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

# Bis[1,3-bis(benzimidazol-2-yl)propane-$\kappa^2N,N'$]copper(II) dinitrate methanol disolvate

**Bo Hu, Min Wang, Xiao-Yan Wang, Xue-Gang Song and Cheng-Gang Wang***

Department of Chemistry, Central China Normal University, Wuhan, Hubei 430079, People's Republic of China
Correspondence e-mail: wangcg23@yahoo.com.cn

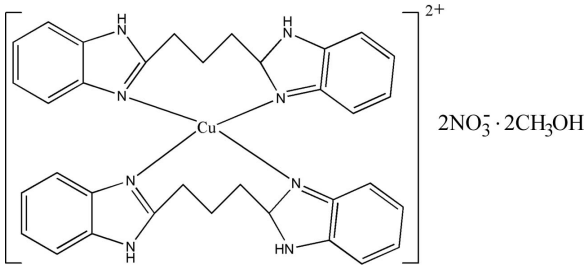
Received 6 April 2007; accepted 13 April 2007

Key indicators: single-crystal X-ray study; $T$ = 297 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.052; $wR$ factor = 0.130; data-to-parameter ratio = 17.1.

In the title compound, $[Cu(C_{17}H_{16}N_4)_2](NO_3)_2\cdot 2C_2H_5OH$, the $Cu^{II}$ ion lies on a crystallographic twofold rotation axis and is in a distorted square-planar coordination geometry formed by four N atoms from two 1,3-bis(benzimidazol-2-yl)propane ligands. The N—Cu—N angles range from 90.25 (7) to 144.89 (11)°. In the crystal structure, a two-dimensional framework is formed by a combination of N—H···O and O—H···O hydrogen bonds.

## Related literature

For related literature, see: Albada *et al.* (1995); Roderick *et al.* (1972); Wang & Joullie (1957), Allen *et al.* (1987); Sun *et al.* (2004).




## Experimental

### Crystal data

$[Cu(C_{17}H_{16}N_4)_2](NO_3)_2\cdot 2C_2H_6O$
$M_r$ = 804.32
Orthorhombic, *Pccn*
$a$ = 14.4793 (10) Å
$b$ = 17.8978 (13) Å
$c$ = 14.3078 (10) Å
$V$ = 3707.8 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.66 mm$^{-1}$
$T$ = 297 (2) K
0.45 × 0.32 × 0.20 mm

### Data collection

Bruker APEX CCD diffractometer
Absorption correction: none
23966 measured reflections
4453 independent reflections
3394 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.042

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.130
$S$ = 1.07
4453 reflections
261 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.48 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.25 e Å$^{-3}$

**Table 1**
Selected bond angles (°).

| | | | |
|---|---|---|---|
| N3—Cu1—N3$^{i}$ | 144.46 (12) | N3—Cu1—N1$^{i}$ | 90.25 (7) |
| N3—Cu1—N1 | 100.35 (7) | N1—Cu1—N1$^{i}$ | 144.89 (11) |

Symmetry code: (i) $-x+\frac{1}{2}, -y+\frac{3}{2}, z$.

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O4—H4$A$···O2$^{ii}$ | 0.816 (10) | 2.014 (17) | 2.814 (4) | 167 (5) |
| O4—H4$A$···O1$^{ii}$ | 0.816 (10) | 2.60 (4) | 3.261 (5) | 139 (5) |
| N2—H2$N$···O3$^{iii}$ | 0.78 (3) | 2.21 (3) | 2.929 (4) | 152 (3) |
| N2—H2$N$···O2$^{iii}$ | 0.78 (3) | 2.37 (3) | 2.969 (3) | 134 (3) |

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work is supported by the Hubei Key Laboratory of Novel Chemical Reactor and Green Chemical Technology (No. RCT2004011).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2363).

