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Synthesis and Structural Characterization of Chloro-(triphenylphosphine)-[1-phenyl-3-(2-pyridyl)-2-thiourea]Cu(I) and Chloro-bis[1-phenyl-3-(2-pyridyl)-2-thiourea]-Cu(I)

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Abstract

The crystal structures of two complexes, Cu(PPh$_3$)(pptu)Cl (I) and Cu(pptu)$_2$Cl (II) [pptu = 1-phenyl-3-(2-pyridyl)-2-thiourea], were determined by single-crystal X-ray diffraction methods at 293 K. Both crystals are monoclinic, space groups $P2_1/c$, with $a = 11.345(3)$, $b = 9.550(2)$, $c = 26.009(8)$ Å, $\beta = 94.36(4)^\circ$ for (I); $a = 9.715(3)$, $b = 19.363(6)$, $c = 14.201(5)$ Å, $\beta = 108.00(3)^\circ$ for (II). The crystal structures were solved by Patterson and Fourier methods and refined by least-squares to a final conventional agreement index $R = 4.7\%$ and 8.1% (1528 and 2270 'observed' reflections) respectively for (I) and (II). In both compounds the coordination around copper is trigonal planar and involves a chlorine atom, a sulphur atom from a pptu molecule and a phosphorus atom from PPh$_3$ for (I), a chlorine atom and two sulphur atoms from pptu molecules for (II). In (I) the coordination is completed to a nearly regular trigonal pyramid, by a long interaction (3.4 Å) between copper and the C_5-C_6 bond of an adjacent benzene ring. In (II) the coordination is completed by two hydrogen atoms of two phenylic rings so that the whole polyhedron can be described as a very elongated trigonal bipyramid ($Cu\cdots H3^{viii} = 2.37$, $Cu\cdots H21^{viii} = 3.01$ Å).

Introduction

In this paper, as part of a more extensive investigation into the chemistry of Cu(I) and Cu(II) complexes [1–3], we report results of studies on the synthesis and structural characterization of two Cu(I) complexes, chloro-(triphenylphosphine)-[1-phenyl-3-(2-pyridyl)-2-thiourea]Cu(I) (I) and chloro-bis[1-phenyl-3-(2-pyridyl)-2-thiourea]Cu(I) (II), obtained by the reaction of the tetrameric [Cu(PPh$_3$)-Cl]$_4$ [4] with 1-phenyl-3-(2-pyridyl)-2-thiourea (pptu). The main purpose is to investigate ligand behaviour and the possible transformation of the pseudo-cubane stereochemistry [5, 6] in connection with different factors such as the oxidation state of the metal, the complexing properties of the ligands containing N, S and P as donor atoms and the experimental conditions employed in the synthesis reactions. The research has shown that different situations are possible. In fact, in (I) the coordination around copper involves the chlorine, phosphine and pptu ligands, while in (II) a chlorine atom but two independent pptu molecules are coordinated to metal.

Experimental

Preparation of Cu(PPh$_3$)(pptu)Cl (I)

An equimolar amount of 1-phenyl-3-(2-pyridyl)-2-thiourea (pptu), dissolved previously in hot toluene, was added to a boiling toluene solution of [Cu(PPh$_3$)-Cl]$_4$. The reaction mixture was heated under reflux for *ca.* 1 h and then allowed to stand at room temperature. After slow evaporation of the solvent a pale yellow oily solid was isolated (yield *ca.* 95%), which by recrystallization from acetone gave crystals of Cu(PPh$_3$)(pptu)Cl.

By the same procedure the reaction of [Cu(PPh$_3$)-Cl]$_4$ with pptu in 1:2 molar ratio again provided complex (I), as confirmed by analytical and spectroscopic data.

Preparation of Cu(pptu)$_2$Cl (II)

Powdered copper(II) nitrate trihydrate was added to a toluene solution of [Cu(PPh$_3$)Cl]$_4$ and pptu (1:1:2 molar ratio) and the suspension was refluxed (1 h). After the reaction was started the colour of the solution gradually changed from colourless to brown-green, while the solid from dark-blue to pale blue. After the evolution of NO$_2$ gas was finished, the solution was cooled and a powdered precipitate of formula Cu(pptu)Cl·H$_2$O (yield *ca.* 70%) together with unreacted copper(II) nitrate was isolated. After filtration the remaining solution was slowly evaporated at room temperature until a small amount of a pale-yellow crystalline product, Cu(pptu)$_2$Cl (II),

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was obtained (yield *ca.* 10%). As by-products triphenylphosphine and, in a very small yield, $Cu(OPPh_3)_2(NO_3)_2$ were also found.

The complex $Cu(OPPh_3)_2(NO_3)_2$, whose X-ray structural analysis is now in progress, was also isolated by reacting $[Cu(PPh_3)Cl]_4$ with $Cu(NO_3)_2 \cdot 3H_2O$ in toluene solution.

The infrared spectra were registered on a Perkin-Elmer Mod. 283 B using KBr disks.

Structure Solution and Refinement

Crystal data and information pertinent to data collection and structural determination are given in Table I.

TABLE I. Crystal Data and Experimental Parameters for (I) and for (II).

Formula	$C_{30}H_{26}ClCuN_3PS$	$C_{24}H_{22}ClCuN_6S_2$
Molecular weight	590.7	557.6
Crystal symmetry	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	11.345(3)	9.715(3)
b, Å	9.550(2)	19.363(6)
c, Å	26.009(8)	14.201(5)
β,°	94.36(4)	108.00(3)
V, Å^3	2809.8	2540.6
Z	4	4
d(calc) g cm^{-3}	1.40	1.46
d(obs) g cm^{-3}	1.39	1.44
Crystal size (mm)	0.08 × 0.04 × 0.48	0.3 × 0.2 × 0.4
μ(Cu-Kα) cm^{-1}	33.6	38.6
Mean μR	0.1	0.6
Scan type	$\omega-2\theta$	$\omega-2\theta$
Collection range	$\pm h, k, l$	$\pm h, k, l$
2θ deg	$6 < 2\theta < 140$	$6 < 2\theta < 120$
Radiation (CuKα)	$\lambda = 1.54178$	$\lambda = 1.54178$
Temperature °C	20	20
Total data collected	5709	3936
Independent data with I > 2σ(I)	1528	2270
Final R (observed reflections only)	4.7%	8.1%

For both compounds accurate unit cell parameters were obtained by least-squares from the angular coordinates of 25 and 20 reflections measured in a θ range of 7–69° and 9–60° respectively for (**I**) and (**II**). All the reflections were collected on a Siemens AED single-crystal computer-controlled diffractometer. No correction for absorption was made as the samples were sufficiently small. Both structures were solved by the heavy-atom technique starting from the three-dimensional Patterson distributions. Successive Fourier syntheses gave the coordinates of all non-hydrogen atoms, which were refined by means of isotropic and anisotropic least-squares calculations. For both compounds unit weights were used.

