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# Di-$\mu$-chlorido-bis{bis[4-(adamantan-1-ylcarbamoyl)pyridine-$\kappa N$]chloridocopper(II)} hemihydrate

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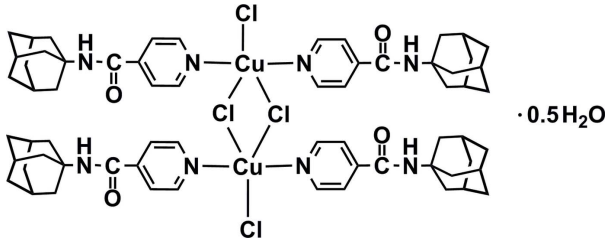
Key indicators: single-crystal X-ray study; $T$ = 295 K; mean $\sigma$(C–C) = 0.007 Å; disorder in solvent or counterion; $R$ factor = 0.069; $wR$ factor = 0.197; data-to-parameter ratio = 16.7.

In the centrosymmetric dimeric title compound, $[Cu_2Cl_4(C_{16}H_{20}N_2O)_4]\cdot 0.5H_2O$, the $Cu^{II}$ atom is in a distorted trigonal–bipyramidal environment defined by two bridging Cl atoms, one terminal Cl atom and two N atoms from two monodentate 4-(adamantan-1-ylcarbamoyl)pyridine ligands. The amine N atoms are involved in intramolecular N—H···O and intermolecular N—H···Cl hydrogen bonds. The latter hydrogen bonds link the complex molecules into a ribbon along [010]. The uncoordinated water molecule is 0.25-occupied.

## Related literature

For the structures of related amino compounds, see: Fu *et al.* (2007, 2008, 2009); Fu & Xiong (2008). For the ferroelectric properties of related amino derivatives, see: Fu *et al.* (2011*a*,*b*,*c*).




## Experimental

### Crystal data

$[Cu_2Cl_4(C_{16}H_{20}N_2O)_4]\cdot 0.5H_2O$ $M_r$ = 1303.25
Triclinic, $P\overline{1}$
$a$ = 6.739 (4) Å
$b$ = 11.149 (6) Å
$c$ = 21.814 (12) Å
$\alpha$ = 92.221 (6)°
$\beta$ = 95.993 (8)°
$\gamma$ = 96.727 (9)°
$V$ = 1616.6 (16) Å$^3$
$Z$ = 1
Mo $K\alpha$ radiation
$\mu$ = 0.88 mm$^{-1}$
$T$ = 295 K
0.30 × 0.25 × 0.15 mm

### Data collection

Rigaku Mercury2 CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min}$ = 0.779, $T_{max}$ = 0.880
16110 measured reflections
6320 independent reflections
4988 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.054

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.197
$S$ = 1.06
6320 reflections
379 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.19 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.77 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1$A$···O1$^{i}$ | 0.86 | 2.35 | 2.969 (5) | 129 |
| N2—H2$A$···Cl1$^{ii}$ | 0.86 | 2.66 | 3.499 (4) | 165 |

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL* and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2504).

## References

Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Fu, D.-W., Ge, J.-Z., Dai, J., Ye, H.-Y. & Qu, Z.-R. (2009). *Inorg. Chem. Commun.* **12**, 994–997.
Fu, D.-W., Song, Y.-M., Wang, G.-X., Ye, Q., Xiong, R.-G., Akutagawa, T., Nakamura, T., Chan, P. W. H. & Huang, S. P. D. (2007). *J. Am. Chem. Soc.* **129**, 5346–5347.
Fu, D.-W. & Xiong, R.-G. (2008). *Dalton Trans.* pp. 3946–3948.
Fu, D.-W., Zhang, W., Cai, H.-L., Ge, J.-Z., Zhang, Y. & Xiong, R.-G. (2011*a*). *Adv. Mater.* **23**, 5658–5662.
Fu, D.-W., Zhang, W., Cai, H.-L., Zhang, Y., Ge, J.-Z., Xiong, R.-G. & Huang, S. P. D. (2011*b*). *J. Am. Chem. Soc.* **133**, 12780–12786.
Fu, D.-W., Zhang, W., Cai, H.-L., Zhang, Y., Ge, J.-Z., Xiong, R.-G., Huang, S. P. D. & Nakamura, T. (2011*c*). *Angew. Chem. Int. Ed.* **50**, 11947–11951.
Fu, D.-W., Zhang, W. & Xiong, R.-G. (2008). *Cryst. Growth Des.* **8**, 3461–3464.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supporting information