## References

Albada, G. A. van, Lakin, M. T., Veldman, N., Spek, A. L. & Reedijk, J. (1995). *Inorg. Chem.* **34**, 4910–4917.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bruker (2000). *SMART*, *SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Roderick, W. R., Nordeen, C. W., Von Esch, A. M. Jr & Appell, R. N. (1972). *J. Med. Chem.* **15**, 655–658.
Sheldrick, G. M. (2001). *SADABS*. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Sun, Y., Liu, X.-H., Zhang, X., Somg, H.-B. & Liu, X.-L. (2004). *Chin. J. Struct. Chem.* **23**, 803–807.
Wang, L. L.-Y. & Joullie, M. M. (1957). *J. Am. Chem. Soc.* **79**, 5706–5708.

  doi:10.1107/S1600536807018570 

# supplementary materials

*Acta Cryst.* (2007). E**63**, m1416 [ **doi:10.1107/S1600536807018570** ]

# Bis[1,3-bis(benzimidazol-2-yl)propane-$\kappa^2N,N'$]copper(II) dinitrate methanol disolvate

**B. Hu, M. Wang, X.-Y. Wang, X.-G. Song and C.-G. Wang**

## Comment

Interest in bis(2-benzimidazolyl)alkanes is widespread, due to their wide-ranging antiviral activity (Roderick *et al.*, 1972). Herein, we report the crystal structure of the title compound (I). In the cation (Fig. 1), the $Cu^{II}$ ion lies on a crystallogrphic twofold axis. Hence, the $Cu^{II}$ ion is coordinated by four N atoms (N1, N3, N1a, N3a [symmety code: (*a*) 1/2 − *x*, 3/2 − *y*, *z*]) from two dbz ligangs. The bond anlges listed in Table 1 indicate a distorted square-planar coordination geomtry.

In the crystal structure, molecules are linked by *N*—$H_{benzimidazole}\cdots O_{nitrate}$ and *O*—$H_{methanol}\cdots O_{nitrate}$ hydrogen bonds, forming a two-dimensional framework structure perpendicular to the *ab* plane (Table 2, Fig. 2).

## Experimental

The ligand 1,3-bis(2-benzimidazolyl)propane (dbz) was synthesized from reported literature earlier (van Albada *et al.*, 1995; Wang

& Joullie, 1957). The title compound was prepared according to the following procedure: The ligand (0.28 g, 1 mmol) in 10 ml me thanol was added slowly to a $Cu(NO_3)_2{\cdot}2H_2O$ (0.12 g, 0.5 mmol) solution of 10 ml me thanol. The mixture was stirred for 1 h. After filtration, the brownish solution was allowed to stand at room temperature. Green block-shaped crystals of (I) were obtained after three weeks.

## Refinement

H atoms bonded to O and N atoms were located in difference maps and then included in the refinement with bond-length restraints of O–H = 0.82 Å and N–H = 0.78 Å, with $U_{iso}$(H)= 1.2$U_{eq}$ (O) and the $U_{iso}$(H) of the N—H atoms refined. H atoms bonded to C atoms were placed in calculated positions and included in the riding-model approximation, with C–H = 0.97—0.98 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C of methylene and aromatic) or 1.5$U_{eq}$(C of methyl).

## Figures

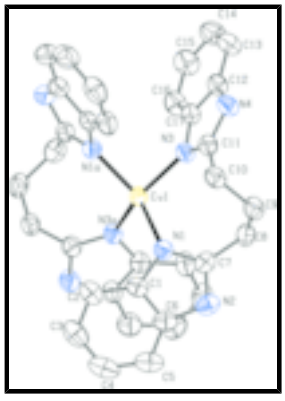


Fig. 1. The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level. The H atoms, anion and solvent molecules are not shown. [symmetry code: (*a*) 1/2 − *x*, 3/2 − *y*, *z*]

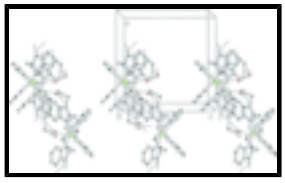


Fig. 2. Part of the crystal structure of (I), showing the formation of hydrogen-bonded (dashed lines) two-dimensional layers.

## Bis[1,3-bis(benzimidazol-2-yl)propane-$\kappa^2N,N'$]copper(II) dinitrate methanol solvate

*Crystal data*

| | |
|---|---|
| $[Cu(C_{17}H_{16}N_4)_2](NO_3)_2{\cdot}2C_2H_6O$ | $F_{000}$ = 1676 |
| $M_r$ = 804.32 | $D_x$ = 1.441 Mg m$^{-3}$ |
| Orthorhombic, *Pccn* | Mo *K*α radiation<br>λ = 0.71073 Å |
| Hall symbol: -P 2ab 2ac | Cell parameters from 5026 reflections |
| *a* = 14.4793 (10) Å | θ = 2.3–25.4º |
| *b* = 17.8978 (13) Å | μ = 0.66 mm$^{-1}$ |
| *c* = 14.3078 (10) Å | *T* = 297 (2) K |
| *V* = 3707.8 (5) Å$^3$ | Block, green |
| *Z* = 4 | 0.45 × 0.32 × 0.20 mm |

