Aquachlorido(2-[[6-(dimethylamino)pyrimidin-4-yl]sulfanyl]pyrimidine-4,6-diamine)copper(II) chloride hydrate

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Aquachlorido(2-[[6-(dimethylamino)pyrimidin-4-yl]sulfanyl]pyrimidine-4,6-diamine)copper(II) chloride hydrate

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A copper(II) complex of the non-symmetric bidentate ligand 2-[[6-(dimethylamino)pyrimidin-4-yl]sulfanyl]pyrimidine-4,6-diamine (L1) is reported. The single-crystal X-ray structure of aqua[aqua/chlorido(0.49/0.51)](2-[[6-(dimethylamino)pyrimidin-4-yl]sulfanyl]pyrimidine-4,6-diamine)copper(II) 0.49-chloride 1.51-hydrate, [CuCl1.51(C10H13N7S)(H2O)1.49]Cl0.49⋅1.51H2O or [(L1)Cl1.51(H2O)1.49Cu]0.49Cl1.51H2O, exhibits distorted square-pyramidal geometry around the metal centre, with disorder in the axial position, occupied by chloride or water. The six-membered metal–chelate ring is in a boat conformation, and short intermolecular S···S interactions are observed. In addition to its capacity for bidentate metal coordination, the ligand has the ability to engage in further supramolecular interactions as both a hydrogen-bond donor and acceptor, and multiple interactions with lattice solvent water molecules are present in the reported structure.

1. Chemical context

Non-symmetric ligand–metal complexes have been explored for their applications in chiral synthesis (Asay & Morales-Morales, 2015; Pfaltz & Drury, 2004), or for their potential to yield new multimetallic topologies which combine homo- and heteroleptic sites into a single molecule (Dawe et al., 2006). Non-symmetric thio-bis-(pyridin-2-yl) or bis-(pyrimidin-2-yl) ligands are known, and upon bidentate coordination with transition metal cations, these form six-membered chelate rings, which adopt a boat-shaped conformation (Fig. 1). Some reported transition metal complexes resulting from this class of ligands have been employed as possible alternatives to traditional chemotherapy drugs (Ray et al., 1994; Mandal et al., 2007), as a step en route to new thrombin inhibitors (Chung et al., 2003), and have led to the formation of one Cu30-nuclear cluster (Li et al., 2012).
In the interest of exploring simultaneous coordination chemistry and anion–ligand affinity via hydrogen-bonding interactions, the non-symmetric ligand 2-[(6-(dimethylamino)-pyrimidin-4-yl)sulfanyl]pyrimidine-4,6-diamine (C_{10}H_{13}N_{7}S; L1), was synthesized, and its metal complex with copper(II) chloride, is reported here. Even upon metal coordination, the ligand can still serve as a hydrogen-bond donor to anions via the amine moieties. Alternatively, these free amines could also act as possible anchors for surface attachment, with a view towards future device applications.

2. Structural commentary

The title compound crystallizes in the monoclinic space group P2_{1}/c with one bidentate ligand bound to a copper(II) cation (via N1 and N4; Fig. 2). The copper(II) cation is five-coordinate, with the remaining coordination sites occupied by a chloride anion (Cl1), a water molecule (O1), and a disordered site, with either chloride (Cl2; Fig. 2a) or water (O2; Fig. 2b) with occupancies of 0.511 (5) and 0.489 (5), respectively. The two largest ligand–metal–ligand bond angles (Table 1) are N4—Cu1—Cl1 and O1—Cu1—N1 [171.10 (6) and 157.01 (8)°, respectively] giving a τ value of 0.23 (where τ = 0 is ideal square-pyramidal geometry, and τ = 1 is ideal trigonal-bipyramidal geometry; Addison et al., 1984), indicating that the geometry is distorted square pyramidal. Examination of the bond lengths (Table 1), is also consistent with the disordered Cl/O as the axial site for this geometry. An intramolecular hydrogen bond is present between the amine group (via N5—H5A) and the apical ligand (Fig. 2; Table 2). The six-membered chelate ring adopts a boat conformation. The angle between the distorted square plane defined by N1/N4/C4/C5 (r.m.s. deviation from the plane is 0.032 Å) and the flap defined by C4/S1/C5 (τ1) is 34.51 (17)°, while the angle between the square plane and the flap defined by N1/Cu1/N4 (τ2) is 46.93 (14)°. The boat-shaped configuration accommodates the C—S and N—Cu bonds, making up the flaps.

