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Preparation and characterization of the complexes $Cu(PTU)_2Cl$, $Cu(ETU)_2Cl$ and $Cu(BTU)_2Cl$ (PTU: R = phenyl, ETU: R = ethyl, BTU: R = benzyl in $CH_3CH{=}CH{-}CO{-}NH{-}CS{-}NH{-}R$); crystal structure of the $Cu(PTU)_2Cl$ complex

Juraj Černák, Jozef Chomič

Department of Inorganic Chemistry, P. J. Šafárik University, Moyzesova 11, CS-041 54 Košice (Czechoslovakia)

Peter Kutschy, Dana Svrčinová and Milan Dzurilla

Department of Organic Chemistry, P. J. Šafárik University, Moyzesova 11, CS-041 54 Košice (Czechoslovakia)

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Abstract

The complexes $Cu(PTU)_2Cl$, $Cu(ETU)_2Cl$ and $Cu(BTU)_2Cl$ (PTU: R = phenyl, ETU: R = ethyl, BTU: R = benzyl in $CH_3CHCHCONHCSNHR$) were prepared by the reaction of $CuCl_2$ with the corresponding derivates of 2-propenoyl thiourea. The complexes were investigated by the methods of CHN analysis, infrared spectroscopy, ^1H and ^{13}C NMR spectroscopy. The crystal structure of $Cu(PTU)_2Cl$ was determined by X-ray analysis: triclinic space group $P\bar{1}$, $a = 15.538(1)$, $b = 14.296(2)$, $c = 12.016(2)$ Å, $\alpha = 102.72(1)$, $\beta = 105.95(1)$, $\gamma = 94.31(1)°$, $D_m = 1.44(1)$, $D_c = 1.44$ g cm^{-3}, $Z = 4$, $R = 0.066$. The unit cell of $Cu(PTU)_2Cl$ contains two centrosymmetrical dimer molecules of the complex (denoted as A and B) with a different coordination sphere of the Cu(I) atoms. In molecule A two atoms of Cu(I) with coordination number 4 are bridged through chloride bridges (Cu–Cl 2.318(2) and Cu–Cl′ 2.762(2) Å) and two molecules of PTU are terminally coordinated through the S atoms. In molecule B the bridges are formed by the atoms of S of one PTU molecule (Cu–S 2.235(2) and Cu–S′ 2.904(2) Å). The other PTU molecule as well as the Cl^- anion are terminally bonded. The results of infrared and NMR spectroscopy indicate that the complexes containing ETU or BTU exhibit analogous structure.

Introduction

The *N*′-2-propenoylthioureas containing different N-substituents $CH_3CH{=}CH{-}CO{-}NH{-}CS{-}NR_1R_2$ were studied as precursors in the preparation of 1,3-thiazines [1], but their ability to form complex compounds has not yet been studied. On the other hand, the complex compounds containing the N-substituted *N*′-benzoyl thioureas $C_6H_5{-}CO{-}N'H{-}CS{-}NR_1R_2$ have been sufficiently investigated. The corresponding benzoyl thioureas act in these complexes either as S-donors, e.g. in $Ag(BDTU)_3SH$ (BDTU = *N*-diethyl-*N*′-benzoyl thiourea) [2] or more frequently as O,S-donors (after deprotonization), e.g. in $Ni[2\text{-}Cl{-}C_2H_4CO{-}N{-}CS{-}N(C_2H_5)_2]_2$ [3] or in $Cu[C_6H_5{-}CO{-}N{-}CS{-}N(C_2H_5)_2]$ [4]. The results published in ref. 5 show that the reactivity of the substituted thiourea is different if it is bonded in a complex. The formation of the complex compounds was also used for concentrating and extracting solutions of metal ions [6]. Such complex compounds may also be interesting from their biological activity point of view because some species of substituted benzoyl thiourea exhibit pesticide efficiency [7].

The aim of this study has been to investigate the synthesis, properties and structure of the complex compounds that arose by the reaction of $CuCl_2$ with $CH_3CH{=}CH{-}CO{-}NH{-}CS{-}NHR$ where $R = C_6H_5$ (PTU), $R = C_2H_5$ (ETU) and $R = CH_2C_6H_5$ (BTU) and to compare them with similar complex compounds described in the literature [2–4].

Experimental

Synthesis and analysis

PTU was prepared according to the literature [1]. ETU was synthesized as follows. A total of 8.3 ml of the 33% solution of ethylamine (0.04 mol) in hexane was dropped (15 min) under stirring and cooling with ice into a solution of 5 g (0.04 mol) of 2-propenoyl isothiocyanate in 200 ml of hexane

[8]. After 30 min the separated solid product was filtered off and crystallized in a benzene–hexane mixture. Yield 5.2 g (71%), m.p. 108–110 °C.

BTU was obtained as follows. A solution of 1.7 ml (0.016 mol) of benzylamine in 20 ml of hexane was dropped under stirring and cooling with ice into a solution consisting of 2 g (0.016 mol) of 2-propenoyl isothiocyanate and 100 ml of hexane. After 20 min the light-yellow product was filtered off. IR and NMR spectra showed that the expected acylthiourea represented the major portion of the product (*c*. 90%). In addition, 1,3-thiazine, which was the cyclization product of acylthiourea, was identified as by-product. As the cyclization took place after the dissolution of acylthiourea in solution, the products could not be separated from each other. Since thiazine does not coordinate to copper, this crude product could be used for the synthesis of the complex. Yield 2.1 g (57%).