*Data collection*

| | |
|---|---|
| Bruker APEX CCD diffractometer | 3394 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int}$ = 0.042 |
| Monochromator: graphite | $\theta_{max}$ = 28.0º |
| *T* = 297(2) K | $\theta_{min}$ = 1.8º |
| φ and ω scans | *h* = −19→18 |
| Absorption correction: none | *k* = −21→23 |
| 23966 measured reflections | *l* = −17→18 |
| 4453 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.052$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.130$ | $w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 1.4161P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.07$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 4453 reflections | $\Delta\rho_{max} = 0.48$ e Å$^{-3}$ |
| 261 parameters | $\Delta\rho_{min} = -0.25$ e Å$^{-3}$ |
| 1 restraint | Extinction correction: none |
| Primary atom site location: structure-invariant direct methods | |

*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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| H4N | 0.293 (2) | 0.4833 (17) | 0.041 (2) | 0.048 (8)* |
| H2N | −0.077 (2) | 0.6948 (16) | 0.111 (2) | 0.048 (8)* |
| Cu1 | 0.2500 | 0.7500 | 0.06676 (3) | 0.03171 (13) |
| N1 | 0.11849 (13) | 0.74057 (10) | 0.10902 (14) | 0.0352 (4) |
| N3 | 0.27403 (13) | 0.64615 (10) | 0.02440 (14) | 0.0342 (4) |
| C1 | 0.07694 (16) | 0.79298 (12) | 0.16863 (16) | 0.0368 (5) |
| C2 | 0.1142 (2) | 0.85029 (14) | 0.22291 (17) | 0.0449 (6) |
| H2 | 0.1773 | 0.8601 | 0.2228 | 0.054* |
| C3 | 0.0542 (2) | 0.89193 (15) | 0.2768 (2) | 0.0554 (7) |
| H3 | 0.0774 | 0.9310 | 0.3127 | 0.067* |
| C4 | −0.0399 (2) | 0.87695 (17) | 0.2789 (2) | 0.0619 (8) |
| H4 | −0.0782 | 0.9062 | 0.3162 | 0.074* |
| C5 | −0.0778 (2) | 0.82015 (17) | 0.2275 (2) | 0.0562 (7) |
| H5 | −0.1407 | 0.8098 | 0.2294 | 0.067* |
| C6 | −0.01757 (17) | 0.77856 (15) | 0.17211 (18) | 0.0430 (6) |
| C7 | 0.04996 (16) | 0.69688 (13) | 0.07935 (16) | 0.0371 (5) |

