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# [1-(2-Oxidobenzylidene)-4-phenylthiosemicarbazidato-$\kappa^3O,N^1,S$](pyridine-$\kappa N$)-copper(II)

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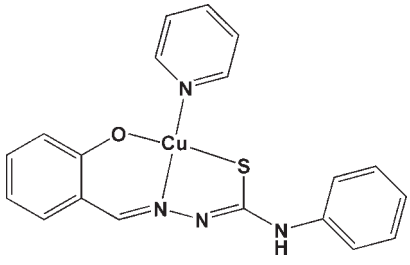
Key indicators: single-crystal X-ray study; $T$ = 173 K; mean $\sigma$(C–C) = 0.004 Å; disorder in main residue; $R$ factor = 0.038; $wR$ factor = 0.080; data-to-parameter ratio = 11.2.

In the structure of the title compound, $[Cu(C_{14}H_{11}N_3OS)(C_5H_5N)]$, the $Cu^{II}$ atom exhibits a slightly distorted square-planar $CuN_2OS$ coordination polyhedron consisting of a phenyl O, an azomethine N and a thioamide S atom from the tridentate thiosemicarbazonate dianion, and the N atom of a pyridine molecule. The thiosemicarbazonate ligand exists in the thiol tautomeric form as an *E* isomer. Rotational disorder of the pyridine and phenyl rings in a 1:1 ratio of the respective components is observed. An extensive network of weak N—H···S, C—H···O, C—H···N and C—H···S hydrogen-bonding interactions consolidates the structure.

## Related literature

For general background to thiosemicarbazonates, see: Garoufilis *et al.* (2009); Stanojkovic *et al.* (2010); Kaur *et al.* (2007). For related structures, see: John *et al.* (2002); Naik *et al.* (2003); Cao *et al.* (2007); Seena & Kurup (2008).




## Experimental

### Crystal data

$[Cu(C_{14}H_{11}N_3OS)(C_5H_5N)]$
$M_r$ = 411.96
Monoclinic, $P2_1/n$
$a$ = 18.2958 (17) Å
$b$ = 4.5610 (5) Å
$c$ = 20.473 (2) Å
$\beta$ = 93.602 (7)°
$V$ = 1705.1 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.42 mm$^{-1}$
$T$ = 173 K
0.50 × 0.06 × 0.05 mm

### Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min}$ = 0.540, $T_{max}$ = 0.938
19901 measured reflections
3493 independent reflections
2522 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.078

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.080
$S$ = 1.02
3493 reflections
311 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.45 e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Cu1—O1 | 1.9126 (19) | Cu1—N4 | 2.010 (2) |
| Cu1—N1 | 1.926 (2) | Cu1—S1 | 2.2626 (8) |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N3—H3$N$···S1$^{i}$ | 0.74 (3) | 2.90 (3) | 3.593 (3) | 157 (3) |
| C10$A$—H10$A$···N2 | 0.95 | 2.28 | 2.852 (7) | 118 |
| C10$B$—H10$B$···N2 | 0.95 | 2.43 | 2.936 (7) | 113 |
| C14$B$—H14$B$···S1$^{i}$ | 0.95 | 2.81 | 3.679 (6) | 152 |
| C15$B$—H15$B$···O1$^{ii}$ | 0.95 | 2.40 | 3.339 (7) | 169 |
| C16$A$—H16$A$···O1$^{iii}$ | 0.95 | 2.53 | 3.371 (7) | 148 |

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2343).

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# supporting information

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## [1-(2-Oxidobenzylidene)-4-phenylthiosemicarbazidato-$\kappa^3O,N^1,S$](pyridine-$\kappa N$)copper(II)

**Vladimir V. Bon, Svitlana I. Orysyk and Vasily I. Pekhnyo**

### S1. Comment

Thiosemicarbazones and their metal complexes attract constant scientific interest due to their antimicrobial, antifungal and antitumoral activities (Garoufilis *et al.*, 2009; Stanojkovic *et al.*, 2010). Moreover, some thiosemicarbazones are used as reagents for determination of Co(II), Ni(II), Cu(II) and Pd(II) by solid phase microextraction in HPLC (Kaur *et al.*, 2007). Several crystal structures of salicylaldehyde (4)-phenylthiosemicarbazone metal complexes with Ni(II), Cu(II), Co(II) and Zn(II) have been reported previously (John *et al.*, 2002; Naik *et al.*, 2003; Cao *et al.*, 2007; Seena & Kurup, 2008).

The title compound crystallizes with one molecule in the asymmetric unit (Fig. 1), which differs from the previously reported Ni compound (Cao *et al.*, 2007) that crystallizes with two different molecules. The copper atom in the title structure exhibits a slightly distorted square-planar coordination with a mean deviation from the Cu1/O1/N1/S1/N4 plane of 0.0485 Å. The doubly deprotonated ligand molecule coordinates to the copper(II) atom in a tridentate manner *via* a phenyl oxygen, an azomethine nitrogen and a thioamide sulfur atom, creating five- and six-membered chelate metalla rings. The pyridine molecule completes the square-planar coordination environment of the Cu(II) atom. Values of Cu—O, Cu—N and Cu—S bond lengths are in a good agreement with related structures (Naik *et al.*, 2003). The C8—S1 (1.749 (3) Å) and C8—N2 (1.299 (3) Å) bond lengths indicate the presence of the thiol tautomeric form of the thiosemicarbazone in the structure. The value of the torsion angle N1—N2—C8—N3 = -179.9 (2)° confirms the presence of the *E*-isomer for the coordinating ligand molecule.