$Cu(PTU)_2Cl$ (**I**) was prepared as follows. A solution of 170 mg of $CuCl_2 \cdot 2H_2O$ (1 mmol) in 30 ml of ethanol was slowly added under stirring to a solution of 440 mg of PTU (2 mmol) in 60 ml of ethanol. After 15 min the separated yellow complex **I** was filtered off. Yield 346 mg (69%), m.p. 193–195 °C. Crystals suitable for structural analysis were obtained by recrystallization from a $CHCl_3$–CH_3OH mixture (3:1). *Anal.* Calc. for $CuCl(C_{11}H_{12}N_2OS)_2$: C, 48.97; H, 4.48; N, 10.38; Cu, 12.65. Found: C, 49.31; H, 4.53; N, 10.33; Cu 12.18%.

The complex compounds $Cu(ETU)_2Cl$ (**II**) and $Cu(BTU)_2Cl$ (**III**) were prepared analogously. For complex **II**, 372 mg of ETU (2 mmol) were weighed and dissolved in 45 ml of ethanol. The product separated after 5 min. Yield 271 mg (62.5%), m.p. 154–156 °C. *Anal.* Calc. for $CuCl(C_9H_{15}N_2OS)_2$: C, 37.92; H, 5.45; N, 12.63; Cu, 14.65. Found: C, 38.03; H, 5.68; N, 12.86; Cu, 14.34%.

For complex **III**, 468 mg of BTU (2 mmol) were weighed and dissolved in 60 ml of ethanol. Yield 470 mg (41%), m.p. 155–157 °C. *Anal.* Calc. for $CuCl(C_{12}H_{14}N_2OS)$: C, 50.78; H, 4.97; N, 9.87; Cu, 11.19. Found: C, 51.06; H, 4.98; N, 9.81; Cu, 11.51%.

The CHN analyses were performed on an CHN analyzer (Hewlett-Packard, model 185). The Cu content was estimated complexometrically.

Physical methods

The infrared spectra were taken on a Specord M 80 (Carl Zeiss, Jena) instrument in the range 4000–200 cm^{-1} using KBr tablets. The ^1H and ^{13}C NMR spectra were measured on a Tesla BS 567 A instrument (25 MHz) in deuterated chloroform using tetramethylsilane as internal standard.

Determination of crystal structure

For determining the crystal structure of **I** a yellow monocrystal of an extended plate shape was chosen. It was cut to dimensions 0.52×0.28×0.11 mm. The preliminary examination performed by means of the Weissenberger chamber suggested a triclinic structure. The exact lattice parameters were obtained by refining the position angles of 30 reflections ($25° < 2\theta < 39°$) measured on a diffractometer. The basic crystallographic data are: $C_{22}H_{24}ClCuN_4O_2S_2$, $M_r = 539.57$, $a = 15.538(1)$, $b = 14.296(2)$, $c = 12.016(2)$ Å, $\alpha = 102.72(1)$, $\beta = 105.95(1)$, $\gamma = 94.31(1)°$, $V = 2477.1(6)$ Å^3, space group $P\bar{1}$, $Z = 4$, $D_c = 1.44$, $D_m = 1.44(1)$ g cm^{-3}, μ(Cu Kα) = 39.15 mm^{-1}, $F(000) = 1112$. The intensities were measured at laboratory temperature on a Siemens AED automatic diffractometer at the Centro di Studio per la Strutturistica Diffractometrica del C.N.R., Parma, Italy. The $\omega/2\theta$ scan technique ($3° < \theta < 70°$) and Ni-filtered Cu Kα radiation ($\lambda = 1.54178$ Å) were used. For the sake of control a reflection $\bar{1}0,4,4$ was measured after each 50 reflections. A total of 9388 reflections was measured among which 4832 reflections were considered as observed ($F_o \geqslant 4\sigma(F_o)$). The measured intensities were corrected for Lorentz and polarization effects. Furthermore the correction for absorption according to the Walker–Stuart method [9] was carried out using the ABSORB programme [10]. The structure was solved by the use of direct methods [11] and by means of the SHELX '86 programme. The positions of the non-hydrogen atoms were refined at first isotropically and later anisotropically per block (over 500 parameters) by using the full-matrix least-squares method. The phenyl rings were refined as rigid bodies. The positions of the structurally important hydrogen atoms (expect H(6a)) were refined while their U values were fixed for 0.06 Å^2 (hydrogen atoms bonded to nitrogen) or for 0.08 Å^2 (hydrogen atoms bonded to carbon). The positions of H atoms in the CH_3 groups were obtained by refining the CH_3 groups as rigid bodies and the positions of the hydrogen atoms bonded to the phenyl rings were calculated on the basis of geometrical considerations. First the weight $\omega = [\sigma^2(F_o)]^{-1}$ was used, which in the last cycles of refinement was replaced by the weight $\omega = [\sigma^2(F_o) + 0.005F_o^{\,2}]^{-1}$ for which, however, no shift depending on the value of F_o was observed. In the last cycles the diffractions 010, $\bar{3}\bar{3}2$, and $0\bar{8}1$ were eliminated from refinement because they had a large error. The final data are: $R = 0.066$, $R_w = 0.089$, $S = 0.86$, $-0.78 < \Delta\rho < 0.41$ e Å^{-3}. The scattering factors for C, H, N, O, S and Cl were taken from the SHELX '76 programme [12] which was used in the course of all the refinement. The scattering factor for Cu was taken from the literature

