metal-organic compounds

Bis{2-bromo-4-chloro-6-[2-(phenyl-sulfonyl)hydrazonomethyl]phenolato-κ^2N,O^1}copper(II)

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The Cu atom in the title compound, $[Cu(C_{13}H_9BrClN_2O_3S)_2]$, is chelated by two deprotonated Schiff base ligands in a square-planar coordination geometry; the Cu atom lies on a center of inversion. The –NH– group of one anion forms an intramolecular hydrogen bond to the phenolate atom of the symmetry-related ion.

Related literature

For the structure of the copper derivative of a similar Schiff base ligand, see: Ali *et al.* (2007).
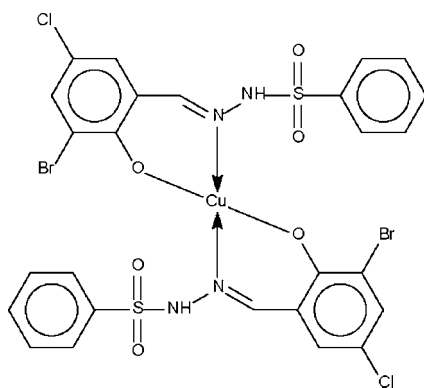
Experimental

Crystal data

$[Cu(C_{13}H_9BrClN_2O_3S)_2]$	$c = 11.7386$ (2) Å
$M_r = 840.82$	$\alpha = 95.955$ (1)°
Triclinic, $P\bar{1}$	$\beta = 90.133$ (1)°
$a = 8.0688$ (1) Å	$\gamma = 115.159$ (1)°
$b = 8.2755$ (1) Å	$V = 704.70$ (2) Å³

$Z = 1$	$T = 100$ (2) K
Mo $K\alpha$ radiation	$0.20 \times 0.09 \times 0.09$ mm
$\mu = 4.00$ mm^{-1}	

Data collection

Bruker SMART APEX diffractometer	8995 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	3214 independent reflections
$T_{min} = 0.502$, $T_{max} = 0.715$	2928 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.061$	
$S = 1.05$	$\Delta\rho_{max} = 0.52$ e Å^{-3}
3214 reflections	$\Delta\rho_{min} = -0.29$ e Å^{-3}
200 parameters	
1 restraint	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.905 (1)	Cu1—N1	1.963 (2)
O1—Cu1—N1	91.28 (6)	O1—Cu1—N1^i	88.72 (6)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2N$\cdots$O1^i	0.88 (1)	2.07 (2)	2.722 (2)	130 (2)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2008).

References

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Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
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supporting information

Bis{2-bromo-4-chloro-6-[2-(phenylsulfonyl)hydrazonomethyl]phenolato-κ^2N,O^1}copper(II)

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S1. Comment

The present study continues with a study on the copper derivative of Schiff-base condensation products from the reaction between substituted salicylaldehydes and benzene sulfonylhydrazine. The two monoanions chelate to the copper atom, which shows square-planar coordination (Ali *et al.*, 2007). The present copper derivative (Scheme I, Fig. 1), which has a bromine substituent in the aromatic system, shows such a geometry; the nature of the substituent in the salicylaldehyde portion does not have an effect on the overall geometry.