Table 1

| Selected geometric parameters (Å, °). |
|--------------------------|--------------------------|
| Cu1—Cl1                  | 2.2689 (7)               |
| Cu1—Cl2                  | 2.5273 (19)              |
| Cu1—O1                   | 2.0158 (19)              |
| Cu1—O2                   | 2.229 (6)                |
| Cu1—N1                   | 2.034 (2)                |
| Cl1—Cu1—Cl2              | 92.89 (5)                |
| O1—Cu1—Cl1               | 91.94 (6)                |
| O1—Cu1—Cl2               | 92.69 (7)                |
| O1—Cu1—O1                | 100.64 (18)              |
| O1—Cu1—N1                | 157.01 (6)               |
| N1—Cu1—O2                | 93.1 (2)                 |
| N1—Cu1—Cl1               | 92.81 (6)                |
| N1—Cu1—Cl2               | 109.51 (8)               |

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which are significantly longer than the C–N bonds in the
square plane (Table 1).

A simpler, symmetric bidentate ligand, di(pyridin-2-yl)-
sulfide (DPS), has been reported to exhibit a very similar
metal coordination environment to the major component
reported here, upon reaction with CuCl$_2$·H$_2$O, to yield
[Cu(DPS)$(H_2O)Cl_2$]·H$_2$O (Teles et al., 2006). In this complex,
the authors report $\tau = 0.06$, with the square plane formed by
the two nitrogen atoms from DPS, a coordinating water
molecule, and one chloride ion (with the second chloride
occupying the axial position). Similar to the reported structure
here, the six-membered chelate ring adopts a boat confor-
mation, which is characteristic for transition metal complexes
with this class of ligands upon bidentate coordination (vide infra).

3. Supramolecular features
In the crystal, molecules of the title complex pack in columns,
parallel to the crystallographic b axis (Fig. 3), with short S···S'
intermolecular distances [3.7327 (3) Å; symmetry code: (i)
$-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$]. Note that each chelated ‘boat’ points
in the same direction within a column, and the opposite direction
is observed in adjacent columns.

4. Database survey
A survey was performed of the Cambridge Structural Data-
base (version 5.38 with May 2017 updates; Groom et al., 2016),
using ConQuest (version 1.19; Bruno et al., 2002), for six-
membered transition metal chelate rings resulting from
bidentate ligand coordination, where the metal was any
transition metal, and the other ring components were N–C–S–
C–N. Further, within the ligand, each C–N was required to be
part of a six-membered ring, where the remaining four atoms
could be any non-metal, and the bond type within the ring was
unspecified (allowed to be ‘any’ bond type). This resulted in 74
hits, which were then manually sorted to omit systems where
the ligand exhibited anything greater than bidenticity, leaving
68 structures for further analysis using Mercury (version 3.9;
Macrae et al., 2006). All of these exhibited boat-shaped
puckering of the chelate ring, with mean values for $\theta_1 = 43$ (7)
and $\theta_2 = 37$ (5)°. While the larger angle for the title complex is
$\theta_2$, both $\theta_1$ and $\theta_2$ are within two standard deviations of
comparable structures from the database.

5. Synthesis and crystallization
2-[(6-Dimethylamino)pyrimidin-4-yl]sulfanylpyrimidine-
4,6-diamine (C$_{10}$H$_{13}$N$_5$S; L1): 0.972 g (7.03 mmol) of potassium
carbonate and 1.000 g (6.24 mmol) of 4,6-diamino-2-
mercaptopyrimidine hydrate were combined in 20 mL of
dimethylformamide, and stirred at 333 K for 20 min, prior to the
addition of 0.524 g (3.51 mmol) of 4,6-dichloropyrimidine (see
reaction scheme). The resulting cloudy orange solution was
refluxed for 24 h. It was then filtered, and the brown filtrate
was reduced in vacuo to yield 0.387 g (1.47 mmol) of orange
solid, after washing with ethanol (42% yield).