In both complexes the hydrogen atoms were located from a ΔF synthesis except H5, H12, H15, H22, H23 for (**I**) and H01, H04 for (**II**), which were calculated with standard geometries. The final R-index was 4.7% for (**I**) and 8.1% for (**II**) (observed reflections only). The highest residual electron density was 0.3 for (**I**), 1.1 for (**II**) and the deepest pit was −0.4 for (**I**), −0.6 for (**II**). All the calculations were performed on the C.D.C. Cyber 76 computer of CINECA, Casalecchio, Bologna using the SHELX system of programs [7]. Atomic scattering factors used throughout the calculations were taken from Cromer & Mann [8] for non-hydrogen atoms and from Stewart, Davidson & Simpson [9] for H atoms. The positions of the atoms, as well as their thermal factors, are reported in Table II for (**I**), in Table III for (**II**).

Results and Discussion

The two complexes are shown in Fig. 1 and in Fig. 2. In both compounds the coordination around copper is trigonal planar and involves a chlorine atom, a sulphur atom from a pptu molecule and a phosphorus atom from PPh_3 for (**I**), a chlorine atom and two sulphur atoms from pptu molecules for (**II**). In (**I**) the coordination polyhedron is completed to a nearly regular trigonal pyramid, by a long interaction (3.4 Å) between copper and the C5–C6 bond of an adjacent benzene ring (Cl–Cu–A[a] = 92.7; S–Cu–A = 94.9; P–Cu–A = 93.3°) (Fig. 3 and Table IV). A fifth position involves a long non bonded interaction (Cu···H30 = 2.93 Å) with a phenyl ring ortho-hydrogen atom (Fig. 3). In (**II**) the coordination is completed by two hydrogen atoms of two phenylic rings which are on opposite sides of the trigonal plane, so that the whole polyhedron can be described as a very elongated trigonal bipyramid ($Cu \cdots H3^{vii} = 2.37$, $Cu \cdots H21^{viii} = 3.01$ Å) (Fig. 4). The angles of coordination are reported in Table V. Interbond angles (in (**I**) Cl–Cu–P < Cl–Cu–S ≅ P–Cu–S in (**II**) S–Cu–S < Cl–Cu–S1 ≅ Cl–Cu–S2) (Tables IV and V)) are influenced, for the given geometry, by distribution of bulk about the metal, by hydrogen bonds Cl···N (3.16 in (**I**), 3.24 and 3.19 Å in (**II**)) and for (**I**) by close chlorine–phenyl hydrogen non-bonded contacts (Cl···H14 = 2.81 Å). The copper atom is out of the coordination plane of 0.14 Å in the direction of the C5–C6 bond for (**I**) and 0.05 Å for (**II**).

Interatomic distances, bond angles and dihedral angles with their estimated standard deviations are shown in Table IV for (**I**) and in Table V for (**II**).

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[a] A is the midpoint of C_5–C_6.

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^2$ Å^2)* for (I) with Standard Deviations.

Atom	*x/a*	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	3349(1)	8080(2)	3685(1)	3.7(1)	3.9(1)	5.0(1)	-1.1(1)	0.1(1)	0.7(1)
Cl	4305(3)	8643(3)	4441(1)	6.6(2)	4.9(2)	4.6(2)	-1.3(2)	-0.4(2)	0.1(2)
S	3575(3)	9337(4)	2982(1)	3.8(2)	4.9(2)	4.3(2)	-1.3(2)	-0.5(2)	1.0(2)
P	1930(3)	6517(3)	3734(3)	3.7(2)	3.9(2)	4.1(2)	-0.8(2)	-0.2(2)	0.4(2)
N1	5256(8)	10550(11)	3572(3)	3.6(6)	4.9(7)	2.8(6)	-1.9(5)	-0.2(5)	0.0(5)
N2	5006(9)	11390(11)	2739(4)	5.2(7)	6.8(8)	3.6(6)	-2.5(6)	-0.5(5)	1.9(6)
N3	6711(9)	12259(13)	3428(4)	5.6(7)	8.5(9)	6.2(8)	-3.2(7)	-0.7(6)	0.8(8)
C1	4438(12)	11436(17)	2227(5)	5.0(1.0)	8.2(1.2)	5.1(1.0)	-3.6(9)	0.2(8)	3.6(9)
C2	3492(14)	12374(17)	2123(6)	7.0(1.1)	9.2(1.3)	6.9(1.3)	-0.6(9)	-0.6(9)	2.3(1.0)
C3	3023(16)	12452(19)	1601(8)	7.5(1.4)	7.6(1.4)	8.8(1.4)	-0.2(1.1)	-0.4(1.1)	3.0(1.1)
C4	3491(16)	11627(25)	1236(7)	7.3(1.2)	14.8(2.1)	6.1(1.3)	-2.2(1.3)	-1.2(1.0)	3.4(1.4)
C5	4382(15)	10691(24)	1323(6)	5.0(1.1)	20.3(2.2)	5.5(1.1)	-2.5(1.3)	-1.6(9)	4.3(1.3)
C6	4847(13)	10582(18)	1822(6)	5.0(1.0)	11.9(1.4)	5.5(1.0)	-2.1(1.0)	0.9(9)	0.3(1.0)
C7	4717(10)	10504(13)	3101(5)	3.0(7)	4.5(9)	4.0(8)	-0.4(7)	-0.2(6)	0.2(7)
C8	6220(10)	11417(14)	3760(5)	3.0(7)	4.9(9)	5.2(9)	-0.3(7)	1.2(6)	-0.2(8)
C9	6599(10)	11363(14)	4280(5)	3.9(8)	4.7(9)	5.8(9)	-1.3(7)	-0.1(6)	-0.7(7)
C10	7525(12)	12160(16)	4459(6)	6.5(1.0)	6.6(1.1)	5.6(1.1)	-1.5(9)	-0.2(8)	-1.6(9)
C11	8041(13)	13026(18)	4127(6)	6.6(1.0)	7.6(1.2)	10.7(1.3)	-3.1(1.1)	-2.5(9)	-2.4(1.2)
C12	7641(12)	13055(17)	3617(6)	7.3(1.0)	9.5(1.2)	9.8(1.4)	-4.9(1.0)	-0.5(9)	1.4(1.2)
C13	2431(10)	4854(12)	4027(5)	3.9(7)	3.2(8)	4.6(8)	0.3(6)	0.4(7)	0.3(7)
C14	3158(10)	4930(13)	4482(5)	4.5(8)	4.0(9)	6.1(9)	0.2(7)	-0.3(7)	0.9(8)
C15	3679(11)	3728(17)	4711(6)	4.6(8)	4.6(1.1)	10.0(1.2)	-0.3(8)	2.2(7)	1.9(1.0)
C16	3396(13)	2442(17)	4477(6)	5.6(1.0)	7.0(1.2)	7.7(1.2)	1.7(9)	2.2(9)	2.4(1.0)
C17	2675(14)	2325(15)	4050(7)	8.4(1.1)	3.8(1.1)	10.1(1.4)	0.1(8)	2.9(1.0)	-1.3(1.0)
C18	2130(11)	3574(15)	3814(6)	6.2(1.0)	5.7(1.0)	8.0(1.2)	-0.5(8)	0.1(8)	-1.5(9)
C19	1078(11)	6057(14)	3148(5)	5.1(9)	6.9(1.0)	4.4(8)	0.4(8)	-0.6(7)	0.0(7)
C20	1654(12)	5993(17)	2683(5)	5.9(1.0)	11.4(1.3)	4.3(8)	-1.4(1.0)	0.3(8)	-1.6(9)
C21	1063(16)	5566(22)	2228(7)	9.5(1.3)	17.1(1.9)	5.4(1.3)	-1.4(1.3)	2.3(1.0)	-2.0(1.3)
C22	-151(18)	5297(21)	2223(7)	10.1(1.5)	16.1(1.8)	5.9(1.3)	-3.1(1.4)	-0.7(1.2)	-1.2(1.3)
C23	-780(14)	5431(24)	2655(6)	6.8(1.2)	21.8(2.4)	5.1(1.1)	-4.2(1.4)	-0.6(1.0)	-1.8(1.4)
C24	-153(12)	5755(19)	3116(5)	5.7(9)	14.6(1.6)	5.0(1.0)	-2.5(1.0)	-1.5(8)	-0.5(1.1)
C25	804(10)	7189(12)	4140(4)	3.7(7)	3.3(9)	3.9(7)	0.2(6)	-0.3(6)	-0.5(7)
C26	168(11)	6334(15)	4447(5)	3.9(8)	5.5(1.0)	6.4(9)	0.1(8)	0.3(7)	2.5(8)
C27	-715(12)	6925(18)	4718(6)	5.5(9)	7.2(1.2)	7.4(1.0)	0.2(9)	0.7(8)	1.0(1.0)
C28	-947(12)	8354(19)	4680(6)	5.1(9)	8.8(1.4)	6.8(1.0)	2.0(9)	0.5(8)	-0.9(1.0)
C29	-277(14)	9176(16)	4368(6)	9.3(1.2)	4.1(1.0)	8.4(1.1)	-0.1(1.0)	0.5(9)	0.3(9)
C30	619(12)	8614(14)	4106(5)	5.5(1.0)	4.4(9)	6.8(1.0)	1.0(8)	1.8(8)	-0.5(8)