S2. Experimental

3-Bromo-5-chlorobenzaldehyde (0.5 g, 0.3 mmol) and benzenesulfonylhydrazine (0.5 g, 0.3 mmol) were condensed in refluxing ethanol (100 ml) for two hours. The solvent was removed to give the Schiff base, which was collected and dried. The ligand (0.6 g, 2 mmol) and copper acetate (0.2 g, 1 mmol) were heated in ethanol (100 ml) for two hours. The solvent was removed and the product recrystallized from DMSO.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95 Å) and were included in the refinement in the riding model approximation, with U(H) set to $1.2U_{eq}$(C). The amino H atom was refined with a distance restraint of N–H 0.88±0.01 Å; its temperature factor was freely refined.
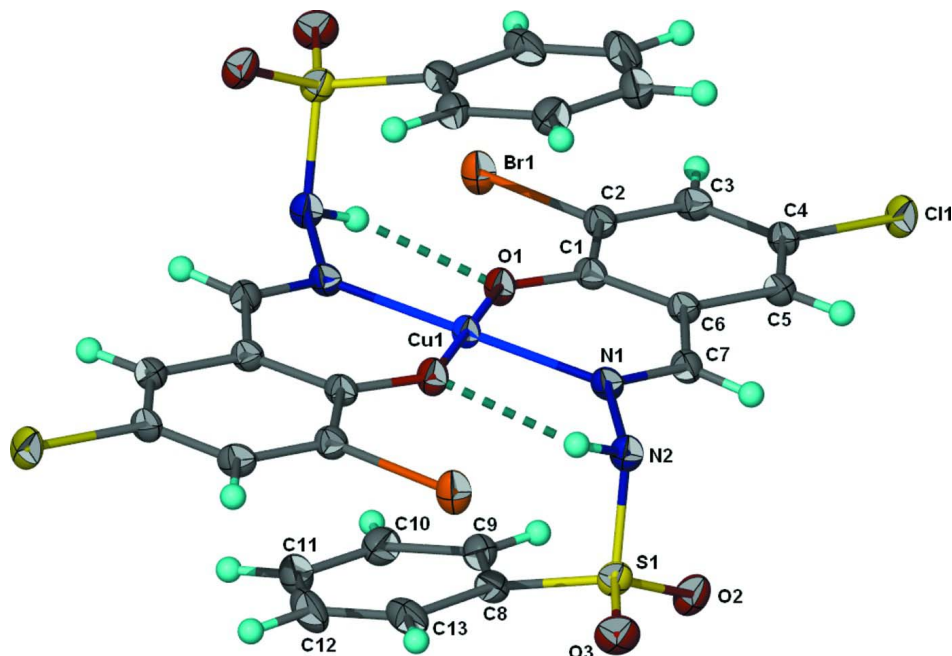
Figure 1

Thermal ellipsoid plot (Barbour, 2001) plot of Cu(C$_{13}$H$_9$BrClN$_2$O$_3$S)$_2$ at the 70% probability level. Hydrogen atoms are drawn as spheres of arbitrary radius. Hydrogen bonds are denoted by dashed lines. The copper atom lies on a center of inversion, and unlabeled atoms are related to their labeled equivalents by $1 - x$, $1 - y$, $1 - z$.

Bis{2-bromo-4-chloro-6-[2-(phenylsulfonyl)hydrazonomethyl]phenolato- κ²N,O¹}copper(II)

Crystal data

[Cu(C$_{13}$H$_9$BrClN$_2$O$_3$S)$_2$]	$Z = 1$
$M_r = 840.82$	$F(000) = 415$
Triclinic, $P\overline{1}$	$D_x = 1.981$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.0688$ (1) Å	Cell parameters from 5423 reflections
$b = 8.2755$ (1) Å	$\theta = 2.7–28.4°$
$c = 11.7386$ (2) Å	$\mu = 4.00$ mm^{-1}
$\alpha = 95.955$ (1)°	$T = 100$ K
$\beta = 90.133$ (1)°	Block, purple
$\gamma = 115.159$ (1)°	$0.20 \times 0.09 \times 0.09$ mm
$V = 704.70$ (2) Å^3	