The title structure contains several planar fragments. The major part Cu1/O1/N1/N2/S1/C1—C9 (denoted as plane A) has a mean deviation from the least squares plane of 0.023 Å. The disordered phenyl ring contains two planar fragments C9/C10A/C11A/C12/C13A/C14A (plane B) and C9/C10B/C11B/C12/C13B/C14B (plane C) with a mean deviation from the corresponding least squares planes of 0.026 and 0.020 Å, respectively. The dihedral angles between planes A/B, A/C and B/C are 17.00 (19)°, 26.3 (2)° and 43.1 (3)°. The mean deviations from the least squares planes for the disordered pyridine ring N4/C15A/C16A/C17/C18A/C19A (plane D) and N4/C15B/C16B/C17/C18B/C19B (plane E) amount to 0.0054 and 0.0329 Å, respectively, with a dihedral angle between planes D and E of 51.2 (3)°.

The crystal packing of the title compound (Fig. 2) is characterised by an alternating arrangement of disordered phenyl and pyridine rings in neighboring molecules (configuration A and B). An extensive network of weak N—H···S, C—H···O, C—H···N and C—H···S hydrogen bonding interactions additionally stabilizes the crystal structure (Table 2).

### S2. Experimental

20 ml ($5\times10^{-3}$ M) of an aqueous solution of copper acetate was stirred in a cone flask for 2 hours with a mixture that contained 10 ml ($10^{-2}$ M) of an ethanolic solution of salicylaldehyde (4)-phenylthiosemicarbazone and 2 ml of pyridine. The resulting solution was left for 3 days in a dark place. As a result, brown needle-like crystals of title compound were

isolated from the solution.

### S3. Refinement

The structure refinement indicates rotational disorder of phenyl (C(9)—C(14)) and pyridine (C(15)—C19)N(4)) rings. For this reason, both positions for the atoms C(10), C(11), C(12), C(13), C(15), C(16), C(18) and C(19) were refined with occupancies of 0.5. All disordered ring atoms were refined anisotropically. The hydrogen atom bonded to N(3) was found from a difference Fourier map and was refined freely. All other hydrogen atoms were constrained geometrically and refined using a "riding model" on the parent atom with d(C—H) = 0.95 Å and Uiso(H) = 1.5Ueq(C).

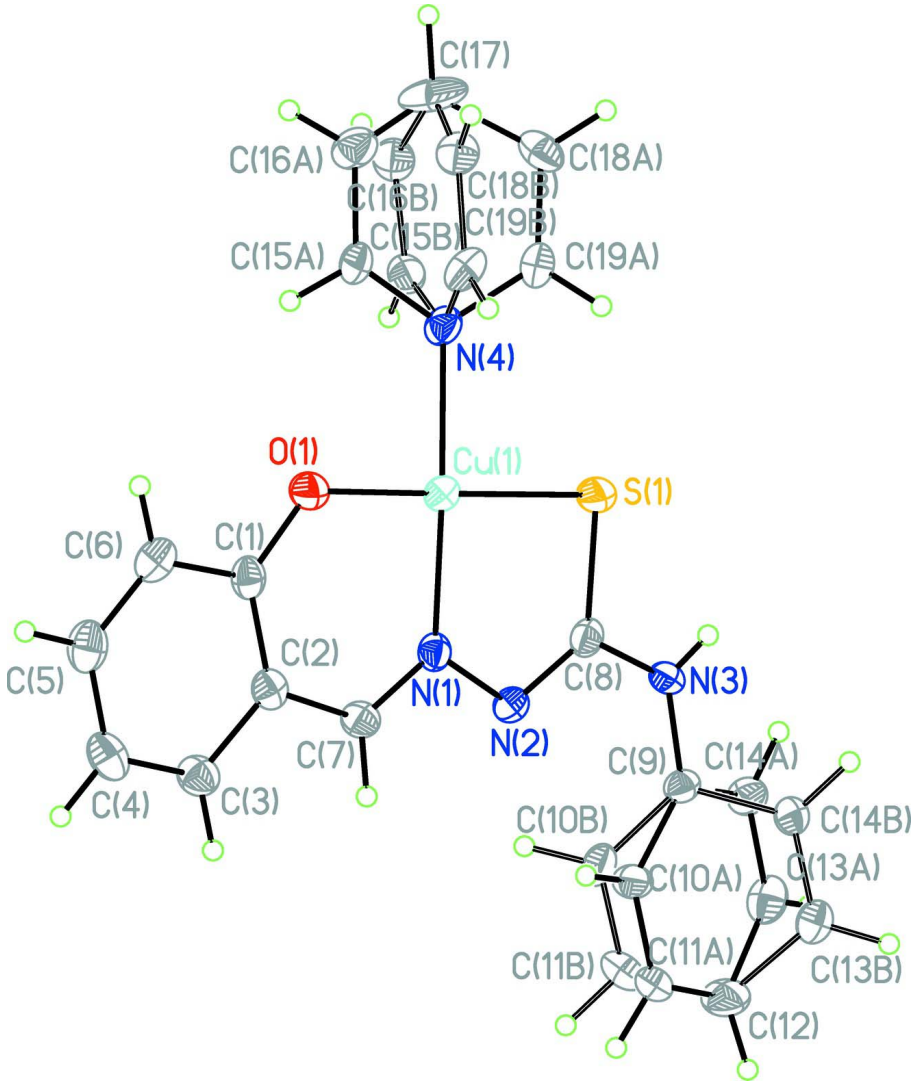


**Figure 1**

View of the molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Both positions of the disordered phenyl and pyridine rings are shown.

