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# *catena*-Poly[[[aquabis(1*H*-imidazole-$\kappa N^3$)copper(II)]-$\mu$-naphthalene-1,4-dicarboxylato-$\kappa^2O^1$:$O^4$] dihydrate]

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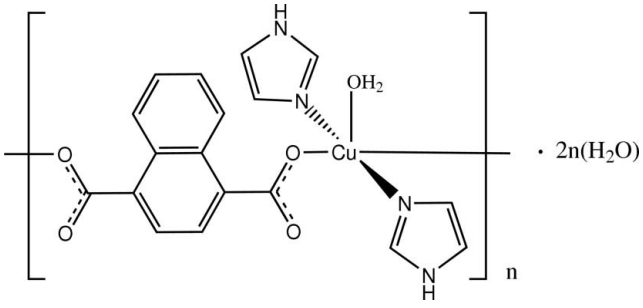
Key indicators: single-crystal X-ray study; $T$ = 295 K; mean $\sigma$(C–C) = 0.004 Å; disorder in solvent or counterion; $R$ factor = 0.036; $wR$ factor = 0.098; data-to-parameter ratio = 14.2.

In the title compound, $\{[Cu(C_{12}H_6O_4)(C_3H_4N_2)_2(H_2O)]\cdot 2H_2O\}_n$, the $Cu^{II}$ cation is coordinated by two naphthalene-1,4-dicarboxylate (naph) dianions, two imidazole molecules and one water molecule in a distorted square-pyramidal geometry. The Cu—O bond distance in the apical direction is 0.509 (3) Å longer than the mean Cu—O bond distance in the basal plane. The naph dianion bridges two $Cu^{II}$ cations, forming a one-dimensional polymeric chain. The coordinated water molecule is hydrogen-bonded to the carboxylate groups and imidazole ligands of adjacent polymeric chains, forming a three-dimensional supramolecular structure. No $\pi$–$\pi$ stacking is observed in the crystal structure. One solvent water molecule is disordered equally over two positions.

## Related literature

For general background, see: Su & Xu (2004); Li *et al.* (2005). For related structures, see: Derissen *et al.* (1979); Li *et al.* (2008).




## Experimental

### *Crystal data*

$[Cu(C_{12}H_6O_4)(C_3H_4N_2)_2(H_2O)]\cdot 2H_2O$
$M_r$ = 467.92
Monoclinic, $P2_1/n$
$a$ = 12.571 (2) Å
$b$ = 14.698 (3) Å
$c$ = 12.636 (2) Å
$\beta$ = 119.011 (6)°
$V$ = 2041.8 (6) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.12 mm$^{-1}$
$T$ = 295 (2) K
0.33 × 0.30 × 0.24 mm

### *Data collection*

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min}$ = 0.660, $T_{max}$ = 0.765
23205 measured reflections
3989 independent reflections
3251 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.043

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.097
$S$ = 1.06
3989 reflections
280 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.50 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.39 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Cu—N1 | 1.992 (2) | Cu—O3$^{i}$ | 2.0116 (17) |
| Cu—N3 | 1.990 (2) | Cu—O5 | 2.506 (2) |
| Cu—O1 | 1.9819 (17) | | |

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1*W*—H1*A*···O3 | 0.87 | 1.99 | 2.846 (3) | 170 |
| O1*W*—H1*B*···O4$^{ii}$ | 0.89 | 1.93 | 2.789 (3) | 162 |
| O2*WA*—H2*A*···O1*W* | 0.91 | 1.97 | 2.828 (13) | 155 |
| O2*WB*—H2*C*···O2*WA* | 0.85 | 1.55 | 2.156 (16) | 126 |
| N2—H2*N*···O1*W*$^{iii}$ | 0.86 | 1.96 | 2.798 (4) | 165 |
| N4—H4*N*···O5$^{iv}$ | 0.86 | 2.02 | 2.866 (3) | 166 |
| O5—H5*A*···O2$^{ii}$ | 0.85 | 1.90 | 2.716 (3) | 162 |
| O5—H5*B*···O4$^{v}$ | 0.85 | 1.95 | 2.791 (3) | 172 |
| C17—H17···O2$^{vi}$ | 0.93 | 2.50 | 3.389 (4) | 160 |

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SG2252).