Hydrogen atoms** (fractional coordinates $\times 10^3$)

Atom	*x/a*	*y/b*	*z/c*	*U*
H2	317(-)	277(-)	255(-)	7.0(-)
H3	233(9)	310(12)	166(4)	8.9(3.9)
H4	297(8)	185(10)	86(3)	7.6(3.1)
H5	471(-)	6(-)	101(-)	10.3(-)
H6	562(10)	-22(13)	194(5)	17.1(4.9)
H9	637(7)	47(9)	447(3)	7.3(3.0)
H10	774(7)	211(10)	482(3)	6.1(2.9)
H11	864(-)	394(-)	421(-)	8.0(-)
H12	808(-)	374(-)	335(-)	8.9(-)
H14	350(6)	591(7)	462(3)	2.4(2.1)
H15	429(-)	380(-)	506(-)	6.4(-)
H16	363(11)	156(14)	480(5)	18.3(5.0)
H17	260(9)	160(11)	383(4)	8.9(3.9)
H18	167(7)	359(8)	344(3)	4.2(2.5)
H20	247(9)	629(11)	267(4)	9.7(4.1)
H21	145(9)	593(10)	187(4)	7.5(3.5)
H22	-63(-)	496(-)	186(-)	10.7(-)

(continued overleaf)

TABLE II *(continued)*

Atom	x/a	y/b	z/c	U
H23	−175(−)	529(−)	263(−)	11.2(−)
H24	−38(10)	560(13)	347(5)	11.1(4.8)
H26	39(9)	527(11)	443(4)	9.9(3.9)
H27	−121(8)	628(10)	503(4)	7.1(3.4)
H28	−166(9)	905(11)	492(4)	10.1(3.9)
H29	−47(9)	28(11)	430(4)	9.1(3.8)
H30	111(9)	938(11)	391(4)	10.1(3.8)
H01	507(8)	991(10)	388(4)	7.8(3.4)
H02	580(−)	219(−)	292(−)	5.0(−)

*The anisotropic temperature factors employed were of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$. **Hydrogen atoms are numbered according to the atoms to which they are attached; H2, H11, H02 not refined; H5, H12, H15, H22, H23 calculated.