TABLE 1. Fractional coordinates of non-hydrogen atoms ($\times 10^4$) and their equivalent temperature factors U_{eq} ($\times 10^2$)

Atom	x	y	z	U^{eq} (Å^2)
Cu(1)	349(1)	9131(1)	677(1)	7.36(5)
Cu(2)	3892(1)	4360(1)	4426(1)	8.55(6)
Cl(1)	−446(1)	8878(1)	−1328(1)	6.86(7)
Cl(2)	3116(1)	4249(2)	2488(2)	8.33(9)
S(a)	−433(1)	8672(2)	1844(2)	7.36(8)
S(b)	1844(1)	9069(1)	1186(1)	5.89(6)
S(c)	5149(1)	3680(1)	4887(1)	6.03(7)
S(d)	3204(1)	4503(1)	5859(2)	6.43(7)
O(a)	−3411(3)	8613(4)	−70(5)	8.8(3)
O(b)	2542(3)	8227(4)	−2319(4)	7.2(2)
O(c)	5731(3)	2545(3)	1349(4)	6.6(2)
O(d)	255(3)	4580(4)	3914(4)	7.7(2)
N(1a)	−1911(3)	8614(5)	50(5)	6.7(3)
N(2a)	−2135(4)	8655(5)	1890(5)	6.9(3)
N(1b)	1616(3)	8570(4)	−1132(4)	5.7(2)
N(2b)	3077(3)	8658(4)	47(5)	5.6(2)
N(1c)	4982(3)	3369(4)	2558(4)	5.3(2)
N(2c)	6120(3)	2690(4)	3650(5)	5.4(2)
N(1d)	1715(3)	4345(4)	4061(4)	5.8(2)
N(2d)	1554(3)	4736(4)	5977(5)	6.0(2)
C(1a)	−3972(5)	8936(6)	−3670(7)	8.3(3)
C(2a)	−3767(5)	8797(5)	−2449(6)	6.5(3)
C(3a)	−2978(5)	8637(6)	−1799(6)	6.7(3)
C(4a)	−2821(4)	8611(5)	−546(6)	6.4(3)
C(5a)	−1557(4)	8656(5)	1268(6)	6.3(3)
C(6a)	−1913(3)	8749(3)	3134(4)	5.8(3)
C(7a)	−2328(3)	8055(3)	3547(4)	6.9(3)
C(8a)	−2144(3)	8148(3)	4773(4)	8.3(4)
C(9a)	−1545(3)	8936(3)	5586(4)	8.6(4)
C(10a)	−1130(3)	9630(3)	5172(4)	9.1(4)
C(11a)	−1314(3)	9537(3)	3946(4)	7.5(3)
C(1b)	189(4)	7326(6)	−5441(6)	7.5(3)
C(2b)	984(5)	7644(6)	−4349(6)	6.6(3)
C(3b)	946(4)	8009(5)	−3251(6)	6.1(3)
C(4b)	1773(4)	8277(5)	−2237(6)	5.7(3)
C(5b)	2221(4)	8750(5)	−3(5)	5.2(3)
C(6b)	3817(2)	8720(3)	1069(4)	5.6(2)
C(7b)	3758(2)	8289(3)	1985(4)	6.5(3)
C(8b)	4526(2)	8336(3)	2939(4)	8.7(4)
C(9b)	5354(2)	8816(3)	2977(4)	9.1(4)
C(10b)	5413(2)	9247(3)	2061(4)	8.7(4)
C(11b)	4644(2)	9199(3)	1107(4)	7.0(3)
C(1c)	4443(5)	3850(6)	−1482(6)	8.1(4)
C(2c)	4850(4)	3404(5)	−486(6)	6.3(3)
C(3c)	4648(4)	3496(5)	527(6)	5.9(3)
C(4c)	5167(4)	3075(5)	1461(6)	5.5(3)
C(5c)	5437(4)	3216(5)	3638(6)	5.3(2)
C(6c)	6718(3)	2533(3)	4709(4)	5.9(3)
C(7c)	7228(3)	3320(3)	5626(4)	6.9(3)
C(8c)	7870(3)	3164(3)	6610(4)	8.7(4)
C(9c)	8002(3)	2221(3)	6679(4)	10.2(5)
C(10c)	7492(3)	1434(3)	5762(4)	9.0(4)
C(11c)	6850(3)	1591(3)	4777(4)	7.6(4)
C(1d)	−382(5)	3677(6)	20(6)	8.2(3)
C(2d)	−141(5)	4001(6)	1371(6)	6.5(3)
C(3d)	651(4)	4046(6)	2107(6)	6.4(3)
C(4d)	818(4)	4354(5)	3428(6)	5.8(3)
C(5d)	2089(4)	4558(5)	5300(5)	5.2(2)
C(6d)	1877(3)	4912(3)	7247(4)	5.6(2)
C(7d)	1701(3)	4187(3)	7798(4)	6.6(3)
C(8d)	2004(3)	4363(3)	9041(4)	7.6(4)
C(9d)	2482(3)	5263(3)	9733(4)	7.5(4)
C(10d)	2658(3)	5988(3)	9182(4)	7.6(3)
C(11d)	2355(3)	5813(3)	7939(4)	6.6(3)