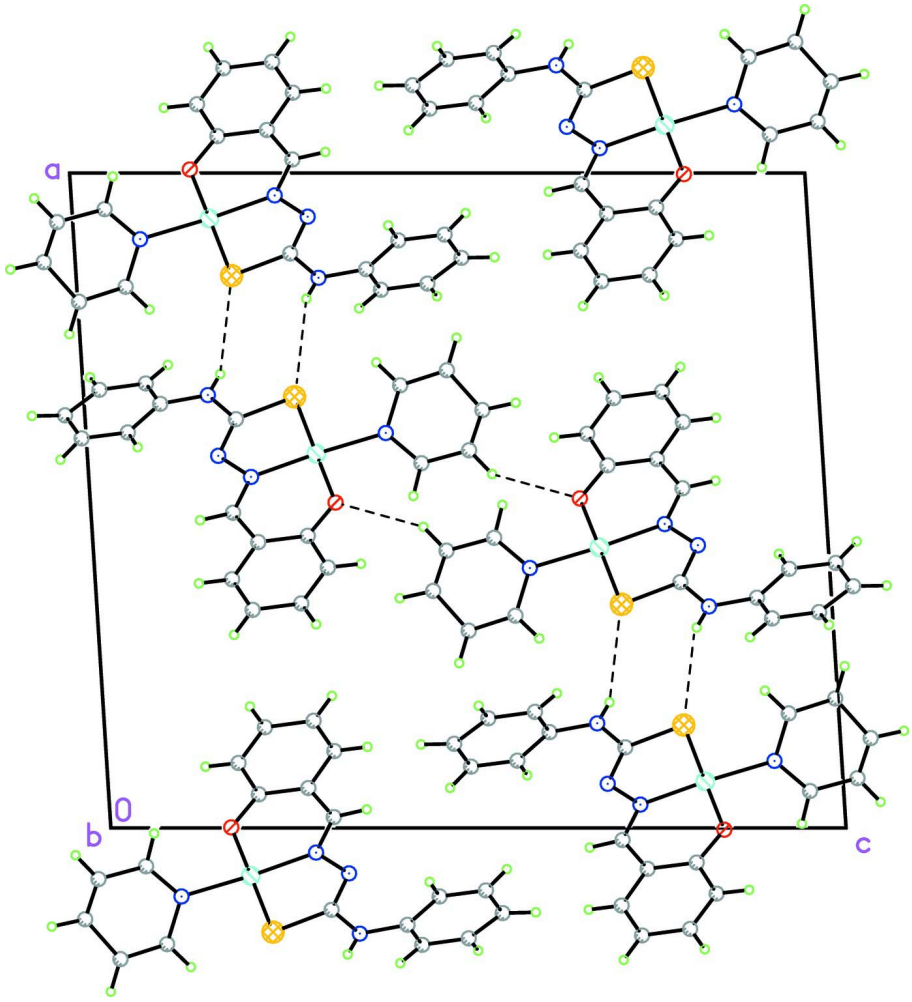


**Figure 2**

Crystal packing of title compound showing only the A position for the disordered phenyl and pyridine rings in a projection along the *b* axis. Dashed lines indicate hydrogen bonds.

**[1-(2-Oxidobenzylidene)-4-phenylthiosemicarbazidato-$\kappa^3O,N^1,S$](pyridine-$\kappa N$)copper(II)**

*Crystal data*

[Cu($C_{14}H_{11}N_3OS$)($C_5H_5N$)]
$M_r$ = 411.96
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a$ = 18.2958 (17) Å
$b$ = 4.5610 (5) Å
$c$ = 20.473 (2) Å
$\beta$ = 93.602 (7)°
$V$ = 1705.1 (3) Å$^3$
$Z$ = 4
$F$(000) = 844
$D_x$ = 1.605 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 2588 reflections
$\theta$ = 2.2–23.9°
$\mu$ = 1.42 mm$^{-1}$
$T$ = 173 K
Needle, brown
0.50 × 0.06 × 0.05 mm

*Data collection*

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.33 pixels mm$^{-1}$
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min}$ = 0.540, $T_{max}$ = 0.938

19901 measured reflections
3493 independent reflections
2522 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.078
$\theta_{max}$ = 26.4°, $\theta_{min}$ = 1.5°
$h$ = −22→22
$k$ = −5→5
$l$ = −25→25

