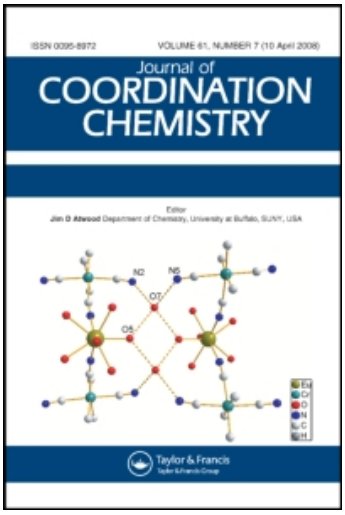

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Synthesis, characterization and crystal structure of copper(I) tetra(phenyl thiourea) chloride

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Synthesis, characterization and crystal structure of copper(I) tetra(phenyl thiourea) chloride

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The title compound $C_{28}H_{32}N_8S_4ClCu$ has been synthesized, crystallized and characterized by density measurement, element analysis and IR spectra. Its crystal structure has been determined by X-ray diffraction methods. The most interesting structure feature of the complex is that the dihedral angle between the thiourea framework and the benzene ring is 52.03(22)°, the minimal value in the literature. All four bonds around Cu(I) are equivalent, but the six S–Cu–S angles are non-equivalent.

Keywords: Supermolecular complex; Phenyl thiourea; Crystal structure; Bioactivity

1. Introduction

Thiourea and its substituted derivatives are of great importance in biology and medicine [1, 2] because of their prominent bioactivity, including anti-HIV properties [3–5]. It appears that Cu(I,II) ions also have this bioactivity. Therefore, we synthesized the title supermolecular complex.

2. Experimental

2.1. *Preparation*

About 0.34 g (2 mmol) of $CuCl_2 \cdot 2H_2O$ and 1.21 g (8 mmol) of phenyl thiourea (PTU) were each dissolved in 10 mL of methanol. The two solutions were mixed together and refluxed for 10 min. Finally, the resulting yellow liquid was cooled, filtered and left for several days until it gave well-formed, yellow, single crystals.

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2.2. *Density measurement*

The density measured by the mixture solution method is 1.39 g cm^{-3}; the actual density is 1.384 g cm^{-3}.

2.3. *Elemental analysis*

C, H and N were analyzed by an Eager-200 element analysis instrument. Anal. Calcd for $C_{28}H_{32}N_8S_4ClCu$ (%): C, 47.51; H, 4.56; N, 15.83. Found: C, 47.55; H, 4.34; N, 15.81.

2.4. *Infrared spectra*

An infrared spectrum was recorded with a Shimadzu IR-470 spectrophotometer (4000–400 cm^{-1}) by use of a powdered sample spread on a KBr plate.

2.5. *Crystal structure determination*

A yellow crystal of the title complex with approximate dimensions $0.32 \times 0.24 \times 0.22$ mm was mounted on a glass fibre. X-ray intensity data were collected on a Bruker APEX area-detector diffractometer up to a 2θ value of 55.0° with graphite-monochromatized MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) by the ω–2θ scan technique. A total 1399 independent reflections were collected, of which 1161 reflections were considered as observed [$I > 2\sigma(I)$] and used for the structure determination. Usual Lp and empirical adsorption corrections were applied [6].

The structure was solved by the Patterson method followed by Fourier syntheses. Structure refinement was carried out by full-matrix least-squares procedures using the SHELXL-97 program [7]. H atoms on imino groups were located in a difference Fourier map, others were located by using the theoretical method. Anisotropic refinement including all the non-H atoms converged to agreement factors with $R = 0.047$ and $Rw = 0.052$, where $w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors were taken from International Tables for X-ray Crystallography [8].

3. Results and discussion

3.1. *Crystal structure*

3.1.1. Crystal data. $[Cu(PTU)_4] \cdot Cl$, $Mw = 707.90$, tetragonal, Space group I-4, $a = b = 11.4734(16)$, $c = 12.904(3)$ Å, $V = 1698.7(5)$ Å^3, $Z = 2$, $D_c = 1.384$ g cm^{-3}, $F(000) = 732$, $\mu(\text{MoK}_\alpha) = 9.99$ cm^{-1}, $T = 295(2)$ K, $\theta = 2.4$–$27.5°$, CCDC 256792.

3.1.2. Data collection. Absorption correction: multi-scan (ABSCOR; Higashi, 1995), $R_{int} = 0.041$, $T_{min} = 0.768$, $T_{max} = 0.887$, $\theta_{max} = 27.5°$, $h = -13 \rightarrow 14$, $k = -8 \rightarrow 14$, $l = -16 \rightarrow 13$.

