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

# Diamminebis[5-(pyrimidin-2-yl-$\kappa N^1$)-tetrazolato-$\kappa N^1$]copper(II) dihydrate

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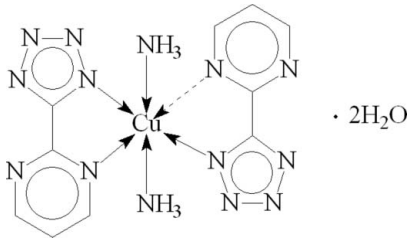
Received 1 May 2007; accepted 11 June 2007

Key indicators: single-crystal X-ray study; $T$ = 294 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.036; $wR$ factor = 0.097; data-to-parameter ratio = 13.8.

The title compound, $[Cu(C_5H_3N_6)_2(NH_3)_2]\cdot 2H_2O$, consists of a mononuclear copper complex and two solvent water molecules. The center $Cu^{II}$ ion is coordinated by two $NH_3$ and two 5-(pyrimidin-2-yl)tetrazolato ligands through the tetrazole N atoms in the 1 positions to form a square geometry. The two axial positions are occupied by weakly coordinated pyrimidinyl N atoms, thus giving rise to a highly distorted octahedral geometry. Furthermore, extensive intermolecular hydrogen-bond interactions lead to the formation of a three-dimensional network.

## Related literature

For related literature, see: Demko & Sharpless (2001); Rodríguez *et al.* (2005).




## Experimental

### Crystal data

$[Cu(C_5H_3N_6)_2(NH_3)_2]\cdot 2H_2O$
$M_r$ = 427.91
Triclinic, $P\overline{1}$
$a$ = 7.1533 (12) Å
$b$ = 9.5708 (16) Å
$c$ = 13.155 (2) Å
$\alpha$ = 97.048 (3)°
$\beta$ = 90.214 (2)°
$\gamma$ = 97.777 (3)°
$V$ = 885.4 (2) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 1.27 mm$^{-1}$
$T$ = 294 (2) K
0.22 × 0.22 × 0.20 mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min}$ = 0.975, $T_{max}$ = 1.000 (expected range = 0.756–0.775)
5086 measured reflections
3549 independent reflections
3104 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.023

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.097
$S$ = 1.04
3549 reflections
257 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.56 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.63 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Cu1—N1 | 2.0170 (18) | Cu1—N11 | 2.429 (2) |
| Cu1—N5 | 2.728 (2) | Cu1—N13 | 1.990 (2) |
| Cu1—N7 | 2.0447 (19) | Cu1—N14 | 1.992 (2) |
| | | | |
| N13—Cu1—N14 | 173.45 (9) | N1—Cu1—N7 | 173.28 (7) |
| N13—Cu1—N1 | 90.18 (8) | N13—Cu1—N11 | 94.55 (8) |
| N14—Cu1—N1 | 91.95 (8) | N14—Cu1—N11 | 91.24 (8) |
| N13—Cu1—N7 | 88.98 (8) | N1—Cu1—N11 | 98.88 (7) |
| N14—Cu1—N7 | 89.61 (8) | N7—Cu1—N11 | 74.54 (7) |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N14—H14$A$···O1$W$ | 0.89 | 2.56 | 3.332 (4) | 145 |
| N14—H14$A$···N4$^{i}$ | 0.89 | 2.59 | 3.209 (3) | 127 |
| N14—H14$B$···N6$^{i}$ | 0.89 | 2.52 | 3.345 (3) | 154 |
| N14—H14$C$···N12$^{ii}$ | 0.89 | 2.48 | 3.339 (3) | 162 |
| N13—H13$A$···N4$^{iii}$ | 0.89 | 2.47 | 3.137 (3) | 132 |
| N13—H13$B$···N12$^{iv}$ | 0.89 | 2.48 | 3.325 (3) | 158 |
| O2$W$—H2$WA$···N9$^{v}$ | 0.85 (1) | 2.07 (2) | 2.901 (3) | 168 (5) |
| O1$W$—H1$WA$···N3$^{i}$ | 0.85 (1) | 2.23 (2) | 3.053 (3) | 165 (5) |
| O1$W$—H1$WA$···N4$^{i}$ | 0.85 (1) | 2.59 (4) | 3.227 (3) | 133 (5) |
| O2$W$—H2$WB$···N8$^{vi}$ | 0.85 (1) | 2.199 (12) | 3.041 (4) | 172 (4) |
| O1$W$—H1$WB$···O2$W$ | 0.84 (1) | 2.01 (2) | 2.825 (4) | 161 (5) |

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

The authors thank Dalian Nationalities University for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ER2035).

