

Tetrakis(phenylthiourea- κ S)copper(I) chlorideYu Liu[‡] and Duan-Jun Xu*Department of Chemistry, Zhejiang University,
People's Republic of China[‡] Department of Chemical Engineering,
Shandong Institute of Light Industry, People's
Republic of China

Correspondence e-mail: xudj@mail.hz.zj.cn

The Cu^I atom of the title complex, [Cu(C₇H₈N₂S)₄]Cl, is located on a $\bar{4}$ inversion axis and has distorted tetrahedral coordination geometry, formed by four phenylthiourea S atoms. Within the phenylthiourea ligands, the C–N(imino) bonds [1.341 (2) Å] are significantly longer than the C–N(amino) bonds [1.316 (3) Å]. The Cl[−] anion is located on another $\bar{4}$ inversion axis and links with four complex cations *via* N–H...Cl hydrogen bonding.

Received 23 June 2004

Accepted 29 June 2004

Online 9 July 2004

Key indicators

Single-crystal X-ray study

T = 295 K

Mean σ (C–C) = 0.004 Å

R factor = 0.026

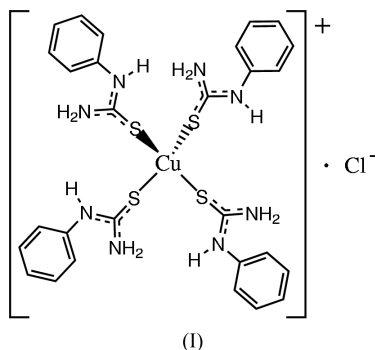
wR factor = 0.065

Data-to-parameter ratio = 18.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

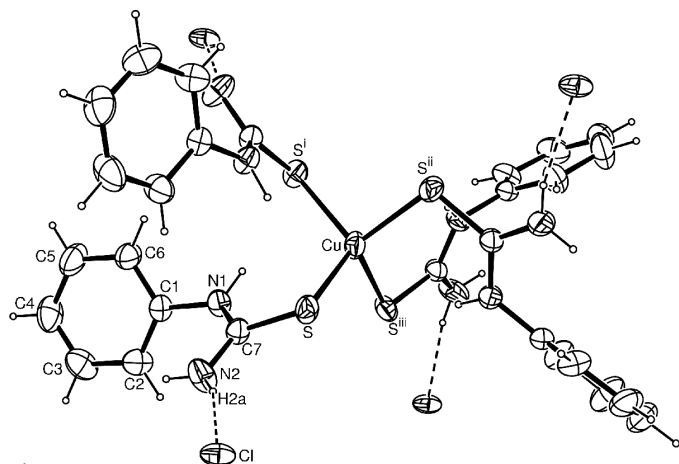
Comment

The significant difference between C–N(imino) and C–N(amino) bond distances within phenylthiourea has recently been revealed (Shen & Xu, 2004). The title complex, (I), incorporating phenylthiourea, has been prepared and its crystal structure determined in order to compare the structure of phenylthiourea in the free compound with that in the metal complex.

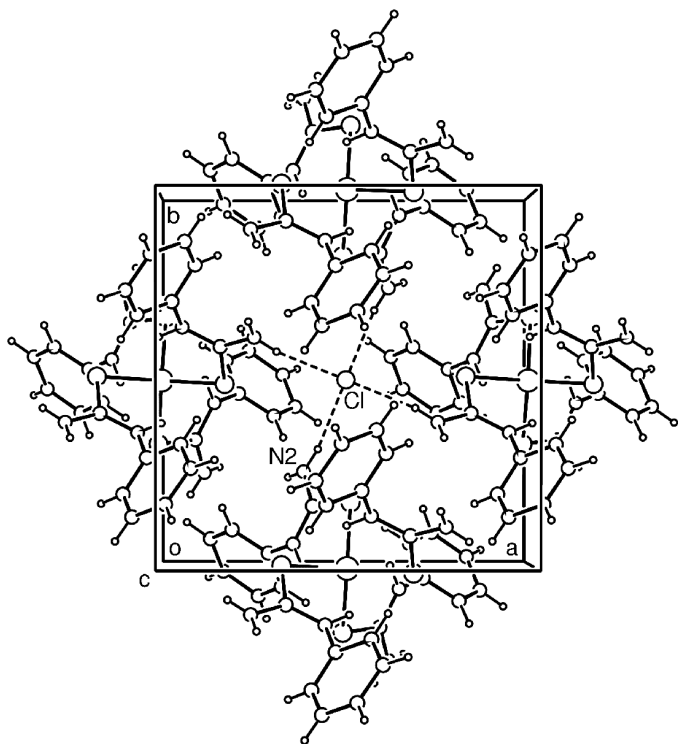


The molecular structure of (I) is illustrated in Fig. 1. The Cu^I atom is located on a $\bar{4}$ inversion axis and has a distorted tetrahedral coordination geometry, formed by four phenylthiourea molecules. The Cu–S bond distance of 2.3313 (5) Å is comparable to 2.3661 (7) Å found in a tetrahedral thiourea complex of Cu^I (Li, 2004), and longer than 2.2121 (10) Å found in a trigonal planar thiourea complex of Cu^I (Wu *et al.*, 2002). The S–Cu–Sⁱ angle [117.38 (2)°] is larger than the S–Cu–Sⁱⁱ angle [105.666 (10)°] (Fig. 1) (for symmetry codes, see Table 1).