TABLE III. Fractional Atomic Coordinates (X10^4) and Thermal Parameters (X10^2 Å^2)* for (II) with Standard Deviations.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	1689(2)	1351(1)	1746(1)	7.3(1)	7.7(1)	9.2(1)	−0.6(1)	5.4(1)	−0.6(1)
Cl	2109(5)	208(2)	1891(4)	15.9(4)	6.1(2)	22.6(5)	−1.2(2)	15.9(4)	−2.0(3)
S1	2942(3)	2041(2)	1072(3)	7.1(2)	6.9(2)	9.8(3)	0.5(2)	5.3(2)	0.6(2)
S2	104(4)	1835(2)	2375(3)	8.3(2)	6.0(2)	11.0(3)	0.8(2)	6.6(2)	1.7(2)
N1	4675(12)	943(6)	1239(9)	9.0(8)	7.5(8)	11.7(1.0)	−1.0(6)	5.5(7)	−0.5(7)
N2	5317(14)	1931(6)	498(10)	12.2(1.1)	8.9(9)	16.2(1.2)	0.0(8)	11.0(1.0)	0.8(8)
N3	6796(11)	720(6)	831(9)	6.7(7)	9.2(9)	11.6(9)	1.2(6)	4.8(7)	0.9(7)
N4	−144(9)	575(4)	3043(6)	6.6(6)	3.8(5)	7.0(6)	0.4(4)	3.5(5)	0.6(5)
N5	−1393(9)	1438(4)	3563(6)	6.3(6)	5.1(6)	8.3(6)	−0.2(5)	4.9(5)	0.3(5)
N6	−1569(10)	107(5)	3973(7)	8.2(7)	5.9(6)	9.5(8)	0.2(5)	5.9(6)	0.4(6)
C1	5234(19)	2639(6)	191(13)	11.1(1.3)	6.0(9)	11.5(1.3)	−0.8(9)	9.4(1.2)	0.4(9)
C2	4081(15)	2886(9)	−533(11)	6.4(9)	11.1(1.3)	6.9(1.0)	−0.4(9)	3.0(8)	−1.0(9)
C3	4098(18)	3540(10)	−819(12)	9.9(1.3)	11.1(1.3)	9.8(1.3)	1.6(1.1)	5.7(1.1)	2.9(1.1)
C4	5226(23)	3958(8)	−403(15)	14.8(1.5)	6.0(1.1)	15.3(1.6)	0.4(1.1)	11.0(1.4)	1.7(1.1)
C5	6386(18)	3729(10)	345(12)	9.3(1.2)	11.7(1.4)	8.5(1.1)	−3.2(1.1)	2.7(9)	0.1(1.1)
C6	6435(16)	3043(9)	652(10)	7.7(1.1)	13.7(1.4)	7.0(1.1)	−0.4(1.0)	3.2(9)	1.9(1.0)
C7	4345(18)	1612(7)	857(13)	16.1(1.5)	6.3(9)	19.6(1.6)	−0.5(9)	14.7(1.4)	−0.3(1.0)
C8	5816(15)	482(7)	1232(11)	7.1(1.0)	7.8(1.0)	12.0(1.3)	1.1(8)	4.5(9)	0.5(9)
C9	5703(13)	−185(7)	1535(11)	5.6(8)	7.8(9)	13.1(1.2)	0.1(7)	3.3(8)	1.6(9)
C10	6615(17)	−659(7)	1345(11)	12.0(1.2)	5.8(1.0)	11.1(1.2)	0.8(9)	3.9(1.0)	−0.6(9)
C11	7681(21)	−433(9)	937(12)	18.1(1.7)	10.8(1.4)	11.4(1.2)	5.4(1.2)	8.5(1.2)	1.7(1.1)
C12	7679(16)	235(9)	693(10)	8.3(1.1)	10.9(1.3)	7.8(1.0)	2.7(1.0)	2.8(8)	0.5(9)
C13	−507(11)	1236(5)	3050(8)	6.4(7)	5.1(6)	7.6(8)	0.1(5)	3.5(6)	0.6(6)
C14	−655(11)	3(5)	3442(8)	6.0(7)	4.6(6)	6.0(7)	0.7(5)	2.2(6)	0.5(5)
C15	−180(14)	−648(6)	3291(10)	8.8(9)	5.9(7)	11.0(1.1)	0.5(7)	6.2(9)	0.2(7)
C16	−688(15)	−1204(7)	3663(11)	10.0(1.0)	5.8(9)	12.0(1.1)	0.3(8)	4.4(9)	0.7(8)
C17	−1649(16)	−1109(7)	4195(12)	12.0(1.1)	5.8(9)	14.5(1.3)	0.2(8)	7.9(1.0)	2.1(9)
C18	−2049(14)	−465(6)	4321(10)	9.8(1.0)	6.7(8)	11.0(1.1)	−0.6(7)	6.8(9)	1.3(8)
C19	−1857(13)	2138(5)	3617(8)	7.0(8)	5.4(7)	7.3(8)	0.5(6)	5.0(7)	0.3(6)
C20	−867(16)	2612(7)	4156(11)	6.6(1.0)	6.6(8)	13.1(1.2)	−1.0(8)	4.7(1.0)	−2.0(8)
C21	−1315(18)	3280(8)	4213(13)	8.4(1.2)	7.1(1.0)	14.4(1.4)	−1.0(9)	5.3(1.0)	−1.5(1.0)
C22	−2729(17)	3467(8)	3692(12)	10.3(1.2)	6.4(1.1)	12.0(1.2)	2.0(9)	7.1(1.0)	1.5(9)
C23	−3693(18)	2997(8)	3183(11)	8.0(1.2)	9.2(1.1)	8.5(1.1)	2.0(1.0)	4.3(1.0)	1.0(9)
C24	−3278(14)	2315(7)	3135(9)	7.0(9)	7.4(9)	6.7(8)	0.7(7)	3.0(7)	0.5(7)

Hydrogen atoms** (fractional coordinates X10^3)

Atom	x/a	y/b	z/c	U
H01	392(−)	74(−)	161(−)	9.4(−)
H03	656(10)	144(5)	80(7)	14.6(3.2)

(continued on facing page)

TABLE III *(continued)*

Atom	*x/a*	*y/b*	*z/c*	*U*
H04	23(–)	41(–)	258(–)	5.8(–)
H05	–164(9)	102(4)	380(6)	9.0(2.8)
H2	317(10)	262(5)	–108(7)	14.3(3.2)
H3	317(9)	375(4)	–159(6)	10.3(2.7)
H4	529(8)	445(4)	–36(6)	8.5(2.5)
H5	729(10)	419(5)	62(7)	12.3(3.2)
H6	740(11)	291(5)	130(7)	11.3(3.6)
H9	523(10)	–35(5)	198(7)	10.9(33)
H10	668(11)	–112(5)	149(7)	9.5(3.5)
H11	819(11)	–80(6)	77(8)	13.8(3.7)
H12	865(10)	40(5)	41(7)	15.6(3.4)
H15	43(11)	–71(5)	293(8)	8.5(3.5)
H16	–33(11)	–170(6)	367(8)	7.9(3.6)
H17	–186(12)	–156(6)	448(8)	8.7(4.0)
H18	–260(11)	–36(5)	484(8)	7.6(3.4)
H20	14(12)	250(6)	452(8)	8.5(4.1)
H21	–37(13)	364(6)	467(9)	11.0(4.3)
H22	–303(12)	390(6)	366(8)	6.6(4.1)
H23	–468(13)	296(6)	268(8)	9.9(3.9)
H24	–400(11)	199(5)	273(7)	7.1(3.3)

*The anisotropic temperature factors employed were of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$. **Hydrogen atoms are numbered according to the atoms to which they are attached; H01 and H04 are calculated.

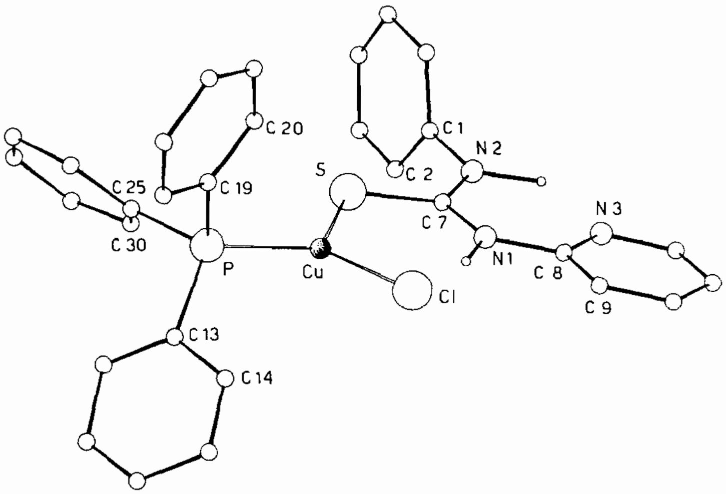

Fig. 1. Molecular structure of (I). Aromatic hydrogen atoms are not included.

