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# (2,2′-Bipyridine-$\kappa^2N,N'$)[*N*-(2-oxido-1-naphthylidene)threoninato-$\kappa^3O^1,N,O^2$]-copper(II)

**Zhanglei Qiu, Lianzhi Li,* Yan Liu, Tao Xu and Daqi Wang**

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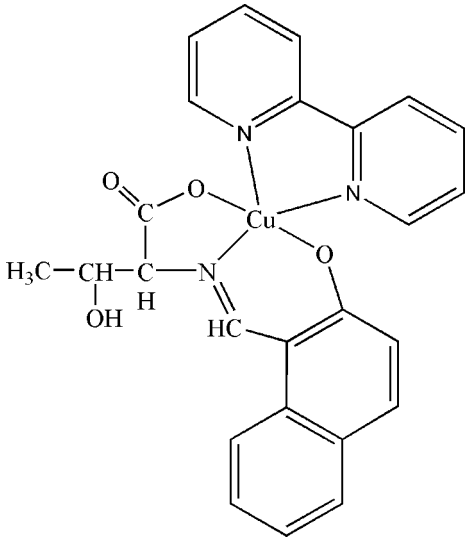
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.034; $wR$ factor = 0.089; data-to-parameter ratio = 17.6.

In the title complex, $[Cu(C_{15}H_{13}NO_4)(C_{10}H_8N_2)]$, the Schiff base ligand is derived from the condensation of 2-hydroxy-1-naphthaldehyde and L-threonine. The $Cu^{II}$ atom is five-coordinated by one N atom and two O atoms from the Schiff base ligand and by two N atoms from a 2,2′-bipyridine ligand in a distorted square-pyramidal geometry. In the crystal structure, the combination of intermolecular O—H···O and C—H···O hydrogen bonds leads to a two-dimensional network.

## Related literature

For related literature, see: Garnovski *et al.* (1993); Kalagouda *et al.* (2006); Wang *et al.* (1999).




## Experimental

### Crystal data

$[Cu(C_{15}H_{13}NO_4)(C_{10}H_8N_2)]$
$M_r$ = 490.99
Orthorhombic, $P2_12_12_1$
$a$ = 9.955 (2) Å
$b$ = 12.180 (3) Å
$c$ = 18.438 (4) Å
$V$ = 2235.6 (9) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.01 mm$^{-1}$
$T$ = 298 (2) K
0.29 × 0.28 × 0.16 mm

### Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.757, $T_{max}$ = 0.855
14242 measured reflections
5278 independent reflections
4243 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.027

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.088
$S$ = 1.04
5278 reflections
300 parameters
492 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.54 e Å$^{-3}$
Absolute structure: Flack (1983), 2229 Friedel pairs
Flack parameter: −0.005 (13)

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

| | | | |
|---|---|---|---|
| Cu1—O4 | 1.925 (2) | Cu1—O1 | 2.0236 (18) |
| Cu1—N1 | 1.926 (2) | Cu1—N2 | 2.231 (3) |
| Cu1—N3 | 2.005 (2) | | |
| O4—Cu1—N1 | 92.62 (8) | N3—Cu1—O1 | 92.57 (9) |
| O4—Cu1—N3 | 91.77 (9) | O4—Cu1—N2 | 109.51 (10) |
| N1—Cu1—N3 | 174.65 (9) | N1—Cu1—N2 | 104.07 (9) |
| O4—Cu1—O1 | 147.49 (9) | N3—Cu1—N2 | 77.29 (10) |
| N1—Cu1—O1 | 82.08 (8) | O1—Cu1—N2 | 102.88 (9) |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O3—H3···O2$^{i}$ | 0.82 | 1.99 | 2.808 (3) | 178 |
| C5—H11···O2$^{i}$ | 0.93 | 2.49 | 3.311 (3) | 147 |
| C12—H27···O2$^{i}$ | 0.93 | 2.50 | 3.431 (4) | 174 |
| C14—H25···O3$^{ii}$ | 0.93 | 2.52 | 3.445 (4) | 177 |

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{5}{2}, -z+2$; (ii) $-x-\frac{1}{2}, -y+2, z-\frac{1}{2}$.