## References

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# supplementary materials

*Acta Cryst.* (2007). E**63**, m1942 [ **doi:10.1107/S1600536807028668** ]

# Diamminebis[5-(pyrimidin-2-yl-$\kappa N^1$)tetrazolato-$\kappa N^1$]copper(II) dihydrate

**J.-T. Liu and S.-D. Fan**

## Comment

The crystal structures of Fe(II) and Co(II) complexes with 5-(pyrimidin-2-yl)tetrazolate ligand have been reported recently (Rodríguez et al., 2005), which feature a two-dimensional square-grid-like network. And, the ligands coordinate to metal atoms through one of the pyrimidinyl nitrogen atoms and the 1- and 3-positon tetrazole nitrogen atoms. The title complex, diamminobis[5-(pyrimidin-2-yl-κN$^1$)tetrazolato-κN$^1$]copper(II) dehydrate (I) performs a mono-nuclear structure (Fig. 1), in which the center $Cu^{II}$ atom, located on a normal position, is normally coordinated by two $NH_3$ and two ligand molecules using tetrazole N atoms in 1-position to form a square geometry. Simultaneously, two apical positions in $Cu^{II}$ atom form weak coordination (Cu1—N11 = 2.429 (2) and Cu1—N5 = 2.728 (2) Å) with two pyrimidinyl N atoms of two ligands, thus giving a highly distorted octahedral geometry (see Table 1). In addition, a three-dimensional supramolecular framework (Fig. 2) is formed by the intermolecular extensive N—H···O, N—H···N, O—H···N and O—H···O hydrogen-bond interactions between parking water molecules and complex molecules. The hydrogen bond parameters are listed in Table 2.

## Experimental

TThe ligand, 2-(1*H*-tetrazol-5-yl)pyrimidine (*L*) was synthesized according to the literature method (Demko & Sharpless, 2001). $CuCl_2·2H_2O$ (34 mg, 0.2 mmol) and *L* (60 mg, 0.4 mmol) were dissolved in ammonium hydroxide (20%, 10 ml). The solution was filtered, and then filtrate was allowed to stand for about 10 days. Blue crystals of (I) were isolated in about 30% yield.

## Refinement

H atoms bound to carbon and amine were included in calculated positions and treated in the subsequent refinement as riding atoms, with C—H = 0.93 and N—H = 0.89 Å and $U_{iso}$(H) = 1.2 and 1.5 $U_{eq}$(C and N), respectively. The H atoms of the water molecules were located in Fourier difference maps and refined with isotropic displacement parameters set at 1.5 times those of the parent O atoms.

## Figures

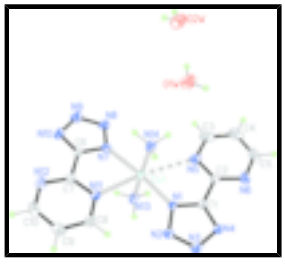

Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level.

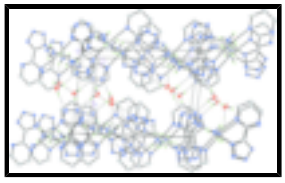

Fig. 2. Three-dimensional hydrogen-bonded network.