| | | | | |
|---|---|---|---|---|
| C8 | 0.05757 (17) | 0.62941 (14) | 0.01904 (18) | 0.0434 (6) |
| H8A | 0.1047 | 0.6377 | −0.0280 | 0.052* |
| H8B | −0.0007 | 0.6213 | −0.0129 | 0.052* |
| C9 | 0.08211 (18) | 0.55980 (13) | 0.07567 (19) | 0.0465 (6) |
| H9A | 0.0857 | 0.5173 | 0.0338 | 0.056* |
| H9B | 0.0331 | 0.5501 | 0.1203 | 0.056* |
| C10 | 0.17360 (16) | 0.56732 (13) | 0.12819 (17) | 0.0405 (5) |
| H10A | 0.1698 | 0.6085 | 0.1721 | 0.049* |
| H10B | 0.1856 | 0.5220 | 0.1633 | 0.049* |
| C11 | 0.25044 (16) | 0.58083 (13) | 0.06119 (16) | 0.0371 (5) |
| C12 | 0.36087 (17) | 0.55352 (13) | −0.03919 (17) | 0.0396 (5) |
| C13 | 0.4271 (2) | 0.52029 (15) | −0.09541 (19) | 0.0516 (7) |
| H13 | 0.4376 | 0.4690 | −0.0940 | 0.062* |
| C14 | 0.4766 (2) | 0.56670 (17) | −0.1534 (2) | 0.0568 (7) |
| H14 | 0.5219 | 0.5465 | −0.1918 | 0.068* |
| C15 | 0.4603 (2) | 0.64322 (17) | −0.1558 (2) | 0.0543 (7) |
| H15 | 0.4951 | 0.6729 | −0.1959 | 0.065* |
| C16 | 0.39374 (18) | 0.67644 (14) | −0.10034 (18) | 0.0465 (6) |
| H16 | 0.3825 | 0.7275 | −0.1030 | 0.056* |
| C17 | 0.34427 (16) | 0.63005 (13) | −0.04022 (16) | 0.0363 (5) |
| C18 | 0.1719 (4) | 0.1726 (3) | 0.0359 (4) | 0.1238 (19) |
| H18A | 0.1675 | 0.2185 | 0.0705 | 0.186* |
| H18B | 0.1110 | 0.1540 | 0.0232 | 0.186* |
| H18C | 0.2035 | 0.1816 | −0.0221 | 0.186* |
| N2 | −0.03139 (15) | 0.71824 (13) | 0.11500 (16) | 0.0444 (5) |
| N4 | 0.30001 (15) | 0.52477 (12) | 0.02574 (16) | 0.0423 (5) |
| N5 | 0.81550 (16) | 0.58786 (18) | 0.1762 (2) | 0.0654 (7) |
| O1 | 0.7826 (3) | 0.53217 (18) | 0.2119 (3) | 0.1170 (11) |
| O2 | 0.81605 (17) | 0.64741 (15) | 0.2217 (2) | 0.0854 (7) |
| O3 | 0.84823 (19) | 0.58743 (19) | 0.0982 (2) | 0.1039 (10) |
| O4 | 0.2211 (2) | 0.11977 (14) | 0.08836 (19) | 0.0816 (7) |
| H4A | 0.216 (4) | 0.122 (3) | 0.1451 (8) | 0.122* |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0331 (2) | 0.0260 (2) | 0.0361 (2) | −0.00241 (15) | 0.000 | 0.000 |
| N1 | 0.0356 (10) | 0.0323 (10) | 0.0376 (10) | −0.0013 (8) | 0.0028 (8) | 0.0005 (8) |
| N3 | 0.0372 (10) | 0.0273 (9) | 0.0380 (10) | −0.0017 (7) | 0.0034 (8) | −0.0023 (8) |
| C1 | 0.0435 (13) | 0.0311 (12) | 0.0357 (12) | 0.0029 (9) | 0.0047 (9) | 0.0073 (9) |
| C2 | 0.0571 (16) | 0.0381 (13) | 0.0395 (13) | −0.0006 (11) | 0.0073 (11) | 0.0030 (11) |
| C3 | 0.084 (2) | 0.0397 (14) | 0.0424 (15) | 0.0062 (14) | 0.0068 (14) | 0.0015 (11) |
| C4 | 0.075 (2) | 0.0527 (17) | 0.0581 (18) | 0.0256 (15) | 0.0183 (15) | 0.0057 (14) |
| C5 | 0.0488 (15) | 0.0561 (17) | 0.0636 (18) | 0.0159 (13) | 0.0125 (13) | 0.0094 (14) |
| C6 | 0.0441 (14) | 0.0407 (13) | 0.0441 (14) | 0.0063 (11) | 0.0030 (10) | 0.0098 (11) |
| C7 | 0.0365 (12) | 0.0381 (12) | 0.0367 (12) | −0.0029 (10) | −0.0020 (9) | 0.0079 (10) |
| C8 | 0.0415 (13) | 0.0463 (14) | 0.0425 (14) | −0.0091 (11) | −0.0029 (10) | −0.0071 (11) |
