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

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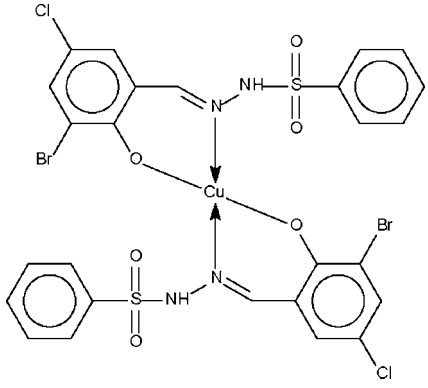
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.021; $wR$ factor = 0.062; data-to-parameter ratio = 16.1.

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

$[Cu(C_{13}H_9BrClN_2O_3S)_2]$
$M_r$ = 840.82
Triclinic, $P\overline{1}$
$a$ = 8.0688 (1) Å
$b$ = 8.2755 (1) Å
$c$ = 11.7386 (2) Å
$\alpha$ = 95.955 (1)°
$\beta$ = 90.133 (1)°
$\gamma$ = 115.159 (1)°
$V$ = 704.70 (2) Å$^3$
$Z$ = 1
Mo $K\alpha$ radiation
$\mu$ = 4.00 mm$^{-1}$
$T$ = 100 (2) K
0.20 × 0.09 × 0.09 mm

### Data collection

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

### Refinement

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

**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···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2N···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).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2424).

## References

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# supplementary materials

*Acta Cryst.* (2008). E**64**, m1039 [ **doi:10.1107/S1600536808022022** ]

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

**J. Yusnita, H. M. Ali, S. Puvaneswary, W. T. Robinson and S. W. Ng**

## 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.

## 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.

## 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 1.2$U_{eq}$(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.

## Figures

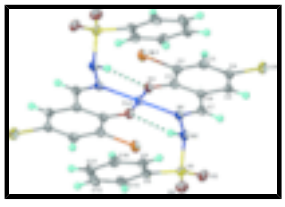


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) plot of $Cu(C_{13}H_9BrClN_2O_3S)_2$ at the 70% probability level. Hydrogen atoms are drawn as spheres of arbitrary radius. Hydrogen bonds are denoted by dashed lines. The copper atom lies on a center of inversion, and unlabeled atoms are related to their labeled equivalents by $1-x$, $1-y$, $1-z$.

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

*Crystal data*

| | |
|---|---|
| $[Cu(C_{13}H_9BrClN_2O_3S)_2]$ | $Z = 1$ |
| $M_r = 840.82$ | $F_{000} = 415$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.981$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation |

| | |
|---|---|
| | λ = 0.71073 Å |
| *a* = 8.0688 (1) Å | Cell parameters from 5423 reflections |
| *b* = 8.2755 (1) Å | θ = 2.7–28.4º |
| *c* = 11.7386 (2) Å | μ = 4.00 mm$^{-1}$ |
| α = 95.955 (1)º | *T* = 100 (2) K |
| β = 90.133 (1)º | Block, purple |
| γ = 115.159 (1)º | 0.20 × 0.09 × 0.09 mm |
| *V* = 704.70 (2) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART APEX diffractometer | 3214 independent reflections |
| Radiation source: fine-focus sealed tube | 2928 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.017 |
| *T* = 100(2) K | $\theta_{max}$ = 27.5º |
| ω scans | $\theta_{min}$ = 1.8º |
| Absorption correction: Multi-scan (SADABS; Sheldrick, 1996) | *h* = −8→10 |
| $T_{min}$ = 0.502, $T_{max}$ = 0.715 | *k* = −10→10 |
| 8995 measured reflections | *l* = −15→15 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.021 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.061 | $w = 1/[\sigma^2(F_o^2) + (0.0332P)^2 + 0.5714P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| *S* = 1.05 | $(\Delta/\sigma)_{max}$ = 0.001 |
| 3214 reflections | $\Delta\rho_{max}$ = 0.52 e Å$^{-3}$ |
| 200 parameters | $\Delta\rho_{min}$ = −0.29 e Å$^{-3}$ |
| 1 restraint | Extinction correction: none |
| Primary atom site location: structure-invariant direct methods | |

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *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, °)*

| | | | |
|---|---|---|---|
| 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—N1$^{i}$ | 88.72 (6) | C4—C5—C6 | 120.01 (19) |
| O1$^{i}$—Cu1—N1$^{i}$ | 91.28 (6) | C4—C5—H5 | 120.0 |
| O1$^{i}$—Cu1—N1 | 88.72 (6) | C6—C5—H5 | 120.0 |
| N1$^{i}$—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 |
| N1$^{i}$—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) |
| O1$^{i}$—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) |
| O1$^{i}$—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) | | |

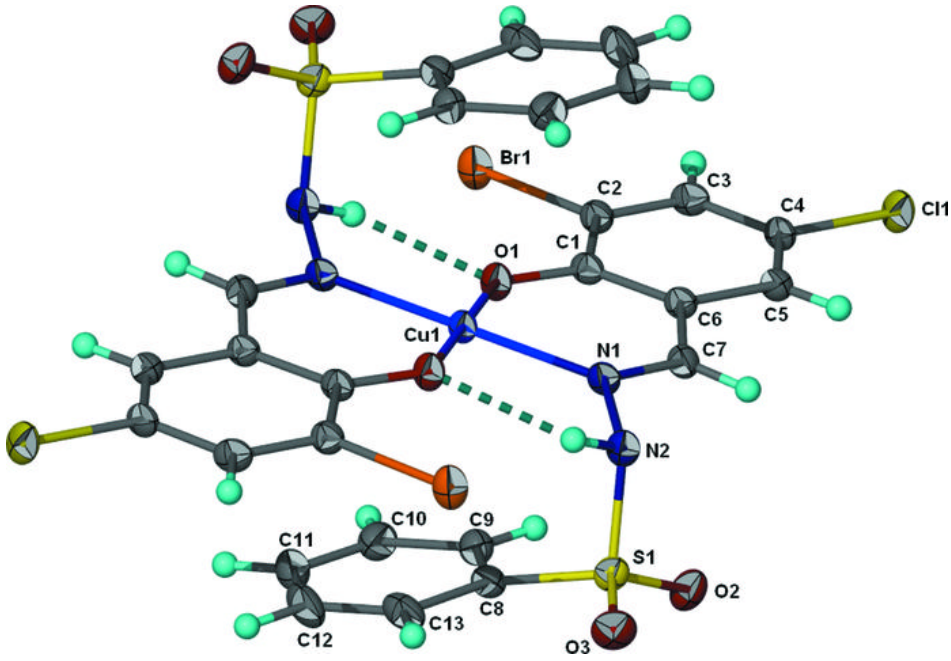
Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2N···O1$^{i}$ | 0.88 (1) | 2.07 (2) | 2.722 (2) | 130 (2) |

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

**Fig. 1**


Br1
C2
C3
C4
Cl1
C1
O1
C6
C5
Cu1
N1
C7
N2
C10
C9
C11
S1
O2
C8
C13
C12
O3