TABLE 2. Fractional coordinates of the refined hydrogen atoms ($\times 10^4$)

Atom	x	y	z
H(4a)	−4190(45)	8867(51)	−1935(60)
H(5a)	−2566(45)	8356(51)	−2155(61)
H(7a)	−2791(40)	8636(43)	1370(53)
H(4b)	1601(46)	7565(49)	−4510(58)
H(5b)	362(46)	8130(49)	−3092(59)
H(6b)	1049(40)	8720(43)	−1098(53)
H(7b)	3159(40)	8437(45)	−650(55)
H(4c)	5282(45)	2945(51)	−694(59)
H(5c)	4056(43)	3844(47)	765(57)
H(6c)	4494(39)	3657(44)	2588(52)
H(7c)	6263(39)	2488(44)	2978(55)
H(4d)	−555(46)	4154(53)	1640(62)
H(5d)	1125(45)	3758(49)	1850(60)
H(6d)	2176(40)	4097(43)	3610(53)
H(7d)	915(40)	4802(43)	5633(52)

[13]. The corrections for anomalous scattering were also used. The final coordinates of non-hydrogen atoms and the corresponding U_{eq} values are listed in Table 1. The coordinates of the refined hydrogen atoms are listed in Table 2. See also 'Supplementary material'.

The geometrical analysis was performed by the use of the PARST programme [14] and the pictures were made by means of the PLUTO programme [15]. The calculations were carried out on computers GOULD-SEL 77/22 (Centro di Studio per la Strutturistica Diffractometrica del C.N.R., Parma, Italy) and EC 1045 (Computer Centre of the Technical College, Košice, Czechoslovakia).

Results and discussion

The unit cell of $Cu(PTU)_2Cl$ contains two centrosymmetrical dimer molecules of the complex with a different coordination sphere of the Cu(I) atoms (Fig. 1) and four crystallographically different ligand molecules of PTU denoted a, b, c and d (Fig. 2). In the first molecule of the complex denoted A two copper atoms are joined through chloride bridges by different bonds (Fig. 3). The first Cu(1)–Cl(1) bond (2.138(2) Å) is normal whereas the second Cu(1)–Cl(1)′ bond is somewhat longer (2.762(2) Å) (Table 3). The remaining two coordination sites about the Cu(1) atoms are occupied by S(a) and S(b) atoms from the PTU molecules. The Cu–S distances are comparable with those found in the $Cu(TU)_2Cl$ complex (TU = thiourea) [16]. As the lengths of the Cu–Cl bonds are not equivalent and with respect to the values of angles in the coordination polyhedron

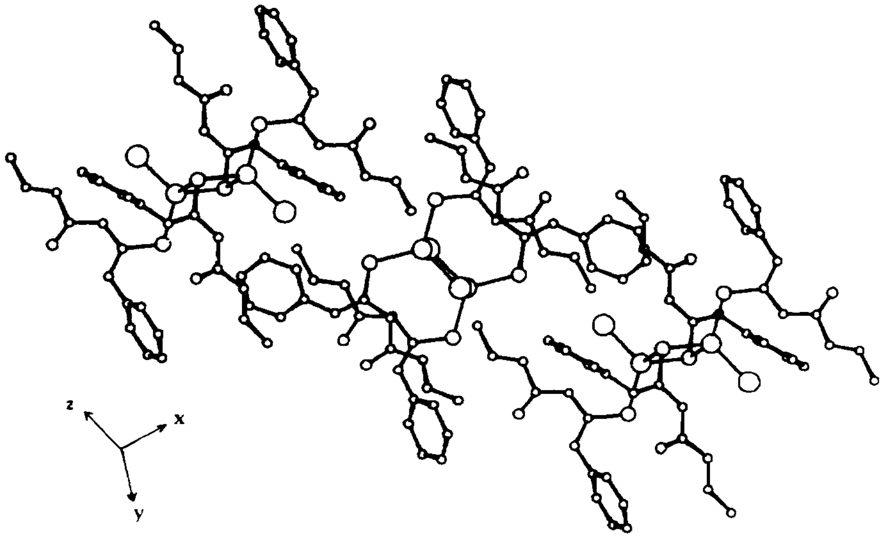

Fig. 1. View showing the packing of molecules in the unit cell.

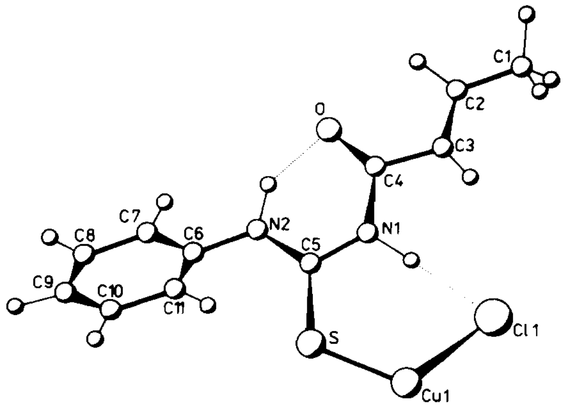

Fig. 2. PTU(a) molecule along with atom numbering scheme. Dotted lines refer to hydrogen bonds.