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# supporting information

*Acta Cryst.* (2008). E**64**, m948–m949 [doi:10.1107/S1600536808018515]

## *catena*-Poly[[[aquabis(1*H*-imidazole-$\kappa N^3$)copper(II)]-$\mu$-naphthalene-1,4-dicarboxylato-$\kappa^2O^1$:$O^4$] dihydrate]

**Jun-Hua Li, Jing-Jing Nie and Duan-Jun Xu**

### S1. Comment

As part of our investigation on the nature of $\pi$-$\pi$ stacking between aromatic rings (Li *et al.*, 2005), the title polymeric complex of $Cu^{II}$ incorporating imidazole and naphthalenedicarboxylate (naph) ligands has been prepared and its crystal structure is reported here.

The $Cu^{II}$ cation is coordinated by two naph dianions, two imidazole molecules and one water molecule in a distorted square pyramidal geometry. The Cu—O(water) bond distance in the apical direction is longer than mean Cu—*O*(carboxyl) bond distance in the basal plane by 0.509 (3) Å. The naph dianion bridges two $Cu^{II}$ cations by two carboxyl groups to form the one dimensional polymeric chain (Fig. 1). Two carboxyl groups of the naph dianion are twisted with respect to the C1-benzene ring with the dihedral angles of 32.0 (2)° and 38.2 (2)°, which are close to that found in the free naphthalenedicarboxylic acid (*ca* 40°; Derissen *et al.*, 1979) but are much smaller than those [52.5 (3)° and 48.7 (3)°] found in a $Mn^{II}$ complex with the uncoordinated naph dianion (Li *et al.*, 2008). The coordinated water molecule (O5) is hydrogen bonded to carboxyl groups and imidazole ligand of adjacent polymeric chains (Table 2) to form the three dimensional supra-molecular structure.

The parallel C8-benzene and $C8^{iii}$-benzene rings from the adjacent polymeric chains overlap as shown in Fig. 2 [symmetry code: (iii) 1 - *x*, 1 - *y*, 2 - *z*] with a face-to-face separation of 3.67 (2) Å indicating no $\pi$-$\pi$ stacking existing between benzene rings, a similar situation to that found in the $Mn^{II}$ complex with uncoordinated naph dianion (Li *et al.*, 2008). The face-to-face distances between parallel N1-imidazole and $N1^{iv}$-imidazole rings and between parallel N3-imidazole and $N3^{v}$-imidazole rings are 3.310 (4) and 3.050 (17) Å, respectively [symmetry codes: (iv) 1 - *x*, -*y*, 1 - *z*; (v) 1 - *x*, 1 - *y*, 1 - *z*]. However the imidazole rings are not overlapping each other in the crystal structure (Fig. 3), therefore no $\pi$-p\ stacking exists between parallel imidazole rings too.

### S2. Experimental

A water-ethanol solution (12 ml, 1:1) containing naphthalene-1,4-dicarboxyllic acid (0.162 g, 0.75 mmol), sodium hydroxide (0.053 g, 1.3 mmol), sodium acetate trihydrate (0.204 g, 1.5 mmol), cupric chloride dihydrate (0.085 g, 0.5 mmol) and imidazole (0.034 g, 0.5 mmol) was refluxed for 3 h. After cooling to room temperature the solution was filtered. The single crystals of the title compound were obtained from the filtrate after 8 d.

### S3. Refinement

The lattice water O2WB is close to an inversion center, while the lattice O2WA is *ca* 1.5 Å apart from $O2WB^{vi}$ [symmetry code: (vi) -*x*, 1 - *y*, 1 - *z*]. The site occupancy factors of the O2WA and O2WB atoms were initially refined and converged to 0.48 and 0.45, and fixed as 0.50 for each at final cycles of refinemens. Water H atoms were placed in a difference Fourier map and refined in riding mode with $U_{iso}(H) = 1.5U_{eq}(O)$. Other H atoms were placed in calculated

positions with C—H = 0.93 Å and N—H = 0.86 Å, and refined in riding mode with $U_{iso}$(H) = 1.2$U_{eq}$(C,*N*).

