

## {4-Bromo-2-[2-(ethylamino)ethylimino-methyl]phenolato- $\kappa^3$ N,N',O}(thiocyanato- $\kappa$ N)copper(II)

Zhi Zhou<sup>a\*</sup> and Rui-Ren Tang<sup>b</sup>

<sup>a</sup>Department of Chemistry, Kaili College, Kaili Guizhou 556000, People's Republic of China, and <sup>b</sup>College of Chemistry and Chemical Engineering, Central South University, Changsha Hunan 410083, People's Republic of China  
Correspondence e-mail: zhou82zhi@126.com

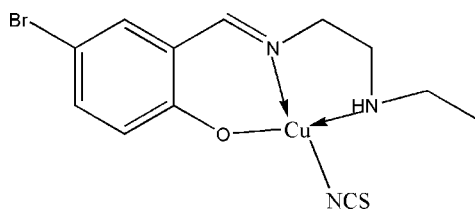
Received 25 October 2007; accepted 5 November 2007

Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.009$  Å;  $R$  factor = 0.061;  $wR$  factor = 0.148; data-to-parameter ratio = 19.0.

In the title compound,  $[\text{Cu}(\text{C}_{11}\text{H}_{14}\text{BrN}_2\text{O})(\text{NCS})]$ , the Cu atom is four-coordinated by the NNO donor set of the Schiff base ligand and by the terminal N atom of the thiocyanate anion, forming a square-planar geometry. An  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bond helps to establish the packing.

### Related literature

For related structures, see: Li *et al.* (2007); Wang *et al.* (2006); Wang & Li (2005); Xu *et al.* (2005); Zhou & Xiao (2007).



### Experimental

#### Crystal data

$[\text{Cu}(\text{C}_{11}\text{H}_{14}\text{BrN}_2\text{O})(\text{NCS})]$   
 $M_r = 391.77$   
 Monoclinic,  $P2_1/n$   
 $a = 6.3368$  (12) Å  
 $b = 19.163$  (4) Å  
 $c = 12.308$  (2) Å  
 $\beta = 100.601$  (3)°

$V = 1469.1$  (5) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 4.34$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 $0.15 \times 0.13 \times 0.10$  mm

#### Data collection

Bruker SMART APEXII CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2004)  
 $T_{\min} = 0.562$ ,  $T_{\max} = 0.671$

12464 measured reflections  
 3350 independent reflections  
 2054 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.073$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$   
 $wR(F^2) = 0.148$   
 $S = 1.02$   
 3350 reflections  
 176 parameters  
 1 restraint

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.74$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.59$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Cu1—O1	1.825 (4)	Cu1—N3	1.870 (5)
Cu1—N1	1.853 (5)	Cu1—N2	1.942 (5)

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2}\cdots\text{S1}^i$	0.90 (5)	2.68 (3)	3.520 (6)	155 (6)

Symmetry code: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ .

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors thank Kaili College for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2616).

### References

- Bruker (2001). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Bruker (2005). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Li, J.-X., Jiang, Y.-M. & Wang, J.-G. (2007). *Acta Cryst.* **E63**, m601–m603.  
 Sheldrick, G. M. (2001). *SHELXTL*. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.  
 Wang, N., Han, X.-E. & Wen, X.-G. (2006). *Acta Cryst.* **E62**, m369–m370.  
 Wang, N. & Li, J.-P. (2005). *Acta Cryst.* **E61**, m1223–m1225.  
 Xu, G.-J., Yan, S.-P., Liao, D.-Z., Jiang, Z.-H. & Cheng, P. (2005). *Acta Cryst.* **E61**, m933–m935.  
 Zhou, Z. & Xiao, Z.-H. (2007). *Acta Cryst.* **E63**, m2012.

**supplementary materials**

*Acta Cryst.* (2007). E63, m2960 [ doi:10.1107/S1600536807056048 ]

## {4-Bromo-2-[2-(ethylamino)ethyliminomethyl]phenolato- $\kappa^3N,N',O$ }(thiocyanato- $\kappa N$ )copper(II)

Z. Zhou and R.-R. Tang

### Comment

Recently, we have reported a Schiff base-nickel(II) complex (Zhou & Xiao, 2007). As an extensive of our work, we report herein the crystal structure of the title mononuclear copper(II) complex, (I), (Fig. 1).