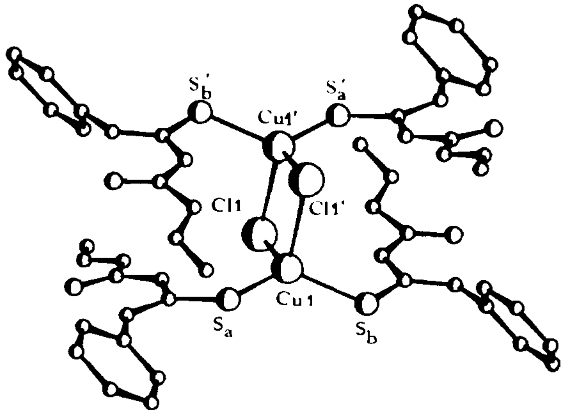

Fig. 3. View of molecule A showing the coordination of the Cu(1) atom.

of the Cu(1) atom (Table 3), this coordination polyhedron may be regarded as a distorted trigonal pyramid. The Cu(1) atom is displaced 0.367(2) Å from the basal plane to the Cl(1)′ atom. The Cu(1)–Cu(1)′ distance is equal to 3.349(2) Å which is a value exceeding 2.981(4) Å found for $Cu(TU)_2Cl$ [16].

The other molecule of the complex denoted B (Fig. 4) is formally considered a dimer though the lengths of the bonds Cu(2)–S(c) and Cu(2)–S(c)′ exhibit a greater difference (2.235(2) and 2.904(2) Å) than observed for the Cu–Cl bonds in molecule A, the second bond being at the limit for a covalent bond. The coordination of the Cu(2) atom may be described as a distorted trigonal pyramidal. In the plane of the pyramid one terminally bonded Cl^- anion and two S atoms from the PTU(c, d) molecules are coordinated. In the axial position is the S′ atom of the PTU(c)′ molecule bound by a weak bond. The Cu(2) atom is displaced by 0.308(2) Å from the trigonal plane towards the S(c)′ atom. The Cu(2)–Cu(2)′ distance (3.527(7) Å) does not indicate any metal–metal interaction.

Similar long and short sulfur and chloride bridges between two copper atoms were found in the $Cu(DTO)Cl_2$ complex (DTO = 3,6-dithiaoctane), in which as a consequence of alternating these sulfur and chloride bridges the chain structure is formed [17]. While the short distances (Cu–S: 2.327(1) Å; Cu–Cl: 2.264(1) Å) are comparable with the corresponding ones in the $Cu(PTU)_2Cl$ complex (Table 3) (considering the different oxidation state of the Cu atoms), the long distances (Cu–S′: 3.361(2) Å; Cu–Cl′: 3.234(1) Å) are much longer for the

TABLE 3. Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses

Bonds and angles in coordination polyhedra[a]			
Cu(1)–Cl(1)	2.318(2)	Cu(2)–Cl(2)	2.273(3)
Cu(1)–Cl(1)^{i}	2.762(2)	Cu(2)–S(c)	2.235(2)
Cu(1)–S(a)	2.257(3)	Cu(2)–S(c)^{ii}	2.904(2)
Cu(1)–S(b)	2.248(2)	Cu(2)–S(d)	2.245(3)
Cl(1)–Cu(1)–S(a)	116.06(10)	Cl(2)–Cu(2)–S(c)	120.80(10)
Cl(1)–Cu(1)–S(b)	118.78(9)	Cl(2)–Cu(2)–S(d)	121.89(11)
Cl(1)–Cu(1)–Cl(1)^{i}	98.03(7)	Cl(2)–Cu(2)–S(c)^{ii}	100.47(9)
S(a)–Cu(1)–S(b)	117.92(10)	S(c)–Cu(2)–S(d)	111.75(8)
S(a)–Cu(1)–Cl(1)^{i}	101.56(9)	S(c)–Cu(2)–S(c)^{ii}	94.36(8)
S(b)–Cu(1)–Cl(1)^{i}	97.52(8)	S(d)–Cu(2)–S(c)^{ii}	98.46(7)