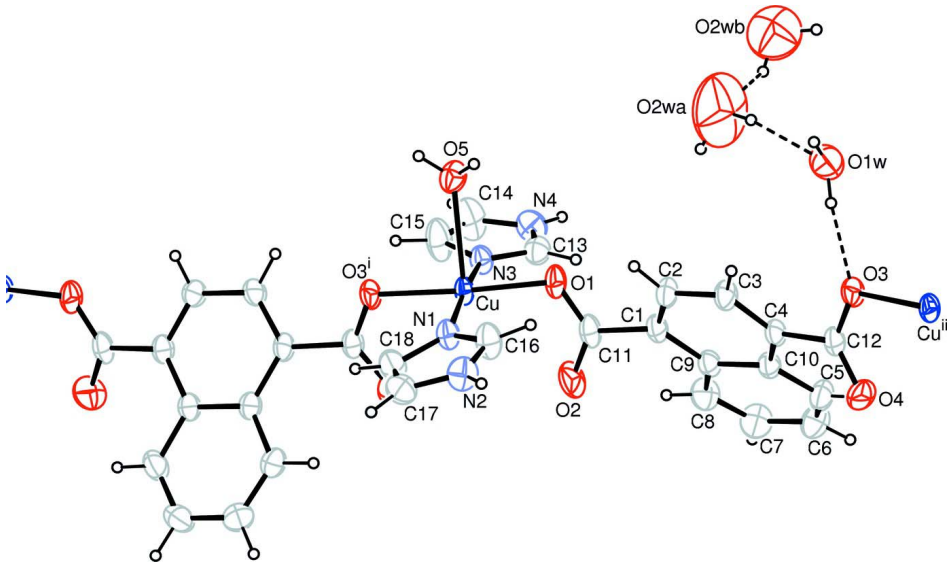


**Figure 1**

A segment of the polymeric chain of the title compound with 30% probability displacement ellipsoids (arbitrary spheres for H atoms); dashed lines indicate hydrogen bonding [symmetry codes: (i) *x* + 1/2, -*y* + 1/2, *z* - 1/2; (ii) *x* - 1/2, -*y* + 1/2, *z* + 1/2].

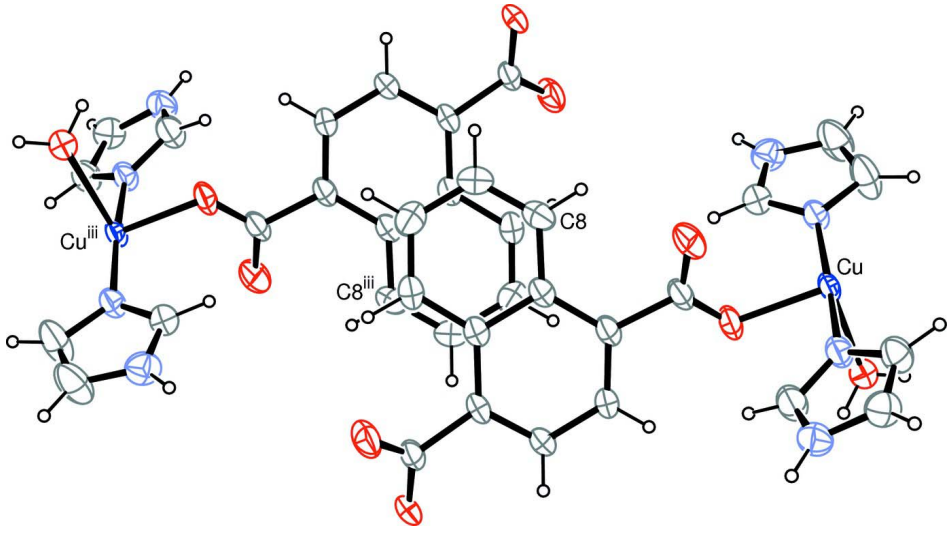


**Figure 2**

A digram showing the ovelapped arrangement of adjacent naphthaline ligands [symmetry code: (iii) 1 - *x*, 1 - *y*, 2 - *z*].

