intramolecular hydrogen bonds					
N(1)···Cl(1)	3.230(3)	N(4)···Cl(1)	3.250(5)	N(5)···O(6)	2.681(4)
N(1)–H(1)···Cl(1)	168.0	N(4)–H(12)···Cl(1)	164.7	N(5)–H(13)···O(6)	153.4
N(2)···O(2)	2.554(5)	N(2)–H(2)···O(2)	147.6		
2					
Cu–S(1)*	2.607(3)	Cu–S(1)	2.268(2)		
Cu–Cl(1)	2.255(2)				
S(2)–Cu–Cl(1)	120.0(1)	S(2)–Cu–S(1)	108.85(9)	Cu–S(2)	2.247(2)
Cl(1)–Cu–S(1)	119.8(1)	Cl(1)–Cu–S(1)*	105.7(1)	S(2)–Cu–S(1)*	104.19(9)
C(1)–S(1)–Cu	111.4(3)	C(1)*–S(1)*–Cu	99.9(3)	S(1)–Cu–S(1)*	93.31(8)
C(10)–S(2)–Cu	111.1(3)	Cu–S(1)–Cu*	86.69(8)		
Intramolecular hydrogen bonds					
Cl(1)–N(1)	3.242(7)	Cl(1)–N(4)	3.251(7)		
Cl(1)···H(3)–N(4)	164.1	Cl(1)···H(1)–N(1)	154.1	O(2)–N(2)	2.657(9)
O(6)–N(5)	2.66(1)	O(6)···H(4)–N(5)	142.1	O(2)···H(2)–N(2)	151.2

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

TABLE V ^{1}H NMR spectra data of the compounds (in ppm)

	*Assignment**				
Compound	NH PhNHC(S)	NH NHC(O)	Aromatic ring	CH [OCH_2]	CH [OCH_3]
H_2net	11.93 (s, 1H)	8.26 (s, 1H)	7.98–8.28 (q, 4H)	4.30–4.35 (q, 2H)	1.36–1.39 (t, 3H)
1	12.08 (s, 1H)	11.00 (s, 1H)	7.74–8.29 (q, 4H)	4.36–4.41 (q, 2H)	1.41–1.44 (t, 3H)
H_2nmt	11.84 (s, 1H)	8.43 (s, 1H)	8.00–8.28 (q, 4H)	—	3.77 (s, 3H)
2	12.13 (s, 1H)	11.80 (s, 1H)	7.85–8.22 (q, 4H)	—	3.84 (s, 3H)

* s = singlet, t = triplet, q = quartet.

TABLE VI ^{13}C NMR spectral data of the compounds (in ppm)

	Assignment									
Cpd^a	$C_1{}^b$	C_2	C_3	C_4	$C_5{}^c$	$C_6{}^c$	$C_7{}^c$	$C_8{}^c$	$C_9{}^c$	$C_{10}{}^c$
H_2net	14.11	63.53	152.80	177.43	145.03	123.15	124.54	143.21	124.54	123.15
1	14.19	63.80	154.30	179.10	145.41	123.55	124.85	143.70	124.85	123.55
H_2nmt	53.57	154.18	179.10	144.68	124.48	124.63	144.58	124.63	124.48	
2	53.74	154.65	181.11	147.23	125.11	125.04	146.16	125.04	125.11	

[a] Cpd = compound; [b] The positions of the carbon atoms are denoted in the structures of the free ligands; [c] For H_2net and complex **1**, the carbon atoms of C_6 and C_{10}, and C_7 and C_9 appear as one signal due to overlapping, so are the carbon atoms of C_5 and C_9, and C_6 and C_8 for the ligand H_2nmt and complex **2**.

Supplementary Data

Full lists of H coordinates, thermal parameters, bond lengths, angles and observed and calculated structure factors are available from the authors upon request.

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