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# Di-$\mu$-chlorido-bis{bis[4-(adamantan-1-ylcarbamoyl)pyridine-$\kappa N$]chloridocopper(II)} hemihydrate

**Ying-Chun Wang**

## S1. Comment

Amino compounds have attracted more attention as phase transition dielectric materials for their applications in memory storage (Fu *et al.*, 2007, 2008, 2009; Fu & Xiong, 2008). With the purpose of obtaining phase transition crystals of amino compounds, various amines have been studied and a series of new materials with this organic molecules have been elaborated (Fu *et al.*, 2011*a*,b,c). In this study, we describe the crystal structure of the title compound.

The asymmetric unit is composed of two 4-[(1-adamantyl)carbamoyl]pyridine ligands, two $Cl^-$ anions, one $Cu^{II}$ ion and a quarter of water molecule (Fig. 1). The two pyridine rings are twisted from each other by a dihedral angle of 11.14 (1)°. The dimeric complex molecule is centrosymmetric. The distorted trigonal-bipyramidal environment around the $Cu^{II}$ ion is defined by two bridging Cl atoms, one terminal Cl atom and two N atoms from two monodentate organic ligands. The geometric parameters in the title compound are in a normal range.

In the crystal, the amino N atoms are involved in an intramolecular N—H···O hydrogen bond and an intermolecular N—H···Cl hydrogen bond. These hydrogen bonds link the complex molecules into a one-dimensional ribbon along [0 1 0] (Table 1 and Fig. 2).

## S2. Experimental

$CuCl_2.6H_2O$ (2 mmol) and 4-[(1-adamantyl)carbamoyl]pyridine (2 mmol) were dissolved in 70% aqueous methanol solution, and then 2 ml HCl was added. Single crystals suitable for X-ray diffraction analysis were obtained from slow evaporation of the solution at room temperature after two weeks.

## S3. Refinement

H atoms attached to C and N atoms were positioned geometrically and treated as riding, with C—H = 0.93 (aromatic), 0.97 (methylene) and 0.98 Å (methine) and N—H = 0.86 Å and with $U_{iso}$(H) = 1.2$U_{eq}$(C, N). H atoms bonded to O atom were located in a difference Fourier map and restrained with H—O = 0.82 (1) Å. In the last stage of refinement, they were treated as riding atoms with $U_{iso}$(H) = 1.5$U_{eq}$(O). The highest residual electron density was found at 0.97 Å from Cl1 atom and the deepest hole at 0.80 Å from Cl1 atom.