In (I) the distance Cu–P (2.206 Å) is within the range of those found in a number of copper(I) compounds with one phosphine ligand [10], but shorter than the similar interactions in the four-coordinate copper atom [11]. However, judging from the values found in $[Cu(PPh_3)Cl]_4$ (2.193; 2.192 Å) [4], the Cu–P distances do not appear to be greatly affected by coordination number but rather by the number of phosphine ligands bound to the same metal center and by steric repulsions [5, 6]. The Cu–Cl bond lengths (2.238 for (I) and 2.248 Å for (II)) are influenced by the change in coordination number [10]. In fact $[Cu(PPh_3)Cl]_4$, starting material in the synthesis of the two complexes owing to tetrahedral environment of metal and triply bridging chlorine atoms, shows Cu–Cl bonds significantly longer (mean value 2.444 Å) than those shown in the present paper.

The Cu–S distances (2.218 Å in (I); 2.214, 2.213 Å in (II)), approximately equal for both compounds, are shorter than those found in other three-coordinate copper(I) complexes with non-bridging

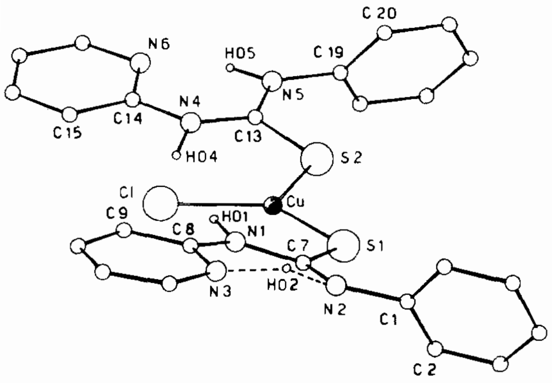

Fig. 2. Molecular structure of (II). Aromatic hydrogen atoms are not included.

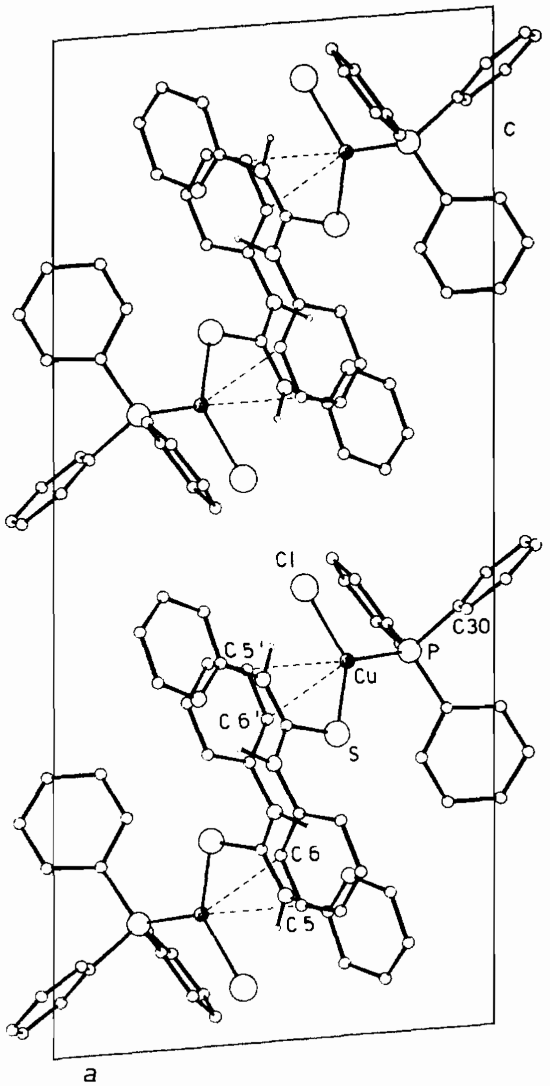

Fig. 3. Projection of (I) on the (010) plane. The aromatic hydrogen atoms have been omitted for clarity.

Cu–S bonds (2.23–2.26 Å) [12–18], and show strong copper–sulphur bond energies. The shortening of the Cu–S and Cu–Cl distances in trigonal Cu(I) compounds (the sum of the single-bond covalent radii is 2.39 and 2.41 Å respectively) has been observed previously [5, 6, 11, 18] and can be attributed to the difference in steric repulsion around the tetrahedral and trigonal copper atoms [19]. However metal–ligands multiple bonding may also account for this shortening. It can be observed that a monomeric trigonal copper(I) complex still has some vacant coordinating positions and so an other different ligand can also be accommodated, as is found in square-planar copper(II) complexes. This fact may have important implications in understanding the biological activity of the redox-couple Cu(I)–Cu(II).

In (I) the three independent phosphorus–carbon bond lengths are in good agreement with those found in other copper(I) triphenylphosphine complexes [4, 10, 11]. The Cu–P–C13 and Cu–P–C19 angles (113.9, 117.7°) deviate significantly from the ideal tetrahedral value, but the Cu–P–C25 (109.9°) is smaller, probably for copper phenyl–hydrogen non-bonded contact. The C–P–C angles are all less than the ideal tetrahedral angle [4, 10, 11] (Table IV). The three carbocyclic phenyl rings are planar within the limits of experimental error, and the C–C distances are in the usual range.

In (I) the Cu–S–C angle is 109.6°. The S–C distance 1.72(1) Å is comparable to those found for free thiourea at 1.720(9) Å from the X-ray data [20]. The central C–N distances of the thiourea group are shorter (1.33, 1.33 Å) than the terminal ones (1.44, 1.43 Å). The orientation of the thiourea and pyridine groups, relative to the central CuClSP unit, appears to be determined by hydrogen interaction between N1 and chlorine atoms (N1···Cl = 3.16 Å) and by short intramolecular hydrogen bond (N2···N3 = 2.67 Å). The torsion angles Cu–S–C–N1 and Cu–S–C–N2, are −2.6° and 1.2° respectively. The benzene and pyridine rings are strictly planar (excluding hydrogen atoms) and the dihedral angle between them is 92.7°. Packing requirements probably give rise to rotation of the benzene moiety so that this latter is placed parallel to coordination plane at 1/2 − x, 1/2 + y, 1/2 − z. So a long interaction between copper and C5–C6 bond, responsible for the formation of dimers (Fig. 3), is determined. The pptu molecule behaves as a monodentate ligand as in $BiCl_3(pptu)_3$ [21], and not as postulated by Krishnaswami and Bharghava [22] from IR spectral studies. The donor

TABLE IV. Interatomic Distances and Angles with Esd for (**I**).

a. Interatomic Ditances (Å)*

Cu–Cl	2.238(4)	Cu–A^a	3.39(2)
Cu–S	2.218(4)		
Cu–P	2.206(4)		