The N–S and N–C bond distances (Table 1) both show electron delocalization within the phenylthiourea moiety. The thiourea mean plane is tilted with respect to the phenyl plane, with a dihedral angle of 52.55 (9)°, which suggests that there is no conjugation effect between the thiourea and phenyl groups. The C7–N1(imino) bond [1.341 (2) Å] is 0.025 (3) Å longer than the C7–N2(amino) bond [1.316 (3) Å]. This difference is essentially the same as found in free phenylthiourea


Figure 1

The molecular structure of (I) with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonding between ions. [Symmetry codes: (i) $1-x, -y, z$; (ii) $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z$; (iii) $\frac{1}{2}-y, x-\frac{1}{2}, \frac{3}{2}-z$].


Figure 2

A molecular packing diagram showing four hydrogen bonds (dashed lines) around the Cl^- anion.

[0.019 (3) Å; Shen & Xu, 2004] and may be due to the induction effect of the phenyl group on the imino group.

The Cl anion is also located on a $\bar{4}$ inversion axis and links with four Cu^{I} complex cations *via* $\text{N2}-\text{H2a}\cdots\text{Cl}$ hydrogen bonds, as shown in Figs. 1 and 2. The $\text{N2}\cdots\text{Cl}$ distance and $\text{N2}-\text{H2a}\cdots\text{Cl}$ angle are 3.4284 (17) Å and 168 (2)°, respectively.

Experimental

An ethanol solution (10 ml) of phenylthiourea (0.30 g, 2 mmol) was mixed with an aqueous solution (3 ml) of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.17 g,

1 mmol). The resulting green solution was refluxed for 1 h and then filtered to remove the white precipitate. Pale-yellow single crystals were obtained from the filtrate after 3 d.

Crystal data

$[\text{Cu}(\text{C}_7\text{H}_8\text{N}_2\text{S})_4]\text{Cl}$
 $M_r = 707.85$
 Tetragonal, $I\bar{4}$
 $a = 11.4847$ (3) Å
 $c = 12.8612$ (4) Å
 $V = 1696.37$ (8) Å³
 $Z = 2$
 $D_x = 1.386$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 7866 reflections
 $\theta = 2.5\text{--}26.0^\circ$
 $\mu = 1.00$ mm⁻¹
 $T = 295$ (2) K
 Prism, pale yellow
 $0.38 \times 0.26 \times 0.24$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\text{min}} = 0.68, T_{\text{max}} = 0.78$
 8326 measured reflections

1957 independent reflections
 1868 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -14 \rightarrow 14$
 $k = -14 \rightarrow 14$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.065$
 $S = 1.09$
 1957 reflections
 104 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 0.2897P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.13$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³
 Absolute structure: Flack (1983), 932 Friedel Pairs
 Flack parameter = 0.001 (12)

Table 1

Selected geometric parameters (Å, °).

Cu—S	2.3313 (5)	N1—Cl	1.429 (2)
S—C7	1.709 (2)	N2—C7	1.316 (3)
N1—C7	1.341 (2)		
S—Cu—S ⁱ	117.38 (2)	S—Cu—S ⁱⁱ	105.666 (10)

Symmetry codes: (i) $1-x, -y, z$; (ii) $\frac{1}{2}+y, \frac{1}{2}-x, \frac{3}{2}-z$.

H atoms of the amino and imino groups were located in a difference Fourier map and refined independently with a fixed isotropic displacement parameter of 0.08 Å². H atoms on the benzene ring were placed in calculated positions, with C—H = 0.93 Å, and included in the final cycles of refinement as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This project was supported by the National Natural Science Foundation of China (29973036 and 20240430654).

References

- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Li, D.-X. (2004). Doctoral Dissertation, Zhejiang University, People's Republic of China.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MSC (2002). *CrystalStructure*. Version 3.00. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Shen, Y.-H. & Xu, D.-J. (2004). *Acta Cryst.* **E60**, o1193–o1194.
- Wu, Z.-Y., Xu, D.-J., Wu, J.-Y. & Chiang, M. Y. (2002). *Acta Cryst.* **C58**, m374–m376.