Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# Bis(2,2′-bipyridine-$\kappa^2N,N'$)(thiocyanato-$\kappa N$)copper(II) perchlorate

**Qian Li,[a] Dong Zhang,[b] Chun-Ling Chen[b] and Lin Yan[c,d]***

[a]Institute of Fine Chemistry and Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, People's Republic of China, [b]Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, People's Republic of China, [c]Institute of Pharmacy, Henan University, Kaifeng 475004, People's Republic of China, and [d]Key Laboratory of Natural Medicine and Immunal Engineering, Henan University, Kaifeng 475004, People's Republic of China
Correspondence e-mail: yanlin_online@163.com

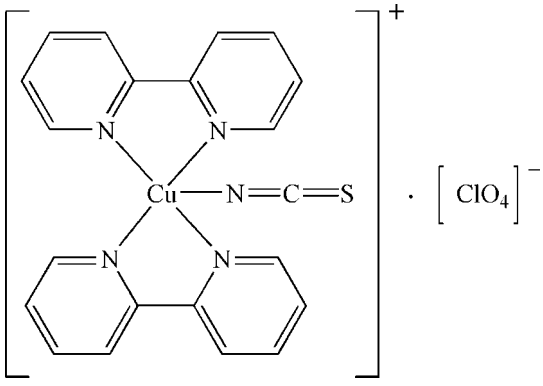
Received 4 August 2009; accepted 5 August 2009

Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.008 Å; disorder in solvent or counterion; $R$ factor = 0.049; $wR$ factor = 0.116; data-to-parameter ratio = 11.7.

The asymmetric unit of title compound, [Cu(NCS)-$(C_{10}H_8N_2)_2$]$ClO_4$, contains a bis(2,2′-bipyridine)(isothiocyanato)copper(II) cation and a perchlorate anion. In the cation, the $Cu^{2+}$ ion is coordinated by four N atoms from two bidentate 2,2′-bipyridine molecules and an N atom from an isothiocyanate anion, resulting in a distorted $CuN_5$ pyramidal configuration. The crystal structure is stabilized by weak intermolecular C—H···O and C—H···S hydrogen bonds, and weak $\pi$–$\pi$ interactions between 2,2′-bipyridine rings [centroid–centroid distance = 3.908 (4) Å]. The perchlorate counteranion is disordered over two positions in a 0.66:0.34 ratio.

## Related literature

For the potenial applications of metal-organic coordination compounds in catalysis, non-linear optics, gas absorption, luminescene and magnetism, see: Kitagawa & Matsuda (2007); Maspoch *et al.* (2007).



## Experimental

### Crystal data

$[Cu(NCS)(C_{10}H_8N_2)_2]ClO_4$
$M_r$ = 533.46
Monoclinic, $P2_1/c$
$a$ = 15.151 (2) Å
$b$ = 8.9518 (13) Å
$c$ = 19.0409 (17) Å
$\beta$ = 120.306 (7)°
$V$ = 2229.6 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.23 mm$^{-1}$
$T$ = 293 K
0.21 × 0.15 × 0.13 mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min}$ = 0.782, $T_{max}$ = 0.856
10831 measured reflections
3917 independent reflections
2370 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.043

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.116
$S$ = 1.03
3917 reflections
335 parameters
44 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.60 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.82 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu1—N5 | 1.968 (4) | Cu1—N2 | 2.058 (4) |
| Cu1—N4 | 1.985 (3) | Cu1—N3 | 2.102 (4) |
| Cu1—N1 | 1.992 (4) | | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C7—H7$A$···O4′$^{i}$ | 0.93 | 2.55 | 3.176 (15) | 125 |
| C10—H10$A$···S1$^{ii}$ | 0.93 | 2.85 | 3.587 (6) | 137 |
| C18—H18$A$···O1′$^{iii}$ | 0.93 | 2.45 | 3.335 (13) | 159 |

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2856).

