

N-(4-Chlorophenyl)-*N'*-(4-nitrobenzoyl)urea

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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.033
 wR factor = 0.088
Data-to-parameter ratio = 11.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\text{C}_{14}\text{H}_{10}\text{ClN}_3\text{O}_4$, was obtained by the reaction of *N*-(4-chlorophenyl)-*N'*-(4-nitrobenzoyl)thiourea with cupric chloride dihydrate. Intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds link the molecules into centrosymmetric dimers. The crystal packing is further stabilized by weak $\text{C}-\text{H}\cdots\text{O}$ interactions.

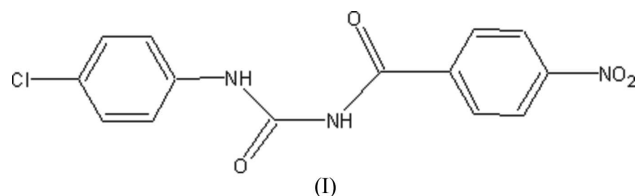
Received 9 September 2005

Accepted 26 September 2005

Online 30 September 2005

Comment

Thiourea derivatives have been studied intensively in recent years (Koch, 2001; Foss *et al.*, 2004; Bombicz *et al.*, 2004). Acyl thiourea derivatives are known to form various coordination compounds with transition metals. They can act as reducing agents to reduce the oxidation state of transition metal ions. They may also produce unexpected compounds in ordinary coordination reactions. Recently, Zhang *et al.* (2003) reported that an oxazoline ring was formed in the coordination reaction of cupric chloride dihydrate with *N*-benzoyl-*N'*-(2-hydroxyethyl)thiourea. In this reaction, desulfurization and cyclization have occurred, and two oxazoline rings were formed in the resulting coordination compound. In the coordination reaction of *N*-ethoxycarbonyl-*N'*-*o*-chlorophenylthiourea with cupric chloride dihydrate in ethanol solution (Su, Xian *et al.*, 2005), an unusual compound was obtained, containing the Cu_6 cluster unit, where the copper(I) ions form a hexagonal ring structure *via* $\text{Cu}-\text{Cu}$ bonds.



The title compound, (I) (Fig. 1), was obtained by the reaction of *N*-*p*-nitrobenzoyl-*N'*-*p*-chlorophenylthiourea with cupric chloride dihydrate, in which the S atom on the thio-carbonyl group of the thiourea ligand was replaced by an O atom. The bond lengths and angles in (I) (Table 1) are normal (Allen *et al.*, 1987). The intramolecular $\text{N1}-\text{H1}\cdots\text{O2}$ hydrogen bond (Table 2) determines the molecular conformation. The intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2) link the molecules into centrosymmetric dimers. The crystal packing (Fig. 2) is further stabilized by weak $\text{C}-\text{H}\cdots\text{O}$ interactions (Table 2).

The title compound was obtained unexpectedly in the coordination reaction of thiourea with copper(II). To validate the results of the structural analysis, IR and ^1H NMR measurements have been carried out. The IR and ^1H NMR

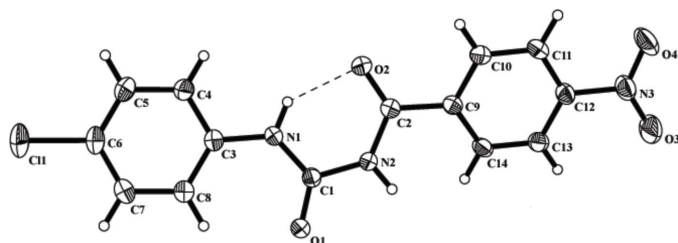


Figure 1
View of (I), with displacement ellipsoids at the 50% probability level. The intramolecular hydrogen bond is indicated by a dashed line.

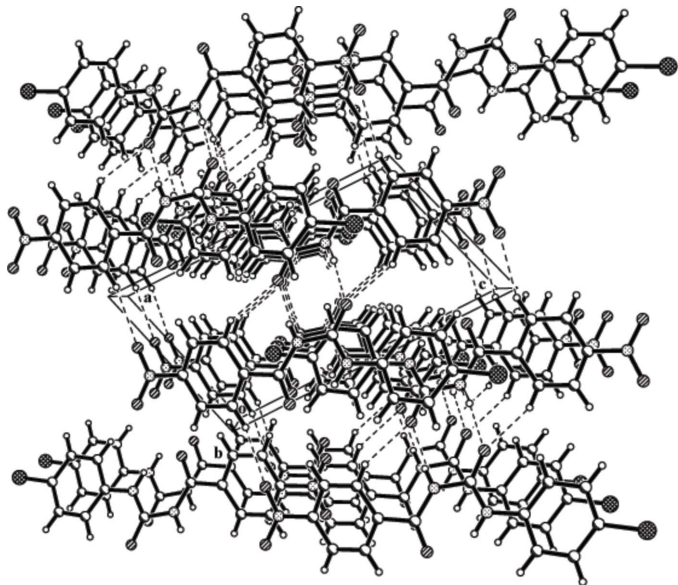


Figure 2
The crystal packing viewed along the *b* axis. Intermolecular hydrogen bonds are indicated by dashed lines.

data indicated that the thiocarbonyl group was replaced by the carbonyl group, *i.e.* the S atom was replaced by the O atom in air when the solution was heated. We suppose that in this process the copper(II) ion acts as an electron transferring unit, allowing the replacement of the S atom by an O atom in air. This reaction is different from other coordination reactions, which commonly form 1:2 thiourea coordination compounds having a central triangular structure (Su *et al.*, 2004); the reasons for this difference are still unknown.

