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# Bis(1,10-phenanthroline-$\kappa^2N,N'$)(sulfato-*O*)copper(II) butane-2,3-diol monosolvate

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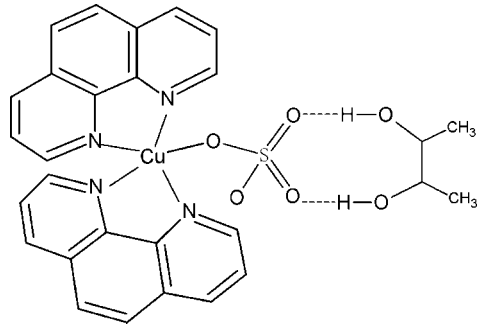
Key indicators: single-crystal X-ray study; $T$ = 223 K; mean $\sigma$(C–C) = 0.015 Å; disorder in main residue; $R$ factor = 0.046; $wR$ factor = 0.135; data-to-parameter ratio = 10.2.

The title compound, $[Cu(SO_4)(C_{12}H_8N_2)_2]\cdot C_4H_{10}O_2$, is comprised of neutral monomeric complex and butane-2,3-diol solvent molecules. In the complex, the $Cu^{II}$ ion is in a distorted square-pyramidal coordination environment defined by four N atoms from two chelating 1,10-phenanthroline ligands and one O atom from a monodentate sulfate anion; the O atom is at the apex. The two chelating $N_2C_2$ groups subtend a dihedral angle of 85.8 (4)°. In the crystal, the neutral monomeric complex and butane-2,3-diol solvent molecules are held together by O—H···O hydrogen bonding, which leads to additional stabilization of the structure. The presence of pseudosymmetry in the structure suggests the higher symmetry space group *C*2/*c*, but attempts to refine the structure in this space group resulted in an unsatisfactory model and high $R$ and $wR$ values. The sulfate anion is disordered over two sets of sites with occupancies of 0.55 (1) and 0.45 (1).

## Related literature

For the ethane-1,2-diol solvate of the title complex, see: Zhong (2011*a*), for the propane-1,2-diol solvate, see: Zhong (2011*b*) and for the propane-1,3-diol solvate, see: Zhong (2012). For related structures of transition metal complexes with a sulfate anion, see: Wang & Zhong (2011); Zhong & Ni (2012); Cui *et al.* (2010); Lu *et al.* (2006).



## Experimental

### Crystal data

$[Cu(SO_4)(C_{12}H_8N_2)_2]\cdot C_4H_{10}O_2$
$M_r$ = 610.13
Monoclinic, *Cc*
$a$ = 17.352 (4) Å
$b$ = 13.070 (3) Å
$c$ = 13.444 (3) Å
$\beta$ = 123.84 (3)°
$V$ = 2532.4 (13) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.00 mm$^{-1}$
$T$ = 223 K
0.32 × 0.27 × 0.21 mm

### Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (*REQAB*; Jacobson, 1998)
$T_{min}$ = 0.741, $T_{max}$ = 0.818
7154 measured reflections
4178 independent reflections
3542 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.026

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.135
$S$ = 0.99
4178 reflections
408 parameters
124 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.60 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.53 e Å$^{-3}$
Absolute structure: Flack (1983), 1317 Friedel pairs
Flack parameter: 0.55 (2)

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

| | | | |
|---|---|---|---|
| Cu1—O1 | 1.922 (11) | Cu1—N4 | 2.014 (7) |
| Cu1—O1′ | 1.944 (10) | Cu1—N3 | 2.091 (6) |
| Cu1—N1 | 2.000 (7) | Cu1—N2 | 2.186 (7) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O5—H5*B*···O3 | 0.82 | 1.92 | 2.73 (2) | 172 |
| O5—H5*B*···O4′ | 0.82 | 2.01 | 2.83 (2) | 176 |
| O6—H6···O3′ | 0.82 | 2.19 | 2.919 (16) | 148 |
| O6—H6···O4 | 0.82 | 1.95 | 2.720 (14) | 156 |

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear* (Rigaku, 2007); data reduction: *CrystalClear* (Rigaku, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2380).

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# supporting information

*Acta Cryst.* (2013). E**69**, m40–m41 [https://doi.org/10.1107/S1600536812049951]

# Bis(1,10-phenanthroline-$\kappa^2N,N'$)(sulfato-*O*)copper(II) butane-2,3-diol monosolvate

**Kai-Long Zhong and Guo-Qing Cao**

## S1. Comment

In the past few years, we have unexpectedly obtained and characterized some transition metal complexes with bidentate-chelating sulfate auxiliary ligand *via* alcohol-solvothermal reaction during attempts to synthesize mixed-ligand coordination polymers, such as cobalt complex (Wang & Zhong, 2011), nickel complex (Zhong & Ni, 2012), zinc complex (Cui *et al.*, 2010), cadmium complex (Lu *et al.*, 2006). The title compound $[CuSO_4(C_{12}H_8N_2)_2].C_4H_{10}O_2$, (I), was obtained by the similar alcohol-solvothermal reaction and its crystal structure has not hitherto been reported.