## References

Bruker (2001). *SAINT-Plus* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Kitagawa, S. & Matsuda, R. (2007). *Coord. Chem. Rev.* **251**, 2490–2509.
Maspoch, D., Ruiz-Molina, D. & Veciana, J. (2007). *Chem. Soc. Rev.* **36**, 770–818.
Sheldrick, G. M. (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

# supporting information

*Acta Cryst.* (2009). E**65**, m1061 [doi:10.1107/S1600536809031067]

## Bis(2,2′-bipyridine-$\kappa^2N,N'$)(thiocyanato-$\kappa N$)copper(II) perchlorate

**Qian Li, Dong Zhang, Chun-Ling Chen and Lin Yan**

### S1. Comment

Recently, more attentions have been paid to metal-organic coordination compounds (MOCPs) due to their potenial applications in catalysis, nonlinear optics, gas absorption, luminescene and magnetism (Maspoch *et al.* 2007, Kitagawa & Matsuda 2007). In the field of coordination chemistry, dual-ligand or multidentate ligands are usually engaged in the costruction of MOCPs, among which N,*N*-bidentate ligands (such as 2,2′-bipyridine) is familiar chelate ligand. Herein, we report the structure of the title compound (I) containing organic dual ligands.

The title compound (I) consists of one $[Cu(C_{10}H_8N_2)_2(SCN)]^+$ complex cations, one disordered $[ClO_4]^-$ anion (Fig.1). In the molecular structure, the $Cu^{2+}$ centre is coordinated by five N atoms, among which four N atoms come from two bidentate 2,2′-bipyridine molecule and another one N atom from an isothiocyanato anion. The environment of the $Cu^{2+}$ cation is in a distorted pyramidal geometry with Cu–N bond lengths ranging from 1.968 (4) to 2.102 (4) Å (Table 1).

In addition, the crystal structure is stability by weak intermolecular C—H···O and C—H···S hydrogen bonds (Table 2), and weak $\pi$-$\pi$ interactions between 2,2′-bipyridine rings with centroid-to centroid distance of 3.908 (4) Å.

### S2. Experimental

2,2′-Bipyridine (1 mol, 0.16 g) was suspended in 20 ml

ethanol solution, to which $Cu(ClO_4)\cdot 2H_2O$ (0.5 mmol, 0.19 g) was added, and then KSCN (0.5 mmol, 0.5 g) were added to the mixture. It was stirred under reflux for 4 h. The solution was cooled and filtered, and the filtrate was kept at the room temperature. After ten days, green blocks of (I) were obtained.

### S3. Refinement

H atoms were treated as riding, with C—H distances of 0.93 Å, and were refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