Experimental

All chemicals used for the preparation of compound (I) were of reagent grade quality. *N*-(4-Chlorophenyl)-*N'*-(4-nitrobenzoyl)thiourea was obtained from a CH_2Cl_2 solution using the known method (Su, Liu *et al.*, 2005). The thiourea ligand and cupric chloride dihydrate were dissolved in ethanol. The two solutions were mixed and heated for a while with stirring; a yellow product was deposited. Single crystals were obtained after one week by slow evaporation of a mixed solution in 1:1 dimethyl sulfoxide/acetone. Yield 28%. Analysis required for $\text{C}_{14}\text{H}_{10}\text{ClN}_3\text{O}_4$: C 52.55, H 3.13, N 13.15%; found: C 50.04, H 2.59, N 13.13%. IR (cm^{-1}): 3131 (NH), 1701 (C=O), 1596, 1525, 1499 (C=C), 1346, 1270, 1227, 1091, 831, 723,

511. ^1H NMR: 7.38–7.70 (*m*, 4H, Cl– C_6H_4), 8.14–8.34 (*m*, 4H, NO_2 – C_6H_4), 10.64 (*s*, 1H, NH), 11.39 (*s*, 1H, NH).

Crystal data

$\text{C}_{14}\text{H}_{10}\text{ClN}_3\text{O}_4$
 $M_r = 319.70$
Triclinic, $P\bar{1}$
 $a = 7.1737$ (10) Å
 $b = 8.2486$ (12) Å
 $c = 12.1873$ (17) Å
 $\alpha = 91.418$ (2)°
 $\beta = 106.157$ (2)°
 $\gamma = 99.400$ (2)°
 $V = 681.50$ (17) Å³

$Z = 2$
 $D_x = 1.558$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 1727 reflections
 $\theta = 2.5$ – 27.7 °
 $\mu = 0.30$ mm⁻¹
 $T = 293$ (2) K
Block, yellow
 $0.26 \times 0.24 \times 0.18$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.911$, $T_{\max} = 0.947$
3693 measured reflections

2368 independent reflections
1941 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.009$
 $\theta_{\max} = 25.0$ °
 $h = -8 \rightarrow 8$
 $k = -9 \rightarrow 8$
 $l = -10 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.088$
 $S = 1.06$
2368 reflections
207 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 0.161P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.26$ e Å⁻³
 $\Delta\rho_{\min} = -0.21$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N1–C1	1.338 (2)	O1–C1	1.2207 (19)
N1–C3	1.412 (2)	O2–C2	1.2204 (19)
N2–C2	1.365 (2)	C2–C9	1.498 (2)
N2–C1	1.404 (2)		
C1–N1–C3	127.58 (14)	N1–C1–N2	116.09 (14)
C2–N2–C1	128.49 (13)	N2–C2–C9	115.93 (14)

Table 2

Hydrogen-bond geometry (Å, °).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N1–H1 \cdots O2	0.87 (1)	1.96 (1)	2.6699 (18)	138 (2)
C8–H8 \cdots O1	0.93	2.28	2.868 (2)	121
N2–H2 \cdots O1 ⁱ	0.86 (1)	2.02 (1)	2.8763 (17)	172 (2)
C10–H10 \cdots O3 ⁱⁱ	0.93	2.58	3.390 (2)	146
C14–H14 \cdots O1 ⁱ	0.93	2.47	3.089 (2)	124

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + 1, y, z$.

The C-bound H atoms were positioned geometrically and allowed to ride on their parent atoms, with $\text{C–H} = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The amine atoms H1 and H2 were located in a difference Fourier map and refined isotropically with a restrained N–H distance of 0.87 (1) Å.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics:

SHELXTL (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

The financial support of the Foundation of Lanzhou Jiaotong University (No. 405003) is gratefully acknowledged.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Bombicz, P., Mutikainen, I., Krunks, M., Leskelä, T., Madarosz, J. & Niinistö, L. (2004). *Inorg. Chim. Acta*, **357**, 513–525.
- Bruker (2000). *SMART, SAINT and SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Foss, O., Husebye, S., Törnroos, K. W. & Fanwick, P. E. (2004). *Polyhedron*, **23**, 3021–3032.
- Koch, K. R. (2001). *Coord. Chem. Rev.* **216–217**, 473–488.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97 and SHELXL97*. University of Göttingen, Germany.
- Su, B. Q., Liu, G. L., Sheng, L., Wang, X. Q. & Xian, L. (2005). *Phosphorus Sulfur Silicon*. In the press.
- Su, B. Q., Xian, L., Song, H. B. & Sheng, L. (2004). *Acta Cryst.* **C60**, m661–m662.
- Su, B. Q., Xian, L., Zhang, B. & Song, H. B. (2005). *J. Chem. Res.* pp. 101–102.
- Zhang, Y. M., Xian, L., Wei, T. B. & Yu, K. B. (2003). *J. Chem. Res.* pp. 798–799.