Data collection

Bruker SMART APEX diffractometer	8995 measured reflections
Radiation source: fine-focus sealed tube	3214 independent reflections
Graphite monochromator	2928 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.017$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.5°$, $\theta_{min} = 1.8°$
$T_{min} = 0.502$, $T_{max} = 0.715$	$h = -8→10$
	$k = -10→10$
	$l = -15→15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.021$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.061$	
$S = 1.05$	H atoms treated by a mixture of independent and constrained refinement
3214 reflections	
200 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0332P)^2 + 0.5714P]$
1 restraint	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} = 0.001$
	$\Delta\rho_{max} = 0.52$ e Å⁻³
	$\Delta\rho_{min} = -0.29$ e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.46994 (3)	0.68016 (3)	0.125566 (17)	0.01926 (7)
Cu1	0.5000	0.5000	0.5000	0.01271 (9)
Cl1	−0.18066 (7)	0.07143 (7)	0.02818 (4)	0.02134 (12)
S1	0.09184 (7)	0.33794 (7)	0.69365 (4)	0.01590 (11)
O1	0.4287 (2)	0.53987 (19)	0.35457 (12)	0.0156 (3)
O2	−0.0713 (2)	0.2946 (2)	0.62483 (13)	0.0201 (3)
O3	0.0825 (2)	0.2833 (2)	0.80598 (13)	0.0223 (3)
N1	0.2591 (2)	0.2994 (2)	0.51073 (14)	0.0139 (3)
N2	0.2075 (2)	0.2348 (2)	0.62019 (14)	0.0149 (3)
H2N	0.309 (2)	0.267 (4)	0.663 (2)	0.025 (7)*
C1	0.2899 (3)	0.4324 (3)	0.28525 (17)	0.0142 (4)
C2	0.2784 (3)	0.4722 (3)	0.17138 (17)	0.0150 (4)
C3	0.1374 (3)	0.3636 (3)	0.09341 (17)	0.0165 (4)
H3	0.1350	0.3938	0.0177	0.020*
C4	−0.0018 (3)	0.2085 (3)	0.12702 (17)	0.0161 (4)
C5	0.0002 (3)	0.1631 (3)	0.23553 (17)	0.0162 (4)
H5	−0.0958	0.0571	0.2570	0.019*
C6	0.1451 (3)	0.2739 (3)	0.31582 (16)	0.0140 (4)
C7	0.1325 (3)	0.2211 (3)	0.42942 (17)	0.0151 (4)
H7	0.0238	0.1219	0.4461	0.018*
C8	0.2345 (3)	0.5685 (3)	0.69679 (18)	0.0168 (4)
C9	0.2357 (3)	0.6526 (3)	0.60000 (18)	0.0175 (4)
H9	0.1500	0.5902	0.5372	0.021*
C10	0.3634 (3)	0.8287 (3)	0.5961 (2)	0.0215 (4)
H10	0.3658	0.8877	0.5305	0.026*
C11	0.4881 (3)	0.9189 (3)	0.6887 (2)	0.0254 (5)
H11	0.5770	1.0388	0.6856	0.030*
C12	0.4833 (3)	0.8350 (3)	0.7848 (2)	0.0269 (5)
H12	0.5673	0.8987	0.8481	0.032*
C13	0.3572 (3)	0.6584 (3)	0.79044 (19)	0.0216 (4)
H13	0.3547	0.6004	0.8566	0.026*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02148 (12)	0.01787 (11)	0.01395 (11)	0.00366 (9)	−0.00187 (8)	0.00401 (7)
Cu1	0.01245 (17)	0.01403 (16)	0.00878 (16)	0.00304 (13)	−0.00122 (12)	0.00080 (12)
Cl1	0.0154 (2)	0.0276 (3)	0.0122 (2)	0.0018 (2)	−0.00463 (18)	−0.00208 (19)
S1	0.0156 (2)	0.0193 (2)	0.0112 (2)	0.0056 (2)	0.00112 (18)	0.00311 (18)
O1	0.0151 (7)	0.0171 (7)	0.0111 (7)	0.0035 (6)	−0.0023 (5)	0.0018 (5)
O2	0.0148 (7)	0.0249 (8)	0.0179 (7)	0.0054 (6)	0.0001 (6)	0.0047 (6)
O3	0.0253 (8)	0.0291 (8)	0.0123 (7)	0.0107 (7)	0.0031 (6)	0.0054 (6)
N1	0.0167 (9)	0.0141 (8)	0.0095 (8)	0.0052 (7)	0.0006 (6)	0.0018 (6)
N2	0.0160 (9)	0.0166 (8)	0.0106 (8)	0.0051 (7)	−0.0009 (6)	0.0029 (6)
C1	0.0146 (10)	0.0162 (9)	0.0121 (9)	0.0074 (8)	−0.0016 (7)	−0.0007 (7)
C2	0.0161 (10)	0.0148 (9)	0.0134 (9)	0.0061 (8)	0.0005 (8)	0.0012 (7)
C3	0.0181 (10)	0.0214 (10)	0.0111 (9)	0.0096 (9)	−0.0002 (8)	0.0014 (8)
C4	0.0132 (10)	0.0196 (10)	0.0129 (9)	0.0060 (8)	−0.0037 (7)	−0.0043 (7)
C5	0.0145 (10)	0.0171 (9)	0.0149 (9)	0.0055 (8)	0.0002 (8)	−0.0014 (7)
C6	0.0147 (10)	0.0158 (9)	0.0112 (9)	0.0064 (8)	−0.0006 (7)	0.0003 (7)
C7	0.0155 (10)	0.0140 (9)	0.0139 (9)	0.0048 (8)	0.0003 (8)	0.0005 (7)
C8	0.0162 (10)	0.0177 (9)	0.0158 (9)	0.0074 (8)	0.0002 (8)	−0.0015 (8)
C9	0.0160 (10)	0.0184 (10)	0.0165 (10)	0.0062 (8)	−0.0006 (8)	0.0001 (8)
C10	0.0200 (11)	0.0198 (10)	0.0242 (11)	0.0079 (9)	0.0035 (9)	0.0027 (9)
C11	0.0190 (11)	0.0190 (11)	0.0330 (13)	0.0053 (9)	0.0000 (10)	−0.0058 (9)
C12	0.0247 (12)	0.0260 (12)	0.0257 (12)	0.0101 (10)	−0.0090 (9)	−0.0118 (9)
C13	0.0249 (12)	0.0246 (11)	0.0169 (10)	0.0137 (9)	−0.0039 (9)	−0.0047 (8)