Triphenylphosphine

P–C13	1.83(1)	C21–C22	1.40(3)
P–C19	1.80(1)	C22–C23	1.38(3)
P–C25	1.83(1)	C23–C24	1.38(2)
C13–C14	1.39(2)	C19–C24	1.42(2)
C14–C15	1.40(2)	C25–C26	1.38(2)
C15–C16	1.40(2)	C26–C27	1.39(2)
C16–C17	1.33(2)	C27–C28	1.39(2)
C17–C18	1.46(2)	C28–C29	1.40(2)
C13–C18	1.37(2)	C29–C30	1.38(2)
C19–C20	1.42(2)	C25–C30	1.38(2)
C20–C21	1.38(2)		

1-Phenyl-3-(2-pyridyl)-2thiourea

S–C7	1.72(1)	C2–C3	1.42(3)
N1–C7	1.33(1)	C3–C4	1.37(3)
N1–C8	1.43(2)	C4–C5	1.36(3)
N2–C1	1.44(2)	C5–C6	1.37(2)
N2–C7	1.33(2)	C1–C6	1.44(2)
N3–C8	1.33(2)	C8–C9	1.39(2)
N3–C12	1.36(2)	C9–C10	1.35(2)
C1–C2	1.41(2)	C10–C11	1.36(2)
		C11–C12	1.37(2)
		N1–H01	1.04(10)
		N2–H02	1.24(–)

b. Selected Bond Angles (deg)

Cl–Cu–S	121.0(2)	C19–P–C25	102.8(6)
Cl–Cu–P	114.8(2)	C13–P–C25	105.7(5)
P–Cu–S	123.0(2)	C13–P–C19	105.7(6)
Cl–Cu–A^a	92.7(4)	S–C7–N2	120.6(9)
S–Cu–A	94.9(4)	S–C7–N1	118.4(9)
P–Cu–A	93.3(5)	N1–C7–N2	120.9(1.1)
Cu–S–C7	109.6(5)	C7–N1–C8	128.5(1.0)
Cu–P–C13	113.9(4)	C7–N2–C1	124.1(1.1)
Cu–P–C19	117.7(5)		
Cu–P–C25	109.9(4)		

^{a}A is the midpoint of the (C5–C6) bond.

c. Dihedral Angles (deg) in pptu

Plane 1	Plane 2	Dihedral angle
phenyl ring	pyridine ring	92.7(4)
phenyl ring	coordination plane	91.4(3)
pyridine ring	coordination plane	4.1(3)

*The 24 independent hydrogen–carbon bond distances range from C–H = 0.89 Å up to C–H = 1.25 Å. The average value is 1.09 Å.

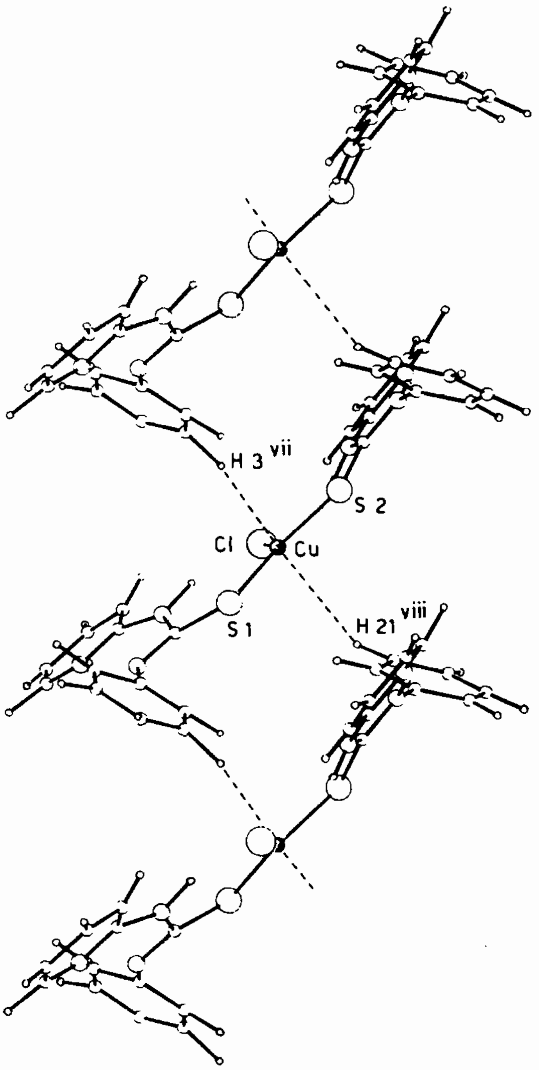

Fig. 4. Packing diagram of (II) showing the copper–hydrogen interactions.

atom is the sulphur, the pyridyl nitrogen being involved in the intramolecular NH···N hydrogen bond.

In (**II**) two independent molecules of pptu are present. There are no significant differences between corresponding distances and angles of the pptu in (**II**) and (**I**) (Tables IV and V). The angles Cu–S1–C7, Cu–S2–C13 are not far from the tetrahedral values (111.1, 110.0°). The dihedral angles between the benzene and pyridine rings in the two independent molecules are similar (65.1, 67.5°) but smaller than those found in (**I**) (92.7°) and in BiCl$_3$(pptu)$_3$ [21] (77.7°). This result is perhaps a consequence of electronic, steric and crystal packing factors. The nitrogen atoms

TABLE V. Interatomic Distances and Angles with Esd for (**II**).

a. Interatomic Distances (Å)*			
Cu–Cl	2.248(4)		
Cu–S1	2.214(5)		
Cu–S2	2.213(5)		
Cu···H3^{vii}	2.37(8)		
Cu···H21^{viii}	3.01(10)		
Molecule 1		Molecule 2	
S1–C7	1.70(2)	S2–C13	1.72(1)
N1–C7	1.40(2)	N4–C13	1.33(1)
N1–C8	1.43(2)	N4–C14	1.40(1)
N2–C1	1.43(2)	N5–C19	1.44(1)
N2–C7	1.35(2)	N5–C13	1.35(2)
N3–C8	1.33(2)	N6–C14	1.35(2)
N3–C12	1.33(2)	N6–C18	1.35(2)
C1–C2	1.35(2)	C19–C20	1.38(2)
C1–C6	1.39(2)	C20–C21	1.38(2)
C2–C3	1.33(3)	C21–C22	1.39(2)
C3–C4	1.34(2)	C22–C23	1.35(2)
C4–C5	1.36(2)	C23–C24	1.39(2)
C5–C6	1.39(3)	C19–C24	1.38(2)
C8–C9	1.38(2)	C14–C15	1.38(2)
C9–C10	1.36(2)	C15–C16	1.36(2)
C10–C11	1.40(3)	C16–C17	1.38(3)
C11–C12	1.34(2)	C17–C18	1.33(2)
N1–H01	1.10(–)	N4–H04	0.91(–)
N2–H02	1.50(9) **	N5–H05	0.94(9)
N3–H02	1.41(9)		
b. Selected Bond Angles (deg)			
C1–Cu–S1	121.7(2)	Cu–S1–C7	111.1(5)
Cl–Cu–S2	120.6(2)	Cu–S2–C13	110.0(4)
S1–Cu–S2	117.6(2)	C7–N1–C8	131.4(1.3)
Cl–Cu···H3^{vii}	77.9(3.0)	C1–N2–C7	124.8(1.4)
S1–Cu···H3^{vii}	103.6(4.3)	C13–N5–C19	124.5(9)
S2–Cu···H3^{vii}	85.1(3.2)	C13–N4–C14	129.0(9)
C1–Cu···H21^{viii}	98.2(4.8)		
S2–Cu···H21^{viii}	93.2(4.9)		
S1–Cu···H21^{viii}	82.1(4.1)		
c. Dihedral Angles (deg)			
	Molecule 1		Molecule 2
pyridine ring phenyl ring	65.1(4)°		67.3(4)°
pyridine ring coordination plane	–5.9(3)		–6.1(3)
pyridine ring CuS2C13N4Cl	8.5(3)		6.0(3)
pyridine ring CuS1C7N1Cl	1.8(3)		13.3(3)
phenyl ring coordination plane	109.5(3)		116.9(3)
pyridine ring N3C8N1C7N2H03	10.3(5)	pyridine ring N6C14N4C13N5H05	2.1(4)
pyridine ring 1 pyridine ring 2	12.0(4)		