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

The authors thank the Natural Science Foundation of Shandong Province (grant No. Y2004B02) for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2129).

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# supporting information

*Acta Cryst.* (2008). E**64**, m745–m746 [doi:10.1107/S1600536808012191]

## (2,2′-Bipyridine-$\kappa^2N,N'$)[*N*-(2-oxido-1-naphthylidene)threoninato-$\kappa^3O^1,N,O^2$]copper(II)

**Zhanglei Qiu, Lianzhi Li, Yan Liu, Tao Xu and Daqi Wang**

### S1. Comment

Amino acids and their derivatives are very important in molecular biology because of their roles in biochemical reactions. Schiff base complexes have continued to play the role of the most important stereochemical models in main group and transition metal coordination chemistry with their easy preparation and structural variation (Garnovski *et al.*, 1993). So efforts have been made to synthesize and characterize amino Schiff base complexes with transition metals and more and more these new complexes have been reported (Kalagouda *et al.*, 2006; Wang *et al.*, 1999). Herein, we report the synthesis and crystal structure of a copper(II) complex with a tridentate Schiff base ligand derived from the condensation of 2-hydroxy-1-naphthaldehyde and L-threonine.

In the title compound (Fig. 1), the $Cu^{II}$ atom is in a distorted square-pyramidal coordination geometry, defined by one N and two O atoms from the Schiff base ligand and two N atoms from a 2, 2′-bipyridine ligand. The Cu atom deviates from the basal equatorial plane (formed by O1, N1, O4 and N3) by 0.230 (2) Å toward N2 atom, with a significantly longer Cu1—N2 bond distance (Table 1). The Cu1—N2 bond deviates greatly from the right position to close the Cu1—N3 bond [the bond angle of N3—Cu1—N2 is 77.3 (1)°]. The bipyridine ligand deviates from planarity, with an angle of 11.7 (1)° between the two pyridyl rings. The least-square plane of the bipyridine ligand is approximately perpendicular to the basal equatorial plane [dihedral angle 100.3 (2)°]. In the crystal, the combination of intermolecular O—H···O and C—H···O hydrogen bonds (Table 2) leads to a two-dimensional network structure (Fig. 2).

### S2. Experimental

L-Threonine (0.119 g, 1 mmol) was dissolved in hot methanol (10 ml), which was then added to a methanol solution (3 ml) of 2-hydroxy-1-naphthaldehyde (0.172 g, 1 mmol). The mixture was stirred at 323 K for 2 h. Subsequently, an aqueous solution (2 ml) of cupric acetate monohydrate (0.200 g, 1 mmol) was added dropwise and stirred for 2 h. A methanol solution (5 ml) of 2,2′-bipyridine (0.156 g, 1 mmol) was added dropwise and stirred for 4 h. The solution was held at room temperature for 10 d and blue block crystals suitable for X-ray diffraction were obtained.

### S3. Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 (aromatic), 0.98(CH) and 0.96($CH_3$) Å, and O—H = 0.82 Å, and with $U_{iso}$(H) = 1.2$U_{eq}$(C) or 1.5$U_{eq}$(C,*O*) for methyl and hydroxyl groups.