Geometric parameters (Å, º)

Br1—C2	1.890 (2)	C3—H3	0.9500
Cu1—O1	1.905 (1)	C4—C5	1.367 (3)
Cu1—O1^i	1.905 (1)	C5—C6	1.415 (3)
Cu1—N1^i	1.963 (2)	C5—H5	0.9500
Cu1—N1	1.963 (2)	C6—C7	1.436 (3)
Cl1—C4	1.744 (2)	C7—H7	0.9500
S1—O3	1.4297 (15)	C8—C9	1.391 (3)
S1—O2	1.4309 (16)	C8—C13	1.393 (3)
S1—N2	1.6945 (19)	C9—C10	1.387 (3)
S1—C8	1.756 (2)	C9—H9	0.9500
O1—C1	1.306 (2)	C10—C11	1.393 (3)
N1—C7	1.296 (3)	C10—H10	0.9500
N1—N2	1.437 (2)	C11—C12	1.376 (4)
N2—H2N	0.88 (1)	C11—H11	0.9500
C1—C6	1.418 (3)	C12—C13	1.390 (3)
C1—C2	1.421 (3)	C12—H12	0.9500
C2—C3	1.377 (3)	C13—H13	0.9500
C3—C4	1.395 (3)		
O1—Cu1—O1^i	180.000 (1)	C5—C4—Cl1	119.90 (16)