## Diamminebis[5-(pyrimidin-2-yl-κN$^1$)tetrazolato-κN$^1$]copper(II) dihydrate

*Crystal data*

| | |
|---|---|
| $[Cu(C_5H_3N_6)_2(NH_3)_2]\cdot 2H_2O$ | $Z = 2$ |
| $M_r = 427.91$ | $F_{000} = 438$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.605$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| $a = 7.1533$ (12) Å | Cell parameters from 3035 reflections |
| $b = 9.5708$ (16) Å | $\theta = 2.5$–$26.4^\circ$ |
| $c = 13.155$ (2) Å | $\mu = 1.28$ mm$^{-1}$ |
| $\alpha = 97.048$ (3)° | $T = 294$ (2) K |
| $\beta = 90.214$ (2)° | Block, blue |
| $\gamma = 97.777$ (3)° | 0.22 × 0.22 × 0.20 mm |
| $V = 885.4$ (2) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 3549 independent reflections |
| Radiation source: fine-focus sealed tube | 3104 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.023$ |
| $T = 294(2)$ K | $\theta_{max} = 26.4^\circ$ |
| φ and ω scans | $\theta_{min} = 1.6^\circ$ |
| Absorption correction: multi-scan (SADABS; Bruker, 1998) | $h = -6\rightarrow 8$ |
| $T_{min} = 0.975$, $T_{max} = 1.000$ | $k = -11\rightarrow 10$ |
| 5086 measured reflections | $l = -16\rightarrow 16$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.036$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.097$ | $w = 1/[\sigma^2(F_o^2) + (0.0583P)^2 + 0.2049P]$<br>where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.04$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 3549 reflections | $\Delta\rho_{max} = 0.56$ e Å$^{-3}$ |

257 parameters

4 restraints

Primary atom site location: structure-invariant direct methods

$\Delta\rho_{min} = -0.63$ e Å$^{-3}$

Extinction correction: SHELXL97, $Fc^{*}=kFc[1+0.001xFc^{2}\lambda^{3}/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.096 (5)

*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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0.23179 (3) | 0.95624 (3) | 0.245828 (19) | 0.02515 (13) |
| N1 | 0.2492 (3) | 1.0675 (2) | 0.38683 (14) | 0.0257 (4) |
| N2 | 0.2601 (3) | 1.2084 (2) | 0.41174 (16) | 0.0352 (5) |
| N3 | 0.2667 (3) | 1.2353 (2) | 0.51209 (17) | 0.0402 (5) |
| N4 | 0.2606 (3) | 1.1139 (2) | 0.55440 (15) | 0.0333 (5) |
| N5 | 0.2149 (3) | 0.7757 (2) | 0.39173 (18) | 0.0384 (5) |
| N6 | 0.2597 (4) | 0.8204 (2) | 0.57417 (18) | 0.0448 (6) |
| N7 | 0.2131 (3) | 0.8657 (2) | 0.09642 (15) | 0.0285 (4) |
| N8 | 0.1767 (3) | 0.7331 (2) | 0.04961 (17) | 0.0389 (5) |
| N9 | 0.1783 (4) | 0.7390 (3) | −0.05057 (18) | 0.0469 (6) |
| N10 | 0.2150 (3) | 0.8732 (3) | −0.07049 (16) | 0.0410 (5) |
| N11 | 0.2867 (3) | 1.1532 (2) | 0.14470 (15) | 0.0314 (4) |
| N12 | 0.2938 (3) | 1.1822 (3) | −0.03200 (16) | 0.0418 (5) |
| C1 | 0.2495 (3) | 1.0122 (2) | 0.47534 (17) | 0.0246 (5) |
| C2 | 0.2402 (3) | 0.8601 (2) | 0.48099 (18) | 0.0282 (5) |
| C3 | 0.2101 (5) | 0.6381 (3) | 0.3973 (3) | 0.0554 (8) |
| H3A | 0.1921 | 0.5751 | 0.3373 | 0.067* |
| C4 | 0.2309 (5) | 0.5847 (3) | 0.4888 (3) | 0.0641 (10) |
| H4A | 0.2287 | 0.4879 | 0.4916 | 0.077* |
| C5 | 0.2547 (5) | 0.6800 (3) | 0.5747 (3) | 0.0642 (10) |
| H5A | 0.2683 | 0.6461 | 0.6373 | 0.077* |
| C6 | 0.2364 (3) | 0.9490 (3) | 0.02177 (17) | 0.0284 (5) |
| C7 | 0.2752 (3) | 1.1045 (3) | 0.04536 (18) | 0.0291 (5) |
| C8 | 0.3217 (4) | 1.2939 (3) | 0.1692 (2) | 0.0407 (6) |
| H8A | 0.3323 | 1.3316 | 0.2379 | 0.049* |
| C9 | 0.3426 (4) | 1.3842 (3) | 0.0953 (2) | 0.0478 (7) |
| H9A | 0.3662 | 1.4822 | 0.1124 | 0.057* |
| C10 | 0.3270 (4) | 1.3236 (3) | −0.0047 (2) | 0.0502 (7) |