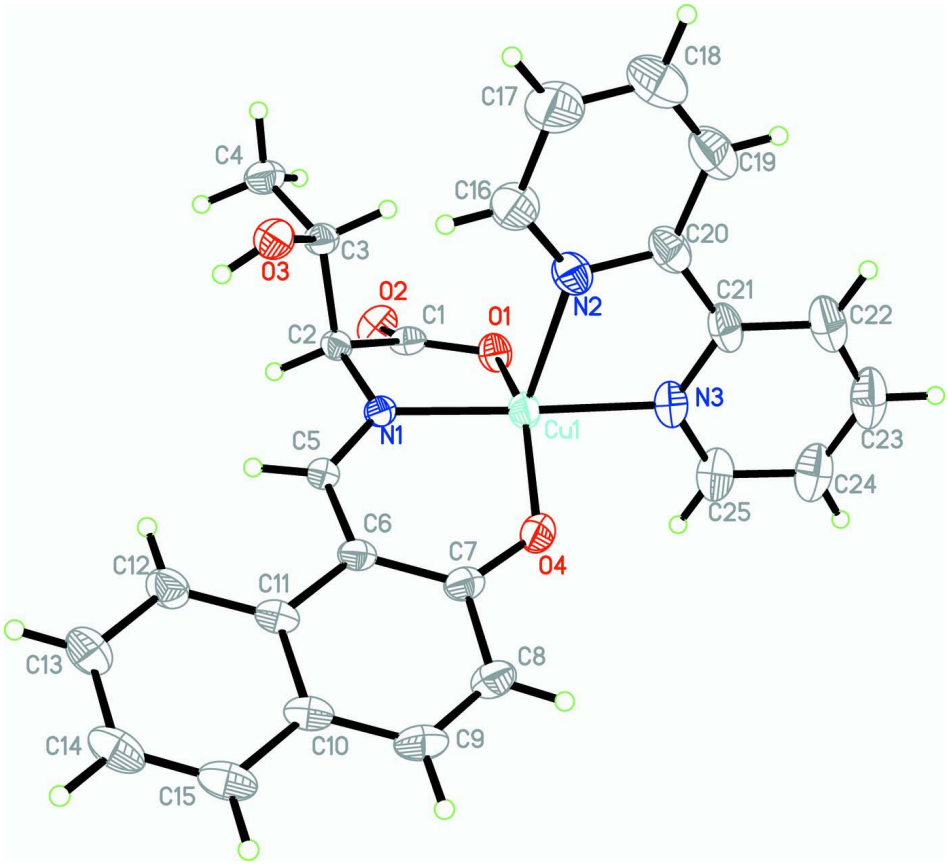


**Figure 1**

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

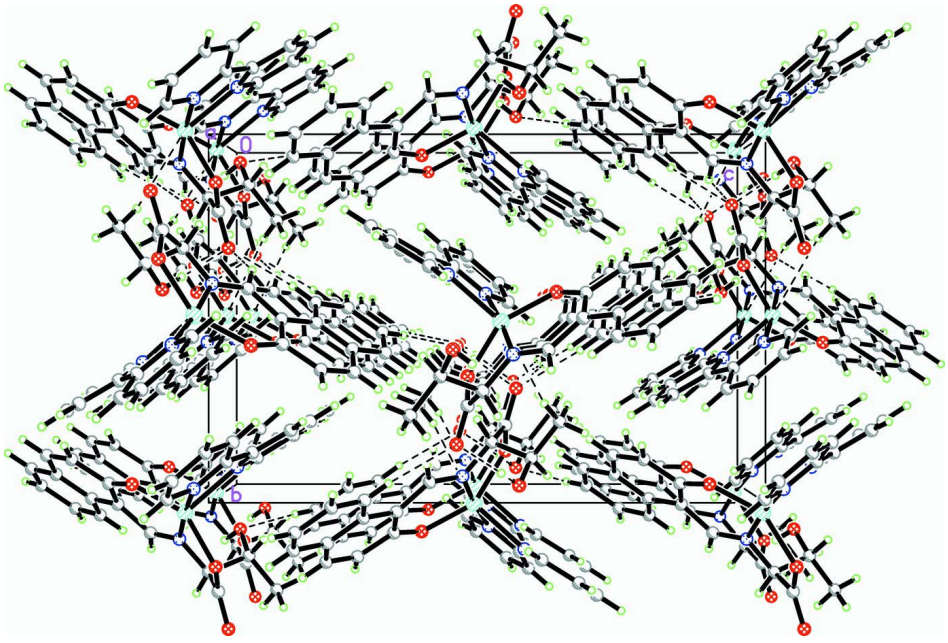

**Figure 2**

Packing diagram of the title compound with hydrogen bonds shown as dashed lines.