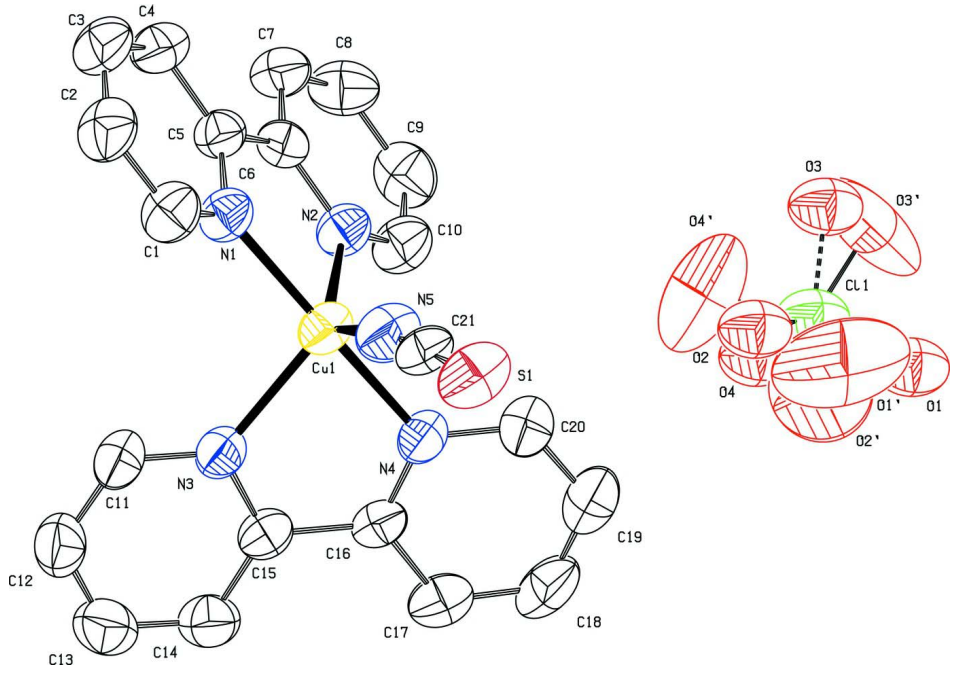



**Figure 1**

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

### Bis(2,2′-bipyridine-$\kappa^2N,N'$)(thiocyanato-$\kappa N$)copper(II) perchlorate

*Crystal data*

$[Cu(NCS)(C_{10}H_8N_2)_2]ClO_4$
$M_r = 533.46$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 15.151$ (2) Å
$b = 8.9518$ (13) Å
$c = 19.0409$ (17) Å
$\beta = 120.306$ (7)°
$V = 2229.6$ (5) Å$^3$
$Z = 4$
$F(000) = 1084$
$D_x = 1.589$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2091 reflections
$\theta = 2.5$–20.5°
$\mu = 1.23$ mm$^{-1}$
$T = 293$ K
Block, green
0.21 × 0.15 × 0.13 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.782$, $T_{max} = 0.856$
10831 measured reflections
3917 independent reflections
2370 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 25.1°$, $\theta_{min} = 2.2°$
$h = -9 \rightarrow 18$
$k = -10 \rightarrow 10$
$l = -22 \rightarrow 20$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.116$
$S = 1.03$
3917 reflections
335 parameters
44 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
$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.60$ e Å$^{-3}$
$\Delta\rho_{min} = -0.82$ e Å$^{-3}$

*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 | 0.28304 (4) | 0.52479 (6) | 0.58542 (3) | 0.0504 (2) | |
| S1 | 0.21213 (11) | 0.09251 (15) | 0.69020 (9) | 0.0736 (4) | |
| N1 | 0.4011 (3) | 0.4415 (4) | 0.5796 (2) | 0.0489 (10) | |
| N2 | 0.3811 (3) | 0.7044 (4) | 0.6288 (2) | 0.0478 (9) | |
| N3 | 0.1728 (3) | 0.5378 (4) | 0.4610 (2) | 0.0475 (9) | |
| N4 | 0.1701 (3) | 0.6262 (4) | 0.5907 (2) | 0.0488 (9) | |
| N5 | 0.2680 (3) | 0.3429 (5) | 0.6365 (3) | 0.0659 (12) | |
| C1 | 0.4060 (4) | 0.3036 (5) | 0.5556 (3) | 0.0588 (13) | |
| H1A | 0.3494 | 0.2416 | 0.5375 | 0.071* | |
| C2 | 0.4912 (4) | 0.2495 (6) | 0.5565 (3) | 0.0637 (14) | |
| H2A | 0.4918 | 0.1535 | 0.5381 | 0.076* | |
| C3 | 0.5754 (4) | 0.3400 (6) | 0.5852 (3) | 0.0657 (14) | |
| H3A | 0.6348 | 0.3055 | 0.5875 | 0.079* | |
| C4 | 0.5712 (4) | 0.4814 (5) | 0.6103 (3) | 0.0576 (13) | |
| H4A | 0.6278 | 0.5439 | 0.6300 | 0.069* | |
| C5 | 0.4828 (3) | 0.5312 (5) | 0.6062 (3) | 0.0453 (11) | |
| C6 | 0.4705 (3) | 0.6823 (5) | 0.6308 (3) | 0.0456 (11) | |
| C7 | 0.5427 (4) | 0.7926 (5) | 0.6539 (3) | 0.0552 (13) | |
| H7A | 0.6031 | 0.7753 | 0.6537 | 0.066* | |
| C8 | 0.5246 (4) | 0.9294 (6) | 0.6772 (3) | 0.0651 (14) | |
| H8A | 0.5732 | 1.0050 | 0.6941 | 0.078* | |
| C9 | 0.4346 (4) | 0.9526 (5) | 0.6753 (3) | 0.0666 (14) | |
| H9A | 0.4209 | 1.0440 | 0.6911 | 0.080* | |
| C10 | 0.3643 (4) | 0.8385 (5) | 0.6498 (3) | 0.0584 (13) | |
| H10A | 0.3021 | 0.8559 | 0.6471 | 0.070* | |