| C9 | 0.0459 (14) | 0.0346 (13) | 0.0589 (16) | −0.0109 (11) | 0.0082 (11) | −0.0028 (11) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C10 | 0.0464 (14) | 0.0302 (12) | 0.0448 (14) | −0.0018 (10) | 0.0081 (10) | 0.0029 (10) |
| C11 | 0.0404 (12) | 0.0317 (11) | 0.0391 (12) | −0.0022 (10) | −0.0016 (10) | −0.0015 (9) |
| C12 | 0.0442 (13) | 0.0341 (12) | 0.0407 (13) | −0.0009 (10) | 0.0020 (10) | −0.0012 (10) |
| C13 | 0.0596 (17) | 0.0414 (14) | 0.0540 (16) | 0.0069 (12) | 0.0091 (13) | −0.0075 (12) |
| C14 | 0.0592 (17) | 0.0622 (18) | 0.0491 (16) | 0.0052 (14) | 0.0167 (13) | −0.0060 (14) |
| C15 | 0.0610 (17) | 0.0585 (17) | 0.0434 (14) | −0.0055 (14) | 0.0155 (13) | 0.0019 (13) |
| C16 | 0.0572 (16) | 0.0381 (13) | 0.0441 (14) | −0.0047 (11) | 0.0067 (12) | 0.0026 (11) |
| C17 | 0.0391 (12) | 0.0349 (12) | 0.0348 (12) | −0.0031 (10) | 0.0006 (9) | −0.0024 (9) |
| C18 | 0.140 (5) | 0.074 (3) | 0.158 (5) | 0.013 (3) | 0.034 (4) | 0.030 (3) |
| N2 | 0.0335 (12) | 0.0476 (12) | 0.0521 (13) | −0.0011 (10) | −0.0017 (9) | 0.0090 (11) |
| N4 | 0.0517 (13) | 0.0253 (10) | 0.0498 (12) | −0.0002 (9) | 0.0078 (10) | −0.0003 (9) |
| N5 | 0.0395 (13) | 0.0756 (19) | 0.081 (2) | −0.0106 (13) | −0.0033 (13) | 0.0111 (16) |
| O1 | 0.133 (3) | 0.084 (2) | 0.134 (3) | −0.032 (2) | 0.020 (2) | 0.025 (2) |
| O2 | 0.0706 (16) | 0.0768 (17) | 0.109 (2) | −0.0088 (13) | 0.0124 (14) | 0.0026 (16) |
| O3 | 0.0819 (18) | 0.147 (3) | 0.0829 (19) | −0.0447 (18) | 0.0125 (15) | −0.0126 (18) |
| O4 | 0.114 (2) | 0.0473 (13) | 0.0834 (17) | 0.0018 (13) | 0.0006 (16) | −0.0110 (13) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu1—N3 | 1.9857 (18) | C9—H9B | 0.9700 |
| Cu1—N3$^{i}$ | 1.9857 (18) | C10—C11 | 1.488 (3) |
| Cu1—N1 | 2.0049 (19) | C10—H10A | 0.9700 |
| Cu1—N1$^{i}$ | 2.0049 (19) | C10—H10B | 0.9700 |
| N1—C7 | 1.333 (3) | C11—N4 | 1.334 (3) |
| N1—C1 | 1.403 (3) | C12—N4 | 1.380 (3) |
| N3—C11 | 1.327 (3) | C12—C13 | 1.386 (4) |
| N3—C17 | 1.404 (3) | C12—C17 | 1.391 (3) |
| C1—C6 | 1.393 (3) | C13—C14 | 1.375 (4) |
| C1—C2 | 1.395 (3) | C13—H13 | 0.9300 |
| C2—C3 | 1.380 (4) | C14—C15 | 1.390 (4) |
| C2—H2 | 0.9300 | C14—H14 | 0.9300 |
| C3—C4 | 1.390 (5) | C15—C16 | 1.382 (4) |
| C3—H3 | 0.9300 | C15—H15 | 0.9300 |
| C4—C5 | 1.369 (5) | C16—C17 | 1.394 (3) |
| C4—H4 | 0.9300 | C16—H16 | 0.9300 |
| C5—C6 | 1.393 (4) | C18—O4 | 1.403 (5) |
| C5—H5 | 0.9300 | C18—H18A | 0.9600 |
| C6—N2 | 1.369 (4) | C18—H18B | 0.9600 |
| C7—N2 | 1.339 (3) | C18—H18C | 0.9600 |
| C7—C8 | 1.488 (3) | N2—H2N | 0.78 (3) |
| C8—C9 | 1.528 (4) | N4—H4N | 0.78 (3) |
| C8—H8A | 0.9700 | N5—O3 | 1.213 (4) |
| C8—H8B | 0.9700 | N5—O1 | 1.217 (4) |
| C9—C10 | 1.529 (4) | N5—O2 | 1.249 (4) |
| C9—H9A | 0.9700 | O4—H4A | 0.816 (10) |
| N3—Cu1—N3$^{i}$ | 144.46 (12) | H9A—C9—H9B | 107.8 |
| N3—Cu1—N1 | 100.35 (7) | C11—C10—C9 | 110.2 (2) |
| N3$^{i}$—Cu1—N1 | 90.25 (7) | C11—C10—H10A | 109.6 |