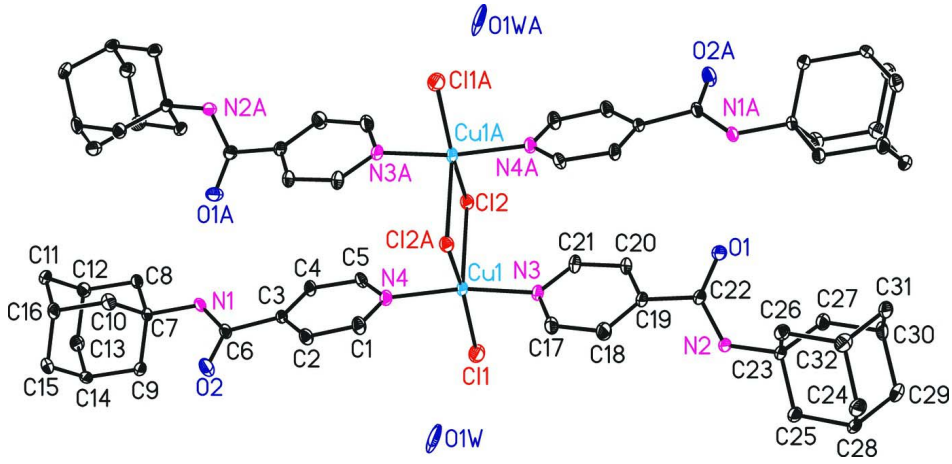


**Figure 1**

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (A) -x, 1-y, 1-z.]

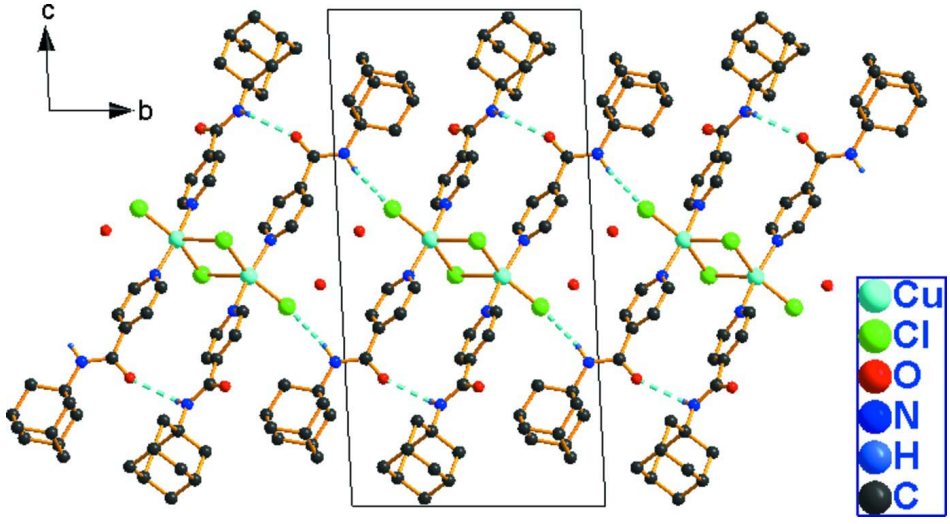


**Figure 2**

The crystal packing of the title compound viewed along the *a* axis, showing the hydrogen bonded ribbon. H atoms not involved in hydrogen bonds (dashed line) have been omitted for clarity.

### Di-*μ*-chlorido-bis{bis[4-(adamantan-1-ylcarbamoyl)pyridine- *κN*]chloridocopper(II)} hemihydrate

*Crystal data*

$[Cu_2Cl_4(C_{16}H_{20}N_2O)_4]\cdot 0.5H_2O$
$M_r = 1303.25$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.739\ (4)$ Å
$b = 11.149\ (6)$ Å
$c = 21.814\ (12)$ Å
$\alpha = 92.221\ (6)°$
$\beta = 95.993\ (8)°$
$\gamma = 96.727\ (9)°$
$V = 1616.6\ (16)$ Å$^3$
$Z = 1$
$F(000) = 683$
$D_x = 1.339$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4355 reflections
$\theta = 2.6–27.5°$
$\mu = 0.88$ mm$^{-1}$
$T = 295$ K
Block, colorless
0.30 × 0.25 × 0.15 mm

*Data collection*

Rigaku Mercury2 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.6612 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min}$ = 0.779, $T_{max}$ = 0.880
16110 measured reflections
6320 independent reflections
4988 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.054
$\theta_{max}$ = 26.0°, $\theta_{min}$ = 1.9°
$h$ = −8→8
$k$ = −13→13
$l$ = −26→26

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.197
$S$ = 1.06
6320 reflections
379 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
$w = 1/[\sigma^2(F_o^2) + (0.1016P)^2 + 0.817P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.19 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.77 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.