3.1.3. Refinement. Refinement on F^2, $R[F^2 > 2\sigma(F^2)] = 0.047$, $wR(F^2) = 0.1073$, $S = 0.945$, 1399 reflections, 95 parameters, $(\Delta/\sigma)_{max} = 0.000$, $\Delta\rho_{max} = 0.26$ e Å^{-3}, $\Delta\rho_{min} = -0.30$ e Å^{-3}.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	$U_{iso/eq}$
Cu	0.0000	0.0000	0.0000	0.0569(3)
Cl	0.0000	0.5000	0.2500	0.0540(5)
S	0.00998(13)	0.17322(9)	0.09424(8)	0.0581(3)
N1	−0.1134(4)	0.2537(4)	0.2496(4)	0.0761(13)
N2	−0.1416(4)	0.0601(3)	0.2121(3)	0.0548(9)
C1	−0.0895(4)	0.1626(4)	0.1922(3)	0.0511(9)
C2	−0.2087(4)	0.0334(4)	0.3030(3)	0.0516(9)
C3	−0.3057(4)	0.0967(5)	0.3288(5)	0.0705(13)
C4	−0.3654(5)	0.0704(6)	0.4192(5)	0.0850(18)
C5	−0.3308(5)	−0.0187(8)	0.4811(5)	0.094(2)
C6	−0.2381(6)	−0.0878(8)	0.4513(5)	0.098(2)
C7	−0.1730(5)	−0.0594(5)	0.3638(4)	0.0705(13)

$U_{eq} = 8/3\pi(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{z23}bb^*cc^*\cos\alpha)$.

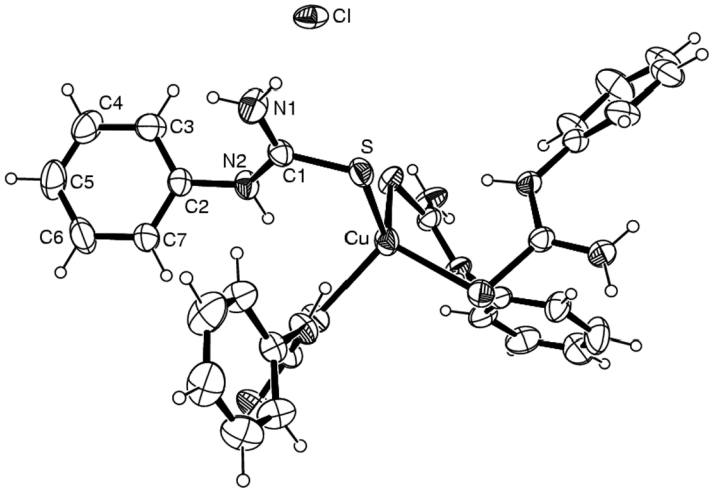

Figure 1. Structure of the title complex showing 30% probability displacement ellipsoids and the atom-numbering scheme.

Fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in table 1. The molecular structure of the title complex is illustrated in figure 1 with the atom-numbering scheme. The crystal packing is illustrated in figure 2.

The Cu(I) has a tetrahedral coordination geometry. Each phenyl thiourea bonds a sulfur atom to a dsp^2 hybridized orbital of Cu(I). All four bonds around Cu(I) are 2.332 (1) Å. However, the six S–Cu–S angles are non-equivalent.

The imino group (N2–H2) on phenyl thiourea and the S atom on the opposite phenyl thiourea $(1-x, 1-y, z)$ form a hydrogen bond (N–H···S). In the same way, the S atom on phenyl thiourea and the imino group (N2–H2) on the opposite phenyl thiourea $(1-x, 1-y, z)$ form another hydrogen bond (N–H···S). A list of H-bonds is given in table 2, and illustrated in figure 3. The other two opposite phenyl thioureas in the