**(2,2′-Bipyridine-$\kappa^2N,N'$)[*N*-(2-oxido-1- naphthylidene)threoninato-$\kappa^3O^1,N,O^2$]copper(II)**

*Crystal data*

$[Cu(C_{15}H_{13}NO_4)(C_{10}H_8N_2)]$
$M_r = 490.99$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 9.955$ (2) Å
$b = 12.180$ (3) Å
$c = 18.438$ (4) Å
$V = 2235.6$ (9) Å$^3$
$Z = 4$
$F(000) = 1012$
$D_x = 1.459$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5604 reflections
$\theta = 2.3$–$26.1°$
$\mu = 1.01$ mm$^{-1}$
$T = 298$ K
Block, blue
0.29 × 0.28 × 0.16 mm

*Data collection*

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.757$, $T_{max} = 0.855$
14242 measured reflections
5278 independent reflections
4243 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.0°$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 16$
$l = -20 \rightarrow 24$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.089$
$S = 1.04$
5278 reflections
300 parameters
492 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
$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å$^{-3}$
$\Delta\rho_{min} = -0.54$ e Å$^{-3}$
Absolute structure: Flack (1983), 2229 Friedel pairs
Absolute structure parameter: −0.005 (13)

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0.32501 (3) | 1.00767 (2) | 0.977106 (17) | 0.03806 (10) |
| N1 | 0.1622 (2) | 1.08781 (15) | 0.95744 (11) | 0.0313 (4) |
| N2 | 0.2672 (3) | 0.89079 (19) | 1.06492 (15) | 0.0491 (6) |
| N3 | 0.5005 (2) | 0.93672 (19) | 1.00252 (14) | 0.0480 (6) |

| | | | | |
|---|---|---|---|---|
| O4 | 0.3191 (2) | 0.93362 (17) | 0.88490 (11) | 0.0498 (5) |
| O2 | 0.29386 (19) | 1.31490 (16) | 1.05070 (12) | 0.0512 (5) |
| O1 | 0.37076 (18) | 1.14608 (15) | 1.03256 (11) | 0.0424 (4) |
| O3 | −0.05190 (19) | 1.07490 (16) | 1.05400 (12) | 0.0474 (5) |
| H3 | −0.0961 | 1.1082 | 1.0236 | 0.071* |
| C1 | 0.2783 (3) | 1.2178 (2) | 1.03223 (14) | 0.0371 (6) |
| C2 | 0.1394 (3) | 1.17825 (19) | 1.00763 (13) | 0.0319 (5) |
| H28 | 0.0912 | 1.2379 | 0.9832 | 0.038* |
| C3 | 0.0596 (3) | 1.1395 (2) | 1.07501 (15) | 0.0368 (6) |
| H29 | 0.1194 | 1.0925 | 1.1037 | 0.044* |
| C4 | 0.0177 (3) | 1.2351 (3) | 1.12313 (16) | 0.0510 (7) |
| H21A | −0.0285 | 1.2076 | 1.1651 | 0.077* |
| H21B | −0.0409 | 1.2830 | 1.0965 | 0.077* |
| H21C | 0.0960 | 1.2750 | 1.1382 | 0.077* |
| C5 | 0.0856 (2) | 1.0765 (2) | 0.90139 (14) | 0.0325 (5) |
| H11 | 0.0125 | 1.1237 | 0.8978 | 0.039* |
| C6 | 0.1028 (2) | 0.9982 (2) | 0.84450 (12) | 0.0363 (5) |
| C7 | 0.2228 (3) | 0.9366 (2) | 0.83774 (15) | 0.0415 (6) |
| C8 | 0.2402 (3) | 0.8722 (3) | 0.77391 (16) | 0.0545 (8) |
| H18 | 0.3199 | 0.8335 | 0.7678 | 0.065* |
| C9 | 0.1453 (4) | 0.8654 (3) | 0.72205 (16) | 0.0560 (8) |
| H19 | 0.1615 | 0.8224 | 0.6813 | 0.067* |
| C10 | 0.0215 (3) | 0.9221 (2) | 0.72803 (15) | 0.0452 (6) |
| C11 | −0.0016 (3) | 0.9893 (2) | 0.78988 (13) | 0.0397 (6) |
| C12 | −0.1269 (3) | 1.0408 (2) | 0.79527 (17) | 0.0495 (7) |
| H27 | −0.1453 | 1.0845 | 0.8354 | 0.059* |
| C13 | −0.2234 (4) | 1.0284 (3) | 0.74247 (19) | 0.0588 (8) |
| H26 | −0.3055 | 1.0640 | 0.7475 | 0.071* |
| C14 | −0.2000 (4) | 0.9635 (3) | 0.68174 (18) | 0.0621 (9) |
| H25 | −0.2659 | 0.9556 | 0.6464 | 0.074* |
| C15 | −0.0795 (4) | 0.9115 (3) | 0.67446 (17) | 0.0572 (8) |
| H15 | −0.0634 | 0.8685 | 0.6337 | 0.069* |
| C16 | 0.1466 (4) | 0.8711 (3) | 1.0941 (2) | 0.0660 (9) |
| H17 | 0.0701 | 0.8976 | 1.0710 | 0.079* |
| C17 | 0.1333 (6) | 0.8119 (3) | 1.1577 (3) | 0.0965 (13) |
| H22 | 0.0488 | 0.7999 | 1.1777 | 0.116* |
| C18 | 0.2463 (6) | 0.7710 (4) | 1.1912 (3) | 0.1063 (14) |
| H36 | 0.2387 | 0.7302 | 1.2336 | 0.128* |
| C19 | 0.3693 (5) | 0.7909 (3) | 1.1617 (3) | 0.0883 (12) |
| H37 | 0.4468 | 0.7665 | 1.1849 | 0.106* |
| C20 | 0.3776 (4) | 0.8483 (2) | 1.09632 (19) | 0.0579 (8) |
| C21 | 0.5052 (3) | 0.8664 (2) | 1.05811 (19) | 0.0524 (7) |
| C22 | 0.6242 (4) | 0.8126 (3) | 1.0751 (2) | 0.0701 (10) |
| H33 | 0.6271 | 0.7624 | 1.1131 | 0.084* |
| C23 | 0.7371 (4) | 0.8343 (3) | 1.0354 (3) | 0.0775 (11) |
| H23 | 0.8169 | 0.7986 | 1.0468 | 0.093* |
| C24 | 0.7348 (3) | 0.9067 (3) | 0.9799 (3) | 0.0719 (10) |
| H24 | 0.8118 | 0.9222 | 0.9532 | 0.086* |