**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 $F^2 > 2$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* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Cu1 | 0.02209 (9) | 0.63814 (5) | 0.46299 (2) | 0.0322 (2) | |
| Cl1 | −0.0961 (3) | 0.78238 (13) | 0.40137 (6) | 0.0589 (4) | |
| Cl2 | −0.24643 (16) | 0.45318 (10) | 0.46545 (5) | 0.0337 (3) | |
| O1 | −0.2052 (7) | 0.8512 (3) | 0.74349 (17) | 0.0636 (12) | |
| O2 | 0.6396 (5) | 0.5226 (3) | 0.24014 (16) | 0.0496 (9) | |
| N1 | 0.3965 (6) | 0.3694 (3) | 0.20396 (17) | 0.0331 (9) | |
| H1A | 0.2815 | 0.3324 | 0.2100 | 0.040* | |
| N2 | −0.1049 (7) | 1.0381 (3) | 0.71060 (17) | 0.0387 (10) | |
| H2A | −0.0776 | 1.0767 | 0.6785 | 0.046* | |
| N3 | −0.0537 (6) | 0.7312 (3) | 0.53575 (17) | 0.0366 (9) | |
| N4 | 0.1535 (6) | 0.5718 (3) | 0.39231 (16) | 0.0334 (8) | |
| C1 | 0.3484 (7) | 0.6058 (5) | 0.3907 (2) | 0.0396 (11) | |
| H1B | 0.4175 | 0.6554 | 0.4232 | 0.048* | |
| C2 | 0.4541 (7) | 0.5711 (4) | 0.3431 (2) | 0.0361 (11) | |
| H2B | 0.5898 | 0.5987 | 0.3432 | 0.043* | |
| C3 | 0.3534 (7) | 0.4941 (4) | 0.29515 (19) | 0.0282 (9) | |