| | | | | |
|---|---|---|---|---|
| H10A | 0.3399 | 1.3827 | −0.0560 | 0.060* |
| N14 | 0.5061 (3) | 0.9386 (3) | 0.24816 (16) | 0.0369 (5) |
| H14A | 0.5254 | 0.8682 | 0.2835 | 0.055* |
| H14B | 0.5704 | 1.0196 | 0.2777 | 0.055* |
| H14C | 0.5449 | 0.9203 | 0.1843 | 0.055* |
| N13 | −0.0473 (3) | 0.9502 (3) | 0.24504 (15) | 0.0383 (5) |
| H13A | −0.0986 | 0.8813 | 0.2801 | 0.057* |
| H13B | −0.0915 | 0.9334 | 0.1807 | 0.057* |
| H13C | −0.0768 | 1.0332 | 0.2739 | 0.057* |
| O1W | 0.6222 (4) | 0.6186 (4) | 0.2726 (2) | 0.0799 (8) |
| H2WA | 0.895 (7) | 0.449 (3) | 0.145 (4) | 0.120* |
| H1WA | 0.655 (7) | 0.643 (6) | 0.3348 (14) | 0.120* |
| O2W | 0.9450 (4) | 0.5292 (3) | 0.17569 (19) | 0.0651 (6) |
| H2WB | 1.008 (6) | 0.579 (4) | 0.135 (3) | 0.098* |
| H1WB | 0.731 (3) | 0.610 (6) | 0.251 (3) | 0.098* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.01906 (17) | 0.0352 (2) | 0.02059 (18) | 0.00532 (11) | −0.00056 (10) | −0.00088 (11) |
| N1 | 0.0269 (10) | 0.0287 (10) | 0.0217 (9) | 0.0063 (8) | 0.0015 (7) | 0.0010 (8) |
| N2 | 0.0455 (13) | 0.0277 (10) | 0.0331 (11) | 0.0075 (9) | 0.0035 (9) | 0.0042 (9) |
| N3 | 0.0575 (15) | 0.0301 (11) | 0.0322 (12) | 0.0083 (10) | 0.0039 (10) | −0.0019 (9) |
| N4 | 0.0457 (12) | 0.0274 (10) | 0.0259 (10) | 0.0048 (9) | 0.0015 (9) | 0.0000 (8) |
| N5 | 0.0390 (12) | 0.0318 (11) | 0.0415 (13) | 0.0038 (9) | 0.0001 (10) | −0.0051 (9) |
| N6 | 0.0580 (15) | 0.0366 (12) | 0.0408 (13) | 0.0028 (11) | −0.0064 (11) | 0.0130 (10) |
| N7 | 0.0244 (10) | 0.0329 (10) | 0.0269 (10) | 0.0040 (8) | −0.0010 (8) | −0.0012 (8) |
| N8 | 0.0427 (13) | 0.0353 (12) | 0.0363 (12) | 0.0059 (10) | −0.0024 (9) | −0.0054 (9) |
| N9 | 0.0540 (15) | 0.0445 (14) | 0.0380 (13) | 0.0049 (11) | −0.0038 (11) | −0.0101 (10) |
| N10 | 0.0474 (13) | 0.0467 (14) | 0.0263 (11) | 0.0057 (11) | −0.0018 (9) | −0.0056 (10) |
| N11 | 0.0341 (11) | 0.0340 (11) | 0.0259 (10) | 0.0057 (9) | 0.0019 (8) | 0.0016 (8) |
| N12 | 0.0441 (13) | 0.0507 (14) | 0.0296 (11) | −0.0030 (11) | −0.0026 (9) | 0.0113 (10) |
| C1 | 0.0214 (10) | 0.0305 (12) | 0.0211 (11) | 0.0040 (9) | 0.0002 (8) | 0.0004 (9) |
| C2 | 0.0238 (11) | 0.0277 (12) | 0.0327 (12) | 0.0026 (9) | 0.0006 (9) | 0.0039 (10) |
| C3 | 0.0542 (19) | 0.0307 (15) | 0.076 (2) | 0.0039 (13) | −0.0033 (16) | −0.0113 (14) |
| C4 | 0.067 (2) | 0.0276 (15) | 0.099 (3) | 0.0053 (14) | −0.006 (2) | 0.0125 (17) |
| C5 | 0.081 (2) | 0.0436 (18) | 0.074 (2) | 0.0062 (17) | −0.0107 (19) | 0.0299 (17) |
| C6 | 0.0199 (10) | 0.0409 (13) | 0.0234 (11) | 0.0045 (9) | −0.0001 (8) | −0.0007 (9) |
| C7 | 0.0202 (11) | 0.0407 (13) | 0.0258 (12) | 0.0033 (9) | 0.0002 (9) | 0.0033 (10) |
| C8 | 0.0456 (15) | 0.0358 (14) | 0.0389 (14) | 0.0051 (11) | 0.0020 (12) | −0.0015 (11) |