| | | | | |
|---|---|---|---|---|
| C25 | 0.6136 (3) | 0.9570 (3) | 0.9642 (2) | 0.0634 (9) |
| H32 | 0.6097 | 1.0066 | 0.9259 | 0.076* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.03383 (16) | 0.04027 (16) | 0.04008 (17) | 0.00393 (14) | −0.00421 (14) | 0.00230 (15) |
| N1 | 0.0301 (10) | 0.0347 (10) | 0.0291 (11) | 0.0002 (9) | 0.0011 (9) | −0.0009 (8) |
| N2 | 0.0536 (15) | 0.0405 (13) | 0.0531 (16) | −0.0017 (11) | −0.0030 (13) | 0.0083 (12) |
| N3 | 0.0409 (13) | 0.0384 (13) | 0.0647 (17) | 0.0035 (10) | −0.0093 (12) | 0.0003 (11) |
| O4 | 0.0456 (11) | 0.0590 (12) | 0.0448 (12) | 0.0165 (10) | −0.0016 (11) | −0.0084 (9) |
| O2 | 0.0434 (11) | 0.0466 (11) | 0.0636 (14) | −0.0096 (9) | 0.0033 (10) | −0.0158 (10) |
| O1 | 0.0341 (9) | 0.0460 (10) | 0.0470 (12) | −0.0025 (8) | −0.0092 (9) | −0.0015 (9) |
| O3 | 0.0356 (10) | 0.0553 (12) | 0.0514 (13) | −0.0103 (9) | 0.0020 (9) | 0.0047 (10) |
| C1 | 0.0398 (13) | 0.0424 (13) | 0.0291 (13) | −0.0075 (11) | 0.0053 (11) | −0.0008 (11) |
| C2 | 0.0348 (12) | 0.0333 (12) | 0.0275 (12) | 0.0016 (10) | −0.0021 (10) | −0.0008 (9) |
| C3 | 0.0339 (13) | 0.0442 (14) | 0.0323 (13) | −0.0029 (11) | 0.0013 (11) | 0.0017 (11) |
| C4 | 0.0536 (18) | 0.0621 (19) | 0.0374 (15) | 0.0016 (15) | 0.0060 (14) | −0.0050 (14) |
| C5 | 0.0326 (12) | 0.0360 (12) | 0.0288 (12) | 0.0016 (10) | −0.0001 (10) | 0.0002 (10) |
| C6 | 0.0456 (13) | 0.0364 (12) | 0.0270 (11) | 0.0003 (13) | 0.0012 (10) | −0.0009 (11) |
| C7 | 0.0486 (15) | 0.0413 (14) | 0.0346 (14) | 0.0009 (12) | 0.0065 (12) | −0.0036 (11) |
| C8 | 0.0637 (19) | 0.0570 (17) | 0.0428 (17) | 0.0105 (15) | 0.0104 (15) | −0.0090 (14) |
| C9 | 0.074 (2) | 0.0580 (16) | 0.0354 (15) | −0.0053 (16) | 0.0078 (15) | −0.0131 (13) |
| C10 | 0.0586 (16) | 0.0469 (15) | 0.0299 (13) | −0.0123 (13) | 0.0007 (13) | −0.0025 (11) |
| C11 | 0.0510 (14) | 0.0392 (13) | 0.0291 (11) | −0.0082 (13) | −0.0017 (11) | 0.0002 (11) |
| C12 | 0.0552 (16) | 0.0542 (15) | 0.0392 (15) | −0.0003 (13) | −0.0115 (13) | −0.0065 (12) |
| C13 | 0.0596 (17) | 0.065 (2) | 0.0515 (17) | −0.0031 (15) | −0.0187 (15) | −0.0011 (15) |
| C14 | 0.076 (2) | 0.0662 (18) | 0.0440 (16) | −0.0210 (16) | −0.0221 (16) | 0.0030 (14) |
| C15 | 0.079 (2) | 0.0582 (17) | 0.0344 (15) | −0.0206 (16) | −0.0067 (15) | −0.0039 (13) |
| C16 | 0.074 (2) | 0.0503 (17) | 0.074 (2) | −0.0007 (16) | 0.0131 (19) | 0.0167 (16) |
| C17 | 0.104 (3) | 0.085 (3) | 0.101 (3) | 0.002 (2) | 0.034 (3) | 0.038 (2) |
| C18 | 0.128 (3) | 0.098 (3) | 0.092 (3) | 0.009 (3) | 0.010 (3) | 0.049 (2) |
| C19 | 0.100 (3) | 0.080 (2) | 0.084 (2) | 0.015 (2) | −0.007 (2) | 0.035 (2) |
| C20 | 0.0753 (19) | 0.0387 (14) | 0.0597 (18) | 0.0037 (15) | −0.0113 (17) | 0.0086 (14) |
| C21 | 0.0575 (17) | 0.0352 (14) | 0.0645 (18) | 0.0071 (13) | −0.0215 (15) | −0.0033 (14) |
| C22 | 0.076 (2) | 0.0502 (17) | 0.084 (2) | 0.0146 (17) | −0.029 (2) | −0.0012 (17) |
| C23 | 0.060 (2) | 0.063 (2) | 0.109 (3) | 0.0182 (17) | −0.031 (2) | −0.020 (2) |
| C24 | 0.0489 (17) | 0.0566 (18) | 0.110 (3) | 0.0058 (15) | −0.010 (2) | −0.015 (2) |
| C25 | 0.0492 (17) | 0.0481 (16) | 0.093 (2) | 0.0030 (13) | −0.0050 (18) | −0.0026 (16) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu1—O4 | 1.925 (2) | C8—H18 | 0.9300 |
| Cu1—N1 | 1.926 (2) | C9—C10 | 1.417 (5) |
| Cu1—N3 | 2.005 (2) | C9—H19 | 0.9300 |
| Cu1—O1 | 2.0236 (18) | C10—C15 | 1.415 (4) |
| Cu1—N2 | 2.231 (3) | C10—C11 | 1.422 (4) |
| N1—C5 | 1.292 (3) | C11—C12 | 1.400 (4) |