	Molecule A		Molecule B	
	a	b	c	d
Bonds in PTU ligand molecules				
C(1)–C(2)	1.475(12)	1.489(8)	1.490(11)	1.516(10)
C(2)–C(3)	1.327(10)	1.327(10)	1.320(11)	1.291(9)
C(3)–C(4)	1.467(11)	1.464(8)	1.465(10)	1.493(10)
C(4)–O	1.206(9)	1.232(8)	1.217(8)	1.205(9)
C(4)–N(1)	1.398(7)	1.395(9)	1.407(9)	1.395(7)
N(1)–C(5)	1.401(9)	1.378(7)	1.370(8)	1.395(7)
C(5)–N(2)	1.317(10)	1.333(8)	1.345(9)	1.315(9)
C(5)–S	1.689(6)	1.675(7)	1.694(7)	1.692(6)
N(2)–C(6)	1.412(8)	1.414(6)	1.428(7)	1.427(7)
Angles in PTU ligand molecules				
C(1)–C(2)–C(3)	126.0(7)	125.2(7)	126.9(7)	125.2(7)
C(2)–C(3)–C(4)	121.4(7)	120.5(6)	120.0(6)	121.3(6)
C(3)–C(4)–O	123.6(6)	124.6(6)	125.2(6)	125.1(6)
C(3)–C(4)–N(1)	112.9(6)	113.7(6)	113.6(6)	112.2(5)
N(1)–C(4)–O	123.5(6)	121.7(6)	121.2(6)	122.7(6)
C(4)–N(1)–C(5)	125.3(5)	128.7(5)	127.7(5)	122.2(5)
N(1)–C(5)–S	118.9(5)	118.9(5)	121.0(5)	118.1(5)
N(1)–C(5)–N(2)	117.2(6)	116.0(5)	116.6(6)	118.9(5)
S–C(5)–N(2)	123.9(5)	125.1(5)	122.4(5)	122.9(5)
C(5)–N(2)–C(6)	126.0(6)	128.0(5)	124.2(5)	122.2(5)
C(5)–S–Cu	112.0(3)	112.8(2)	110.3(2)	111.1(2)

[a] Symmetry codes: ^{i} $-x$, $2-y$, $-z$; ^{ii} $1-x$, $1-y$, $1-z$.

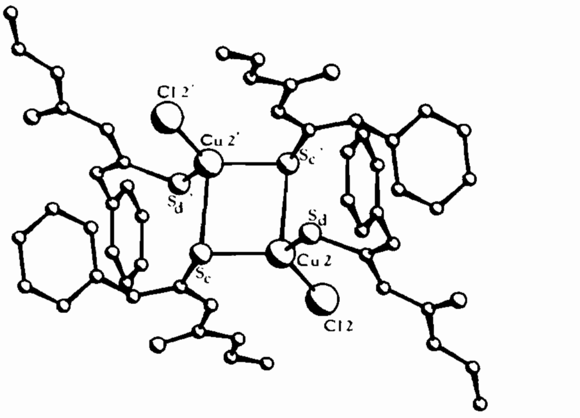

Fig. 4. View of molecule B showing the coordination of the Cu(2) atom.

$Cu(DTO)Cl_2$ complex as could be expected for the axial bonds of the tetragonal Cu(II) complex.

Provided we do not take into consideration the weak Cu(2)–S(c)′ bond, all molecules of ATU function as neutral terminal ligands bonded through the S atom. The values of the Cu–S–C angle are within the range 110.3–112.8° and the lowest value was found for the PTU(c) molecule. In this molecule the S atom forms an additional bond to the Cu(2) atom. These values are higher than the range 107.1–110.2° observed for $Ag(BDTU)_3SH$ [2]. The difference may be due to the fact that the steric repulsion around the larger Ag(I) atom is smaller. In all molecules a *trans* arrangement of substituents about the C=C double bond exists (Fig. 2) which is evidently a consequence of steric repulsion of the voluminous substituents. The rotameric configuration

TABLE 4. Important bond distances (Å) in the R–CO–N–CS–N′R_2R_2 ligands and their complexes

Compound	C_O–O	C_O–N	N–C_S	C_S–S	C_S–N′	Reference
EBDTU	1.218	1.360	1.428	1.658	1.327	3
Cu(PTU)$_2$Cl	1.22	1.40	1.39	1.69	1.33	this work
Ag(BDTU)$_3$SH	1.22	1.38	1.42	1.68	1.32	2
Cu(EBTU-H)$_2$	1.26	1.32	1.34	1.74	1.33	4
Ni(EBDTU-H)$_2$	1.25	1.32	1.36	1.73	1.33	3

TABLE 5. Hydrogen bonds and contacts less than 3.5 Å. Distances in (Å) and angles in degrees

	Molecule A		Molecule B	
	a	b	c	d
Intramolecular hydrogen bonds				
N(2)–H(7)	1.03(6)	0.88(7)	0.89(7)	0.99(6)
N(2)...O	2.614(7)	2.647(7)	2.620(8)	2.685(6)
N(2)–H(7)...O	141(5)	140(6)	133(6)	126(5)
N(1)–H(6)	1.08(-)	0.93(7)	0.90(6)	1.05(7)
N(1)...Cl	3.207(6)	3.218(5)	3.234(5)	3.244(6)
N–H...Cl	166(-)	170(5)	173(5)	153(5)
Donor–H		Donor...acceptor		Donor–H...acceptor
Intermolecular hydrogen bonds[a]				
N(2b)–H(7b) 0.88(7)		N(2b)...O(c)^{i} 3.181(7)		N(2b)–H(7b)...O(c)^{i} 134(5)
N(2c)–H(7c) 0.89(7)		N(2c)...O(b)^{i} 3.148(8)		N(2c)–H(7c)...O(b)^{i} 139(5)
N(2d)–H(7d) 0.99(6)		N(2d)...O(d)^{ii} 3.071(7)		N(2d)–H(7d)...O(d)^{ii} 143(5)
Intermolecular contacts less than 3.5 Å[b]				
S(b)...C(3a)^{i}	3.429(8)		S(b)...C(9c)^{ii}	3.443(5)
O(a)...C(3c)^{iii}	3.302(9)		O(a)...C(4c)^{iii}	3.285(7)
O(b)...O(c)^{iv}	3.012(7)		O(b)...C(11c)^{iv}	3.394(8)
O(b)...C(6c)^{iv}	3.373(7)		O(c)...C(11b)^{iv}	3.296(6)
O(c)...C(6b)^{iv}	3.347(7)		O(c)...C(10d)^{ii}	3.428(7)
O(c)...C(11d)^{ii}	3.429(6)		O(c)...O(c)^{v}	2.963(7)
O(c)...C(6d)^{v}	3.423(7)		N(1c)...C(2a)^{iii}	3.461(9)
C(2a)...C(5c)^{iii}	3.476(9)			