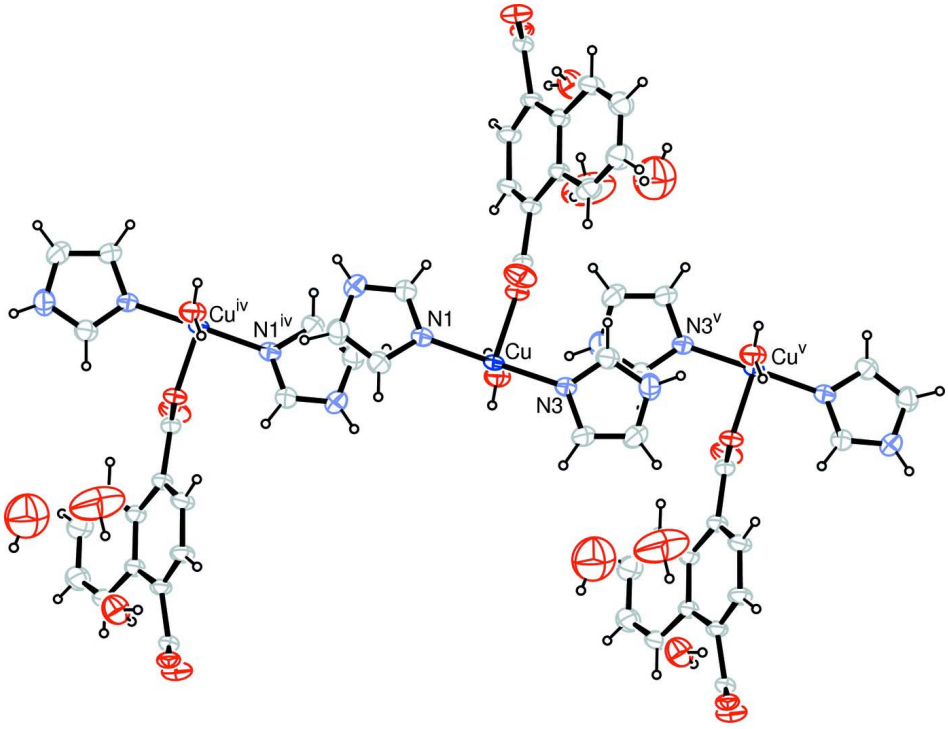


**Figure 3**

A diagram showing the contacts between imidazole rings [symmetry codes: (iv) 1 - *x*, -*y*, 1 - *z*; (v) 1 - *x*, 1 - *y*, 1 - *z*].

***catena*-Poly[[[aquabis(1*H*-imidazole-$\kappa$N$^3$)copper(II)]- $\mu$-naphthalene-1,4-dicarboxylato-$\kappa^2O^1$:$O^4$] dihydrate]**

*Crystal data*

$[Cu(C_{12}H_6O_4)(C_3H_4N_2)_2(H_2O)]\cdot 2H_2O$
$M_r = 467.92$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 12.571$ (2) Å
$b = 14.698$ (3) Å
$c = 12.636$ (2) Å
$\beta = 119.011$ (6)°
$V = 2041.8$ (6) Å$^3$
$Z = 4$
$F(000) = 964$
$D_x = 1.522$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5466 reflections
$\theta = 2.0$–$24.5°$
$\mu = 1.12$ mm$^{-1}$
$T = 295$ K
Prism, blue
0.33 × 0.30 × 0.24 mm