![Figure 3](image-url)

Packed unit cell for [(L1)Cu$_{1.51}$(H$_2$O)$_{1.49}$Cu$][0.49Cl]$·1.51H$_2$O. Only atoms
in the major occupancy component are shown. All solvent water
molecules and hydrogen atoms have been omitted for clarity.

Aquachlorido(2-[(6-(dimethylamino)pyrimidin-4-yl)sulfanyl]pyrimidine-4,6-diamine)copper(II) chloride hydrate
[CuCl$_{1.51}$(C$_{10}$H$_{13}$N$_5$S)(H$_2$O)$_{1.49}$]Cl$_{0.49}$·1.51H$_2$O: 0.050 g
(0.19 mmol) of L1 and 0.048 g (0.28 mmol) of CuCl$_2$·2H$_2$O
were separately dissolved in 5 mL of 1:1 methanol/acetonitrile.
The solution of CuCl$_2$ was added dropwise to the solution of
L1. The resulting cloudy brown solution was stirred vigorously
with heating (333 K) for 20 min. This was filtered, yielding
0.007 g of brown, amorphous powder, and a clear green filtrate.
that was left for slow evaporation. Green, prismatic X-ray quality crystals grew from the filtrate over the course of six weeks. 3.6 mg (0.0080 mmol) of analytically pure crystals were harvested as soon as they formed, though the mother liquor was still highly coloured, accounting for the low (4.2%) yield. These crystals were analyzed via small molecule X-ray diffraction, and elemental analysis. Analysis calculated for \([\text{CuCl}_{1.51}(\text{C}_{10}\text{H}_{13}\text{N}_{7}\text{S})(\text{H}_{2}\text{O})]_{1.49}\text{Cl}_{0.49}\text{H}_{2}\text{O}\) – Cu1.51(C10H13N7S)(H2O)1.49 – Cl0.49 H2O. 

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Moyaert et al. • [CuCl₁.₅₁(C₁₉H₁₃N₇S)(H₂O)₁.₄₉]Cl₀.₄₉·₁.₅₁H₂O

Acta Cryst. (2017). E73, 1534–1538
Aquachlorido(2-[(6-(dimethylamino)pyrimidin-4-yl)sulfanyl]pyrimidine-4,6-diamine)copper(II) chloride hydrate

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Computing details

Data collection: APEX2 (Bruker, 2012); cell refinement: CrysAlis PRO (Rigaku OD, 2015); data reduction: CrysAlis PRO (Rigaku OD, 2015); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2016 (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

Aquachlorido(0.49/0.51)(2-[(6-(dimethylamino)pyrimidin-4-yl)sulfanyl]pyrimidine-4,6-diamine)copper(II) 0.49-chloride 1.51-hydrate

Crystal data

[CuCl1.51(C10H13N7S)(H2O)1.49]·0.49Cl·1.51H2O

F(000) = 924

Dx = 1.718 Mg m−3

Cu Kα radiation, λ = 1.54178 Å

Cell parameters from 13698 reflections

θ = 4.0–66.3°

μ = 5.94 mm−1

T = 110 K

Prism, green

0.27 × 0.19 × 0.17 mm

Data collection

Bruker APEX2 CCD with CrysAlis PRO

imported SAXI images
diffractometer

Radiation source: fine-focus sealed X-ray tube,

Enhance (Cu) X-ray Source

Graphite monochromator

ω and φ scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku Oxford Diffraction, 2015)

Refinement

Refinement on F²

Least-squares matrix: full

R(F² > 2σ(F²)) = 0.030

wR(F²) = 0.079

S = 1.04

3000 reflections

261 parameters

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

Acta Cryst. (2017). E73, 1534-1538
$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.8086P]$  
where $P = (F_o^2 + 2F_c^2)/3$  
$(\Delta \sigma)_{\text{max}} = 0.001$

$\Delta \rho_{\text{max}} = 0.32 \text{ e Å}^{-3}$  
$\Delta \rho_{\text{min}} = -0.32 \text{ e Å}^{-3}$