[a] Symmetry codes: ^{i} $1-x, 1-y, -z$; ^{ii} $-x, 1-y, 1-z$. [b] Symmetry codes: ^{i} $-x, 2-y, -z$; ^{ii} $1-x, 1-y, 1-z$; ^{iii} $-x, 1-y, -z$; ^{iv} $1-x, 1-y, -z$; ^{v} $-x, 1-y, 1-z$.

of the other part of the PTU molecules is E,Z' and is consistent with that observed for the Ag(BDTU)$_3$SH complex [2].

There are small but in some cases significant (more than 3σ) differences in bond lengths and angles in individual PTU molecules (Table 3). As for the bond lengths, these differences, however, do not exceed the value of 4σ and are likely due to steric effects (crystal packing forces). The determined mean values of the bond lengths are comparable with those found for the Ag(BDTU)$_3$SH complex [2] (Table 4). On the other hand, the bond lengths observed for the complexes containing the derivatives of benzoyl thiourea bound by chelate bonds are different. For instance, in the case of chelate bonding of the ligand the length of the C–S bond exceeds 1.70 Å while a value equal to 1.658(2) Å was found for the Cl–C_6H_4–CO–NH–CS–N$(C_2H_5)_2$ ligand itself [3]. In our case, the bond length is in the middle of both these values. The shortening of the C(S)–NHR bond with respect to the value expected for a single bond which was also observed for other ligands is significant (Table 4). It indicates a delocalization of the π-electron density and the double character of the bond. A similar shortening of this bond was also observed for the Cu(PPTU)$_2$Cl complex (PPTU= 1-phenyl-3(2-pyridyl)-thiourea) [18].

The values of the angles are consistent with the expected values and do not significantly differ from those found for the Ag(BDTU)$_3$SH complex [2]. The most important difference between individual PTU molecules was found for an angle of the C(5)–N(2)–C(6) type. In molecule b it has the value of 128.0(5)° while its value in molecule d is 122.2(5)°.

From the structure point of view the presence of a hydrogen atom bonded to the thioamidic nitrogen atom N(2) of the PTU molecule is important (Fig. 2). It forms an intramolecular bond to an oxygen atom of the acyl group (Table 5) and can be one of the causes that PTU is bonded as a terminal ligand and not as a chelate ligand. In this case, the higher affinity of the sulfur atom to Cu(I) evidently plays a certain role. The results in Table 5 show that an intramolecular hydrogen bond of the NH...Cl type also arises and undoubtedly contributes to the stabilization of the complex molecules.

The NH...O hydrogen bonds and the van der Waals forces are effective between individual complex molecules. There are 15 contacts shorter than 3.5 Å (Table 5).

The measured infrared spectra of complexes **I**, **II** and **III** (Table 6) do not show significant changes when compared with the spectra of the corresponding free ligands. This is in agreement with the solved crystal structure of **I** and suggests that the oxygen atom of the carbonyl group is not involved in coordination bonding. The assignment of the observed absorption bands to individual types of vibration is very difficult and almost impracticable. It results from the fact that most absorption bands originate from coupled vibration modes occurring either in amidic or thioamidic parts of the ligand molecule [19]. For this reason, only some significant absorption bands are listed in Table 6. Besides the absorption bands given in Table 6, some bands over 3000 cm^{-1} originating from the vibration ν(C$_{ar}$–H) were observed for complexes **I** and **III**. In the region 3000–2850 cm^{-1} weak absorption bands corresponding to the vibrations ν(C–H) were observed in the spectrum of complex **II** while these vibrations manifest themselves only as very weak shoulders in the spectra of complexes **I** and **III**. The most significant changes in the spectra of complexes with respect to those of the free derivatives of 2-propenoyl thiourea are expressed by a change in intensity ratio as well as by a shift in absorption bands appearing in the region 600–750 cm^{-1} (Table 6). This is doubtlessly due to coordination of thiourea through the sulfur atom [3]. The obtained results are in agreement with the assumption that ETU and BTU in complexes **II** and **III**, respectively, are terminally bonded through the sulfur atom as found for PTU in complex **I** and that the structures of these complexes must be analogous.