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.080
$S$ = 1.02
3493 reflections
311 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 1.1058P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.33 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.45 e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Cu1 | 0.428933 (18) | 0.04089 (8) | 0.687460 (17) | 0.02260 (12) | |
| S1 | 0.34247 (4) | 0.37030 (18) | 0.71230 (4) | 0.0274 (2) | |
| N1 | 0.46424 (12) | 0.0759 (5) | 0.77777 (11) | 0.0194 (5) | |
| N2 | 0.43213 (12) | 0.2699 (5) | 0.82056 (11) | 0.0207 (6) | |
| N3 | 0.33957 (14) | 0.6080 (6) | 0.82989 (13) | 0.0224 (6) | |
| H3N | 0.3077 (15) | 0.674 (6) | 0.8115 (14) | 0.017 (9)* | |
| N4 | 0.39751 (13) | 0.0530 (5) | 0.59166 (11) | 0.0223 (6) | |
| O1 | 0.50312 (10) | −0.2308 (4) | 0.66541 (9) | 0.0253 (5) | |
| C1 | 0.55353 (15) | −0.3487 (6) | 0.70570 (15) | 0.0217 (7) | |
| C2 | 0.56305 (14) | −0.2790 (6) | 0.77319 (14) | 0.0200 (7) | |
| C3 | 0.61943 (15) | −0.4170 (6) | 0.81158 (15) | 0.0251 (7) | |
| H3A | 0.6257 | −0.3696 | 0.8568 | 0.030* | |
| C4 | 0.66565 (16) | −0.6175 (7) | 0.78620 (16) | 0.0288 (8) | |
| H4A | 0.7035 | −0.7072 | 0.8131 | 0.035* | |
| C5 | 0.65588 (16) | −0.6865 (7) | 0.72001 (16) | 0.0306 (8) | |

| | | | | | |
|---|---|---|---|---|---|
| H5A | 0.6874 | −0.8251 | 0.7016 | 0.037* | |
| C6 | 0.60151 (16) | −0.5578 (7) | 0.68106 (15) | 0.0270 (7) | |
| H6A | 0.5959 | −0.6106 | 0.6361 | 0.032* | |
| C7 | 0.51859 (15) | −0.0705 (6) | 0.80498 (14) | 0.0214 (7) | |
| H7A | 0.5301 | −0.0368 | 0.8503 | 0.026* | |
| C8 | 0.37630 (15) | 0.4103 (6) | 0.79364 (14) | 0.0203 (7) | |
| C9 | 0.35281 (15) | 0.6925 (6) | 0.89537 (13) | 0.0187 (6) | |
| C12 | 0.37031 (17) | 0.8705 (7) | 1.02567 (15) | 0.0313 (8) | |
| H12A | 0.3713 | 0.9194 | 1.0708 | 0.038* | |
| C17 | 0.3627 (2) | 0.0996 (7) | 0.45900 (16) | 0.0404 (9) | |
| H17A | 0.3515 | 0.1147 | 0.4132 | 0.048* | |
| C10A | 0.3965 (3) | 0.5278 (16) | 0.9414 (3) | 0.0229 (15) | 0.50 |
| H10A | 0.4190 | 0.3501 | 0.9292 | 0.027* | 0.50 |
| C11A | 0.4055 (4) | 0.633 (2) | 1.0048 (4) | 0.029 (2) | 0.50 |
| H11A | 0.4380 | 0.5320 | 1.0350 | 0.035* | 0.50 |
| C13A | 0.3313 (3) | 1.0474 (15) | 0.9773 (3) | 0.0267 (14) | 0.50 |
| H13A | 0.3120 | 1.2319 | 0.9892 | 0.032* | 0.50 |
| C14A | 0.3216 (3) | 0.9506 (15) | 0.9135 (3) | 0.0238 (14) | 0.50 |
| H14A | 0.2933 | 1.0630 | 0.8821 | 0.029* | 0.50 |
| C15A | 0.4434 (3) | 0.1199 (15) | 0.5460 (3) | 0.0262 (15) | 0.50 |
| H15A | 0.4932 | 0.1536 | 0.5598 | 0.031* | 0.50 |
| C16A | 0.4238 (4) | 0.1436 (16) | 0.4804 (3) | 0.0291 (16) | 0.50 |
| H16A | 0.4599 | 0.1967 | 0.4513 | 0.035* | 0.50 |
| C18A | 0.3023 (3) | 0.0198 (13) | 0.5036 (3) | 0.0263 (14) | 0.50 |
| H18A | 0.2530 | −0.0121 | 0.4879 | 0.032* | 0.50 |
| C19A | 0.3251 (3) | −0.0019 (13) | 0.5681 (3) | 0.0226 (14) | 0.50 |
| H19A | 0.2904 | −0.0568 | 0.5985 | 0.027* | 0.50 |
| C10B | 0.4197 (4) | 0.6784 (15) | 0.9301 (3) | 0.0228 (15) | 0.50 |
| H10B | 0.4615 | 0.6127 | 0.9090 | 0.027* | 0.50 |
| C11B | 0.4269 (5) | 0.7590 (17) | 0.9955 (4) | 0.0270 (19) | 0.50 |
| H11B | 0.4727 | 0.7347 | 1.0194 | 0.032* | 0.50 |
| C13B | 0.2999 (3) | 0.8776 (14) | 0.9931 (3) | 0.0250 (14) | 0.50 |
| H13B | 0.2583 | 0.9315 | 1.0160 | 0.030* | 0.50 |
| C14B | 0.2924 (3) | 0.8055 (14) | 0.9280 (3) | 0.0226 (14) | 0.50 |
| H14B | 0.2464 | 0.8313 | 0.9045 | 0.027* | 0.50 |
| C15B | 0.4194 (3) | 0.2973 (15) | 0.5609 (3) | 0.0230 (14) | 0.50 |
| H15B | 0.4436 | 0.4488 | 0.5857 | 0.028* | 0.50 |
| C16B | 0.4073 (3) | 0.3304 (16) | 0.4944 (3) | 0.0259 (15) | 0.50 |
| H16B | 0.4265 | 0.4928 | 0.4720 | 0.031* | 0.50 |
| C18B | 0.3501 (3) | −0.1385 (13) | 0.4924 (3) | 0.0241 (14) | 0.50 |
| H18B | 0.3295 | −0.3044 | 0.4701 | 0.029* | 0.50 |
| C19B | 0.3662 (3) | −0.1547 (14) | 0.5595 (3) | 0.0258 (15) | 0.50 |
| H19B | 0.3533 | −0.3272 | 0.5821 | 0.031* | 0.50 |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.02066 (19) | 0.0297 (2) | 0.0176 (2) | 0.00297 (17) | 0.00239 (14) | −0.00190 (17) |