| C9 | 0.0487 (17) | 0.0344 (14) | 0.0589 (19) | −0.0019 (12) | 0.0016 (14) | 0.0089 (13) |
| C10 | 0.0549 (18) | 0.0475 (17) | 0.0496 (17) | −0.0036 (14) | 0.0000 (14) | 0.0239 (14) |
| N14 | 0.0262 (10) | 0.0590 (14) | 0.0258 (10) | 0.0120 (10) | −0.0029 (8) | 0.0000 (9) |
| N13 | 0.0230 (10) | 0.0663 (15) | 0.0250 (10) | 0.0072 (10) | −0.0001 (8) | 0.0023 (10) |
| O1W | 0.0835 (19) | 0.094 (2) | 0.0572 (16) | 0.0256 (17) | −0.0117 (15) | −0.0251 (15) |
| O2W | 0.0788 (18) | 0.0543 (14) | 0.0550 (14) | 0.0030 (12) | 0.0053 (12) | −0.0155 (11) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu1—N1 | 2.0170 (18) | N12—C10 | 1.345 (4) |
| Cu1—N5 | 2.728 (2) | C1—C2 | 1.459 (3) |
| Cu1—N7 | 2.0447 (19) | C3—C4 | 1.379 (5) |
| Cu1—N11 | 2.429 (2) | C3—H3A | 0.9300 |
| Cu1—N13 | 1.990 (2) | C4—C5 | 1.357 (5) |
| Cu1—N14 | 1.992 (2) | C4—H4A | 0.9300 |
| N1—C1 | 1.337 (3) | C5—H5A | 0.9300 |
| N1—N2 | 1.339 (3) | C6—C7 | 1.471 (3) |
| N2—N3 | 1.313 (3) | C8—C9 | 1.374 (4) |
| N3—N4 | 1.344 (3) | C8—H8A | 0.9300 |
| N4—C1 | 1.329 (3) | C9—C10 | 1.369 (4) |
| N5—C3 | 1.324 (4) | C9—H9A | 0.9300 |
| N5—C2 | 1.338 (3) | C10—H10A | 0.9300 |
| N6—C2 | 1.339 (3) | N14—H14A | 0.8900 |
| N6—C5 | 1.341 (4) | N14—H14B | 0.8900 |
| N7—N8 | 1.332 (3) | N14—H14C | 0.8900 |
| N7—C6 | 1.336 (3) | N13—H13A | 0.8900 |
| N8—N9 | 1.326 (3) | N13—H13B | 0.8900 |
| N9—N10 | 1.334 (3) | N13—H13C | 0.8900 |
| N10—C6 | 1.332 (3) | O1W—H1WA | 0.846 (10) |
| N11—C7 | 1.331 (3) | O1W—H1WB | 0.843 (10) |
| N11—C8 | 1.334 (3) | O2W—H2WA | 0.849 (10) |
| N12—C7 | 1.329 (3) | O2W—H2WB | 0.848 (10) |
| N13—Cu1—N14 | 173.45 (9) | C4—C3—H3A | 118.8 |
| N13—Cu1—N1 | 90.18 (8) | C5—C4—C3 | 117.0 (3) |
| N14—Cu1—N1 | 91.95 (8) | C5—C4—H4A | 121.5 |
| N13—Cu1—N7 | 88.98 (8) | C3—C4—H4A | 121.5 |
| N14—Cu1—N7 | 89.61 (8) | N6—C5—C4 | 123.4 (3) |
| N1—Cu1—N7 | 173.28 (7) | N6—C5—H5A | 118.3 |
| N13—Cu1—N11 | 94.55 (8) | C4—C5—H5A | 118.3 |
| N14—Cu1—N11 | 91.24 (8) | N10—C6—N7 | 111.5 (2) |
| N1—Cu1—N11 | 98.88 (7) | N10—C6—C7 | 127.4 (2) |
| N7—Cu1—N11 | 74.54 (7) | N7—C6—C7 | 121.1 (2) |
| C1—N1—N2 | 106.16 (18) | N12—C7—N11 | 126.4 (2) |
| C1—N1—Cu1 | 125.67 (16) | N12—C7—C6 | 118.5 (2) |
| N2—N1—Cu1 | 128.17 (15) | N11—C7—C6 | 115.1 (2) |
| N3—N2—N1 | 107.98 (19) | N11—C8—C9 | 121.5 (3) |
| N2—N3—N4 | 110.3 (2) | N11—C8—H8A | 119.2 |
| C1—N4—N3 | 104.76 (19) | C9—C8—H8A | 119.2 |
| C3—N5—C2 | 115.6 (3) | C10—C9—C8 | 117.1 (3) |
| C2—N6—C5 | 114.4 (3) | C10—C9—H9A | 121.5 |
| N8—N7—C6 | 105.87 (19) | C8—C9—H9A | 121.5 |
| N8—N7—Cu1 | 134.76 (17) | N12—C10—C9 | 122.9 (3) |
| C6—N7—Cu1 | 119.35 (16) | N12—C10—H10A | 118.6 |
| N9—N8—N7 | 107.8 (2) | C9—C10—H10A | 118.6 |
| N8—N9—N10 | 110.8 (2) | Cu1—N14—H14A | 109.5 |