*The 18 independent hydrogen-carbon bond distances range from C–H = 0.88 Å up to C–H 1.25 Å. The average value is of 1.04 Å. **The HO2 hydrogen atom is half-way through N2, N3 atoms (Fig. 2).

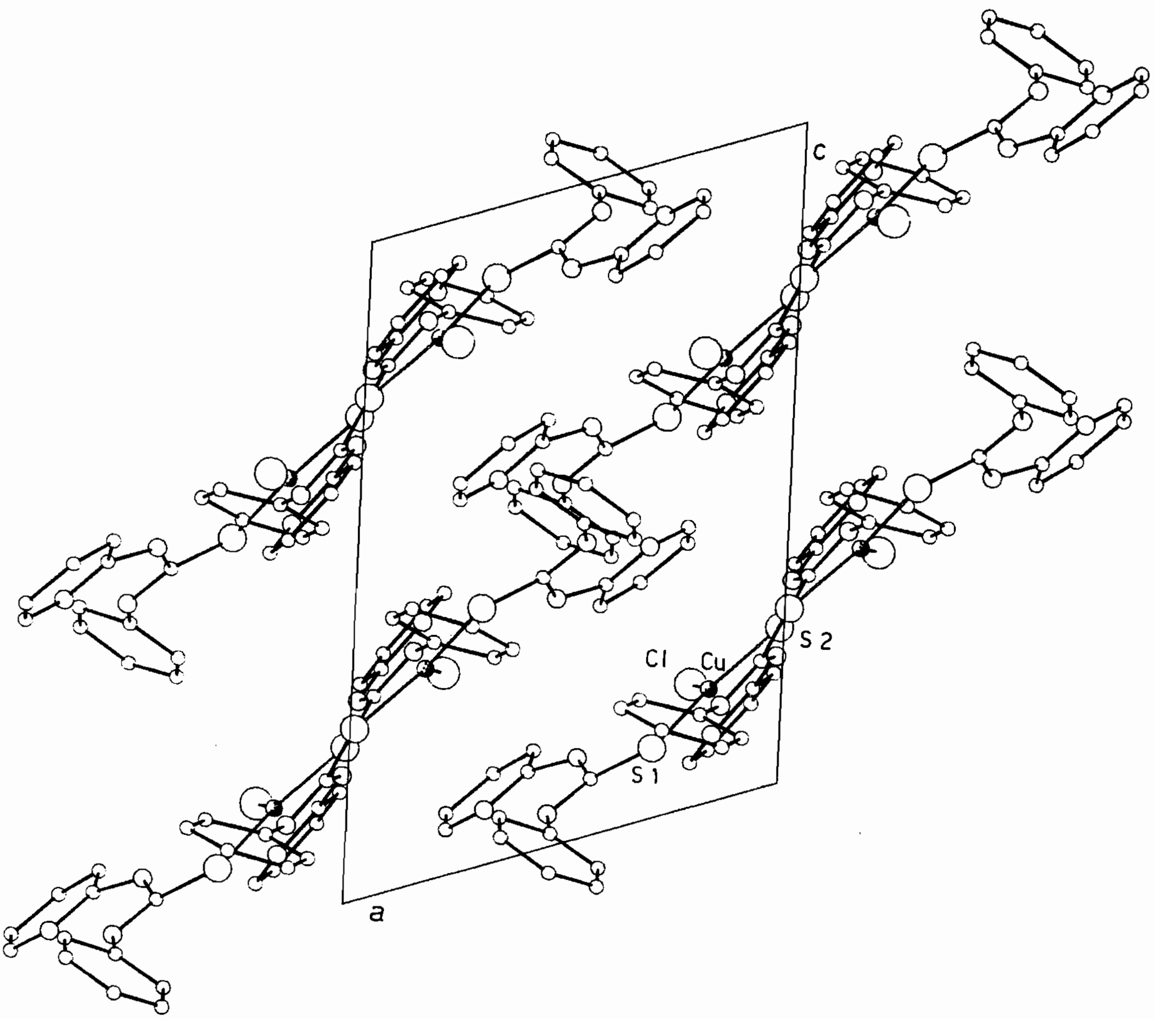

Fig. 5. Projection of (II) on the (010) plane. The hydrogen atoms have been omitted for clarity.

TABLE VI. Contacts less than 3.7 Å.