| | | | | | | |
|---|---|---|---|---|---|---|
| S1 | 0.0248 (4) | 0.0390 (5) | 0.0181 (4) | 0.0082 (4) | −0.0003 (3) | −0.0037 (4) |
| N1 | 0.0165 (12) | 0.0212 (13) | 0.0207 (14) | 0.0006 (11) | 0.0025 (10) | −0.0039 (11) |
| N2 | 0.0205 (13) | 0.0245 (14) | 0.0173 (14) | 0.0026 (11) | 0.0024 (11) | −0.0042 (11) |
| N3 | 0.0187 (14) | 0.0313 (16) | 0.0166 (14) | 0.0067 (12) | −0.0022 (12) | −0.0006 (12) |
| N4 | 0.0238 (13) | 0.0227 (14) | 0.0208 (14) | 0.0049 (12) | 0.0055 (11) | −0.0011 (12) |
| O1 | 0.0236 (11) | 0.0313 (12) | 0.0208 (11) | 0.0048 (10) | −0.0005 (9) | −0.0031 (10) |
| C1 | 0.0172 (15) | 0.0207 (16) | 0.0276 (18) | −0.0021 (13) | 0.0043 (13) | 0.0027 (14) |
| C2 | 0.0184 (15) | 0.0165 (15) | 0.0252 (17) | −0.0038 (12) | 0.0017 (13) | 0.0027 (13) |
| C3 | 0.0254 (16) | 0.0245 (17) | 0.0251 (17) | 0.0002 (14) | −0.0015 (13) | −0.0031 (14) |
| C4 | 0.0231 (16) | 0.0250 (18) | 0.038 (2) | 0.0038 (14) | −0.0031 (15) | 0.0021 (15) |
| C5 | 0.0280 (17) | 0.0256 (18) | 0.039 (2) | 0.0064 (15) | 0.0084 (16) | −0.0021 (16) |
| C6 | 0.0297 (17) | 0.0267 (17) | 0.0255 (17) | 0.0006 (14) | 0.0081 (14) | −0.0019 (14) |
| C7 | 0.0213 (15) | 0.0228 (16) | 0.0198 (16) | −0.0038 (13) | −0.0010 (13) | −0.0040 (13) |
| C8 | 0.0177 (15) | 0.0228 (17) | 0.0208 (16) | −0.0019 (13) | 0.0049 (12) | −0.0010 (13) |
| C9 | 0.0204 (15) | 0.0203 (16) | 0.0154 (16) | −0.0019 (13) | 0.0017 (12) | −0.0016 (13) |
| C12 | 0.0372 (19) | 0.036 (2) | 0.0198 (17) | 0.0057 (16) | −0.0021 (15) | −0.0090 (15) |
| C17 | 0.078 (3) | 0.028 (2) | 0.0147 (18) | 0.014 (2) | 0.0007 (19) | −0.0043 (15) |
| C10A | 0.026 (4) | 0.025 (4) | 0.017 (4) | 0.007 (3) | −0.001 (3) | −0.001 (3) |
| C11A | 0.020 (4) | 0.047 (6) | 0.019 (4) | 0.005 (4) | −0.003 (3) | 0.000 (4) |
| C13A | 0.028 (3) | 0.021 (3) | 0.032 (4) | 0.000 (3) | 0.007 (3) | −0.008 (3) |
| C14A | 0.025 (3) | 0.025 (4) | 0.022 (4) | −0.001 (3) | 0.002 (3) | 0.003 (3) |
| C15A | 0.020 (3) | 0.036 (4) | 0.023 (4) | 0.007 (3) | 0.006 (3) | −0.006 (3) |
| C16A | 0.036 (4) | 0.028 (4) | 0.024 (4) | 0.007 (3) | 0.007 (3) | 0.006 (3) |
| C18A | 0.025 (3) | 0.023 (4) | 0.029 (4) | 0.004 (3) | −0.009 (3) | −0.006 (3) |
| C19A | 0.019 (3) | 0.021 (4) | 0.028 (4) | 0.000 (3) | 0.007 (3) | −0.001 (3) |
| C10B | 0.023 (4) | 0.022 (4) | 0.025 (4) | 0.004 (3) | 0.009 (3) | 0.002 (3) |
| C11B | 0.024 (5) | 0.029 (5) | 0.028 (5) | 0.002 (3) | −0.009 (4) | 0.000 (4) |
| C13B | 0.024 (3) | 0.025 (4) | 0.026 (4) | 0.002 (3) | 0.006 (3) | −0.002 (3) |
| C14B | 0.020 (3) | 0.026 (4) | 0.022 (4) | 0.006 (3) | 0.002 (3) | 0.002 (3) |
| C15B | 0.020 (3) | 0.026 (4) | 0.023 (4) | 0.002 (3) | −0.001 (3) | −0.007 (3) |
| C16B | 0.026 (4) | 0.024 (4) | 0.028 (4) | 0.002 (3) | 0.002 (3) | 0.006 (3) |
| C18B | 0.027 (3) | 0.020 (3) | 0.025 (4) | −0.003 (3) | 0.002 (3) | −0.009 (3) |
| C19B | 0.030 (4) | 0.024 (4) | 0.024 (4) | −0.004 (3) | 0.011 (3) | −0.002 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu1—O1 | 1.9126 (19) | C12—C11A | 1.344 (10) |
| Cu1—N1 | 1.926 (2) | C12—C13B | 1.414 (7) |
| Cu1—N4 | 2.010 (2) | C12—C13A | 1.433 (7) |
| Cu1—S1 | 2.2626 (8) | C12—H12A | 0.9500 |
| S1—C8 | 1.749 (3) | C17—C16A | 1.191 (7) |
| N1—C7 | 1.294 (3) | C17—C18B | 1.311 (7) |
| N1—N2 | 1.400 (3) | C17—C16B | 1.491 (8) |
| N2—C8 | 1.299 (3) | C17—C18A | 1.522 (7) |
| N3—C8 | 1.370 (4) | C17—H17A | 0.9500 |
| N3—C9 | 1.401 (4) | C10A—C11A | 1.383 (10) |
| N3—H3N | 0.74 (3) | C10A—H10A | 0.9500 |
| N4—C19B | 1.270 (6) | C11A—H11A | 0.9500 |