| | | | |
|---|---|---|---|
| N1—C2 | 1.457 (3) | C12—C13 | 1.376 (4) |
| N2—C16 | 1.338 (4) | C12—H27 | 0.9300 |
| N2—C20 | 1.345 (4) | C13—C14 | 1.390 (5) |
| N3—C21 | 1.337 (4) | C13—H26 | 0.9300 |
| N3—C25 | 1.352 (4) | C14—C15 | 1.363 (5) |
| O4—C7 | 1.295 (4) | C14—H25 | 0.9300 |
| O2—C1 | 1.240 (3) | C15—H15 | 0.9300 |
| O1—C1 | 1.269 (3) | C16—C17 | 1.384 (5) |
| O3—C3 | 1.415 (3) | C16—H17 | 0.9300 |
| O3—H3 | 0.8200 | C17—C18 | 1.376 (7) |
| C1—C2 | 1.533 (4) | C17—H22 | 0.9300 |
| C2—C3 | 1.548 (4) | C18—C19 | 1.362 (7) |
| C2—H28 | 0.9800 | C18—H36 | 0.9300 |
| C3—C4 | 1.522 (4) | C19—C20 | 1.397 (5) |
| C3—H29 | 0.9800 | C19—H37 | 0.9300 |
| C4—H21A | 0.9600 | C20—C21 | 1.469 (5) |
| C4—H21B | 0.9600 | C21—C22 | 1.390 (5) |
| C4—H21C | 0.9600 | C22—C23 | 1.366 (6) |
| C5—C6 | 1.428 (3) | C22—H33 | 0.9300 |
| C5—H11 | 0.9300 | C23—C24 | 1.352 (6) |
| C6—C7 | 1.417 (4) | C23—H23 | 0.9300 |
| C6—C11 | 1.452 (3) | C24—C25 | 1.384 (5) |
| C7—C8 | 1.425 (4) | C24—H24 | 0.9300 |
| C8—C9 | 1.346 (5) | C25—H32 | 0.9300 |