The Cu atom in (I) is four-coordinated by the NNO donor set of the Schiff base ligand and by the terminal N atom of the thiocyanate anion, forming a square-planar geometry. The bond lengths and bond angles (Table 1) subtended at the metal centre are comparable to the values in similar copper(II) complexes (Xu *et al.*, 2005; Wang & Li, 2005; Wang *et al.*, 2006; Li *et al.*, 2007).

An N—H $\cdots$ S hydrogen bond helps to establish the packing (Table 2).

### Experimental

5-Bromosalicylaldehyde (0.1 mmol, 20.1 mg), *N*-ethylethane-1,2-diamine (0.1 mmol, 8.8 mg), ammonium thiocyanate (0.1 mmol, 7.6 mg) and copper acetate (0.1 mmol, 20.0 mg) were mixed in a methanol solution (10 ml). The mixture was stirred at room temperature for 30 min to give a deep blue solution. Blue blocks of (I) were formed by slow evaporation of the solution in air.

### Refinement

The N-bound H atom was located in a difference map and freely refined.

The C-bound H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.97 Å and with  $U_{\text{iso}}(\text{H}) = 1.2$  or 1.5 times  $U_{\text{eq}}(\text{C})$ .

### Figures

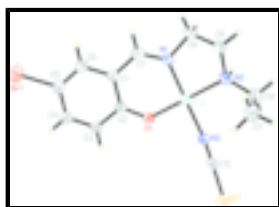


Fig. 1. The molecular structure of (I), with 30% probability displacement ellipsoids (arbitrary spheres for the H atoms).

## {4-Bromo-2-[2-(ethylamino)ethyliminomethyl]phenolato- $\kappa^3N,N',O$ }(thiocyanato- $\kappa N$ )copper(II)

### Crystal data

[Cu(C <sub>11</sub> H <sub>14</sub> BrN <sub>2</sub> O)(NCS)]	$F_{000} = 780$
$M_r = 391.77$	$D_x = 1.771 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
Hall symbol: -P 2yn	$\lambda = 0.71073 \text{ \AA}$
$a = 6.3368 (12) \text{ \AA}$	Cell parameters from 1356 reflections
$b = 19.163 (4) \text{ \AA}$	$\theta = 2.4\text{--}24.9^\circ$
$c = 12.308 (2) \text{ \AA}$	$\mu = 4.34 \text{ mm}^{-1}$
$\beta = 100.601 (3)^\circ$	$T = 298 (2) \text{ K}$
$V = 1469.1 (5) \text{ \AA}^3$	Block, blue
$Z = 4$	$0.15 \times 0.13 \times 0.10 \text{ mm}$

### Data collection

Bruker SMART APEXII CCD diffractometer	3350 independent reflections
Radiation source: fine-focus sealed tube	2054 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.073$
$T = 298(2) \text{ K}$	$\theta_{\text{max}} = 27.5^\circ$
$\omega$ scans	$\theta_{\text{min}} = 2.0^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.562, T_{\text{max}} = 0.671$	$k = -24 \rightarrow 24$
12464 measured reflections	$l = -15 \rightarrow 15$