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|---|---|---|---|
| N4—C15A | 1.330 (6) | C13A—C14A | 1.380 (8) |
| N4—C15B | 1.353 (7) | C13A—H13A | 0.9500 |
| N4—C19A | 1.403 (6) | C14A—H14A | 0.9500 |
| O1—C1 | 1.313 (3) | C15A—C16A | 1.373 (9) |
| C1—C6 | 1.411 (4) | C15A—H15A | 0.9500 |
| C1—C2 | 1.418 (4) | C16A—H16A | 0.9500 |
| C2—C3 | 1.406 (4) | C18A—C19A | 1.363 (8) |
| C2—C7 | 1.434 (4) | C18A—H18A | 0.9500 |
| C3—C4 | 1.370 (4) | C19A—H19A | 0.9500 |
| C3—H3A | 0.9500 | C10B—C11B | 1.387 (11) |
| C4—C5 | 1.392 (4) | C10B—H10B | 0.9500 |
| C4—H4A | 0.9500 | C11B—H11B | 0.9500 |
| C5—C6 | 1.368 (4) | C13B—C14B | 1.371 (8) |
| C5—H5A | 0.9500 | C13B—H13B | 0.9500 |
| C6—H6A | 0.9500 | C14B—H14B | 0.9500 |
| C7—H7A | 0.9500 | C15B—C16B | 1.374 (8) |
| C9—C14A | 1.369 (7) | C15B—H15B | 0.9500 |
| C9—C10B | 1.379 (7) | C16B—H16B | 0.9500 |
| C9—C10A | 1.413 (7) | C18B—C19B | 1.388 (8) |
| C9—C14B | 1.424 (6) | C18B—H18B | 0.9500 |
| C12—C11B | 1.338 (9) | C19B—H19B | 0.9500 |

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|---|---|---|---|
| O1—Cu1—N1 | 94.59 (9) | C18B—C17—C16B | 116.1 (4) |
| O1—Cu1—N4 | 87.20 (9) | C16A—C17—C18A | 121.2 (5) |
| N1—Cu1—N4 | 172.99 (10) | C16A—C17—H17A | 119.4 |
| O1—Cu1—S1 | 178.70 (7) | C18B—C17—H17A | 122.7 |
| N1—Cu1—S1 | 85.77 (7) | C16B—C17—H17A | 120.4 |
| N4—Cu1—S1 | 92.29 (7) | C18A—C17—H17A | 119.4 |
| C8—S1—Cu1 | 94.17 (10) | C11A—C10A—C9 | 118.1 (6) |
| C7—N1—N2 | 113.4 (2) | C11A—C10A—H10A | 121.0 |
| C7—N1—Cu1 | 124.9 (2) | C9—C10A—H10A | 121.0 |
| N2—N1—Cu1 | 121.63 (17) | C12—C11A—C10A | 123.1 (7) |
| C8—N2—N1 | 113.3 (2) | C12—C11A—H11A | 118.4 |
| C8—N3—C9 | 129.6 (3) | C10A—C11A—H11A | 118.4 |
| C8—N3—H3N | 113 (2) | C14A—C13A—C12 | 120.2 (5) |
| C9—N3—H3N | 117 (2) | C14A—C13A—H13A | 119.9 |
| C19B—N4—C15B | 120.6 (4) | C12—C13A—H13A | 119.9 |
| C15A—N4—C19A | 115.0 (4) | C9—C14A—C13A | 120.1 (6) |
| C19B—N4—Cu1 | 125.3 (3) | C9—C14A—H14A | 120.0 |
| C15A—N4—Cu1 | 122.5 (3) | C13A—C14A—H14A | 120.0 |
| C15B—N4—Cu1 | 113.7 (3) | N4—C15A—C16A | 124.6 (6) |
| C19A—N4—Cu1 | 122.4 (3) | N4—C15A—H15A | 117.7 |
| C1—O1—Cu1 | 126.73 (18) | C16A—C15A—H15A | 117.7 |
| O1—C1—C6 | 118.7 (3) | C17—C16A—C15A | 121.9 (6) |
| O1—C1—C2 | 124.0 (3) | C17—C16A—H16A | 119.1 |
| C6—C1—C2 | 117.3 (3) | C15A—C16A—H16A | 119.1 |
| C3—C2—C1 | 119.0 (3) | C19A—C18A—C17 | 114.2 (5) |
| C3—C2—C7 | 117.4 (3) | C19A—C18A—H18A | 122.9 |