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| O4—Cu1—N1 | 92.62 (8) | C9—C8—H18 | 118.8 |
| O4—Cu1—N3 | 91.77 (9) | C7—C8—H18 | 118.8 |
| N1—Cu1—N3 | 174.65 (9) | C8—C9—C10 | 121.6 (3) |
| O4—Cu1—O1 | 147.49 (9) | C8—C9—H19 | 119.2 |
| N1—Cu1—O1 | 82.08 (8) | C10—C9—H19 | 119.2 |
| N3—Cu1—O1 | 92.57 (9) | C15—C10—C9 | 121.3 (3) |
| O4—Cu1—N2 | 109.51 (10) | C15—C10—C11 | 119.8 (3) |
| N1—Cu1—N2 | 104.07 (9) | C9—C10—C11 | 118.9 (3) |
| N3—Cu1—N2 | 77.29 (10) | C12—C11—C10 | 117.3 (3) |
| O1—Cu1—N2 | 102.88 (9) | C12—C11—C6 | 123.7 (2) |
| C5—N1—C2 | 119.8 (2) | C10—C11—C6 | 118.9 (3) |
| C5—N1—Cu1 | 126.40 (17) | C13—C12—C11 | 121.5 (3) |
| C2—N1—Cu1 | 113.27 (15) | C13—C12—H27 | 119.3 |
| C16—N2—C20 | 119.4 (3) | C11—C12—H27 | 119.3 |
| C16—N2—Cu1 | 129.6 (2) | C12—C13—C14 | 121.0 (3) |
| C20—N2—Cu1 | 110.3 (2) | C12—C13—H26 | 119.5 |
| C21—N3—C25 | 119.3 (3) | C14—C13—H26 | 119.5 |
| C21—N3—Cu1 | 119.1 (2) | C15—C14—C13 | 119.4 (3) |
| C25—N3—Cu1 | 121.6 (2) | C15—C14—H25 | 120.3 |
| C7—O4—Cu1 | 127.02 (18) | C13—C14—H25 | 120.3 |
| C1—O1—Cu1 | 114.08 (16) | C14—C15—C10 | 120.9 (3) |
| C3—O3—H3 | 109.5 | C14—C15—H15 | 119.5 |
| O2—C1—O1 | 124.4 (2) | C10—C15—H15 | 119.5 |