| | | | | | |
|---|---|---|---|---|---|
| C11 | 0.1745 (4) | 0.4783 (5) | 0.3972 (3) | 0.0570 (13) | |
| H11A | 0.2310 | 0.4217 | 0.4067 | 0.068* | |
| C12 | 0.0976 (4) | 0.4968 (5) | 0.3191 (3) | 0.0642 (14) | |
| H12A | 0.1007 | 0.4517 | 0.2764 | 0.077* | |
| C13 | 0.0156 (4) | 0.5828 (6) | 0.3046 (3) | 0.0702 (15) | |
| H13A | −0.0374 | 0.5987 | 0.2516 | 0.084* | |
| C14 | 0.0126 (4) | 0.6453 (5) | 0.3689 (3) | 0.0617 (14) | |
| H14A | −0.0424 | 0.7049 | 0.3600 | 0.074* | |
| C15 | 0.0910 (3) | 0.6196 (5) | 0.4464 (3) | 0.0462 (11) | |
| C16 | 0.0909 (3) | 0.6708 (5) | 0.5202 (3) | 0.0467 (11) | |
| C17 | 0.0122 (4) | 0.7529 (6) | 0.5185 (3) | 0.0660 (15) | |
| H17A | −0.0420 | 0.7867 | 0.4694 | 0.079* | |
| C18 | 0.0157 (4) | 0.7834 (6) | 0.5909 (4) | 0.0721 (16) | |
| H18A | −0.0365 | 0.8384 | 0.5908 | 0.087* | |
| C19 | 0.0945 (4) | 0.7339 (5) | 0.6616 (4) | 0.0675 (15) | |
| H19A | 0.0970 | 0.7527 | 0.7107 | 0.081* | |
| C20 | 0.1706 (4) | 0.6553 (5) | 0.6597 (3) | 0.0612 (14) | |
| H20A | 0.2250 | 0.6206 | 0.7085 | 0.073* | |
| C21 | 0.2448 (3) | 0.2379 (5) | 0.6594 (3) | 0.0514 (12) | |
| Cl1 | 0.24431 (10) | 0.98729 (15) | 0.40224 (9) | 0.0726 (4) | |
| O1′ | 0.1951 (6) | 1.1109 (9) | 0.4087 (6) | 0.190 (5) | 0.66 |
| O2′ | 0.1768 (7) | 0.8670 (8) | 0.3661 (5) | 0.193 (5) | 0.66 |
| O3′ | 0.3286 (6) | 0.9451 (11) | 0.4777 (4) | 0.177 (5) | 0.66 |
| O4′ | 0.2788 (8) | 1.0206 (15) | 0.3457 (6) | 0.268 (7) | 0.66 |
| O1 | 0.1870 (7) | 0.9781 (12) | 0.4423 (6) | 0.0755 (10) | 0.34 |
| O2 | 0.2143 (8) | 0.8817 (10) | 0.3404 (6) | 0.0728 (10) | 0.34 |
| O3 | 0.3518 (6) | 0.9693 (14) | 0.4598 (7) | 0.0730 (10) | 0.34 |
| O4 | 0.2356 (9) | 1.1359 (8) | 0.3709 (6) | 0.0730 (10) | 0.34 |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0461 (4) | 0.0518 (4) | 0.0585 (4) | 0.0054 (3) | 0.0303 (3) | 0.0020 (3) |
| S1 | 0.0721 (10) | 0.0594 (9) | 0.1024 (12) | 0.0078 (7) | 0.0536 (9) | 0.0197 (8) |
| N1 | 0.049 (2) | 0.045 (2) | 0.057 (2) | 0.0044 (19) | 0.030 (2) | −0.0022 (19) |