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.061$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.148$	$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 0.919P]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
3350 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
176 parameters	$\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$
1 restraint	$\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.76392 (11)	0.19400 (4)	0.04069 (6)	0.0411 (2)
Br1	1.26434 (12)	-0.06356 (4)	-0.27110 (7)	0.0665 (3)
S1	0.0947 (3)	0.28292 (10)	-0.10857 (15)	0.0584 (5)
O1	0.6977 (6)	0.1300 (2)	-0.0701 (3)	0.0427 (10)
N1	1.0370 (7)	0.1586 (2)	0.0899 (4)	0.0374 (11)
N2	0.8306 (9)	0.2596 (3)	0.1625 (4)	0.0514 (14)
N3	0.4882 (8)	0.2303 (3)	-0.0064 (4)	0.0461 (13)
C1	1.0482 (9)	0.0795 (3)	-0.0614 (5)	0.0367 (13)
C2	0.8301 (9)	0.0898 (3)	-0.1105 (4)	0.0351 (13)
C3	0.7508 (10)	0.0525 (3)	-0.2095 (5)	0.0497 (16)
H3	0.6083	0.0578	-0.2439	0.060*
C4	0.8822 (10)	0.0090 (3)	-0.2544 (6)	0.0501 (16)
H4	0.8279	-0.0152	-0.3190	0.060*
C5	1.0960 (10)	0.0003 (3)	-0.2050 (6)	0.0471 (15)
C6	1.1782 (10)	0.0347 (3)	-0.1109 (5)	0.0423 (14)
H6	1.3217	0.0287	-0.0787	0.051*
C7	1.1358 (9)	0.1143 (3)	0.0405 (5)	0.0433 (15)
H7	1.2763	0.1034	0.0731	0.052*
C8	1.1484 (10)	0.1894 (3)	0.1934 (5)	0.0490 (16)
H8A	1.3019	0.1908	0.1947	0.059*
H8B	1.1224	0.1621	0.2559	0.059*
C9	1.0620 (10)	0.2614 (3)	0.1986 (6)	0.0549 (18)
H9A	1.0969	0.2789	0.2737	0.066*
H9B	1.1260	0.2923	0.1513	0.066*
C10	0.7238 (12)	0.3277 (4)	0.1615 (6)	0.0610 (19)
H10A	0.7791	0.3516	0.2303	0.073*
H10B	0.5714	0.3201	0.1584	0.073*
C11	0.7524 (13)	0.3740 (4)	0.0674 (7)	0.078 (2)
H11A	0.9028	0.3801	0.0674	0.117*
H11B	0.6881	0.4186	0.0755	0.117*
H11C	0.6848	0.3531	-0.0011	0.117*
C12	0.3270 (9)	0.2526 (3)	-0.0482 (5)	0.0391 (14)
H2	0.801 (11)	0.237 (3)	0.222 (4)	0.080*

## supplementary materials

---

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0367 (4)	0.0458 (5)	0.0390 (4)	-0.0040 (3)	0.0024 (3)	-0.0002 (3)
Br1	0.0680 (5)	0.0485 (4)	0.0901 (6)	-0.0006 (3)	0.0334 (4)	-0.0116 (4)
S1	0.0429 (10)	0.0786 (13)	0.0543 (11)	0.0118 (8)	0.0104 (8)	0.0249 (9)
O1	0.034 (2)	0.043 (2)	0.047 (2)	-0.0003 (18)	-0.0052 (18)	-0.0099 (19)
N1	0.034 (3)	0.041 (3)	0.035 (3)	-0.004 (2)	0.000 (2)	0.004 (2)
N2	0.052 (3)	0.057 (3)	0.042 (3)	-0.004 (3)	0.001 (3)	-0.010 (3)
N3	0.034 (3)	0.058 (3)	0.045 (3)	0.004 (2)	0.004 (2)	-0.011 (2)
C1	0.033 (3)	0.031 (3)	0.046 (4)	-0.005 (2)	0.008 (3)	0.006 (3)
C2	0.038 (3)	0.029 (3)	0.035 (3)	-0.003 (2)	-0.001 (3)	0.005 (2)
C3	0.045 (4)	0.037 (3)	0.059 (4)	0.004 (3)	-0.010 (3)	-0.009 (3)
C4	0.047 (4)	0.045 (4)	0.055 (4)	-0.010 (3)	0.001 (3)	-0.010 (3)
C5	0.051 (4)	0.033 (3)	0.059 (4)	0.000 (3)	0.015 (3)	0.002 (3)
C6	0.041 (3)	0.034 (3)	0.054 (4)	0.002 (3)	0.014 (3)	0.007 (3)
C7	0.032 (3)	0.044 (4)	0.051 (4)	-0.004 (3)	-0.001 (3)	0.015 (3)
C8	0.048 (4)	0.058 (4)	0.037 (3)	-0.013 (3)	-0.003 (3)	0.002 (3)
C9	0.048 (4)	0.065 (4)	0.050 (4)	-0.013 (3)	0.003 (3)	-0.023 (3)
C10	0.068 (5)	0.061 (5)	0.056 (4)	0.001 (4)	0.015 (4)	-0.014 (4)
C11	0.090 (6)	0.058 (5)	0.080 (6)	0.002 (4)	-0.001 (5)	-0.014 (4)
C12	0.034 (3)	0.048 (4)	0.038 (3)	-0.007 (3)	0.013 (3)	-0.009 (3)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Cu1—O1	1.825 (4)	C3—H3	0.9300
Cu1—N1	1.853 (5)	C4—C5	1.389 (8)
Cu1—N3	1.870 (5)	C4—H4	0.9300
Cu1—N2	1.942 (5)	C5—C6	1.351 (8)
Br1—C5	1.902 (6)	C6—H6	0.9300
S1—C12	1.629 (6)	C7—H7	0.9300
O1—C2	1.304 (6)	C8—C9	1.491 (8)
N1—C7	1.274 (7)	C8—H8A	0.9700
N1—C8	1.462 (7)	C8—H8B	0.9700
N2—C9	1.452 (8)	C9—H9A	0.9700
N2—C10	1.471 (8)	C9—H9B	0.9700
N2—H2	0.90 (5)	C10—C11	1.496 (10)
N3—C12	1.140 (7)	C10—H10A	0.9700
C1—C6	1.404 (8)	C10—H10B	0.9700
C1—C2	1.417 (7)	C11—H11A	0.9600
C1—C7	1.438 (8)	C11—H11B	0.9600
C2—C3	1.422 (8)	C11—H11C	0.9600
C3—C4	1.364 (8)		
O1—Cu1—N1	94.06 (19)	C5—C6—C1	120.4 (6)
O1—Cu1—N3	86.84 (19)	C5—C6—H6	119.8
N1—Cu1—N3	179.0 (2)	C1—C6—H6	119.8
O1—Cu1—N2	177.8 (2)	N1—C7—C1	125.5 (5)