| | | | |
|---|---|---|---|
| C6—N10—N9 | 104.1 (2) | Cu1—N14—H14B | 109.5 |
| C7—N11—C8 | 116.9 (2) | H14A—N14—H14B | 109.5 |
| C7—N11—Cu1 | 109.90 (16) | Cu1—N14—H14C | 109.5 |
| C8—N11—Cu1 | 133.21 (17) | H14A—N14—H14C | 109.5 |
| C7—N12—C10 | 115.2 (2) | H14B—N14—H14C | 109.5 |
| N4—C1—N1 | 110.8 (2) | Cu1—N13—H13A | 109.5 |
| N4—C1—C2 | 126.1 (2) | Cu1—N13—H13B | 109.5 |
| N1—C1—C2 | 123.1 (2) | H13A—N13—H13B | 109.5 |
| N5—C2—N6 | 127.2 (2) | Cu1—N13—H13C | 109.5 |
| N5—C2—C1 | 116.0 (2) | H13A—N13—H13C | 109.5 |
| N6—C2—C1 | 116.8 (2) | H13B—N13—H13C | 109.5 |
| N5—C3—C4 | 122.4 (3) | H1WA—O1W—H1WB | 96 (5) |
| N5—C3—H3A | 118.8 | H2WA—O2W—H2WB | 112 (5) |
| N13—Cu1—N1—C1 | 92.85 (19) | C3—N5—C2—N6 | −0.5 (4) |
| N14—Cu1—N1—C1 | −80.95 (19) | C3—N5—C2—C1 | 178.8 (2) |
| N11—Cu1—N1—C1 | −172.51 (18) | C5—N6—C2—N5 | 0.8 (4) |
| N13—Cu1—N1—N2 | −86.2 (2) | C5—N6—C2—C1 | −178.4 (3) |
| N14—Cu1—N1—N2 | 100.0 (2) | N4—C1—C2—N5 | 175.0 (2) |
| N11—Cu1—N1—N2 | 8.5 (2) | N1—C1—C2—N5 | −5.5 (3) |
| C1—N1—N2—N3 | 0.0 (3) | N4—C1—C2—N6 | −5.7 (4) |
| Cu1—N1—N2—N3 | 179.19 (16) | N1—C1—C2—N6 | 173.8 (2) |
| N1—N2—N3—N4 | 0.1 (3) | C2—N5—C3—C4 | −0.4 (5) |
| N2—N3—N4—C1 | −0.2 (3) | N5—C3—C4—C5 | 0.7 (5) |
| N13—Cu1—N7—N8 | −83.5 (2) | C2—N6—C5—C4 | −0.4 (5) |
| N14—Cu1—N7—N8 | 90.1 (2) | C3—C4—C5—N6 | −0.3 (6) |
| N11—Cu1—N7—N8 | −178.6 (2) | N9—N10—C6—N7 | −0.3 (3) |
| N14—Cu1—N7—C6 | −91.74 (18) | N9—N10—C6—C7 | −178.6 (2) |
| N11—Cu1—N7—C6 | −0.35 (16) | N8—N7—C6—N10 | 0.3 (3) |
| C6—N7—N8—N9 | −0.1 (3) | Cu1—N7—C6—N10 | −178.39 (16) |
| Cu1—N7—N8—N9 | 178.26 (17) | N8—N7—C6—C7 | 178.7 (2) |