*Data collection*

Rigaku R-AXIS RAPID IP diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.0 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.660$, $T_{max} = 0.765$
23205 measured reflections
3989 independent reflections
3251 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 26.0°$, $\theta_{min} = 1.9°$
$h = -15\rightarrow15$
$k = -18\rightarrow17$
$l = -15\rightarrow15$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.097$
$S = 1.06$
3989 reflections
280 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 1.2324P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ e Å$^{-3}$
$\Delta\rho_{min} = -0.39$ 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) |
|---|---|---|---|---|---|
| Cu | 0.61473 (3) | 0.26395 (2) | 0.57692 (3) | 0.02692 (12) | |
| N1 | 0.60619 (19) | 0.13328 (15) | 0.6141 (2) | 0.0324 (5) | |
| N2 | 0.5581 (2) | 0.00805 (16) | 0.6757 (2) | 0.0408 (6) | |
| H2N | 0.5252 | −0.0276 | 0.7056 | 0.049* | |
| N3 | 0.64575 (19) | 0.39456 (14) | 0.56052 (19) | 0.0310 (5) | |
| N4 | 0.6481 (2) | 0.54324 (16) | 0.5765 (2) | 0.0423 (6) | |
| H4N | 0.6401 | 0.5966 | 0.5997 | 0.051* | |
| O1 | 0.52250 (17) | 0.29662 (13) | 0.66172 (17) | 0.0356 (4) | |
| O2 | 0.69612 (18) | 0.29561 (17) | 0.8353 (2) | 0.0515 (6) | |
| O3 | 0.19639 (16) | 0.27227 (12) | 0.98022 (16) | 0.0311 (4) | |
| O4 | 0.37130 (19) | 0.25600 (14) | 1.14909 (18) | 0.0436 (5) | |
| O5 | 0.41477 (17) | 0.27662 (13) | 0.38636 (17) | 0.0387 (5) | |
| H5A | 0.3510 | 0.2580 | 0.3861 | 0.058* | |
| H5B | 0.4082 | 0.2721 | 0.3166 | 0.058* | |
| O1W | 0.0571 (2) | 0.37164 (15) | 0.7624 (2) | 0.0548 (6) | |
| H1A | 0.1072 | 0.3426 | 0.8274 | 0.082* | |
| H1B | 0.0011 | 0.3328 | 0.7129 | 0.082* | |
| O2WA | 0.1105 (11) | 0.4187 (8) | 0.5762 (10) | 0.181 (5) | 0.50 |
| H2A | 0.0710 | 0.4002 | 0.6169 | 0.271* | 0.50 |
| H2B | 0.1794 | 0.3868 | 0.6144 | 0.271* | 0.50 |
| O2WB | −0.0010 (9) | 0.5394 (6) | 0.5243 (9) | 0.127 (3) | 0.50 |
| H2C | 0.0693 | 0.5188 | 0.5711 | 0.190* | 0.50 |
| H2D | −0.0381 | 0.5579 | 0.5650 | 0.190* | 0.50 |
| C1 | 0.5111 (2) | 0.30793 (18) | 0.8430 (2) | 0.0294 (6) | |
| C2 | 0.3978 (2) | 0.26894 (18) | 0.7913 (2) | 0.0325 (6) | |