**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.

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

|     | x    | y    | z    | $U_{\text{iso}}$/$U_{\text{eq}}$ | Occ. (<1) |
|-----|------|------|------|-------------------------|----------|
| Cu1 | 0.65886 (3) | 0.87641 (5) | 0.36726 (2) | 0.02056 (12) | 0.02412 (16) |
| Cl1 | 0.59471 (5) | 0.68609 (9) | 0.43587 (3) | 0.0250 (6) | 0.511 (5) |
| Cl2 | 0.81961 (17) | 1.0193 (3) | 0.45364 (9) | 0.0250 (6) | 0.511 (5) |
| Cl3 | 0.9316 (3) | 0.7674 (6) | 0.55061 (13) | 0.0648 (12) | 0.489 (5) |
| S1  | 0.47778 (6) | 0.94220 (9) | 0.22968 (3) | 0.02244 (16) | 0.511 (5) |
| O1  | 0.77219 (16) | 0.6829 (3) | 0.34783 (8) | 0.0256 (4) | 0.511 (5) |
| H1A | 0.743 (3) | 0.635 (4) | 0.3084 (9) | 0.051 (11)* | 0.511 (5) |
| H1B | 0.790 (3) | 0.586 (4) | 0.3750 (15) | 0.062 (12)* | 0.511 (5) |
| O3  | 0.9002 (6) | 0.6924 (9) | 0.5536 (4) | 0.0305 (15) | 0.511 (5) |
| H3A | 0.873556 | 0.784224 | 0.524170 | 0.046* | 0.511 (5) |
| H3B | 0.982596 | 0.704284 | 0.569168 | 0.046* | 0.511 (5) |
| O4  | 1.148 (5) | 0.571 (8) | 0.560 (3) | 0.056 (3) | 0.511 (5) |
| H4A | 1.164621 | 0.489914 | 0.531128 | 0.084* | 0.511 (5) |
| H4B | 1.218311 | 0.634714 | 0.578705 | 0.084* | 0.511 (5) |
| O2  | 0.7814 (6) | 1.0316 (10) | 0.4446 (3) | 0.0250 (6) | 0.489 (5) |
| H2A | 0.816574 | 1.128467 | 0.429387 | 0.038* | 0.489 (5) |
| H2B | 0.842833 | 0.962117 | 0.467637 | 0.038* | 0.489 (5) |
| O5  | 1.141 (5) | 0.553 (9) | 0.557 (3) | 0.056 (3) | 0.489 (5) |
| H5C | 1.094042 | 0.658743 | 0.549583 | 0.084* | 0.489 (5) |
| H5D | 1.164982 | 0.487073 | 0.526489 | 0.084* | 0.489 (5) |
| N1  | 0.50737 (19) | 1.0333 (3) | 0.35292 (9) | 0.0214 (5) | 0.0229 (5) |
| N2  | 0.31504 (19) | 1.0711 (3) | 0.28275 (10) | 0.0238 (5) | 0.0229 (5) |
| N3  | 0.86159 (19) | 1.1243 (3) | 0.25035 (10) | 0.0238 (5) | 0.0214 (5) |
| N4  | 0.70468 (19) | 1.0147 (3) | 0.29669 (9) | 0.0213 (5) | 0.0214 (5) |
| N5  | 0.5433 (2) | 1.1471 (4) | 0.45509 (11) | 0.0286 (5) | 0.0214 (5) |
| H5A | 0.614 (3) | 1.106 (5) | 0.4577 (15) | 0.034* | 0.0214 (5) |
| H5B | 0.517 (3) | 1.185 (5) | 0.4834 (16) | 0.034* | 0.0214 (5) |
| N6  | 0.1509 (2) | 1.1695 (4) | 0.32017 (14) | 0.0321 (6) | 0.0321 (6) |
| H6A | 0.122 (3) | 1.202 (5) | 0.3488 (17) | 0.033 (9)* | 0.0321 (6) |
| H6B | 0.109 (3) | 1.134 (5) | 0.2867 (17) | 0.037 (10)* | 0.0321 (6) |
| N7  | 0.8262 (2) | 1.1817 (3) | 0.14302 (10) | 0.0266 (5) | 0.0266 (5) |
| C1  | 0.4646 (2) | 1.1146 (4) | 0.40076 (12) | 0.0232 (6) | 0.0266 (5) |
| C2  | 0.3434 (2) | 1.1595 (4) | 0.39165 (12) | 0.0250 (6) | 0.0232 (6) |
| H2  | 0.312207 | 1.208633 | 0.425222 | 0.030* | 0.0250 (6) |
| C3  | 0.2696 (2) | 1.1307 (4) | 0.33244 (13) | 0.0246 (6) | 0.0246 (6) |
| C4  | 0.4299 (2) | 1.0264 (3) | 0.29687 (11) | 0.0204 (5) | 0.0204 (5) |
### Atomic displacement parameters (Å²)