| N7—N8—N9—N10 | −0.1 (3) | Cu1—N7—C6—C7 | 0.0 (3) |
| N8—N9—N10—C6 | 0.3 (3) | C10—N12—C7—N11 | −0.2 (4) |
| N13—Cu1—N11—C7 | −86.98 (16) | C10—N12—C7—C6 | 179.3 (2) |
| N14—Cu1—N11—C7 | 89.95 (16) | C8—N11—C7—N12 | −0.5 (4) |
| N1—Cu1—N11—C7 | −177.88 (15) | Cu1—N11—C7—N12 | 178.6 (2) |
| N7—Cu1—N11—C7 | 0.69 (15) | C8—N11—C7—C6 | 180.0 (2) |
| N13—Cu1—N11—C8 | 91.9 (2) | Cu1—N11—C7—C6 | −0.9 (2) |
| N14—Cu1—N11—C8 | −91.1 (2) | N10—C6—C7—N12 | −0.7 (4) |
| N1—Cu1—N11—C8 | 1.0 (2) | N7—C6—C7—N12 | −178.8 (2) |
| N7—Cu1—N11—C8 | 179.6 (3) | N10—C6—C7—N11 | 178.8 (2) |
| N3—N4—C1—N1 | 0.2 (3) | N7—C6—C7—N11 | 0.7 (3) |
| N3—N4—C1—C2 | 179.8 (2) | C7—N11—C8—C9 | 0.8 (4) |
| N2—N1—C1—N4 | −0.2 (3) | Cu1—N11—C8—C9 | −178.1 (2) |
| Cu1—N1—C1—N4 | −179.34 (15) | N11—C8—C9—C10 | −0.4 (4) |
| N2—N1—C1—C2 | −179.7 (2) | C7—N12—C10—C9 | 0.6 (4) |
| Cu1—N1—C1—C2 | 1.1 (3) | C8—C9—C10—N12 | −0.4 (5) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N14—H14A···O1W | 0.89 | 2.56 | 3.332 (4) | 145 |
| N14—H14A···N4$^{i}$ | 0.89 | 2.59 | 3.209 (3) | 127 |
| N14—H14B···N6$^{i}$ | 0.89 | 2.52 | 3.345 (3) | 154 |
| N14—H14C···N12$^{ii}$ | 0.89 | 2.48 | 3.339 (3) | 162 |
| N13—H13A···N4$^{iii}$ | 0.89 | 2.47 | 3.137 (3) | 132 |
| N13—H13B···N12$^{iv}$ | 0.89 | 2.48 | 3.325 (3) | 158 |
| O2W—H2WA···N9$^{v}$ | 0.85 (1) | 2.07 (2) | 2.901 (3) | 168 (5) |
| O1W—H1WA···N3$^{i}$ | 0.85 (1) | 2.23 (2) | 3.053 (3) | 165 (5) |
| O1W—H1WA···N4$^{i}$ | 0.85 (1) | 2.59 (4) | 3.227 (3) | 133 (5) |
| O2W—H2WB···N8$^{vi}$ | 0.85 (1) | 2.199 (12) | 3.041 (4) | 172 (4) |
| O1W—H1WB···O2W | 0.84 (1) | 2.01 (2) | 2.825 (4) | 161 (5) |