| | | | |
|---|---|---|---|
| N3—Cu1—N1$^{i}$ | 90.25 (7) | C9—C10—H10A | 109.6 |
| N3$^{i}$—Cu1—N1$^{i}$ | 100.35 (7) | C11—C10—H10B | 109.6 |
| N1—Cu1—N1$^{i}$ | 144.89 (11) | C9—C10—H10B | 109.6 |
| C7—N1—C1 | 105.46 (19) | H10A—C10—H10B | 108.1 |
| C7—N1—Cu1 | 131.33 (16) | N3—C11—N4 | 111.9 (2) |
| C1—N1—Cu1 | 122.29 (15) | N3—C11—C10 | 126.2 (2) |
| C11—N3—C17 | 105.48 (19) | N4—C11—C10 | 121.7 (2) |
| C11—N3—Cu1 | 131.19 (16) | N4—C12—C13 | 132.3 (2) |
| C17—N3—Cu1 | 121.32 (15) | N4—C12—C17 | 105.3 (2) |
| C6—C1—C2 | 119.8 (2) | C13—C12—C17 | 122.4 (2) |
| C6—C1—N1 | 108.6 (2) | C14—C13—C12 | 116.8 (2) |
| C2—C1—N1 | 131.6 (2) | C14—C13—H13 | 121.6 |
| C3—C2—C1 | 117.7 (3) | C12—C13—H13 | 121.6 |
| C3—C2—H2 | 121.2 | C13—C14—C15 | 121.4 (3) |
| C1—C2—H2 | 121.2 | C13—C14—H14 | 119.3 |
| C2—C3—C4 | 121.7 (3) | C15—C14—H14 | 119.3 |
| C2—C3—H3 | 119.2 | C16—C15—C14 | 121.9 (3) |
| C4—C3—H3 | 119.2 | C16—C15—H15 | 119.1 |
| C5—C4—C3 | 121.6 (3) | C14—C15—H15 | 119.1 |
| C5—C4—H4 | 119.2 | C15—C16—C17 | 117.1 (2) |
| C3—C4—H4 | 119.2 | C15—C16—H16 | 121.4 |
| C4—C5—C6 | 116.9 (3) | C17—C16—H16 | 121.4 |
| C4—C5—H5 | 121.6 | C12—C17—C16 | 120.3 (2) |
| C6—C5—H5 | 121.6 | C12—C17—N3 | 108.7 (2) |
| N2—C6—C5 | 132.0 (3) | C16—C17—N3 | 131.0 (2) |
| N2—C6—C1 | 105.6 (2) | O4—C18—H18A | 109.5 |
| C5—C6—C1 | 122.4 (3) | O4—C18—H18B | 109.5 |
| N1—C7—N2 | 111.5 (2) | H18A—C18—H18B | 109.5 |
| N1—C7—C8 | 127.3 (2) | O4—C18—H18C | 109.5 |
| N2—C7—C8 | 121.2 (2) | H18A—C18—H18C | 109.5 |
| C7—C8—C9 | 111.8 (2) | H18B—C18—H18C | 109.5 |
| C7—C8—H8A | 109.3 | C7—N2—C6 | 108.9 (2) |
| C9—C8—H8A | 109.3 | C7—N2—H2N | 124 (2) |
| C7—C8—H8B | 109.3 | C6—N2—H2N | 126 (2) |
| C9—C8—H8B | 109.3 | C11—N4—C12 | 108.6 (2) |
| H8A—C8—H8B | 107.9 | C11—N4—H4N | 123 (2) |
| C8—C9—C10 | 112.97 (19) | C12—N4—H4N | 128 (2) |
| C8—C9—H9A | 109.0 | O3—N5—O1 | 122.3 (4) |
| C10—C9—H9A | 109.0 | O3—N5—O2 | 118.9 (3) |
| C8—C9—H9B | 109.0 | O1—N5—O2 | 118.9 (3) |
| C10—C9—H9B | 109.0 | C18—O4—H4A | 117 (4) |
| N3—Cu1—N1—C7 | −30.8 (2) | N2—C7—C8—C9 | −93.1 (3) |
| N3$^{i}$—Cu1—N1—C7 | 115.1 (2) | C7—C8—C9—C10 | −59.3 (3) |
| N1$^{i}$—Cu1—N1—C7 | −136.3 (2) | C8—C9—C10—C11 | −59.8 (3) |
| N3—Cu1—N1—C1 | 161.87 (17) | C17—N3—C11—N4 | 0.3 (3) |
| N3$^{i}$—Cu1—N1—C1 | −52.24 (18) | Cu1—N3—C11—N4 | −163.27 (17) |
| N1$^{i}$—Cu1—N1—C1 | 56.35 (16) | C17—N3—C11—C10 | −174.9 (2) |