The X-ray diffraction experiment found that the title complex is isotypical to the previously reported $[CuSO_4(C_{12}H_8N_2)_2].C_2H_6O_2$ (Zhong, 2011*a*), (II), $[CuSO_4(C_{12}H_8N_2)_2].CH_2OHCHOHCH_3$ (Zhong, 2011*b*), (III), and $[CuSO_4(C_{12}H_8N_2)_2].CH_2OHCH_2CH_2OH$ (Zhong, 2012), (IV). The geometry of the phenanthroline and sulfate ligands are in good agreement with those reported in the (II), (III) and (IV). The $Cu^{II}$ metal ion is five-coordinated by four N atoms from two chelating phen ligands and an O atoms from a monodentate sulfate ligand, resulting in a distorted $CuN_4O$ square-pyramidal environment. The N1, N2, N3 and N4 atoms comprise a square, and the O1 atom site the apex of a square pyramid surrounding each metal atom (Fig 1). The dihedral angle of the two chelating N2C2 groups is 85.8 (4)°, which is larger than those reported in (II) [71.1 (2)°], (III) [84.9 (4)°] and (IV) [71.10 (15) Å], respectively. The Cu—O bond distance [1.922 (11) Å - 1.944 (10) Å], the Cu—N bond distance [2.000 (7) - 2.186 (7) Å], and the N—Cu—N bite angle [79.8 (3) - 81.6 (3)°] are comparable to those observed in (II), (III) and (IV) (Table 1).

In the crystal, the sulfate group is disordered over two positions with refined site occupancies of 0.55 (1) and 0.45 (1), and is hydrogen bonded to the solvent butane-2,3-diol molecule (Table 2 & Fig. 1).

## S2. Experimental

The single crystals of (I) suitable to X-ray analysis were obtained by 0.2 mmol phen, 0.1 mmol $CuSO_4.5H_2O$, 2.0 ml propane-1,3-diol and 1.0 ml water mixed and placed in a thick Pyrex tube, which was sealed and heated to 453 K for 72 h.

## S3. Refinement

The H atoms of phen were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C). The H atoms of propane-1,3-diol were placed in geometrically idealized positions and refined as riding atoms, with C—H($CH_3$) = 0.96 Å, C—H(CH) = 0.98 Å and O—H = 0.82 Å; $U_{iso}$(H) = 1.2$U_{eq}$(C) and 1.5$U_{eq}$(O). The presence of pseudo-symmetry in the structure suggests a higher symmetry space group *C*2/*c*. But attempts to refine the structure in the space group *C*2/*c* resulted in an unsatisfactory model and high *R* and *wR* values. Hence the requirement to solve in *Cc*. The reported Flack parameter was refined as s full least-squares and obtained by TWIN/BASF procedure in *SHELXL* (Sheldrick, 2008).

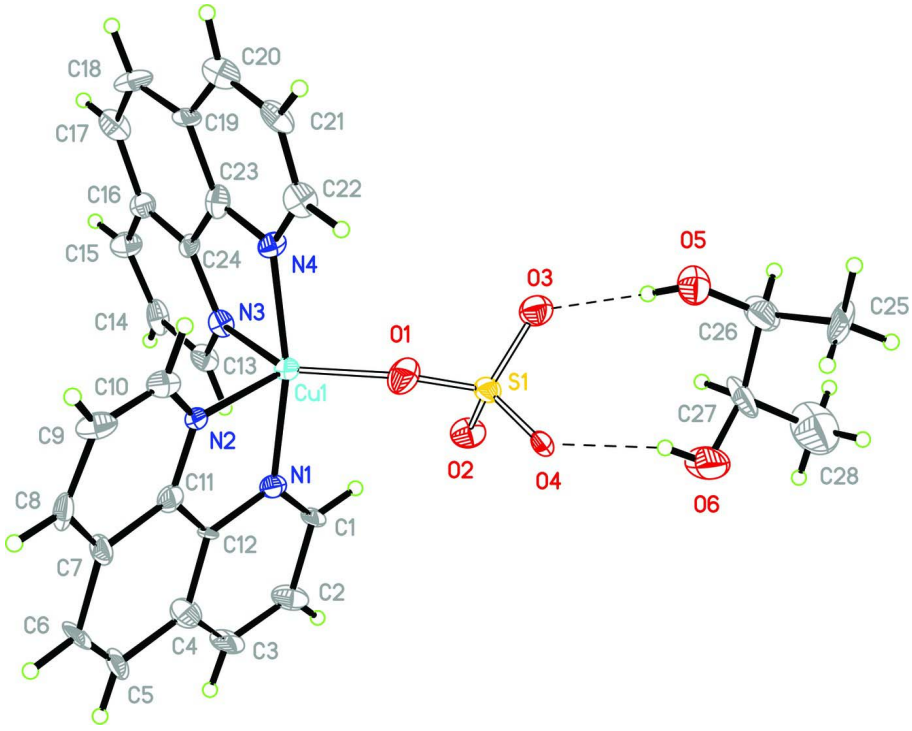


**Figure 1**

The molecular structure showing the atom-numbering scheme and with displacement ellipsoids drawn at the 35% probability level. Hydrogen bonds O—H···O are shown as dashed lines.

**Bis(1,10-phenanthroline-$\kappa^2N,N'$)(sulfato-*O*)copper(II) butane-2,3-diol monosolvate**

*Crystal data*

$[Cu(SO_4)(C_{12}H_8N_2)_2]\cdot C_4H_{10}O_2$
$M_r = 610.13$
Monoclinic, *Cc*
Hall symbol: C -2yc
$a = 17.352$ (4) Å
$b = 13.070$ (3) Å
$c = 13.444$ (3) Å
$\beta = 123.84$ (3)°
$V = 2532.4$ (13) Å$^3$
$Z = 4$
$F(000) = 1260$
$D_x = 1.600$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5509 reflections
$\theta = 3.2$–$27.5°$
$\mu = 1.00$ mm$^{-1}$
$T = 223$ K
Block, green
0.32 × 0.27 × 0.21 mm