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

**Fig. 1**

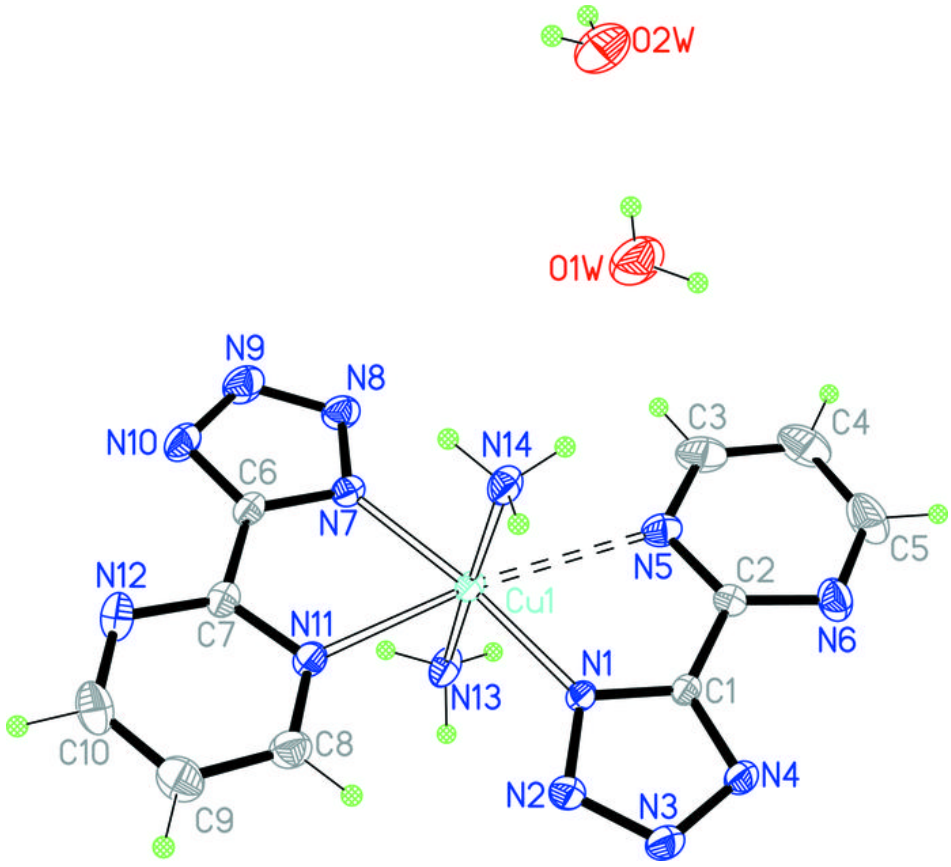
O2W
O1W
N9
N8
N10
C6
N7
N14
C3
C4
C5
N5
C2
N6
N12
C7
N11
Cu1
N1
C1
N13
C10
C8
N4
N2
N3
C9

**Fig. 2**