| N2 | 0.047 (2) | 0.043 (2) | 0.056 (3) | 0.0038 (18) | 0.028 (2) | −0.0002 (19) |
| N3 | 0.046 (2) | 0.052 (2) | 0.051 (2) | 0.0014 (19) | 0.029 (2) | 0.0017 (19) |
| N4 | 0.047 (2) | 0.054 (2) | 0.054 (3) | 0.0036 (19) | 0.032 (2) | 0.001 (2) |
| N5 | 0.058 (3) | 0.068 (3) | 0.077 (3) | 0.003 (2) | 0.038 (3) | 0.009 (2) |
| C1 | 0.063 (3) | 0.048 (3) | 0.071 (4) | 0.004 (3) | 0.038 (3) | −0.003 (3) |
| C2 | 0.071 (4) | 0.054 (3) | 0.074 (4) | 0.018 (3) | 0.042 (3) | 0.001 (3) |
| C3 | 0.057 (4) | 0.073 (4) | 0.075 (4) | 0.020 (3) | 0.039 (3) | 0.002 (3) |
| C4 | 0.043 (3) | 0.066 (3) | 0.064 (3) | 0.006 (2) | 0.027 (3) | 0.000 (3) |
| C5 | 0.040 (3) | 0.049 (3) | 0.047 (3) | 0.004 (2) | 0.022 (2) | 0.003 (2) |
| C6 | 0.041 (3) | 0.051 (3) | 0.039 (3) | 0.004 (2) | 0.016 (2) | 0.004 (2) |
| C7 | 0.042 (3) | 0.058 (3) | 0.063 (3) | −0.003 (2) | 0.024 (3) | −0.003 (3) |
| C8 | 0.052 (3) | 0.056 (3) | 0.075 (4) | −0.007 (3) | 0.023 (3) | −0.003 (3) |
| C9 | 0.077 (4) | 0.050 (3) | 0.065 (4) | 0.005 (3) | 0.031 (3) | −0.009 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C10 | 0.056 (3) | 0.053 (3) | 0.071 (4) | 0.006 (3) | 0.036 (3) | −0.002 (3) |
| C11 | 0.059 (3) | 0.065 (3) | 0.061 (3) | 0.002 (3) | 0.040 (3) | 0.000 (3) |
| C12 | 0.070 (4) | 0.078 (4) | 0.057 (4) | −0.012 (3) | 0.041 (3) | −0.008 (3) |
| C13 | 0.056 (4) | 0.090 (4) | 0.057 (4) | −0.013 (3) | 0.022 (3) | 0.007 (3) |
| C14 | 0.048 (3) | 0.072 (4) | 0.061 (4) | 0.005 (3) | 0.024 (3) | 0.006 (3) |
| C15 | 0.044 (3) | 0.042 (3) | 0.056 (3) | −0.001 (2) | 0.028 (3) | 0.002 (2) |
| C16 | 0.037 (3) | 0.047 (3) | 0.058 (3) | −0.001 (2) | 0.026 (3) | −0.002 (2) |
| C17 | 0.049 (3) | 0.072 (4) | 0.075 (4) | 0.013 (3) | 0.030 (3) | 0.004 (3) |
| C18 | 0.063 (4) | 0.070 (4) | 0.103 (5) | 0.004 (3) | 0.057 (4) | −0.014 (4) |
| C19 | 0.075 (4) | 0.065 (4) | 0.085 (4) | −0.009 (3) | 0.057 (4) | −0.013 (3) |
| C20 | 0.063 (3) | 0.069 (3) | 0.060 (3) | 0.000 (3) | 0.037 (3) | −0.002 (3) |