| | | | | |
|---|---|---|---|---|
| H2 | 0.3638 | 0.2466 | 0.7127 | 0.039* |
| C3 | 0.3324 (2) | 0.26212 (18) | 0.8547 (2) | 0.0327 (6) |
| H3 | 0.2564 | 0.2343 | 0.8181 | 0.039* |
| C4 | 0.3787 (2) | 0.29591 (18) | 0.9699 (2) | 0.0283 (5) |
| C5 | 0.5331 (3) | 0.3954 (2) | 1.1323 (2) | 0.0376 (6) |
| H5 | 0.4903 | 0.3923 | 1.1750 | 0.045* |
| C6 | 0.6357 (3) | 0.4476 (2) | 1.1762 (3) | 0.0441 (7) |
| H6 | 0.6605 | 0.4810 | 1.2468 | 0.053* |
| C7 | 0.7035 (3) | 0.4508 (2) | 1.1152 (3) | 0.0452 (7) |
| H7 | 0.7740 | 0.4856 | 1.1463 | 0.054* |
| C8 | 0.6671 (3) | 0.4035 (2) | 1.0115 (3) | 0.0399 (7) |
| H8 | 0.7144 | 0.4053 | 0.9733 | 0.048* |
| C9 | 0.5581 (2) | 0.35118 (17) | 0.9593 (2) | 0.0287 (5) |
| C10 | 0.4903 (2) | 0.34582 (17) | 1.0226 (2) | 0.0284 (5) |
| C11 | 0.5842 (3) | 0.30043 (18) | 0.7771 (3) | 0.0329 (6) |
| C12 | 0.3125 (2) | 0.27394 (17) | 1.0399 (2) | 0.0289 (6) |
| C13 | 0.6235 (2) | 0.46473 (19) | 0.6125 (2) | 0.0352 (6) |
| H13 | 0.5945 | 0.4598 | 0.6674 | 0.042* |
| C14 | 0.6877 (3) | 0.5244 (2) | 0.4974 (3) | 0.0585 (9) |
| H14 | 0.7112 | 0.5661 | 0.4572 | 0.070* |
| C15 | 0.6865 (3) | 0.4329 (2) | 0.4878 (3) | 0.0561 (9) |
| H15 | 0.7099 | 0.4006 | 0.4391 | 0.067* |
| C16 | 0.5431 (3) | 0.0979 (2) | 0.6621 (3) | 0.0418 (7) |
| H16 | 0.4940 | 0.1315 | 0.6838 | 0.050* |
| C17 | 0.6345 (3) | −0.0168 (2) | 0.6339 (3) | 0.0405 (7) |
| H17 | 0.6612 | −0.0754 | 0.6316 | 0.049* |
| C18 | 0.6642 (3) | 0.05965 (19) | 0.5964 (3) | 0.0389 (6) |
| H18 | 0.7161 | 0.0627 | 0.5635 | 0.047* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu | 0.03055 (19) | 0.02963 (19) | 0.03180 (19) | 0.00027 (12) | 0.02397 (15) | −0.00133 (13) |
| N1 | 0.0350 (12) | 0.0336 (13) | 0.0378 (12) | 0.0004 (10) | 0.0250 (10) | −0.0019 (10) |
| N2 | 0.0484 (14) | 0.0342 (14) | 0.0467 (14) | −0.0069 (11) | 0.0287 (12) | 0.0010 (11) |
| N3 | 0.0341 (12) | 0.0315 (12) | 0.0365 (12) | 0.0011 (9) | 0.0241 (10) | 0.0009 (9) |
| N4 | 0.0448 (14) | 0.0314 (13) | 0.0511 (15) | −0.0005 (10) | 0.0234 (12) | −0.0021 (11) |
| O1 | 0.0446 (11) | 0.0381 (11) | 0.0412 (11) | 0.0005 (8) | 0.0344 (10) | −0.0015 (8) |
| O2 | 0.0333 (12) | 0.0736 (15) | 0.0599 (14) | 0.0010 (10) | 0.0323 (11) | −0.0102 (11) |
| O3 | 0.0295 (10) | 0.0387 (10) | 0.0359 (10) | −0.0006 (8) | 0.0243 (9) | 0.0022 (8) |
| O4 | 0.0398 (11) | 0.0662 (14) | 0.0322 (11) | 0.0016 (10) | 0.0233 (9) | 0.0083 (9) |
| O5 | 0.0379 (11) | 0.0476 (12) | 0.0360 (10) | −0.0086 (9) | 0.0222 (9) | −0.0074 (9) |
| O1W | 0.0509 (13) | 0.0544 (14) | 0.0585 (14) | 0.0047 (11) | 0.0261 (11) | −0.0028 (11) |
| O2WA | 0.216 (12) | 0.203 (12) | 0.214 (12) | −0.016 (9) | 0.175 (11) | 0.029 (9) |
| O2WB | 0.117 (6) | 0.131 (8) | 0.126 (7) | −0.021 (6) | 0.054 (6) | −0.012 (6) |
| C1 | 0.0315 (14) | 0.0311 (14) | 0.0351 (14) | 0.0024 (11) | 0.0236 (12) | 0.0008 (11) |