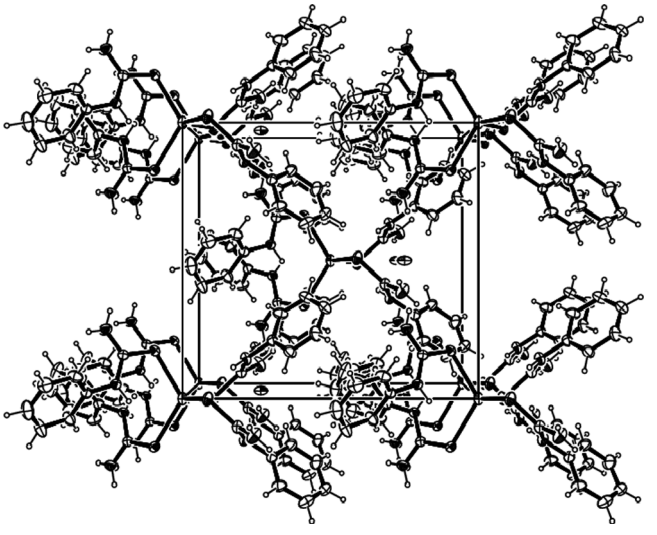

Figure 2. A view of the crystal packing showing 30% probability displacement ellipsoids down the *a* axis for $[Cu(PTU)_4]\cdot Cl$.

Table 2. Hydrogen bonds in title complex.

H-bonds	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
N2–H2···S[a]	0.86	2.67	3.429(4)	148
N1–H1B···Cl	0.86	2.27	3.111(5)	165

Symmetry code: [a]$1-x, 1-y, z$.

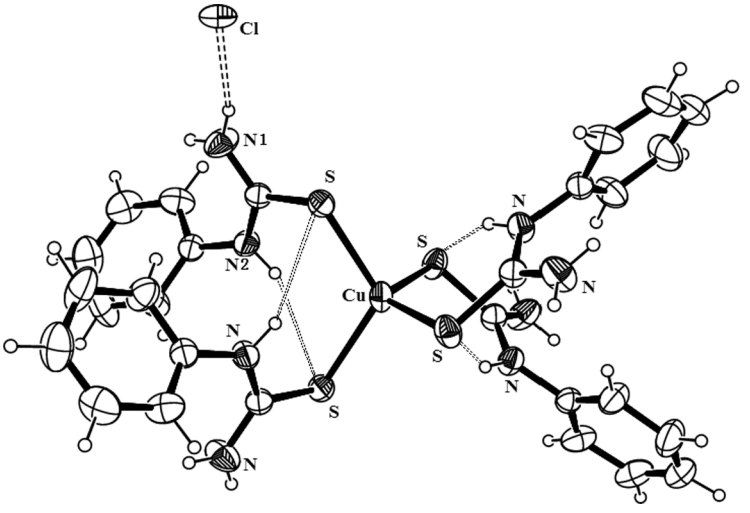

Figure 3. The hydrogen bonds within two pair of PTUs as well as between amino group and chlorine anion. The hydrogen bonding gives two types of S–Cu–S bond angles.

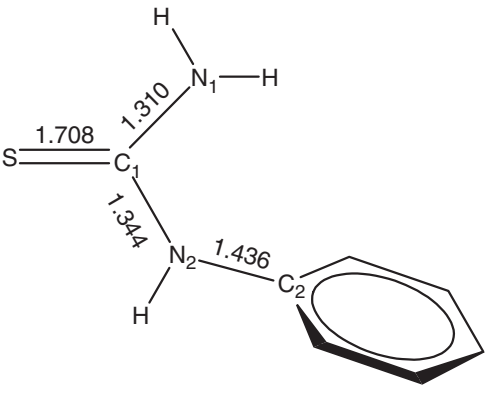

Figure 4. The bond distances of the thiourea framework in crystal.

complex also have the same interaction. The S–Cu–S angles between phenyl thioureas which have two hydrogen bonds are 117.16(5)°, and all the others are 105.77(2)°.

The most interesting structure feature of the complex is that the dihedral angle of the thiourea framework and the benzene ring is 52.03(22)°. This is the smallest value in the literature. Wang reports 63.5 and 68.6° [9] and Mao reports 70.1 and 80.3° for this dihedral angle [10]. This indicates that conjugate effects between the thiourea framework and the benzene ring do not exist. The bond length of C2–N2, 1.436(5) Å, is consistent with the above conclusion. The bonds for thiourea are shown in figure 4.

3.2. *Infrared spectra*

The stretching vibrations of the N–H bond in the amino groups and imino group, which links the hydrogen bond, are 3241.82 and 3127.74 cm^{-1}, respectively. The free N–H bond, which does not link the hydrogen bonds in the amino group, is 3427.47 cm^{-1}. The distortion vibration of the amino group is 1617.98 cm^{-1}.

Furthermore, the stretching vibrations at 1513.96, 1448.03, 1319.28, 1297.53, 1057.57, 751.05 and 696.70 cm^{-1} indicate the coupling between the C=S double bond and two different C–N single bonds. These specific infrared vibrations of the complex crystal are similar with those of free phenyl thiourea.

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