|     |   $U^{11}$ |   $U^{22}$ |   $U^{33}$ |   $U^{12}$ |   $U^{13}$ |   $U^{23}$ |
|-----|------------|------------|------------|------------|------------|------------|
| Cu1 |  0.0206 (2)|  0.0275 (2)|  0.0147 (2)|  0.00178 (16)|  0.00640 (14)|  0.00253 (14)|
| Cl1 |  0.0240 (3)|  0.0325 (3)|  0.0171 (3)|  0.0027 (3)|  0.0072 (2)|  0.0045 (2)|
| Cl2 |  0.0180 (12)|  0.0367 (7)|  0.0183 (8)|  0.0039 (8)|  0.0000 (2)|  0.0004 (5)|
| Cl3 |  0.055 (2)|  0.110 (3)|  0.0285 (11)|  0.0397 (19)|  0.0078 (11)|  0.0013 (16)|
| S1  |  0.0219 (3)|  0.0293 (3)|  0.0168 (3)|  0.0034 (3)|  0.0060 (2)|  0.0018 (2)|
| O1  |  0.0215 (10)|  0.0351 (11)|  0.0208 (10)|  0.0028 (8)|  0.0059 (8)|  0.0012 (8)|
| O2  |  0.021 (3)|  0.038 (3)|  0.035 (3)|  0.007 (2)|  0.011 (2)|  0.012 (2)|
| O3  |  0.080 (5)|  0.054 (8)|  0.034 (4)|  0.022 (4)|  0.013 (3)|  0.009 (4)|
| N1  |  0.080 (5)|  0.054 (8)|  0.034 (4)|  0.022 (4)|  0.013 (3)|  0.009 (4)|
| N2  |  0.0239 (11)|  0.0268 (12)|  0.0149 (10)|  0.0019 (9)|  0.0075 (9)|  0.0032 (9)|
| N3  |  0.0216 (11)|  0.0266 (12)|  0.0209 (11)|  0.0009 (9)|  0.0059 (9)|  0.0051 (9)|
| N4  |  0.0212 (11)|  0.0319 (12)|  0.0188 (11)|  0.0002 (10)|  0.0055 (9)|  0.0019 (9)|
| N5  |  0.0212 (11)|  0.0276 (12)|  0.0156 (10)|  0.0006 (9)|  0.0051 (8)|  0.0001 (8)|
| N6  |  0.0288 (13)|  0.0421 (15)|  0.0162 (11)|  0.0084 (11)|  0.0080 (10)|  0.0024 (10)|
| N7  |  0.0233 (13)|  0.0439 (16)|  0.0306 (15)|  0.0030 (11)|  0.0092 (12)|  0.0048 (12)|
| C1  |  0.0251 (12)|  0.0394 (14)|  0.0175 (11)|  0.0014 (10)|  0.0092 (9)|  0.0033 (9)|
| C2  |  0.0276 (14)|  0.0244 (14)|  0.0199 (13)|  0.0024 (11)|  0.0100 (11)|  0.0068 (10)|
| C3  |  0.0285 (15)|  0.0282 (14)|  0.0213 (13)|  0.0046 (11)|  0.0117 (11)|  0.0054 (10)|
| C4  |  0.0253 (14)|  0.0234 (14)|  0.0277 (14)|  0.0016 (11)|  0.0113 (11)|  0.0011 (11)|
| C5  |  0.0236 (14)|  0.0200 (13)|  0.0191 (12)|  0.0006 (11)|  0.0083 (10)|  0.0044 (10)|
| C6  |  0.0222 (13)|  0.0215 (13)|  0.0189 (12)|  0.0023 (10)|  0.0068 (10)|  0.0024 (10)|
| C7  |  0.0222 (13)|  0.0251 (14)|  0.0144 (12)|  0.0013 (11)|  0.0057 (10)|  0.0001 (10)|
| C8  |  0.0275 (14)|  0.0234 (13)|  0.0196 (13)|  0.0005 (11)|  0.0091 (11)|  0.0029 (10)|
| C9  |  0.0238 (14)|  0.0292 (14)|  0.0174 (12)|  0.0023 (11)|  0.0047 (10)|  0.0013 (10)|
| C10 |  0.0341 (16)|  0.0502 (18)|  0.0193 (14)|  0.0019 (14)|  0.0079 (12)|  0.0053 (12)|
**Geometric parameters (Å, °)**