| | | | | |
|---|---|---|---|---|
| C4 | 0.1504 (7) | 0.4574 (4) | 0.29694 (19) | 0.0325 (10) |
| H4A | 0.0793 | 0.4052 | 0.2658 | 0.039* |
| C5 | 0.0534 (7) | 0.4988 (4) | 0.34532 (19) | 0.0321 (10) |
| H5A | −0.0838 | 0.4758 | 0.3454 | 0.038* |
| C6 | 0.4783 (7) | 0.4621 (4) | 0.2442 (2) | 0.0321 (10) |
| C7 | 0.4921 (6) | 0.3277 (4) | 0.15020 (18) | 0.0259 (9) |
| C8 | 0.3411 (6) | 0.2306 (4) | 0.1135 (2) | 0.0307 (10) |
| H8A | 0.2182 | 0.2645 | 0.1006 | 0.037* |
| H8B | 0.3085 | 0.1640 | 0.1395 | 0.037* |
| C9 | 0.5378 (7) | 0.4319 (4) | 0.1079 (2) | 0.0347 (10) |
| H9A | 0.4147 | 0.4651 | 0.0944 | 0.042* |
| H9B | 0.6302 | 0.4957 | 0.1305 | 0.042* |
| C10 | 0.6852 (7) | 0.2739 (5) | 0.1707 (2) | 0.0373 (11) |
| H10A | 0.6559 | 0.2074 | 0.1970 | 0.045* |
| H10B | 0.7807 | 0.3349 | 0.1942 | 0.045* |
| C11 | 0.6269 (8) | 0.1311 (4) | 0.0778 (2) | 0.0441 (13) |
| H11A | 0.5975 | 0.0639 | 0.1037 | 0.053* |
| H11B | 0.6850 | 0.1012 | 0.0422 | 0.053* |
| C12 | 0.4312 (7) | 0.1841 (4) | 0.0564 (2) | 0.0391 (11) |
| H12A | 0.3350 | 0.1212 | 0.0335 | 0.047* |
| C13 | 0.4807 (8) | 0.2882 (4) | 0.0147 (2) | 0.0411 (11) |
| H13A | 0.3589 | 0.3220 | 0.0004 | 0.049* |
| H13B | 0.5385 | 0.2587 | −0.0210 | 0.049* |
| C14 | 0.6310 (7) | 0.3860 (4) | 0.0516 (2) | 0.0328 (10) |
| H14A | 0.6630 | 0.4534 | 0.0254 | 0.039* |
| C15 | 0.8239 (7) | 0.3321 (4) | 0.0733 (2) | 0.0403 (11) |
| H15A | 0.8838 | 0.3034 | 0.0378 | 0.048* |
| H15B | 0.9199 | 0.3938 | 0.0961 | 0.048* |
| C16 | 0.7755 (7) | 0.2287 (5) | 0.1139 (2) | 0.0414 (12) |
| H16A | 0.8994 | 0.1945 | 0.1273 | 0.050* |
| C17 | 0.0825 (9) | 0.8159 (5) | 0.5631 (3) | 0.0540 (15) |
| H17A | 0.2040 | 0.8309 | 0.5465 | 0.065* |
| C18 | 0.0550 (9) | 0.8840 (5) | 0.6154 (2) | 0.0527 (14) |
| H18A | 0.1539 | 0.9448 | 0.6324 | 0.063* |
| C19 | −0.1204 (8) | 0.8601 (4) | 0.6415 (2) | 0.0392 (11) |
| C20 | −0.2667 (8) | 0.7724 (4) | 0.6124 (2) | 0.0401 (11) |
| H20A | −0.3891 | 0.7557 | 0.6284 | 0.048* |
| C21 | −0.2304 (7) | 0.7102 (4) | 0.5598 (2) | 0.0394 (11) |
| H21A | −0.3299 | 0.6522 | 0.5404 | 0.047* |
| C22 | −0.1500 (9) | 0.9173 (4) | 0.7036 (2) | 0.0435 (12) |
| C23 | −0.0991 (7) | 1.1090 (4) | 0.76943 (19) | 0.0312 (10) |
| C24 | −0.3064 (7) | 1.0948 (4) | 0.7938 (2) | 0.0378 (11) |
| H24A | −0.4059 | 1.1214 | 0.7636 | 0.045* |
| H24B | −0.3466 | 1.0104 | 0.8007 | 0.045* |
| C25 | −0.0430 (8) | 1.2429 (4) | 0.7573 (2) | 0.0371 (11) |
| H25A | −0.1427 | 1.2686 | 0.7269 | 0.045* |
| H25B | 0.0862 | 1.2536 | 0.7411 | 0.045* |
| C26 | 0.0598 (7) | 1.0685 (4) | 0.8172 (2) | 0.0362 (10) |