*Data collection*

Rigaku Mercury CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite Monochromator monochromator
Detector resolution: 28.5714 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (REQAB; Jacobson, 1998)
$T_{min} = 0.741$, $T_{max} = 0.818$
7154 measured reflections
4178 independent reflections
3542 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.3°$
$h = -15\rightarrow22$
$k = -16\rightarrow15$
$l = -17\rightarrow16$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.135$
$S = 0.99$
4178 reflections
408 parameters
124 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.60$ e Å$^{-3}$
$\Delta\rho_{min} = -0.53$ e Å$^{-3}$
Absolute structure: Flack (1983), 1317 Friedel pairs
Absolute structure parameter: 0.55 (2)

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Cu1 | 0.26519 (10) | 0.30074 (3) | 0.29387 (13) | 0.02436 (16) | |
| S1 | 0.2748 (3) | 0.5417 (4) | 0.2771 (4) | 0.0265 (13) | 0.547 (12) |
| S1′ | 0.2569 (3) | 0.5422 (4) | 0.3106 (4) | 0.0170 (14) | 0.453 (12) |
| O1 | 0.2897 (10) | 0.4419 (8) | 0.3416 (12) | 0.043 (3) | 0.547 (12) |
| O1′ | 0.2430 (10) | 0.4435 (7) | 0.2448 (11) | 0.027 (3) | 0.453 (12) |
| O2 | 0.2706 (8) | 0.5188 (9) | 0.1677 (9) | 0.037 (3) | 0.547 (12) |
| O2′ | 0.2653 (8) | 0.5225 (8) | 0.4213 (8) | 0.023 (3) | 0.453 (12) |
| O3 | 0.1922 (11) | 0.5995 (16) | 0.2536 (19) | 0.041 (5) | 0.547 (12) |
| O3′ | 0.3442 (10) | 0.5860 (12) | 0.3305 (17) | 0.021 (3) | 0.453 (12) |
| O4 | 0.3552 (9) | 0.6066 (10) | 0.3586 (11) | 0.021 (3) | 0.547 (12) |
| O4′ | 0.1754 (13) | 0.6044 (16) | 0.2259 (16) | 0.027 (5) | 0.453 (12) |
| O5 | 0.2174 (4) | 0.7813 (3) | 0.3686 (4) | 0.0442 (11) | |
| H5B | 0.2079 | 0.7299 | 0.3282 | 0.066* | |
| O6 | 0.3460 (5) | 0.8062 (5) | 0.2956 (8) | 0.096 (3) | |
| H6 | 0.3455 | 0.7532 | 0.3279 | 0.144* | |
| N1 | 0.3506 (5) | 0.2822 (5) | 0.2394 (6) | 0.0244 (14) | |
| N2 | 0.3706 (5) | 0.2068 (4) | 0.4426 (6) | 0.0236 (15) | |
| N3 | 0.1647 (5) | 0.2096 (5) | 0.1528 (5) | 0.0220 (14) | |
| N4 | 0.1742 (5) | 0.2848 (5) | 0.3410 (6) | 0.0232 (14) | |
| C1 | 0.3444 (6) | 0.3269 (7) | 0.1484 (8) | 0.0282 (17) | |
| H1A | 0.3000 | 0.3772 | 0.1053 | 0.034* | |
| C2 | 0.4087 (7) | 0.2967 (7) | 0.1148 (9) | 0.038 (2) | |
| H2A | 0.4052 | 0.3285 | 0.0505 | 0.046* | |