| Bond          | Distance   | Bond          | Distance   |
|---------------|------------|---------------|------------|
| Cu1—Cl1       | 2.2689 (7) | Cu1—Cl2       | 2.5273 (19) |
| Cu1—O1        | 2.0158 (19)| Cu1—O2        | 2.229 (6)  |
| Cu1—N1        | 2.034 (2)  | Cu1—N4        | 1.996 (2)  |
| S1—C4         | 1.777 (2)  | S1—C5         | 1.774 (3)  |
| Cu1—O1—H1A    | 0.915 (14) | O1—H1A        | 0.911 (15) |
| O1—Cu1—Cl1    | 91.94 (6)  | O1—H1B        | 0.911 (15) |
| O1—Cu1—Cl2    | 92.69 (7)  | O3—H3A        | 0.9233     |
| O1—Cu1—O2     | 100.64 (18)| O3—H3B        | 0.9290     |
| N1—Cu1—Cl1    | 92.81 (6)  | N5—H5A        | 0.84 (3)   |
| N1—Cu1—Cl2    | 92.69 (7)  | N5—H5B        | 0.79 (3)   |
| N1—Cu1—O2     | 101.55 (18)| N5—H5C        | 0.9144     |
| N1—Cu1—N4     | 157.01 (8) | N5—H5D        | 0.9107     |
| N1—Cu1—O4     | 93.1 (2)   | N1—C1         | 1.376 (3)  |
| N1—Cu1—Cl1    | 92.81 (6)  | N1—C4         | 1.332 (3)  |
| N2—C3         | 1.368 (4)  | O1—H1A        | 0.915 (14) |
| N2—C4         | 1.318 (3)  | O1—H1B        | 0.911 (15) |
| N3—C7         | 1.366 (3)  | O3—H3A        | 1.0119     |
| N3—C8         | 1.320 (3)  | O3—H3B        | 0.9233     |
| Cl1—Cu1—Cl2   | 92.89 (5)  | C7—N7—C10     | 120.8 (2)  |
| N1—C1—C2      | 120.3 (2)  | C10—N7—C9     | 120.8 (2)  |
| N2—C3—C2      | 122.3 (2)  | N5—C1—C2      | 122.3 (2)  |
| N2—C3—N6      | 117.4 (2)  | N5—C1—C2      | 122.3 (2)  |
| N3—C7—C6      | 117.0 (3)  | N5—C1—C2      | 122.3 (2)  |
| N3—C8—C9      | 116.97 (19)| N5—C1—C2      | 122.3 (2)  |
| C5—S1—C4      | 104.53 (12)| N5—C1—C2      | 122.3 (2)  |
| Cu1—O2—H2A    | 110 (2)    | N2—C4—S1      | 119.87 (19)|
| Cu1—O2—H2B    | 107 (3)    | N2—C4—S1      | 119.87 (19)|
| Cu1—O1—H1A    | 118 (3)    | N2—C4—S1      | 119.87 (19)|
| H1A—O1—H1B    | 104.53 (12)| N4—C5—S1      | 120.15 (18)|
| H3A—O3—H3B    | 109.4      | N4—C5—S1      | 120.15 (18)|
| H4A—O4—H4B    | 108.7      | N4—C5—S1      | 120.15 (18)|
| Cu1—O2—H2A    | 111.7      | N3—C7—C6      | 120.7 (2)  |
Cu1—O2—H2B 114.0  N7—C7—N3 117.4 (2)  117.4 (2)
H2A—O2—H2B 106.1  N7—C7—C6 122.0 (2)  122.0 (2)
H5C—O5—H5D 123.9  N3—C8—N4 127.4 (2)  127.4 (2)
C1—N1—Cu1 124.00 (17)  N7—C9—H9A 109.5  109.5
C4—N1—Cu1 118.91 (17)  N7—C9—H9B 109.5  109.5
C4—N1—C1 115.4 (2)  N7—C9—H9C 109.5  109.5
C4—N2—C3 115.5 (2)  H9A—C9—H9B 109.5  109.5
C8—N3—C7 116.2 (2)  H9A—C9—H9C 109.5  109.5
C5—N4—Cu1 120.02 (17)  H9B—C9—H9C 109.5  109.5
C8—N4—Cu1 122.97 (17)  N7—C10—H10A 109.5  109.5
C8—N4—C5 115.7 (2)  N7—C10—H10B 109.5  109.5
H5A—N5—H5B 126 (3)  N7—C10—H10C 109.5  109.5
C1—N5—H5A 116 (2)  N7—C10—H10B 109.5  109.5
C1—N5—H5B 116 (2)  N7—C10—H10C 109.5  109.5
H6A—N6—H6B 122 (4)  H10A—C10—H10B 109.5  109.5
C3—N6—H6A 119 (2)  H10A—C10—H10C 109.5  109.5
C3—N6—H6B 118 (2)  H10B—C10—H10C 109.5  109.5
C7—N7—C9 120.8 (2)