| C21 | 0.040 (3) | 0.053 (3) | 0.064 (3) | 0.010 (2) | 0.029 (3) | 0.001 (3) |
| Cl1 | 0.0573 (8) | 0.0714 (9) | 0.0791 (10) | 0.0056 (7) | 0.0270 (8) | −0.0106 (7) |
| O1′ | 0.128 (7) | 0.134 (7) | 0.300 (13) | 0.047 (6) | 0.102 (8) | −0.069 (7) |
| O2′ | 0.201 (10) | 0.176 (8) | 0.174 (9) | −0.140 (8) | 0.072 (7) | −0.028 (7) |
| O3′ | 0.183 (9) | 0.215 (10) | 0.062 (5) | 0.082 (8) | 0.008 (6) | 0.001 (5) |
| O4′ | 0.224 (13) | 0.41 (2) | 0.259 (14) | −0.040 (12) | 0.189 (13) | 0.037 (12) |
| O1 | 0.0592 (14) | 0.0735 (14) | 0.0817 (15) | 0.0063 (13) | 0.0267 (13) | −0.0106 (13) |
| O2 | 0.0582 (14) | 0.0710 (14) | 0.0786 (15) | 0.0059 (13) | 0.0266 (13) | −0.0119 (13) |
| O3 | 0.0569 (13) | 0.0713 (14) | 0.0797 (15) | 0.0063 (13) | 0.0263 (13) | −0.0118 (13) |
| O4 | 0.0577 (13) | 0.0715 (14) | 0.0796 (15) | 0.0058 (13) | 0.0270 (13) | −0.0097 (13) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu1—N5 | 1.968 (4) | C11—C12 | 1.360 (7) |
| Cu1—N4 | 1.985 (3) | C11—H11A | 0.9300 |
| Cu1—N1 | 1.992 (4) | C12—C13 | 1.365 (6) |
| Cu1—N2 | 2.058 (4) | C12—H12A | 0.9300 |
| Cu1—N3 | 2.102 (4) | C13—C14 | 1.369 (6) |
| S1—C21 | 1.605 (5) | C13—H13A | 0.9300 |
| N1—C1 | 1.331 (5) | C14—C15 | 1.368 (6) |
| N1—C5 | 1.342 (5) | C14—H14A | 0.9300 |
| N2—C10 | 1.331 (5) | C15—C16 | 1.478 (6) |
| N2—C6 | 1.349 (5) | C16—C17 | 1.387 (6) |
| N3—C11 | 1.339 (5) | C17—C18 | 1.380 (7) |
| N3—C15 | 1.342 (5) | C17—H17A | 0.9300 |
| N4—C16 | 1.332 (5) | C18—C19 | 1.347 (7) |
| N4—C20 | 1.335 (5) | C18—H18A | 0.9300 |
| N5—C21 | 1.163 (5) | C19—C20 | 1.368 (6) |
| C1—C2 | 1.371 (6) | C19—H19A | 0.9300 |
| C1—H1A | 0.9300 | C20—H20A | 0.9300 |
| C2—C3 | 1.371 (6) | Cl1—O1′ | 1.374 (5) |
| C2—H2A | 0.9300 | Cl1—O2 | 1.395 (7) |
| C3—C4 | 1.366 (6) | Cl1—O2′ | 1.403 (5) |
| C3—H3A | 0.9300 | Cl1—O3′ | 1.409 (5) |
| C4—C5 | 1.376 (6) | Cl1—O1 | 1.419 (6) |
| C4—H4A | 0.9300 | Cl1—O4 | 1.437 (7) |
| C5—C6 | 1.473 (6) | Cl1—O3 | 1.442 (7) |