O1—Cu1—N1	91.28 (6)	C3—C4—Cl1	119.02 (15)
O1—Cu1—N1ⁱ	88.72 (6)	C4—C5—C6	120.01 (19)
O1ⁱ—Cu1—N1ⁱ	91.28 (6)	C4—C5—H5	120.0
O1ⁱ—Cu1—N1	88.72 (6)	C6—C5—H5	120.0
N1ⁱ—Cu1—N1	180.0	C5—C6—C1	120.83 (18)
O3—S1—O2	120.99 (10)	C5—C6—C7	116.47 (18)
O3—S1—N2	104.25 (9)	C1—C6—C7	122.65 (18)
O2—S1—N2	105.94 (9)	N1—C7—C6	124.48 (19)
O3—S1—C8	110.55 (10)	N1—C7—H7	117.8
O2—S1—C8	109.09 (10)	C6—C7—H7	117.8
N2—S1—C8	104.59 (10)	C9—C8—C13	121.3 (2)
C1—O1—Cu1	128.38 (13)	C9—C8—S1	118.74 (16)
C7—N1—N2	114.29 (17)	C13—C8—S1	119.62 (17)
C7—N1—Cu1	126.86 (14)	C10—C9—C8	119.2 (2)
N2—N1—Cu1	118.75 (12)	C10—C9—H9	120.4
N1—N2—S1	112.10 (13)	C8—C9—H9	120.4
N1—N2—H2N	107.8 (18)	C9—C10—C11	119.9 (2)
S1—N2—H2N	103.9 (18)	C9—C10—H10	120.1
O1—C1—C6	124.07 (18)	C11—C10—H10	120.1
O1—C1—C2	119.77 (18)	C12—C11—C10	120.3 (2)
C6—C1—C2	116.16 (18)	C12—C11—H11	119.9
C3—C2—C1	122.80 (19)	C10—C11—H11	119.9
C3—C2—Br1	119.33 (15)	C11—C12—C13	120.9 (2)
C1—C2—Br1	117.84 (15)	C11—C12—H12	119.5
C2—C3—C4	119.11 (18)	C13—C12—H12	119.5
C2—C3—H3	120.4	C12—C13—C8	118.4 (2)
C4—C3—H3	120.4	C12—C13—H13	120.8
C5—C4—C3	121.08 (19)	C8—C13—H13	120.8
N1ⁱ—Cu1—O1—C1	163.78 (17)	C4—C5—C6—C7	177.20 (19)
N1—Cu1—O1—C1	−16.22 (17)	O1—C1—C6—C5	−179.35 (19)
O1—Cu1—N1—C7	11.64 (18)	C2—C1—C6—C5	0.6 (3)
O1ⁱ—Cu1—N1—C7	−168.36 (18)	O1—C1—C6—C7	3.4 (3)
O1—Cu1—N1—N2	−164.50 (14)	C2—C1—C6—C7	−176.57 (19)
O1ⁱ—Cu1—N1—N2	15.50 (14)	N2—N1—C7—C6	173.81 (18)
C7—N1—N2—S1	−84.65 (18)	Cu1—N1—C7—C6	−2.5 (3)
Cu1—N1—N2—S1	91.96 (14)	C5—C6—C7—N1	174.74 (19)
O3—S1—N2—N1	−169.59 (13)	C1—C6—C7—N1	−7.9 (3)
O2—S1—N2—N1	61.73 (15)	O3—S1—C8—C9	−169.03 (17)
C8—S1—N2—N1	−53.47 (15)	O2—S1—C8—C9	−33.7 (2)
Cu1—O1—C1—C6	11.6 (3)	N2—S1—C8—C9	79.30 (19)
Cu1—O1—C1—C2	−168.43 (14)	O3—S1—C8—C13	17.7 (2)
O1—C1—C2—C3	179.09 (19)	O2—S1—C8—C13	153.05 (17)
C6—C1—C2—C3	−0.9 (3)	N2—S1—C8—C13	−93.98 (19)
O1—C1—C2—Br1	0.9 (3)	C13—C8—C9—C10	0.9 (3)
C6—C1—C2—Br1	−179.07 (14)	S1—C8—C9—C10	−172.22 (17)
C1—C2—C3—C4	0.7 (3)	C8—C9—C10—C11	−0.1 (3)
Br1—C2—C3—C4	178.82 (15)	C9—C10—C11—C12	−1.1 (3)

C2—C3—C4—C5	−0.2 (3)	C10—C11—C12—C13	1.4 (4)
C2—C3—C4—Cl1	179.83 (16)	C11—C12—C13—C8	−0.5 (4)
C3—C4—C5—C6	−0.1 (3)	C9—C8—C13—C12	−0.6 (3)
Cl1—C4—C5—C6	179.93 (15)	S1—C8—C13—C12	172.46 (18)
C4—C5—C6—C1	−0.2 (3)		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N2—H2*N*⋯O1[i]	0.88 (1)	2.07 (2)	2.722 (2)	130 (2)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.