Hydrogen-bond geometry (Å, °)

|          | D—H   | H···A  | D···A   | D—H···A |
|----------|-------|--------|---------|---------|
| O1—H1A···S1i | 0.92 (1)  | 2.83 (3)  | 3.439 (2)  | 125 (3) |
| O1—H1A···N2i | 0.92 (1)  | 1.99 (2)  | 2.897 (3)  | 170 (3) |
| O1—H1B···O4ii | 0.91 (2)  | 1.82 (6)  | 2.71 (6)  | 167 (4) |
| O1—H1B···O5ii | 0.91 (2)  | 1.80 (6)  | 2.69 (6)  | 162 (4) |
| O3—H3A···Cl2 | 0.92     | 2.28     | 3.200 (7) | 176     |
| O3—H3B···O4 | 0.93     | 2.17     | 2.94 (6)  | 139     |
| O4—H4A···Cl1i | 0.91    | 2.97     | 3.46 (6)  | 116     |
| O4—H4A···O3ii | 0.91    | 2.25     | 3.07 (6)  | 150     |
| O4—H4B···Cl2ii | 0.93   | 2.61     | 3.01 (6)  | 107     |
| O2—H2A···O5iii | 0.91    | 2.36     | 3.13 (6)  | 144     |
| O2—H2A···Cl3 | 0.91     | 2.33     | 3.177 (7) | 154     |
| O5—H5C···Cl3 | 0.93    | 2.02     | 2.83 (6)  | 145     |
| O5—H5C···O2iii | 0.93    | 2.64     | 3.13 (6)  | 114     |
| O5—H5D···Cl1iv | 0.91    | 2.96     | 3.45 (6)  | 116     |
| O5—H5D···Cl3v | 0.91    | 2.56     | 3.27 (6)  | 135     |
| N5—H5E···Cl1 | 0.84 (3)  | 3.08 (3)  | 3.430 (3)  | 108 (2) |
| N5—H5E···Cl2 | 0.84 (3)  | 2.46 (3)  | 3.295 (3)  | 172 (3) |
| N5—H5E···O2 | 0.84 (3)  | 2.07 (3)  | 2.903 (7)  | 167 (3) |
| N5—H5E···Cl1v | 0.79 (3)  | 2.56 (4)  | 3.353 (3)  | 173 (3) |
| N6—H6A···Cl3w | 0.80 (4)  | 2.41 (4)  | 3.187 (4)  | 165 (3) |
| N6—H6A···O3w | 0.80 (4)  | 2.32 (4)  | 3.094 (8)  | 163 (3) |
| N6—H6B···N3w | 0.81 (4)  | 2.76 (4)  | 3.323 (3)  | 128 (3) |

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