| | | | |
|---|---|---|---|
| C6—C7 | 1.372 (6) | Cl1—O4′ | 1.446 (6) |
| C7—C8 | 1.377 (6) | O1′—O4 | 1.180 (11) |
| C7—H7A | 0.9300 | O1′—O1 | 1.385 (11) |
| C8—C9 | 1.362 (7) | O2′—O2 | 0.927 (11) |
| C8—H8A | 0.9300 | O2′—O1 | 1.701 (11) |
| C9—C10 | 1.375 (6) | O3′—O3 | 0.638 (17) |
| C9—H9A | 0.9300 | O4′—O4 | 1.429 (12) |
| C10—H10A | 0.9300 | O4′—O2 | 1.553 (12) |
| | | | |
| N5—Cu1—N4 | 92.02 (16) | N3—C15—C16 | 114.5 (4) |
| N5—Cu1—N1 | 92.83 (16) | C14—C15—C16 | 123.8 (4) |
| N4—Cu1—N1 | 174.75 (15) | N4—C16—C17 | 120.5 (4) |
| N5—Cu1—N2 | 133.48 (16) | N4—C16—C15 | 115.7 (4) |
| N4—Cu1—N2 | 95.11 (14) | C17—C16—C15 | 123.7 (5) |
| N1—Cu1—N2 | 80.08 (15) | C18—C17—C16 | 118.9 (5) |
| N5—Cu1—N3 | 112.25 (16) | C18—C17—H17A | 120.6 |
| N4—Cu1—N3 | 79.43 (15) | C16—C17—H17A | 120.6 |
| N1—Cu1—N3 | 100.55 (14) | C19—C18—C17 | 120.1 (5) |
| N2—Cu1—N3 | 114.25 (14) | C19—C18—H18A | 119.9 |
| C1—N1—C5 | 119.0 (4) | C17—C18—H18A | 119.9 |
| C1—N1—Cu1 | 125.0 (3) | C18—C19—C20 | 118.5 (5) |
| C5—N1—Cu1 | 116.0 (3) | C18—C19—H19A | 120.8 |
| C10—N2—C6 | 117.8 (4) | C20—C19—H19A | 120.8 |
| C10—N2—Cu1 | 128.0 (3) | N4—C20—C19 | 122.7 (5) |
| C6—N2—Cu1 | 114.1 (3) | N4—C20—H20A | 118.7 |
| C11—N3—C15 | 117.8 (4) | C19—C20—H20A | 118.7 |
| C11—N3—Cu1 | 129.2 (3) | N5—C21—S1 | 179.5 (6) |
| C15—N3—Cu1 | 112.9 (3) | O1′—Cl1—O2 | 131.4 (6) |
| C16—N4—C20 | 119.3 (4) | O1′—Cl1—O2′ | 111.6 (5) |
| C16—N4—Cu1 | 116.5 (3) | O2—Cl1—O2′ | 38.7 (5) |
| C20—N4—Cu1 | 124.2 (3) | O1′—Cl1—O3′ | 112.2 (5) |
| C21—N5—Cu1 | 170.6 (4) | O2—Cl1—O3′ | 114.9 (6) |
| N1—C1—C2 | 122.6 (5) | O2′—Cl1—O3′ | 110.8 (5) |
| N1—C1—H1A | 118.7 | O1′—Cl1—O1 | 59.4 (5) |
| C2—C1—H1A | 118.7 | O2—Cl1—O1 | 112.8 (6) |
| C1—C2—C3 | 118.5 (5) | O2′—Cl1—O1 | 74.1 (5) |
| C1—C2—H2A | 120.7 | O3′—Cl1—O1 | 85.6 (5) |
| C3—C2—H2A | 120.7 | O1′—Cl1—O4 | 49.6 (5) |
| C4—C3—C2 | 119.2 (5) | O2—Cl1—O4 | 110.7 (6) |
| C4—C3—H3A | 120.4 | O2′—Cl1—O4 | 128.0 (6) |
| C2—C3—H3A | 120.4 | O3′—Cl1—O4 | 121.2 (6) |
| C3—C4—C5 | 119.8 (5) | O1—Cl1—O4 | 108.9 (5) |
| C3—C4—H4A | 120.1 | O1′—Cl1—O3 | 118.5 (7) |
| C5—C4—H4A | 120.1 | O2—Cl1—O3 | 109.2 (6) |
| N1—C5—C4 | 120.9 (4) | O2′—Cl1—O3 | 123.4 (7) |
| N1—C5—C6 | 115.4 (4) | O3′—Cl1—O3 | 25.8 (7) |
| C4—C5—C6 | 123.8 (4) | O1—Cl1—O3 | 110.4 (6) |
| N2—C6—C7 | 122.0 (4) | O4—Cl1—O3 | 104.5 (6) |