| | | | | |
|---|---|---|---|---|
| C3 | 0.4728 (6) | 0.2229 (7) | 0.1768 (8) | 0.0375 (18) |
| H3A | 0.5100 | 0.2000 | 0.1517 | 0.045* |
| C4 | 0.4826 (7) | 0.1813 (8) | 0.2797 (9) | 0.038 (2) |
| C5 | 0.5554 (7) | 0.1082 (5) | 0.3559 (8) | 0.032 (2) |
| H5A | 0.5958 | 0.0858 | 0.3355 | 0.039* |
| C6 | 0.5640 (6) | 0.0738 (6) | 0.4535 (8) | 0.036 (2) |
| H6A | 0.6112 | 0.0273 | 0.5009 | 0.043* |
| C7 | 0.5031 (6) | 0.1051 (6) | 0.4909 (8) | 0.0281 (18) |
| C8 | 0.5105 (7) | 0.0762 (5) | 0.5960 (9) | 0.032 (2) |
| H8A | 0.5567 | 0.0309 | 0.6490 | 0.038* |
| C9 | 0.4489 (6) | 0.1151 (7) | 0.6208 (8) | 0.038 (2) |
| H9A | 0.4540 | 0.0982 | 0.6915 | 0.046* |
| C10 | 0.3805 (6) | 0.1789 (7) | 0.5391 (7) | 0.0277 (18) |
| H10A | 0.3384 | 0.2035 | 0.5554 | 0.033* |
| C11 | 0.4289 (5) | 0.1747 (6) | 0.4123 (7) | 0.0270 (18) |
| C12 | 0.4198 (5) | 0.2096 (5) | 0.3075 (7) | 0.0183 (15) |
| C13 | 0.1532 (6) | 0.1797 (6) | 0.0470 (7) | 0.0293 (19) |
| H13A | 0.1933 | 0.2046 | 0.0273 | 0.035* |
| C14 | 0.0804 (6) | 0.1109 (6) | −0.0329 (7) | 0.032 (2) |
| H14A | 0.0736 | 0.0927 | −0.1043 | 0.039* |
| C15 | 0.0208 (6) | 0.0714 (7) | −0.0069 (8) | 0.033 (2) |
| H15A | −0.0248 | 0.0245 | −0.0575 | 0.040* |
| C16 | 0.0311 (6) | 0.1046 (6) | 0.1007 (8) | 0.0284 (18) |
| C17 | −0.0306 (6) | 0.0719 (6) | 0.1307 (7) | 0.035 (2) |
| H17A | −0.0777 | 0.0261 | 0.0808 | 0.042* |
| C18 | −0.0226 (6) | 0.1067 (7) | 0.2327 (8) | 0.037 (2) |
| H18A | −0.0630 | 0.0823 | 0.2521 | 0.045* |
| C19 | 0.0465 (5) | 0.1794 (6) | 0.3089 (6) | 0.0215 (15) |
| C20 | 0.0547 (6) | 0.2284 (8) | 0.4077 (7) | 0.0346 (18) |
| H20A | 0.0129 | 0.2132 | 0.4283 | 0.042* |
| C21 | 0.1237 (7) | 0.2981 (6) | 0.4733 (9) | 0.036 (2) |
| H21A | 0.1324 | 0.3270 | 0.5420 | 0.043* |
| C22 | 0.1777 (6) | 0.3233 (7) | 0.4369 (6) | 0.0324 (19) |
| H22A | 0.2228 | 0.3726 | 0.4816 | 0.039* |
| C23 | 0.1077 (6) | 0.2146 (6) | 0.2782 (7) | 0.0281 (18) |
| C24 | 0.1010 (5) | 0.1709 (6) | 0.1728 (6) | 0.0194 (15) |
| C25 | 0.2642 (9) | 0.9498 (6) | 0.4054 (10) | 0.059 (3) |
| H25A | 0.2309 | 0.9594 | 0.4425 | 0.089* |
| H25B | 0.2663 | 1.0133 | 0.3711 | 0.089* |
| H25C | 0.3262 | 0.9275 | 0.4643 | 0.089* |
| C26 | 0.2142 (7) | 0.8676 (6) | 0.3052 (8) | 0.053 (2) |
| H26A | 0.1498 | 0.8877 | 0.2462 | 0.063* |
| C27 | 0.2654 (7) | 0.8516 (5) | 0.2453 (8) | 0.058 (2) |
| H27A | 0.2238 | 0.8072 | 0.1771 | 0.069* |
| C28 | 0.2703 (13) | 0.9468 (10) | 0.1881 (16) | 0.101 (5) |
| H28A | 0.3013 | 0.9326 | 0.1487 | 0.151* |
| H28B | 0.3040 | 0.9982 | 0.2482 | 0.151* |
| H28C | 0.2086 | 0.9709 | 0.1304 | 0.151* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0249 (3) | 0.0219 (2) | 0.0321 (3) | −0.0008 (5) | 0.0194 (2) | −0.0011 (5) |
| S1 | 0.026 (3) | 0.027 (2) | 0.029 (2) | −0.0005 (17) | 0.017 (2) | −0.0049 (19) |
| S1′ | 0.017 (3) | 0.014 (2) | 0.017 (2) | −0.0005 (17) | 0.008 (2) | −0.0029 (18) |
| O1 | 0.054 (5) | 0.037 (5) | 0.044 (5) | −0.006 (3) | 0.031 (4) | 0.005 (3) |
| O1′ | 0.045 (5) | 0.009 (4) | 0.029 (5) | 0.001 (3) | 0.023 (4) | 0.004 (3) |
| O2 | 0.043 (5) | 0.049 (5) | 0.029 (4) | −0.002 (3) | 0.025 (3) | −0.002 (3) |
| O2′ | 0.022 (4) | 0.024 (4) | 0.015 (4) | −0.009 (3) | 0.006 (3) | 0.001 (3) |
| O3 | 0.034 (6) | 0.042 (6) | 0.047 (7) | 0.000 (4) | 0.022 (4) | 0.005 (4) |
| O3′ | 0.017 (5) | 0.016 (5) | 0.028 (5) | −0.001 (3) | 0.011 (4) | −0.003 (4) |
| O4 | 0.017 (4) | 0.019 (5) | 0.021 (5) | 0.004 (3) | 0.007 (3) | −0.004 (3) |
| O4′ | 0.029 (6) | 0.028 (6) | 0.024 (6) | 0.002 (4) | 0.016 (4) | 0.003 (4) |
| O5 | 0.066 (3) | 0.038 (2) | 0.041 (2) | 0.001 (2) | 0.037 (2) | −0.0007 (19) |
| O6 | 0.076 (4) | 0.060 (4) | 0.188 (7) | 0.039 (3) | 0.096 (5) | 0.071 (4) |
| N1 | 0.023 (3) | 0.026 (3) | 0.027 (3) | −0.003 (3) | 0.016 (3) | −0.002 (3) |
| N2 | 0.027 (3) | 0.017 (3) | 0.038 (4) | −0.001 (2) | 0.025 (3) | 0.000 (2) |
| N3 | 0.019 (3) | 0.026 (3) | 0.011 (3) | 0.002 (2) | 0.002 (2) | −0.001 (2) |
| N4 | 0.022 (3) | 0.027 (3) | 0.019 (3) | −0.008 (3) | 0.010 (3) | −0.007 (3) |
| C1 | 0.033 (4) | 0.026 (3) | 0.047 (5) | 0.009 (3) | 0.036 (4) | 0.008 (3) |
| C2 | 0.034 (4) | 0.055 (5) | 0.035 (4) | 0.002 (3) | 0.025 (4) | −0.009 (3) |
| C3 | 0.038 (4) | 0.046 (4) | 0.048 (4) | 0.005 (3) | 0.035 (4) | −0.011 (4) |
| C4 | 0.043 (5) | 0.035 (4) | 0.048 (5) | 0.003 (4) | 0.033 (4) | −0.007 (3) |
| C5 | 0.034 (5) | 0.017 (3) | 0.044 (5) | 0.008 (3) | 0.021 (4) | −0.004 (3) |
| C6 | 0.023 (4) | 0.025 (4) | 0.054 (5) | 0.009 (3) | 0.018 (4) | −0.016 (3) |
| C7 | 0.023 (4) | 0.019 (3) | 0.031 (4) | 0.007 (3) | 0.009 (3) | 0.007 (3) |
| C8 | 0.029 (5) | 0.015 (3) | 0.033 (5) | −0.002 (3) | 0.006 (4) | 0.008 (3) |
| C9 | 0.034 (5) | 0.053 (5) | 0.039 (5) | −0.006 (4) | 0.028 (4) | 0.001 (4) |
| C10 | 0.026 (4) | 0.034 (4) | 0.026 (4) | −0.009 (4) | 0.016 (4) | −0.014 (3) |
| C11 | 0.019 (4) | 0.022 (3) | 0.031 (4) | −0.006 (3) | 0.008 (3) | −0.004 (3) |
| C12 | 0.013 (3) | 0.016 (3) | 0.034 (4) | 0.001 (3) | 0.018 (3) | −0.002 (3) |
| C13 | 0.031 (4) | 0.030 (3) | 0.026 (4) | −0.001 (4) | 0.015 (4) | −0.013 (3) |
| C14 | 0.039 (5) | 0.020 (3) | 0.020 (4) | 0.001 (3) | 0.005 (4) | −0.009 (3) |
| C15 | 0.021 (5) | 0.043 (4) | 0.028 (4) | −0.005 (4) | 0.009 (4) | −0.003 (4) |
| C16 | 0.022 (4) | 0.030 (4) | 0.029 (4) | 0.007 (3) | 0.012 (3) | 0.015 (4) |
| C17 | 0.026 (4) | 0.036 (4) | 0.030 (4) | 0.002 (3) | 0.007 (4) | −0.013 (3) |
| C18 | 0.022 (4) | 0.060 (5) | 0.034 (5) | −0.005 (4) | 0.018 (4) | 0.009 (4) |
| C19 | 0.009 (3) | 0.033 (3) | 0.020 (3) | 0.005 (3) | 0.007 (3) | 0.007 (3) |
| C20 | 0.029 (4) | 0.051 (4) | 0.019 (3) | 0.012 (3) | 0.010 (3) | 0.005 (3) |
| C21 | 0.044 (5) | 0.036 (4) | 0.033 (4) | 0.007 (3) | 0.025 (4) | −0.013 (3) |
| C22 | 0.024 (4) | 0.039 (4) | 0.017 (4) | −0.001 (3) | 0.001 (3) | −0.006 (3) |
| C23 | 0.033 (4) | 0.023 (4) | 0.019 (4) | 0.001 (3) | 0.008 (3) | 0.003 (3) |
| C24 | 0.026 (4) | 0.017 (3) | 0.019 (3) | 0.000 (3) | 0.015 (3) | 0.002 (3) |
| C25 | 0.104 (6) | 0.036 (4) | 0.074 (5) | −0.044 (4) | 0.071 (5) | −0.042 (4) |
| C26 | 0.070 (5) | 0.046 (4) | 0.069 (5) | 0.016 (4) | 0.055 (5) | 0.009 (4) |
| C27 | 0.104 (7) | 0.031 (3) | 0.082 (6) | 0.038 (4) | 0.079 (6) | 0.028 (4) |
| C28 | 0.149 (10) | 0.089 (8) | 0.110 (8) | 0.024 (7) | 0.100 (7) | 0.021 (6) |