| C2 | 0.0341 (15) | 0.0403 (16) | 0.0315 (14) | −0.0037 (11) | 0.0225 (12) | −0.0070 (11) |
| C3 | 0.0287 (14) | 0.0423 (16) | 0.0350 (14) | −0.0053 (11) | 0.0218 (12) | −0.0046 (12) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C4 | 0.0290 (13) | 0.0336 (14) | 0.0311 (13) | 0.0035 (10) | 0.0215 (11) | 0.0028 (11) |
| C5 | 0.0421 (16) | 0.0464 (17) | 0.0325 (14) | −0.0013 (13) | 0.0245 (13) | −0.0036 (12) |
| C6 | 0.0501 (18) | 0.0453 (18) | 0.0374 (16) | −0.0077 (14) | 0.0217 (14) | −0.0098 (13) |
| C7 | 0.0369 (16) | 0.0500 (19) | 0.0490 (18) | −0.0146 (13) | 0.0211 (14) | −0.0088 (14) |
| C8 | 0.0360 (15) | 0.0437 (17) | 0.0478 (17) | −0.0077 (13) | 0.0265 (14) | −0.0009 (13) |
| C9 | 0.0290 (13) | 0.0304 (14) | 0.0329 (13) | 0.0021 (10) | 0.0200 (11) | 0.0016 (10) |
| C10 | 0.0309 (13) | 0.0295 (14) | 0.0304 (13) | 0.0027 (10) | 0.0192 (11) | 0.0016 (10) |
| C11 | 0.0417 (17) | 0.0273 (14) | 0.0469 (17) | −0.0020 (11) | 0.0351 (14) | −0.0013 (11) |
| C12 | 0.0332 (14) | 0.0292 (14) | 0.0345 (14) | 0.0018 (11) | 0.0245 (12) | −0.0001 (11) |
| C13 | 0.0354 (15) | 0.0381 (16) | 0.0348 (14) | −0.0012 (12) | 0.0192 (12) | −0.0017 (12) |
| C14 | 0.080 (2) | 0.0393 (19) | 0.087 (3) | 0.0010 (16) | 0.065 (2) | 0.0105 (17) |
| C15 | 0.087 (3) | 0.0380 (18) | 0.081 (2) | 0.0069 (16) | 0.070 (2) | 0.0094 (16) |
| C16 | 0.0528 (18) | 0.0339 (16) | 0.0551 (18) | −0.0020 (13) | 0.0390 (16) | −0.0023 (13) |
| C17 | 0.0414 (16) | 0.0339 (16) | 0.0454 (16) | 0.0028 (12) | 0.0206 (14) | 0.0011 (13) |
| C18 | 0.0403 (16) | 0.0370 (16) | 0.0467 (17) | 0.0057 (12) | 0.0268 (14) | 0.0023 (13) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu—N1 | 1.992 (2) | C1—C2 | 1.371 (4) |
| Cu—N3 | 1.990 (2) | C1—C9 | 1.439 (4) |
| Cu—O1 | 1.9819 (17) | C1—C11 | 1.515 (3) |
| Cu—O3$^{i}$ | 2.0116 (17) | C2—C3 | 1.404 (4) |
| Cu—O5 | 2.506 (2) | C2—H2 | 0.9300 |
| N1—C16 | 1.317 (3) | C3—C4 | 1.372 (4) |
| N1—C18 | 1.382 (3) | C3—H3 | 0.9300 |
| N2—C16 | 1.333 (4) | C4—C10 | 1.430 (4) |
| N2—C17 | 1.351 (4) | C4—C12 | 1.514 (3) |
| N2—H2N | 0.8600 | C5—C6 | 1.365 (4) |
| N3—C13 | 1.323 (3) | C5—C10 | 1.421 (4) |
| N3—C15 | 1.372 (4) | C5—H5 | 0.9300 |
| N4—C13 | 1.331 (4) | C6—C7 | 1.400 (4) |
| N4—C14 | 1.344 (4) | C6—H6 | 0.9300 |
| N4—H4N | 0.8600 | C7—C8 | 1.352 (4) |
| O1—C11 | 1.278 (3) | C7—H7 | 0.9300 |
| O2—C11 | 1.234 (3) | C8—C9 | 1.424 (4) |
| O3—C12 | 1.277 (3) | C8—H8 | 0.9300 |
| O3—Cu$^{ii}$ | 2.0116 (17) | C9—C10 | 1.426 (3) |
| O4—C12 | 1.237 (3) | C13—H13 | 0.9300 |
| O5—H5A | 0.8450 | C14—C15 | 1.351 (5) |
| O5—H5B | 0.8478 | C14—H14 | 0.9300 |
| O1W—H1A | 0.8670 | C15—H15 | 0.9300 |
| O1W—H1B | 0.8864 | C16—H16 | 0.9300 |
| O2WA—H2A | 0.9128 | C17—C18 | 1.340 (4) |
| O2WA—H2B | 0.8933 | C17—H17 | 0.9300 |
| O2WB—H2C | 0.8461 | C18—H18 | 0.9300 |
| O2WB—H2D | 0.8876 | | |
| | | | |
| O1—Cu—N3 | 91.04 (8) | C6—C5—H5 | 119.3 |