The ^{1}H and ^{13}C NMR spectra (Table 7) confirm the structure of the prepared compounds. They contain the corresponding signals of protons or carbon atoms of the 2-propenoyl thiourea grouping as well as of the aminic residues R. The found experimental values of the coupling constants (16 Hz) for the hydrogen atoms in the –HC=CH– group indicate their *trans* arrangement. This observation is in line with the solved crystal structure of **I** and with the measured IR spectra of the complexes **I–III**. The

TABLE 6. Selected infrared spectroscopic data (cm^{-1})^a

Cu(PTU)$_2$Cl	PTU	Cu(ETU)$_2$Cl	ETU	Cu(BTU)$_2$	BTU	Assignment
3144m	3176m, b	3184s	3228m, b	3156m, b	3220m, b 3200m, b	ν(NH)
1688v	1680vs	1684vs	1680s	1696v, s 1687v, s	1680v, s	ν(C=O)
1642s	1642vs	1642vs	1644vs	1644s	1638s	ν(C=C)
1592m	1598m			1570m		
1542vs, b	1520vs, b	1542vs	1542s	1520m, b	1550vs, b	ν(NHCS)
966m	964m	960s	960m	962s	956s	γ(=CH)
756m						
731w, sh			740m	736s	738s	
714s	720m	706vs	712m		705s, sh	δ(C=S)
694m	692s			698vs	696vs	

^{a}s, strong; v, very; m, medium; w, weak, b, broad, sh, shoulder.

TABLE 7. Chemical shifts δ (ppm) in the ^{1}H and ^{13}C NMR spectra[a]

	Cu(PTU)$_2$Cl	PTU	Cu(ETU)$_2$Cl	ETU	Cu(BTU)$_2$Cl	BTU
^{1}H						
CH$_3$–	2.00d	1.88d	1.95d	1.95d	1.95d	2.10d
–CH=	7.18m	7.10m	7.18m	7.18m	7.10m	7.37m
=CH–CO	6.48d	5.93d	6.40d	5.95d	6.37d	5.95d
–NH–	9.41s	11.51s	10.70s	11.20s	11.47s	11.00s
–R(–CH$_3$)			1.25t	1.25t		
–R(–CH$_2$–)			3.65q	3.65q	4.80d	4.87d
–R(–Ph)	7.50m	7.45m			7.37m	7.37m

	Cu(PTU)$_2$Cl	PTU	Cu(ETU)$_2$Cl	Cu(BTU)$_2$Cl
^{13}C[b]				
CH$_3$–	18.44q	18.29q	18.32q	18.33q
–CH=	147.97d	146.99d	147.03d	147.44d
=CH–(CO)	124.00d	123.55d	124.00d	123.96d
C=O	167.30s	165.73s	167.03s	167.11s
C=S	179.10s	178.95s	178.72s	179.21s
R(–C$_{ar}$)	136.47m	137.74m		129.00m
	129.08m	128.85m		128.22m
	127.73m	126.84m		127.92m
	125.27m	124.30m		
R(–CH$_2$)			39.34t	49.27t
R(–CH$_3$)			13.51q	

[a] s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet. [b] ETU was not sufficiently soluble, BTU cyclized in solvent.

corresponding $\gamma(=CH)$ absorption band at about 960 cm^{-1} was also observed (Table 6).

Supplementary material

Tables of the observed and calculated structure factors (29 pages) and anisotropic temperature factors can be obtained from the authors on request.

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References

1 M. Dzurilla, P. Kutschy and P. Kirstian, *Synthesis*, (1985) 933–934.
2 U. Braun, R. Richter, J. Sieler, A. I. Yanovski and Yu. T. Struchkov, *Z. Anorg. Allg. Chem., 529* (1985) 201–208.
3 R. A. Bailey, K. L. Rothaupt and R. K. Kullnig, *Inorg. Chim. Acta, 147* (1988) 233–236.
4 R. Richter, L. Beyer and J. Kaiser, *Z. Anorg. Allg. Chem., 461* (1980) 67–73.
5 L. Beyer, J. Hartung and R. Widera, *Tetrahedron, 40* (1984) 405–412.
6 P. Muehl and E. Hoyer, *Z. Chem., 26* (1986) 81.
7 N. N. Melnikov, *Pesticidy*, Chimija, Moscow, 1987, p. 326.
8 *Br. Patent 880 807* (1958); *Chem. Abstr., 53* (1959) 5134.
9 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158–166.
10 F. Ugozzoli, *Comput. Chem., 11* (1987) 109–120.
11 G. M. Sheldrick, *SHELXS '86*, program for solution of crystal structures, University of Göttingen, F.R.G., 1986.
12 G. M. Sheldrick, *SHELX '76*, program for crystal structure determination, University of Cambridge, U.K., 1976.
13 *International Tables for X-ray Crystallography*, Vol. IV. Kynoch Press, Birmingham, U.K., 1974 (present distributor Kluwer, Dordrecht, The Netherlands).
14 M. Nardelli, *Comput. Chem., 7* (1983) 95–98.
15 W. D. S. Motherwell, *PLUTO*, program for plotting molecular and crystal structures, University of Cambridge, U.K., 1976.
16 W. A. Spofford and E. L. Amma, *Acta Crystallogr., Sect. B, 26* (1970) 1474–1483.
17 M. M. Olmstead, W. K. Musker, L. W. Ter Haar and W. E. Hatfield, *J. Am. Chem. Soc., 104* (1982) 6227–6231.
18 M. Belicchi Ferrari, G. Gaspari Fava, C. Pelizzi and P. Tarasconi, *Inorg. Chim. Acta, 97* (1985) 99–109.
19 M. Horak and D. Papousek, *Infrared Spectra and Structure of the Molecules*, Academia, Prague, Czechoslovakia, 1976.