*Geometric parameters (Å, º)*

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|---|---|---|---|
| Cu1—O1 | 1.922 (11) | C7—C11 | 1.445 (11) |
| Cu1—O1′ | 1.944 (10) | C8—C9 | 1.382 (14) |
| Cu1—N1 | 2.000 (7) | C8—H8A | 0.9300 |
| Cu1—N4 | 2.014 (7) | C9—C10 | 1.364 (12) |
| Cu1—N3 | 2.091 (6) | C9—H9A | 0.9300 |
| Cu1—N2 | 2.186 (7) | C10—H10A | 0.9300 |
| S1—O2 | 1.463 (10) | C11—C12 | 1.404 (12) |
| S1—O4 | 1.471 (12) | C13—C14 | 1.430 (11) |
| S1—O3 | 1.490 (15) | C13—H13A | 0.9300 |
| S1—O1 | 1.506 (11) | C14—C15 | 1.365 (14) |
| S1′—O2′ | 1.435 (10) | C14—H14A | 0.9300 |
| S1′—O4′ | 1.470 (15) | C15—C16 | 1.423 (14) |
| S1′—O3′ | 1.498 (14) | C15—H15A | 0.9300 |
| S1′—O1′ | 1.507 (10) | C16—C24 | 1.361 (12) |
| O5—C26 | 1.396 (9) | C16—C17 | 1.405 (12) |
| O5—H5B | 0.8200 | C17—C18 | 1.377 (12) |
| O6—C27 | 1.307 (9) | C17—H17A | 0.9300 |
| O6—H6 | 0.8200 | C18—C19 | 1.423 (12) |
| N1—C1 | 1.306 (10) | C18—H18A | 0.9300 |
| N1—C12 | 1.399 (10) | C19—C20 | 1.408 (11) |
| N2—C10 | 1.265 (11) | C19—C23 | 1.412 (11) |
| N2—C11 | 1.350 (11) | C20—C21 | 1.366 (13) |
| N3—C24 | 1.372 (10) | C20—H20A | 0.9300 |
| N3—C13 | 1.379 (10) | C21—C22 | 1.318 (14) |
| N4—C23 | 1.341 (10) | C21—H21A | 0.9300 |
| N4—C22 | 1.352 (11) | C22—H22A | 0.9300 |
| C1—C2 | 1.472 (12) | C23—C24 | 1.472 (11) |
| C1—H1A | 0.9300 | C25—C26 | 1.555 (13) |
| C2—C3 | 1.352 (13) | C25—H25A | 0.9600 |
| C2—H2A | 0.9300 | C25—H25B | 0.9600 |
| C3—C4 | 1.406 (13) | C25—H25C | 0.9600 |
| C3—H3A | 0.9300 | C26—C27 | 1.510 (9) |
| C4—C12 | 1.384 (11) | C26—H26A | 0.9800 |
| C4—C5 | 1.455 (13) | C27—C28 | 1.490 (14) |
| C5—C6 | 1.314 (13) | C27—H27A | 0.9800 |
| C5—H5A | 0.9300 | C28—H28A | 0.9600 |
| C6—C7 | 1.460 (12) | C28—H28B | 0.9600 |
| C6—H6A | 0.9300 | C28—H28C | 0.9600 |
| C7—C8 | 1.398 (14) | | |