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| O2—C1—C2 | 119.6 (2) | N2—C16—C17 | 121.3 (4) |
| O1—C1—C2 | 116.1 (2) | N2—C16—H17 | 119.3 |
| N1—C2—C1 | 106.54 (19) | C17—C16—H17 | 119.3 |
| N1—C2—C3 | 111.06 (19) | C18—C17—C16 | 119.4 (5) |
| C1—C2—C3 | 108.7 (2) | C18—C17—H22 | 120.3 |
| N1—C2—H28 | 110.1 | C16—C17—H22 | 120.3 |
| C1—C2—H28 | 110.1 | C19—C18—C17 | 119.5 (4) |
| C3—C2—H28 | 110.1 | C19—C18—H36 | 120.3 |
| O3—C3—C4 | 111.7 (2) | C17—C18—H36 | 120.3 |
| O3—C3—C2 | 110.6 (2) | C18—C19—C20 | 119.1 (4) |
| C4—C3—C2 | 112.0 (2) | C18—C19—H37 | 120.4 |
| O3—C3—H29 | 107.4 | C20—C19—H37 | 120.4 |
| C4—C3—H29 | 107.4 | N2—C20—C19 | 121.1 (4) |
| C2—C3—H29 | 107.4 | N2—C20—C21 | 116.2 (3) |
| C3—C4—H21A | 109.5 | C19—C20—C21 | 122.7 (4) |
| C3—C4—H21B | 109.5 | N3—C21—C22 | 120.3 (4) |
| H21A—C4—H21B | 109.5 | N3—C21—C20 | 115.7 (3) |
| C3—C4—H21C | 109.5 | C22—C21—C20 | 123.9 (3) |
| H21A—C4—H21C | 109.5 | C23—C22—C21 | 119.3 (4) |
| H21B—C4—H21C | 109.5 | C23—C22—H33 | 120.4 |
| N1—C5—C6 | 126.0 (2) | C21—C22—H33 | 120.4 |
| N1—C5—H11 | 117.0 | C24—C23—C22 | 121.2 (3) |
| C6—C5—H11 | 117.0 | C24—C23—H23 | 119.4 |
| C7—C6—C5 | 121.3 (2) | C22—C23—H23 | 119.4 |
| C7—C6—C11 | 120.2 (2) | C23—C24—C25 | 117.5 (4) |
| C5—C6—C11 | 118.3 (2) | C23—C24—H24 | 121.3 |
| O4—C7—C6 | 125.5 (2) | C25—C24—H24 | 121.3 |
| O4—C7—C8 | 116.7 (3) | N3—C25—C24 | 122.4 (4) |
| C6—C7—C8 | 117.8 (3) | N3—C25—H32 | 118.8 |
| C9—C8—C7 | 122.4 (3) | C24—C25—H32 | 118.8 |
| | | | |
| C1—C2—C3—C4 | 71.0 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3···O2$^{i}$ | 0.82 | 1.99 | 2.808 (3) | 178 |
| C5—H11···O2$^{i}$ | 0.93 | 2.49 | 3.311 (3) | 147 |
| C12—H27···O2$^{i}$ | 0.93 | 2.50 | 3.431 (4) | 174 |
| C14—H25···O3$^{ii}$ | 0.93 | 2.52 | 3.445 (4) | 177 |

Symmetry codes: (i) $x-1/2, -y+5/2, -z+2$; (ii) $-x-1/2, -y+2, z-1/2$.