| | | | |
|---|---|---|---|
| N3$^{i}$—Cu1—N3—C11 | −146.5 (2) | Cu1—N3—C11—C10 | 21.5 (4) |
| N1—Cu1—N3—C11 | −41.2 (2) | C9—C10—C11—N3 | 82.5 (3) |
| N1$^{i}$—Cu1—N3—C11 | 105.1 (2) | C9—C10—C11—N4 | −92.3 (3) |
| N3$^{i}$—Cu1—N3—C17 | 52.10 (16) | N4—C12—C13—C14 | 180.0 (3) |
| N1—Cu1—N3—C17 | 157.37 (17) | C17—C12—C13—C14 | −0.1 (4) |
| N1$^{i}$—Cu1—N3—C17 | −56.28 (18) | C12—C13—C14—C15 | −0.5 (5) |
| C7—N1—C1—C6 | −0.3 (2) | C13—C14—C15—C16 | 0.0 (5) |
| Cu1—N1—C1—C6 | 169.84 (15) | C14—C15—C16—C17 | 1.1 (4) |
| C7—N1—C1—C2 | 176.9 (2) | N4—C12—C17—C16 | −178.9 (2) |
| Cu1—N1—C1—C2 | −13.0 (3) | C13—C12—C17—C16 | 1.2 (4) |
| C6—C1—C2—C3 | −1.5 (3) | N4—C12—C17—N3 | 0.3 (3) |
| N1—C1—C2—C3 | −178.5 (2) | C13—C12—C17—N3 | −179.7 (2) |
| C1—C2—C3—C4 | 1.2 (4) | C15—C16—C17—C12 | −1.6 (4) |
| C2—C3—C4—C5 | −0.1 (4) | C15—C16—C17—N3 | 179.4 (3) |
| C3—C4—C5—C6 | −0.7 (4) | C11—N3—C17—C12 | −0.4 (3) |
| C4—C5—C6—N2 | 178.3 (3) | Cu1—N3—C17—C12 | 165.21 (16) |
| C4—C5—C6—C1 | 0.3 (4) | C11—N3—C17—C16 | 178.7 (3) |
| C2—C1—C6—N2 | −177.6 (2) | Cu1—N3—C17—C16 | −15.7 (4) |
| N1—C1—C6—N2 | 0.0 (3) | N1—C7—N2—C6 | −0.6 (3) |
| C2—C1—C6—C5 | 0.8 (4) | C8—C7—N2—C6 | 176.1 (2) |
| N1—C1—C6—C5 | 178.4 (2) | C5—C6—N2—C7 | −177.8 (3) |
| C1—N1—C7—N2 | 0.6 (3) | C1—C6—N2—C7 | 0.4 (3) |
| Cu1—N1—C7—N2 | −168.34 (16) | N3—C11—N4—C12 | −0.1 (3) |
| C1—N1—C7—C8 | −175.9 (2) | C10—C11—N4—C12 | 175.4 (2) |
| Cu1—N1—C7—C8 | 15.1 (4) | C13—C12—N4—C11 | 179.8 (3) |
| N1—C7—C8—C9 | 83.1 (3) | C17—C12—N4—C11 | −0.1 (3) |