(a) for (I)			
Cu$\cdots$C5$^{\mathrm{i}}$	3.44(2)	C2$\cdots$C23$^{\mathrm{ii}}$	3.68(2)
Cu$\cdots$C6$^{\mathrm{i}}$	3.47(2)	Cl$\cdots$N1	3.16(1)
Cu$\cdots$C30	3.40(1)	Cl$\cdots$C9$^{\mathrm{iii}}$	3.55(1)
N2$\cdots$N3	2.67(1)	S$\cdots$Cl$^{\mathrm{i}}$	3.64(2)
N3$\cdots$C5$^{\mathrm{v}}$	3.58(3)	S$\cdots$C23$^{\mathrm{ii}}$	3.62(2)
N3$\cdots$C6$^{\mathrm{v}}$	3.67(2)	N1$\cdots$C3$^{\mathrm{i}}$	3.59(2)
C3$\cdots$N1$^{\mathrm{v}}$	3.59(2)	N1$\cdots$C17$^{\mathrm{iv}}$	3.68(2)
C12$\cdots$C5$^{\mathrm{v}}$	3.42(3)	C28$\cdots$C29$^{\mathrm{vi}}$	3.62(2)
C21$\cdots$N3$^{\mathrm{i}}$	3.54(2)	C29$\cdots$C29$^{\mathrm{vi}}$	3.66(2)
C21$\cdots$C12$^{\mathrm{i}}$	3.62(3)		
(b) for (II)			
Cu$\cdots$C3$^{\mathrm{vii}}$	3.53(1)	C14$\cdots$C10$^{\mathrm{x}}$	3.56(2)
Cl$\cdots$N1	3.24(1)	C15$\cdots$C10$^{\mathrm{x}}$	3.47(2)
Cl$\cdots$N4	3.19(1)	C16$\cdots$C10$^{\mathrm{x}}$	3.67(2)
N2$\cdots$N3	2.71(2)	N4$\cdots$C11$^{\mathrm{x}}$	3.65(2)
N5$\cdots$N6	2.66(1)	C14$\cdots$C11$^{\mathrm{x}}$	3.53(2)
N3$\cdots$C22$^{\mathrm{ix}}$	3.58(2)	C15$\cdots$C11$^{\mathrm{x}}$	3.37(2)
Cl$\cdots$C23$^{\mathrm{ix}}$	3.55(3)	N4$\cdots$C12$^{\mathrm{x}}$	3.42(1)
Cl$\cdots$C24$^{\mathrm{ix}}$	3.64(3)	C23$\cdots$C2$^{\mathrm{xi}}$	3.66(3)
C2$\cdots$C24$^{\mathrm{ix}}$	3.65(2)	C10$\cdots$N1$^{\mathrm{xii}}$	3.54(2)
C24$\cdots$N2$^{\mathrm{x}}$	3.64(2)	C11$\cdots$N1$^{\mathrm{xii}}$	3.38(2)
N4$\cdots$N3$^{\mathrm{x}}$	3.61(1)	C9$\cdots$N3$^{\mathrm{xii}}$	3.64(2)
C13$\cdots$N3$^{\mathrm{x}}$	3.56(1)	C10$\cdots$C7$^{\mathrm{xii}}$	3.50(2)
C23$\cdots$C6$^{\mathrm{x}}$	3.64(2)	C11$\cdots$C7$^{\mathrm{xii}}$	3.53(2)
C24$\cdots$C7$^{\mathrm{x}}$	3.61(2)	C10$\cdots$N2$^{\mathrm{xii}}$	3.66(2)

i	$1 - x, y - 1/2, 1/2 - z$	vii	$x, 1/2 - y, 1/2 + z$
ii	$\bar{x}, y + 1/2, 1/2 - z$	viii	$x, 1/2 - y, z - 1/2$
iii	$1 - x, 2 - y, 1 - z$	ix	$x + 1, 1/2 - y, z - 1/2$
iv	$x, y + 1, z$	x	$x - 1, y, z$
v	$1 - x, y + 1/2, 1/2 - z$	xi	$x - 1, 1/2 - y, 1/2 + z$
vi	$\bar{x}, 2 - y, 1 - z$	xii	$1 - x, \bar{y}, \bar{z}$

of the thiourea groups are involved in hydrogen bonds (N5···N6 = 2.66, N2···N3 = 2.71, N4···Cl = 3.19, N1···Cl = 3.24 Å) and the organic molecules behave as monodentate ligands through sulphur atoms as found in (**I**). The pyridine moieties are perfectly planar and almost coplanar with the thiourea groups and the coordination plane (Table V).

The phenyl ring of both pptu molecules is tilted and directs a hydrogen atom towards the copper atom opposite (Table V and Fig. 4).

In (**I**) the formation of dimers is observed (Fig. 3). There is no evidence for quasi-graphitic stacking of phenyl rings, as found in other similar compounds [10, 11], but the shorter contacts involve only the pyridinic groups.

In (**II**) the molecules are linked in polymeric chains running along [001] by axial copper-hydrogen interactions (Fig. 4). The packing is favoured by the tendency of pyridinic rings, belonging to different molecules related by the inversion centre and translated by the screw axis, to form almost parallel

TABLE VII. Selected Infrared Spectroscopic Data (cm^{-1}).

[Cu(PPh$_3$)Cl]$_4$	pptu	Cu(pptu)$_2$Cl	Cu(PPh$_3$)(pptu)Cl	Assignment
	3220m			
		3200mw	3200mw	
	3170mw			ν(NH)
		3160m	3160mw	
	3100mw	3100mw	3100mw	
	3080w	3080w	3080w	
3050m				
	3040m,br	3040m,br	3040m	ν(CH)
			3020(sh)	
			3000m,br	
	1600vs	1600vs	1600vs	ν(CC), δ(NH)py
1580w				ν(CC)
	1550vs			
		1540s	1540s	
	1530vs	1530vs	1530vs	
	1490w	1490(sh)	1490(sh)	ν(CC), ν(CN)py
1480s		1480vs		
	1470vs		1470vs	
	1445w	1445w	1445w	
1435vs		1435s		ν(CC), ν(CS), ν(NCN)
	1430s		1430vs	
1185w			1185s	
		1150vs		δ(CH)in
	1140vs		1140vs	
1095s			1095s	δ(CH)in, ν(PC)
1030m			1030m	δ(CH)in
1000m			1000m	
		780(sh)	780vs	
	775vs	775vs		δ(CH)out
			755s	
750(sh)				
745vs	740s	740s	740vs	
		730(sh)	730(sh)	ν(CS), ν(NCN)
	720w,br	720w,br		
700vs			700vs	δ(CH)out, ν(PC)
	690vs	690vs	690vs	ν(NH), ν(CS), ν(NCN)
	655s	645(sh)		
	640s	635s	635s	
530s				
520vs	515vs		520vs	ring skeletal
500s		500s	500s	
495(sh)			490s	
440w,br				
			430w,br	ring skeletal, ν(PC)
420(sh)				

couples which generate charge-transfer interactions [10] (Fig. 5). The distances between the pairs of pyridine molecules are in the range 3.37–3.67 Å. Contacts <3.7 Å are listed in Table VI for both complexes.

The vibrational spectra were registered in the range 4000–200 cm^{-1}. Selected absorption bands of the two reagents, [Cu(PPh$_3$)Cl]$_4$ and pptu, and of the two complexes Cu(PPh$_3$)(pptu)Cl and Cu(pptu)$_2$Cl are reported and compared in Table VII.

The i.r. spectra of the two complexes are almost similar, both being mainly characterized by vibrational absorptions of coordinated pptu, which are scarcely influenced by coordination to copper. The more significant shifts are observed for the bands of the NH and CS groups, while the vibrational absorptions of the aromatic rings are practically unchanged with respect to those of free pptu.

The ν(NH) bands in particular undergo more remarkable shifts towards lower frequency values, which can be explained by the hydrogen bonds present in the two complexes.

The coordination influences the bands of the C=S groups which shift in the range of 5–10 cm^{-1}; these values are in agreement with those reported for other thiourea–metal complexes [22–24]. It is interesting to note that in Cu(pptu)$_2$Cl some bands are split with respect to those present in the spectrum of Cu(PPh$_3$)(pptu)Cl; this fact can be due to the presence in the former compound of two molecules of pptu.

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