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|---|---|---|---|
| C1—C2—C7 | 123.5 (3) | C17—C18A—H18A | 122.9 |
| C4—C3—C2 | 122.4 (3) | C18A—C19A—N4 | 123.0 (5) |
| C4—C3—H3A | 118.8 | C18A—C19A—H19A | 118.5 |
| C2—C3—H3A | 118.8 | N4—C19A—H19A | 118.5 |
| C3—C4—C5 | 118.4 (3) | C9—C10B—C11B | 120.8 (6) |
| C3—C4—H4A | 120.8 | C9—C10B—H10B | 119.6 |
| C5—C4—H4A | 120.8 | C11B—C10B—H10B | 119.6 |
| C6—C5—C4 | 121.0 (3) | C12—C11B—C10B | 121.2 (7) |
| C6—C5—H5A | 119.5 | C12—C11B—H11B | 119.4 |
| C4—C5—H5A | 119.5 | C10B—C11B—H11B | 119.4 |
| C5—C6—C1 | 121.9 (3) | C14B—C13B—C12 | 119.0 (5) |
| C5—C6—H6A | 119.1 | C14B—C13B—H13B | 120.5 |
| C1—C6—H6A | 119.1 | C12—C13B—H13B | 120.5 |
| N1—C7—C2 | 126.1 (3) | C13B—C14B—C9 | 120.7 (5) |
| N1—C7—H7A | 117.0 | C13B—C14B—H14B | 119.7 |
| C2—C7—H7A | 117.0 | C9—C14B—H14B | 119.7 |
| N2—C8—N3 | 119.6 (3) | N4—C15B—C16B | 121.2 (6) |
| N2—C8—S1 | 125.1 (2) | N4—C15B—H15B | 119.4 |
| N3—C8—S1 | 115.3 (2) | C16B—C15B—H15B | 119.4 |
| C14A—C9—N3 | 116.5 (4) | C15B—C16B—C17 | 116.9 (5) |
| C10B—C9—N3 | 125.1 (4) | C15B—C16B—H16B | 121.5 |
| C14A—C9—C10A | 120.2 (4) | C17—C16B—H16B | 121.5 |
| N3—C9—C10A | 123.3 (4) | C17—C18B—C19B | 121.8 (5) |
| C10B—C9—C14B | 117.7 (4) | C17—C18B—H18B | 119.1 |
| N3—C9—C14B | 117.1 (3) | C19B—C18B—H18B | 119.1 |
| C11B—C12—C13B | 120.0 (5) | N4—C19B—C18B | 122.3 (6) |
| C11A—C12—C13A | 117.5 (5) | N4—C19B—H19B | 118.8 |
| C11A—C12—H12A | 121.2 | C18B—C19B—H19B | 118.8 |
| C13A—C12—H12A | 121.2 | | |

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|---|---|---|---|
| N1—Cu1—S1—C8 | 1.70 (11) | C13B—C12—C13A—C14A | −77.5 (7) |
| N4—Cu1—S1—C8 | −171.55 (12) | C10B—C9—C14A—C13A | −36.8 (7) |
| O1—Cu1—N1—C7 | −3.4 (2) | N3—C9—C14A—C13A | 179.2 (5) |
| S1—Cu1—N1—C7 | 177.9 (2) | C10A—C9—C14A—C13A | −1.6 (8) |
| O1—Cu1—N1—N2 | 176.30 (19) | C14B—C9—C14A—C13A | 78.3 (8) |
| S1—Cu1—N1—N2 | −2.45 (18) | C12—C13A—C14A—C9 | −3.7 (9) |
| C7—N1—N2—C8 | −178.1 (2) | C19B—N4—C15A—C16A | 44.8 (8) |
| Cu1—N1—N2—C8 | 2.2 (3) | C15B—N4—C15A—C16A | −86.2 (8) |
| O1—Cu1—N4—C19B | 70.3 (4) | C19A—N4—C15A—C16A | 1.6 (9) |
| S1—Cu1—N4—C19B | −110.8 (4) | Cu1—N4—C15A—C16A | −177.0 (5) |
| O1—Cu1—N4—C15A | −55.3 (4) | C18B—C17—C16A—C15A | −44.0 (8) |
| S1—Cu1—N4—C15A | 123.5 (4) | C16B—C17—C16A—C15A | 77.8 (8) |
| O1—Cu1—N4—C15B | −103.2 (3) | C18A—C17—C16A—C15A | 1.2 (10) |
| S1—Cu1—N4—C15B | 75.7 (3) | N4—C15A—C16A—C17 | −1.4 (12) |
| O1—Cu1—N4—C19A | 126.2 (3) | C16A—C17—C18A—C19A | −1.4 (8) |
| S1—Cu1—N4—C19A | −55.0 (3) | C18B—C17—C18A—C19A | 69.4 (6) |
| N1—Cu1—O1—C1 | 4.4 (2) | C16B—C17—C18A—C19A | −41.7 (6) |
| N4—Cu1—O1—C1 | 177.6 (2) | C17—C18A—C19A—N4 | 1.8 (8) |