| | | | | | |
|---|---|---|---|---|---|
| H26A | 0.1899 | 1.0776 | 0.8015 | 0.043* | |
| H26B | 0.0251 | 0.9840 | 0.8249 | 0.043* | |
| C27 | 0.1282 (8) | 1.2794 (4) | 0.8652 (2) | 0.0430 (12) | |
| H27A | 0.2582 | 1.2893 | 0.8494 | 0.052* | |
| H27B | 0.1380 | 1.3287 | 0.9033 | 0.052* | |
| C28 | −0.0326 (8) | 1.3205 (4) | 0.8176 (2) | 0.0383 (11) | |
| H28A | 0.0036 | 1.4058 | 0.8097 | 0.046* | |
| C29 | −0.2370 (8) | 1.3047 (4) | 0.8434 (2) | 0.0456 (13) | |
| H29A | −0.3384 | 1.3326 | 0.8143 | 0.055* | |
| H29B | −0.2292 | 1.3527 | 0.8818 | 0.055* | |
| C30 | −0.2954 (8) | 1.1707 (5) | 0.8546 (2) | 0.0437 (12) | |
| H30A | −0.4264 | 1.1604 | 0.8707 | 0.052* | |
| C31 | −0.1339 (9) | 1.1290 (4) | 0.9021 (2) | 0.0471 (13) | |
| H31A | −0.1282 | 1.1756 | 0.9409 | 0.057* | |
| H31B | −0.1692 | 1.0444 | 0.9096 | 0.057* | |
| C32 | 0.0700 (8) | 1.1463 (4) | 0.8777 (2) | 0.0413 (12) | |
| H32A | 0.1715 | 1.1203 | 0.9082 | 0.050* | |
| O1W | 0.500 (3) | 0.9159 (17) | 0.4447 (12) | 0.125 (11) | 0.25 |
| H1WA | 0.5145 | 0.9475 | 0.4800 | 0.187* | 0.25 |
| H1WB | 0.3799 | 0.8940 | 0.4340 | 0.187* | 0.25 |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0445 (4) | 0.0306 (3) | 0.0236 (3) | 0.0077 (2) | 0.0115 (2) | −0.0042 (2) |
| Cl1 | 0.0939 (12) | 0.0497 (8) | 0.0404 (8) | 0.0268 (8) | 0.0188 (7) | 0.0097 (6) |
| Cl2 | 0.0341 (6) | 0.0375 (6) | 0.0288 (6) | 0.0025 (5) | 0.0040 (4) | −0.0028 (4) |
| O1 | 0.123 (4) | 0.0302 (19) | 0.039 (2) | −0.006 (2) | 0.039 (2) | −0.0058 (16) |
| O2 | 0.044 (2) | 0.055 (2) | 0.046 (2) | −0.0154 (17) | 0.0200 (16) | −0.0178 (17) |
| N1 | 0.036 (2) | 0.032 (2) | 0.031 (2) | −0.0051 (16) | 0.0170 (16) | −0.0065 (16) |
| N2 | 0.068 (3) | 0.026 (2) | 0.023 (2) | −0.0004 (19) | 0.0162 (18) | −0.0035 (15) |
| N3 | 0.049 (2) | 0.031 (2) | 0.031 (2) | 0.0095 (18) | 0.0103 (18) | −0.0014 (16) |
| N4 | 0.040 (2) | 0.035 (2) | 0.026 (2) | 0.0097 (17) | 0.0078 (16) | −0.0021 (15) |
| C1 | 0.040 (3) | 0.049 (3) | 0.028 (2) | 0.002 (2) | 0.006 (2) | −0.010 (2) |
| C2 | 0.036 (2) | 0.043 (3) | 0.028 (2) | −0.004 (2) | 0.0075 (19) | −0.0079 (19) |
| C3 | 0.037 (2) | 0.027 (2) | 0.022 (2) | 0.0064 (18) | 0.0099 (17) | 0.0005 (17) |
| C4 | 0.035 (2) | 0.037 (3) | 0.025 (2) | 0.002 (2) | 0.0053 (18) | −0.0101 (18) |
| C5 | 0.031 (2) | 0.042 (3) | 0.024 (2) | 0.000 (2) | 0.0089 (17) | −0.0023 (18) |
| C6 | 0.038 (2) | 0.035 (2) | 0.024 (2) | 0.002 (2) | 0.0110 (18) | −0.0039 (18) |
| C7 | 0.030 (2) | 0.027 (2) | 0.022 (2) | 0.0042 (18) | 0.0085 (16) | −0.0023 (16) |