Symmetry codes: (i) −*x*+1/2, −*y*+3/2, *z*.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O4—H4A···O2$^{ii}$ | 0.816 (10) | 2.014 (17) | 2.814 (4) | 167 (5) |
| O4—H4A···O1$^{ii}$ | 0.816 (10) | 2.60 (4) | 3.261 (5) | 139 (5) |
| N2—H2N···O3$^{iii}$ | 0.78 (3) | 2.21 (3) | 2.929 (4) | 152 (3) |
| N2—H2N···O2$^{iii}$ | 0.78 (3) | 2.37 (3) | 2.969 (3) | 134 (3) |

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

**Fig. 1**

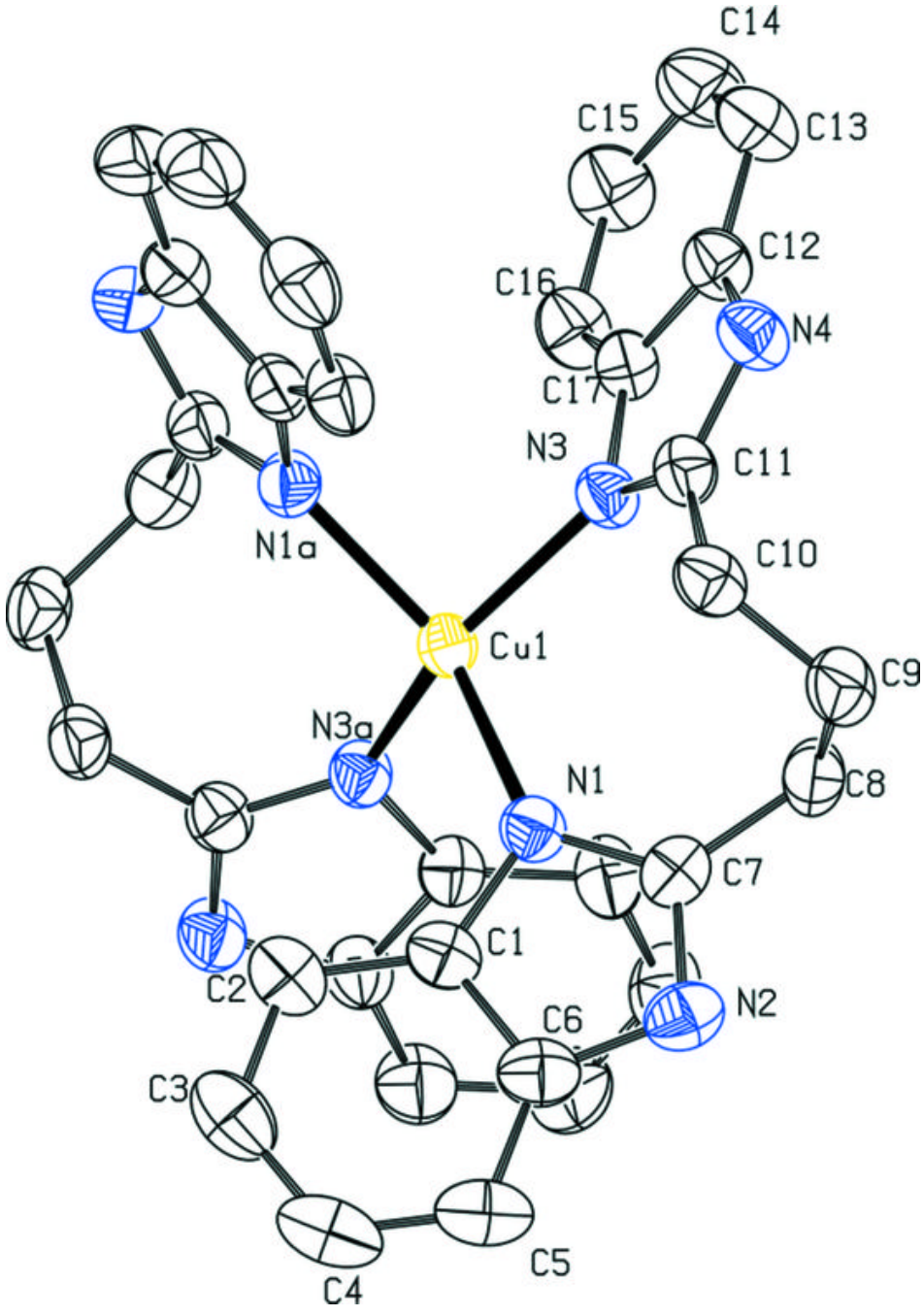

C14
C15
C13
C12
C16
N4
C17
N3
C11
N1a
C10
Cu1
C9
N3a
N1
C8
C7
C1
C2
N2
C6
C3
C5
C4

**Fig. 2**