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|---|---|---|---|
| O1—Cu1—O1′ | 32.6 (2) | N2—C10—C9 | 124.3 (8) |
| O1—Cu1—N1 | 99.6 (4) | N2—C10—H10A | 117.9 |
| O1′—Cu1—N1 | 92.2 (4) | C9—C10—H10A | 117.9 |
| O1—Cu1—N4 | 93.5 (4) | N2—C11—C12 | 121.1 (7) |
| O1′—Cu1—N4 | 99.5 (4) | N2—C11—C7 | 119.1 (8) |
| N1—Cu1—N4 | 166.8 (3) | C12—C11—C7 | 119.7 (8) |

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| O1—Cu1—N3 | 140.1 (4) | C4—C12—N1 | 121.5 (7) |
| O1′—Cu1—N3 | 109.3 (4) | C4—C12—C11 | 121.2 (7) |
| N1—Cu1—N3 | 90.7 (3) | N1—C12—C11 | 116.9 (7) |
| N4—Cu1—N3 | 79.8 (3) | N3—C13—C14 | 120.9 (8) |
| O1—Cu1—N2 | 108.5 (4) | N3—C13—H13A | 119.6 |
| O1′—Cu1—N2 | 139.1 (4) | C14—C13—H13A | 119.6 |
| N1—Cu1—N2 | 81.6 (3) | C15—C14—C13 | 121.6 (8) |
| N4—Cu1—N2 | 93.3 (3) | C15—C14—H14A | 119.2 |
| N3—Cu1—N2 | 111.08 (12) | C13—C14—H14A | 119.2 |
| O2—S1—O4 | 111.2 (9) | C14—C15—C16 | 117.5 (7) |
| O2—S1—O3 | 112.8 (11) | C14—C15—H15A | 121.3 |
| O4—S1—O3 | 105.5 (12) | C16—C15—H15A | 121.3 |
| O2—S1—O1 | 107.4 (7) | C24—C16—C17 | 120.5 (8) |
| O4—S1—O1 | 106.5 (8) | C24—C16—C15 | 118.5 (8) |
| O3—S1—O1 | 113.4 (12) | C17—C16—C15 | 121.0 (8) |
| O2′—S1′—O4′ | 113.7 (11) | C18—C17—C16 | 121.0 (8) |
| O2′—S1′—O3′ | 112.0 (9) | C18—C17—H17A | 119.5 |
| O4′—S1′—O3′ | 111.5 (12) | C16—C17—H17A | 119.5 |
| O2′—S1′—O1′ | 110.2 (7) | C17—C18—C19 | 121.0 (8) |
| O4′—S1′—O1′ | 104.4 (10) | C17—C18—H18A | 119.5 |
| O3′—S1′—O1′ | 104.3 (10) | C19—C18—H18A | 119.5 |
| S1—O1—Cu1 | 134.8 (9) | C20—C19—C23 | 115.4 (7) |
| S1′—O1′—Cu1 | 133.3 (8) | C20—C19—C18 | 125.8 (8) |
| C26—O5—H5B | 109.5 | C23—C19—C18 | 118.5 (7) |
| C27—O6—H6 | 109.5 | C21—C20—C19 | 120.3 (8) |
| C1—N1—C12 | 120.6 (7) | C21—C20—H20A | 119.9 |
| C1—N1—Cu1 | 126.8 (6) | C19—C20—H20A | 119.9 |
| C12—N1—Cu1 | 112.6 (5) | C22—C21—C20 | 118.4 (8) |
| C10—N2—C11 | 121.6 (7) | C22—C21—H21A | 120.8 |
| C10—N2—Cu1 | 131.8 (6) | C20—C21—H21A | 120.8 |
| C11—N2—Cu1 | 106.6 (5) | C21—C22—N4 | 126.6 (8) |
| C24—N3—C13 | 115.4 (6) | C21—C22—H22A | 116.7 |
| C24—N3—Cu1 | 112.8 (5) | N4—C22—H22A | 116.7 |
| C13—N3—Cu1 | 131.8 (6) | N4—C23—C19 | 124.2 (8) |
| C23—N4—C22 | 114.9 (8) | N4—C23—C24 | 116.8 (8) |
| C23—N4—Cu1 | 115.1 (6) | C19—C23—C24 | 119.0 (7) |
| C22—N4—Cu1 | 129.3 (6) | C16—C24—N3 | 126.2 (7) |
| N1—C1—C2 | 119.2 (8) | C16—C24—C23 | 119.7 (7) |
| N1—C1—H1A | 120.4 | N3—C24—C23 | 113.9 (7) |
| C2—C1—H1A | 120.4 | C26—C25—H25A | 109.5 |
| C3—C2—C1 | 120.4 (9) | C26—C25—H25B | 109.5 |
| C3—C2—H2A | 119.8 | H25A—C25—H25B | 109.5 |
| C1—C2—H2A | 119.8 | C26—C25—H25C | 109.5 |
| C2—C3—C4 | 119.4 (8) | H25A—C25—H25C | 109.5 |
| C2—C3—H3A | 120.3 | H25B—C25—H25C | 109.5 |
| C4—C3—H3A | 120.3 | O5—C26—C27 | 112.2 (6) |
| C12—C4—C3 | 118.7 (8) | O5—C26—C25 | 102.5 (7) |
| C12—C4—C5 | 119.4 (9) | C27—C26—C25 | 110.4 (9) |