| | | | |
|---|---|---|---|
| N2—C6—C5 | 114.3 (4) | O1′—Cl1—O4′ | 108.5 (5) |
| C7—C6—C5 | 123.6 (4) | O2—Cl1—O4′ | 66.3 (6) |
| C6—C7—C8 | 119.2 (4) | O2′—Cl1—O4′ | 104.0 (5) |
| C6—C7—H7A | 120.4 | O3′—Cl1—O4′ | 109.4 (5) |
| C8—C7—H7A | 120.4 | O1—Cl1—O4′ | 164.2 (6) |
| C9—C8—C7 | 119.1 (5) | O4—Cl1—O4′ | 59.4 (5) |
| C9—C8—H8A | 120.4 | O3—Cl1—O4′ | 84.0 (7) |
| C7—C8—H8A | 120.4 | O4—O1′—Cl1 | 68.0 (4) |
| C8—C9—C10 | 118.8 (5) | O4—O1′—O1 | 129.8 (6) |
| C8—C9—H9A | 120.6 | Cl1—O1′—O1 | 61.9 (4) |
| C10—C9—H9A | 120.6 | O2—O2′—Cl1 | 70.2 (6) |
| N2—C10—C9 | 123.0 (5) | O2—O2′—O1 | 123.5 (7) |
| N2—C10—H10A | 118.5 | Cl1—O2′—O1 | 53.4 (3) |
| C9—C10—H10A | 118.5 | O3—O3′—Cl1 | 80.0 (9) |
| N3—C11—C12 | 123.1 (5) | O4—O4′—Cl1 | 60.0 (4) |
| N3—C11—H11A | 118.4 | O4—O4′—O2 | 102.7 (6) |
| C12—C11—H11A | 118.4 | Cl1—O4′—O2 | 55.3 (4) |
| C11—C12—C13 | 118.7 (5) | O1′—O1—Cl1 | 58.7 (4) |
| C11—C12—H12A | 120.7 | O1′—O1—O2′ | 95.7 (6) |
| C13—C12—H12A | 120.7 | Cl1—O1—O2′ | 52.5 (3) |
| C12—C13—C14 | 119.2 (5) | O2′—O2—Cl1 | 71.1 (6) |
| C12—C13—H13A | 120.4 | O2′—O2—O4′ | 127.8 (8) |
| C14—C13—H13A | 120.4 | Cl1—O2—O4′ | 58.4 (4) |
| C15—C14—C13 | 119.6 (5) | O3′—O3—Cl1 | 74.2 (9) |
| C15—C14—H14A | 120.2 | O1′—O4—O4′ | 122.4 (7) |
| C13—C14—H14A | 120.2 | O1′—O4—Cl1 | 62.4 (4) |
| N3—C15—C14 | 121.6 (4) | O4′—O4—Cl1 | 60.6 (4) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C7—H7*A*···O4′$^{i}$ | 0.93 | 2.55 | 3.176 (15) | 125 |
| C10—H10*A*···S1$^{ii}$ | 0.93 | 2.85 | 3.587 (6) | 137 |
| C18—H18*A*···O1′$^{iii}$ | 0.93 | 2.45 | 3.335 (13) | 159 |

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