N1—Cu1—N2	85.8 (2)	N1—C7—H7	117.3
N3—Cu1—N2	93.3 (2)	C1—C7—H7	117.3
C2—O1—Cu1	127.4 (3)	N1—C8—C9	106.8 (5)
C7—N1—C8	118.9 (5)	N1—C8—H8A	110.4
C7—N1—Cu1	126.8 (4)	C9—C8—H8A	110.4
C8—N1—Cu1	114.2 (4)	N1—C8—H8B	110.4
C9—N2—C10	114.7 (5)	C9—C8—H8B	110.4
C9—N2—Cu1	108.5 (4)	H8A—C8—H8B	108.6
C10—N2—Cu1	122.3 (4)	N2—C9—C8	108.8 (5)
C9—N2—H2	96 (5)	N2—C9—H9A	109.9
C10—N2—H2	105 (5)	C8—C9—H9A	109.9
Cu1—N2—H2	106 (5)	N2—C9—H9B	109.9
C12—N3—Cu1	171.2 (5)	C8—C9—H9B	109.9
C6—C1—C2	120.3 (5)	H9A—C9—H9B	108.3
C6—C1—C7	119.9 (5)	N2—C10—C11	114.3 (6)
C2—C1—C7	119.8 (5)	N2—C10—H10A	108.7
O1—C2—C1	124.4 (5)	C11—C10—H10A	108.7
O1—C2—C3	118.3 (5)	N2—C10—H10B	108.7
C1—C2—C3	117.3 (5)	C11—C10—H10B	108.7
C4—C3—C2	120.5 (6)	H10A—C10—H10B	107.6
C4—C3—H3	119.7	C10—C11—H11A	109.5
C2—C3—H3	119.7	C10—C11—H11B	109.5
C3—C4—C5	121.0 (6)	H11A—C11—H11B	109.5
C3—C4—H4	119.5	C10—C11—H11C	109.5
C5—C4—H4	119.5	H11A—C11—H11C	109.5
C6—C5—C4	120.5 (6)	H11B—C11—H11C	109.5
C6—C5—Br1	121.5 (5)	N3—C12—S1	178.8 (6)
C4—C5—Br1	117.9 (5)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...S1 <sup>i</sup>	0.90 (5)	2.68 (3)	3.520 (6)	155 (6)

Symmetry codes: (i)  $x+1/2, -y+1/2, z+1/2$ .

Fig. 1