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| C3—C4—C5 | 121.9 (9) | O5—C26—H26A | 110.5 |
| C6—C5—C4 | 119.9 (9) | C27—C26—H26A | 110.5 |
| C6—C5—H5A | 120.1 | C25—C26—H26A | 110.5 |
| C4—C5—H5A | 120.1 | O6—C27—C28 | 107.1 (9) |
| C5—C6—C7 | 123.2 (8) | O6—C27—C26 | 124.3 (7) |
| C5—C6—H6A | 118.4 | C28—C27—C26 | 112.2 (8) |
| C7—C6—H6A | 118.4 | O6—C27—H27A | 103.6 |
| C8—C7—C11 | 116.9 (8) | C28—C27—H27A | 103.6 |
| C8—C7—C6 | 126.6 (8) | C26—C27—H27A | 103.6 |
| C11—C7—C6 | 116.4 (8) | C27—C28—H28A | 109.5 |
| C9—C8—C7 | 119.8 (8) | C27—C28—H28B | 109.5 |
| C9—C8—H8A | 120.1 | H28A—C28—H28B | 109.5 |
| C7—C8—H8A | 120.1 | C27—C28—H28C | 109.5 |
| C10—C9—C8 | 118.3 (8) | H28A—C28—H28C | 109.5 |
| C10—C9—H9A | 120.9 | H28B—C28—H28C | 109.5 |
| C8—C9—H9A | 120.9 | | |

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| O2—S1—O1—Cu1 | −23.9 (15) | C11—C7—C8—C9 | −0.8 (12) |
| O4—S1—O1—Cu1 | −143.0 (11) | C6—C7—C8—C9 | 177.9 (8) |
| O3—S1—O1—Cu1 | 101.4 (15) | C7—C8—C9—C10 | 1.9 (12) |
| O1′—Cu1—O1—S1 | −14.2 (12) | C11—N2—C10—C9 | −0.1 (13) |
| N1—Cu1—O1—S1 | 64.7 (12) | Cu1—N2—C10—C9 | 176.6 (6) |
| N4—Cu1—O1—S1 | −116.4 (12) | C8—C9—C10—N2 | −1.5 (13) |
| N3—Cu1—O1—S1 | −38.2 (16) | C10—N2—C11—C12 | −177.2 (7) |
| N2—Cu1—O1—S1 | 149.0 (11) | Cu1—N2—C11—C12 | 5.4 (8) |
| O2′—S1′—O1′—Cu1 | −18.3 (14) | C10—N2—C11—C7 | 1.3 (11) |
| O4′—S1′—O1′—Cu1 | −140.8 (13) | Cu1—N2—C11—C7 | −176.1 (6) |
| O3′—S1′—O1′—Cu1 | 102.1 (13) | C8—C7—C11—N2 | −0.8 (11) |
| O1—Cu1—O1′—S1′ | −17.4 (12) | C6—C7—C11—N2 | −179.6 (7) |
| N1—Cu1—O1′—S1′ | −121.9 (12) | C8—C7—C11—C12 | 177.7 (7) |
| N4—Cu1—O1′—S1′ | 64.2 (12) | C6—C7—C11—C12 | −1.1 (11) |
| N3—Cu1—O1′—S1′ | 146.6 (11) | C3—C4—C12—N1 | −3.4 (13) |
| N2—Cu1—O1′—S1′ | −42.2 (15) | C5—C4—C12—N1 | 177.7 (7) |
| O1—Cu1—N1—C1 | −65.3 (8) | C3—C4—C12—C11 | −176.6 (8) |
| O1′—Cu1—N1—C1 | −33.4 (8) | C5—C4—C12—C11 | 4.5 (12) |
| N4—Cu1—N1—C1 | 119.4 (13) | C1—N1—C12—C4 | −1.3 (12) |
| N3—Cu1—N1—C1 | 76.0 (7) | Cu1—N1—C12—C4 | 176.2 (6) |
| N2—Cu1—N1—C1 | −172.8 (8) | C1—N1—C12—C11 | 172.3 (8) |
| O1—Cu1—N1—C12 | 117.4 (6) | Cu1—N1—C12—C11 | −10.3 (8) |
| O1′—Cu1—N1—C12 | 149.3 (6) | N2—C11—C12—C4 | 176.3 (8) |
| N4—Cu1—N1—C12 | −57.9 (17) | C7—C11—C12—C4 | −2.2 (11) |
| N3—Cu1—N1—C12 | −101.3 (5) | N2—C11—C12—N1 | 2.8 (10) |
| N2—Cu1—N1—C12 | 10.0 (5) | C7—C11—C12—N1 | −175.7 (7) |
| O1—Cu1—N2—C10 | 77.2 (8) | C24—N3—C13—C14 | −1.5 (10) |
| O1′—Cu1—N2—C10 | 91.0 (9) | Cu1—N3—C13—C14 | 176.2 (5) |
| N1—Cu1—N2—C10 | 174.6 (8) | N3—C13—C14—C15 | −0.9 (12) |
| N4—Cu1—N2—C10 | −17.6 (8) | C13—C14—C15—C16 | 2.7 (12) |
| N3—Cu1—N2—C10 | −97.9 (7) | C14—C15—C16—C24 | −2.0 (12) |