| | | | |
|---|---|---|---|
| O1—Cu—N1 | 89.64 (8) | C10—C5—H5 | 119.3 |
| N3—Cu—N1 | 172.02 (9) | C5—C6—C7 | 120.2 (3) |
| O1—Cu—O3$^{i}$ | 175.67 (8) | C5—C6—H6 | 119.9 |
| N3—Cu—O3$^{i}$ | 90.49 (8) | C7—C6—H6 | 119.9 |
| N1—Cu—O3$^{i}$ | 89.41 (8) | C8—C7—C6 | 120.4 (3) |
| O5—Cu—N1 | 98.89 (8) | C8—C7—H7 | 119.8 |
| O5—Cu—N3 | 89.09 (8) | C6—C7—H7 | 119.8 |
| O5—Cu—O1 | 85.66 (7) | C7—C8—C9 | 121.6 (3) |
| O5—Cu—O3$^{i}$ | 90.32 (7) | C7—C8—H8 | 119.2 |
| C16—N1—C18 | 104.3 (2) | C9—C8—H8 | 119.2 |
| C16—N1—Cu | 127.07 (19) | C8—C9—C10 | 118.2 (2) |
| C18—N1—Cu | 128.61 (18) | C8—C9—C1 | 122.6 (2) |
| C16—N2—C17 | 107.4 (2) | C10—C9—C1 | 119.1 (2) |
| C16—N2—H2N | 126.3 | C5—C10—C9 | 118.2 (2) |
| C17—N2—H2N | 126.3 | C5—C10—C4 | 122.6 (2) |
| C13—N3—C15 | 104.5 (2) | C9—C10—C4 | 119.1 (2) |
| C13—N3—Cu | 126.94 (18) | O2—C11—O1 | 124.2 (2) |
| C15—N3—Cu | 128.44 (19) | O2—C11—C1 | 119.8 (2) |
| C13—N4—C14 | 107.9 (3) | O1—C11—C1 | 115.9 (2) |
| C13—N4—H4N | 126.0 | O4—C12—O3 | 123.3 (2) |
| C14—N4—H4N | 126.0 | O4—C12—C4 | 119.7 (2) |
| C11—O1—Cu | 115.93 (16) | O3—C12—C4 | 117.0 (2) |
| C12—O3—Cu$^{ii}$ | 114.83 (16) | N3—C13—N4 | 111.5 (2) |
| H5A—O5—H5B | 110.9 | N3—C13—H13 | 124.3 |
| H1A—O1W—H1B | 108.4 | N4—C13—H13 | 124.3 |
| H2A—O2WA—H2B | 100.9 | N4—C14—C15 | 106.2 (3) |
| H2C—O2WB—H2D | 111.6 | N4—C14—H14 | 126.9 |
| C2—C1—C9 | 119.3 (2) | C15—C14—H14 | 126.9 |
| C2—C1—C11 | 118.3 (2) | C14—C15—N3 | 109.9 (3) |
| C9—C1—C11 | 122.4 (2) | C14—C15—H15 | 125.0 |
| C1—C2—C3 | 121.2 (2) | N3—C15—H15 | 125.0 |
| C1—C2—H2 | 119.4 | N1—C16—N2 | 111.8 (3) |
| C3—C2—H2 | 119.4 | N1—C16—H16 | 124.1 |
| C4—C3—C2 | 121.0 (2) | N2—C16—H16 | 124.1 |
| C4—C3—H3 | 119.5 | C18—C17—N2 | 106.5 (3) |
| C2—C3—H3 | 119.5 | C18—C17—H17 | 126.7 |
| C3—C4—C10 | 119.7 (2) | N2—C17—H17 | 126.7 |
| C3—C4—C12 | 118.1 (2) | C17—C18—N1 | 109.9 (2) |
| C10—C4—C12 | 122.1 (2) | C17—C18—H18 | 125.1 |
| C6—C5—C10 | 121.4 (2) | N1—C18—H18 | 125.1 |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*W*—H1*A*···O3 | 0.87 | 1.99 | 2.846 (3) | 170 |
| O1*W*—H1*B*···O4$^{iii}$ | 0.89 | 1.93 | 2.789 (3) | 162 |

| | | | | |
|---|---|---|---|---|
| O2*WA*—H2*A*···O1*W* | 0.91 | 1.97 | 2.828 (13) | 155 |
| O2*WB*—H2*C*···O2*WA* | 0.85 | 1.55 | 2.156 (16) | 126 |
| N2—H2*N*···O1*W*$^{iv}$ | 0.86 | 1.96 | 2.798 (4) | 165 |
| N4—H4*N*···O5$^{v}$ | 0.86 | 2.02 | 2.866 (3) | 166 |
| O5—H5*A*···O2$^{iii}$ | 0.85 | 1.90 | 2.716 (3) | 162 |
| O5—H5*B*···O4$^{vi}$ | 0.85 | 1.95 | 2.791 (3) | 172 |
| C17—H17···O2$^{vii}$ | 0.93 | 2.50 | 3.389 (4) | 160 |

Symmetry codes: (iii) $x-1/2, -y+1/2, z-1/2$; (iv) $-x+1/2, y-1/2, -z+3/2$; (v) $-x+1, -y+1, -z+1$; (vi) $x, y, z-1$; (vii) $-x+3/2, y-1/2, -z+3/2$.