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| Cu1—O1—C1—C6 | 176.65 (19) | C19B—N4—C19A—C18A | −73.6 (7) |
| Cu1—O1—C1—C2 | −3.4 (4) | C15A—N4—C19A—C18A | −2.0 (8) |
| O1—C1—C2—C3 | −179.4 (3) | C15B—N4—C19A—C18A | 43.1 (7) |
| C6—C1—C2—C3 | 0.6 (4) | Cu1—N4—C19A—C18A | 176.6 (4) |
| O1—C1—C2—C7 | −0.2 (4) | C14A—C9—C10B—C11B | 42.1 (8) |
| C6—C1—C2—C7 | 179.8 (3) | N3—C9—C10B—C11B | −178.0 (5) |
| C1—C2—C3—C4 | −0.1 (4) | C10A—C9—C10B—C11B | −78.4 (9) |
| C7—C2—C3—C4 | −179.3 (3) | C14B—C9—C10B—C11B | 2.9 (9) |
| C2—C3—C4—C5 | −0.3 (4) | C11A—C12—C11B—C10B | 82.0 (13) |
| C3—C4—C5—C6 | 0.0 (5) | C13B—C12—C11B—C10B | 7.1 (10) |
| C4—C5—C6—C1 | 0.6 (5) | C13A—C12—C11B—C10B | −36.3 (8) |
| O1—C1—C6—C5 | 179.1 (3) | C9—C10B—C11B—C12 | −4.4 (11) |
| C2—C1—C6—C5 | −0.9 (4) | C11B—C12—C13B—C14B | −8.5 (9) |
| N2—N1—C7—C2 | −178.4 (2) | C11A—C12—C13B—C14B | −40.6 (8) |
| Cu1—N1—C7—C2 | 1.3 (4) | C13A—C12—C13B—C14B | 70.9 (7) |
| C3—C2—C7—N1 | −179.6 (3) | C12—C13B—C14B—C9 | 7.3 (9) |
| C1—C2—C7—N1 | 1.2 (4) | C14A—C9—C14B—C13B | −84.6 (8) |
| N1—N2—C8—N3 | −179.9 (2) | C10B—C9—C14B—C13B | −4.6 (8) |
| N1—N2—C8—S1 | −0.2 (3) | N3—C9—C14B—C13B | 176.3 (5) |
| C9—N3—C8—N2 | 0.5 (5) | C10A—C9—C14B—C13B | 32.3 (8) |
| C9—N3—C8—S1 | −179.3 (2) | C19B—N4—C15B—C16B | 1.2 (8) |
| Cu1—S1—C8—N2 | −1.4 (3) | C15A—N4—C15B—C16B | 62.1 (7) |
| Cu1—S1—C8—N3 | 178.4 (2) | C19A—N4—C15B—C16B | −46.9 (7) |
| C8—N3—C9—C14A | 161.8 (4) | Cu1—N4—C15B—C16B | 175.0 (5) |
| C8—N3—C9—C10B | 25.5 (6) | N4—C15B—C16B—C17 | 5.9 (9) |
| C8—N3—C9—C10A | −17.5 (6) | C16A—C17—C16B—C15B | −81.2 (8) |
| C8—N3—C9—C14B | −155.4 (4) | C18B—C17—C16B—C15B | −11.6 (8) |
| C14A—C9—C10A—C11A | 1.0 (9) | C18A—C17—C16B—C15B | 38.9 (7) |
| C10B—C9—C10A—C11A | 74.9 (9) | C16A—C17—C18B—C19B | 48.0 (7) |
| N3—C9—C10A—C11A | −179.8 (5) | C16B—C17—C18B—C19B | 10.8 (8) |
| C14B—C9—C10A—C11A | −38.5 (8) | C18A—C17—C18B—C19B | −77.4 (6) |
| C11B—C12—C11A—C10A | −83.6 (13) | C15A—N4—C19B—C18B | −39.3 (7) |
| C13B—C12—C11A—C10A | 34.8 (9) | C15B—N4—C19B—C18B | −2.7 (8) |
| C13A—C12—C11A—C10A | −10.2 (10) | C19A—N4—C19B—C18B | 81.0 (7) |
| C9—C10A—C11A—C12 | 5.2 (11) | Cu1—N4—C19B—C18B | −175.8 (4) |
| C11B—C12—C13A—C14A | 40.7 (8) | C17—C18B—C19B—N4 | −3.9 (9) |
| C11A—C12—C13A—C14A | 9.4 (8) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3*N*···S1$^{i}$ | 0.74 (3) | 2.90 (3) | 3.593 (3) | 157 (3) |
| C10*A*—H10*A*···N2 | 0.95 | 2.28 | 2.852 (7) | 118 |
| C10*B*—H10*B*···N2 | 0.95 | 2.43 | 2.936 (7) | 113 |
| C14*B*—H14*B*···S1$^{i}$ | 0.95 | 2.81 | 3.679 (6) | 152 |

| | | | | |
|---|---|---|---|---|
| C15*B*—H15*B*···O1$^{ii}$ | 0.95 | 2.40 | 3.339 (7) | 169 |
| C16*A*—H16*A*···O1$^{iii}$ | 0.95 | 2.53 | 3.371 (7) | 148 |

Symmetry codes: (i) −*x*+1/2, *y*+1/2, −*z*+3/2; (ii) *x*, *y*+1, *z*; (iii) −*x*+1, −*y*, −*z*+1.