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|---|---|---|---|
| O1—Cu1—N2—C11 | −105.6 (6) | C14—C15—C16—C17 | 176.5 (8) |
| O1′—Cu1—N2—C11 | −91.8 (7) | C24—C16—C17—C18 | 0.6 (13) |
| N1—Cu1—N2—C11 | −8.2 (5) | C15—C16—C17—C18 | −177.8 (8) |
| N4—Cu1—N2—C11 | 159.6 (5) | C16—C17—C18—C19 | 2.1 (13) |
| N3—Cu1—N2—C11 | 79.2 (6) | C17—C18—C19—C20 | 172.6 (9) |
| O1—Cu1—N3—C24 | −94.2 (8) | C17—C18—C19—C23 | −0.5 (12) |
| O1′—Cu1—N3—C24 | −107.6 (6) | C23—C19—C20—C21 | −5.8 (12) |
| N1—Cu1—N3—C24 | 159.8 (5) | C18—C19—C20—C21 | −179.1 (8) |
| N4—Cu1—N3—C24 | −11.0 (5) | C19—C20—C21—C22 | 4.8 (13) |
| N2—Cu1—N3—C24 | 78.6 (6) | C20—C21—C22—N4 | −2.1 (14) |
| O1—Cu1—N3—C13 | 88.0 (9) | C23—N4—C22—C21 | 0.6 (13) |
| O1′—Cu1—N3—C13 | 74.6 (8) | Cu1—N4—C22—C21 | −168.9 (7) |
| N1—Cu1—N3—C13 | −18.0 (7) | C22—N4—C23—C19 | −1.9 (12) |
| N4—Cu1—N3—C13 | 171.2 (7) | Cu1—N4—C23—C19 | 169.2 (6) |
| N2—Cu1—N3—C13 | −99.2 (7) | C22—N4—C23—C24 | 179.7 (7) |
| O1—Cu1—N4—C23 | 151.3 (7) | Cu1—N4—C23—C24 | −9.2 (9) |
| O1′—Cu1—N4—C23 | 119.0 (7) | C20—C19—C23—N4 | 4.5 (12) |
| N1—Cu1—N4—C23 | −33.4 (18) | C18—C19—C23—N4 | 178.3 (8) |
| N3—Cu1—N4—C23 | 10.9 (5) | C20—C19—C23—C24 | −177.2 (7) |
| N2—Cu1—N4—C23 | −99.9 (6) | C18—C19—C23—C24 | −3.4 (11) |
| O1—Cu1—N4—C22 | −39.2 (8) | C17—C16—C24—N3 | −179.0 (7) |
| O1′—Cu1—N4—C22 | −71.4 (8) | C15—C16—C24—N3 | −0.6 (12) |
| N1—Cu1—N4—C22 | 136.2 (13) | C17—C16—C24—C23 | −4.6 (12) |
| N3—Cu1—N4—C22 | −179.6 (8) | C15—C16—C24—C23 | 173.9 (8) |
| N2—Cu1—N4—C22 | 69.6 (8) | C13—N3—C24—C16 | 2.3 (11) |
| C12—N1—C1—C2 | 2.7 (12) | Cu1—N3—C24—C16 | −175.9 (6) |
| Cu1—N1—C1—C2 | −174.3 (6) | C13—N3—C24—C23 | −172.4 (7) |
| N1—C1—C2—C3 | 0.6 (13) | Cu1—N3—C24—C23 | 9.4 (8) |
| C1—C2—C3—C4 | −5.2 (13) | N4—C23—C24—C16 | −175.6 (7) |
| C2—C3—C4—C12 | 6.5 (14) | C19—C23—C24—C16 | 6.0 (11) |
| C2—C3—C4—C5 | −174.7 (8) | N4—C23—C24—N3 | −0.5 (10) |
| C12—C4—C5—C6 | −3.6 (13) | C19—C23—C24—N3 | −178.9 (7) |
| C3—C4—C5—C6 | 177.6 (9) | O5—C26—C27—O6 | −42.6 (15) |
| C4—C5—C6—C7 | 0.2 (13) | C25—C26—C27—O6 | 71.1 (12) |
| C5—C6—C7—C8 | −176.6 (9) | O5—C26—C27—C28 | −174.2 (10) |
| C5—C6—C7—C11 | 2.0 (12) | C25—C26—C27—C28 | −60.6 (10) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O5—H5*B*···O3 | 0.82 | 1.92 | 2.73 (2) | 172 |
| O5—H5*B*···O4′ | 0.82 | 2.01 | 2.83 (2) | 176 |
| O6—H6···O3′ | 0.82 | 2.19 | 2.919 (16) | 148 |
| O6—H6···O4 | 0.82 | 1.95 | 2.720 (14) | 156 |