| C8 | 0.029 (2) | 0.033 (2) | 0.031 (2) | 0.0011 (19) | 0.0078 (18) | −0.0048 (18) |
| C9 | 0.045 (3) | 0.028 (2) | 0.034 (3) | 0.010 (2) | 0.012 (2) | 0.0000 (19) |
| C10 | 0.034 (2) | 0.048 (3) | 0.032 (3) | 0.011 (2) | 0.0015 (19) | 0.006 (2) |
| C11 | 0.060 (3) | 0.028 (2) | 0.050 (3) | 0.013 (2) | 0.027 (3) | 0.002 (2) |
| C12 | 0.045 (3) | 0.036 (3) | 0.035 (3) | −0.003 (2) | 0.011 (2) | −0.011 (2) |
| C13 | 0.053 (3) | 0.045 (3) | 0.026 (2) | 0.008 (2) | 0.008 (2) | −0.003 (2) |
| C14 | 0.045 (3) | 0.028 (2) | 0.028 (2) | 0.005 (2) | 0.014 (2) | 0.0065 (18) |
| C15 | 0.035 (3) | 0.044 (3) | 0.045 (3) | 0.006 (2) | 0.018 (2) | 0.002 (2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C16 | 0.031 (2) | 0.048 (3) | 0.052 (3) | 0.023 (2) | 0.016 (2) | 0.014 (2) |
| C17 | 0.064 (4) | 0.042 (3) | 0.058 (4) | −0.006 (3) | 0.034 (3) | −0.014 (3) |
| C18 | 0.063 (3) | 0.043 (3) | 0.049 (3) | −0.012 (3) | 0.021 (3) | −0.019 (2) |
| C19 | 0.063 (3) | 0.028 (2) | 0.029 (2) | 0.006 (2) | 0.017 (2) | −0.0049 (19) |
| C20 | 0.054 (3) | 0.038 (3) | 0.031 (3) | 0.008 (2) | 0.018 (2) | −0.010 (2) |
| C21 | 0.041 (3) | 0.040 (3) | 0.035 (3) | 0.008 (2) | −0.001 (2) | −0.008 (2) |
| C22 | 0.073 (4) | 0.026 (2) | 0.032 (3) | 0.000 (2) | 0.020 (2) | −0.007 (2) |
| C23 | 0.045 (3) | 0.024 (2) | 0.025 (2) | 0.0017 (19) | 0.0082 (19) | −0.0059 (17) |
| C24 | 0.042 (3) | 0.035 (3) | 0.035 (3) | 0.000 (2) | 0.008 (2) | −0.009 (2) |
| C25 | 0.058 (3) | 0.027 (2) | 0.027 (2) | 0.006 (2) | 0.007 (2) | −0.0005 (18) |
| C26 | 0.045 (3) | 0.029 (2) | 0.037 (3) | 0.013 (2) | 0.008 (2) | 0.0047 (19) |
| C27 | 0.052 (3) | 0.036 (3) | 0.037 (3) | −0.002 (2) | 0.002 (2) | −0.008 (2) |
| C28 | 0.061 (3) | 0.022 (2) | 0.032 (3) | 0.002 (2) | 0.009 (2) | −0.0041 (18) |
| C29 | 0.058 (3) | 0.031 (3) | 0.051 (3) | 0.013 (2) | 0.013 (3) | −0.010 (2) |
| C30 | 0.045 (3) | 0.045 (3) | 0.043 (3) | 0.003 (2) | 0.023 (2) | −0.012 (2) |
| C31 | 0.082 (4) | 0.034 (3) | 0.026 (3) | 0.003 (3) | 0.015 (2) | −0.004 (2) |
| C32 | 0.050 (3) | 0.038 (3) | 0.034 (3) | 0.009 (2) | −0.005 (2) | 0.000 (2) |
| O1W | 0.074 (13) | 0.072 (13) | 0.23 (3) | −0.003 (11) | 0.064 (16) | −0.097 (16) |

*Geometric parameters (Å, º)*

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| Cu1—N3 | 2.006 (4) | C13—H13B | 0.9700 |
| Cu1—N4 | 2.015 (4) | C14—C15 | 1.533 (7) |
| Cu1—Cl1 | 2.2961 (16) | C14—H14A | 0.9800 |
| Cu1—Cl2$^{i}$ | 2.3978 (15) | C15—C16 | 1.507 (7) |
| Cu1—Cl2 | 2.5854 (16) | C15—H15A | 0.9700 |
| O1—C22 | 1.222 (6) | C15—H15B | 0.9700 |
| O2—C6 | 1.223 (5) | C16—H16A | 0.9800 |
| N1—C6 | 1.355 (6) | C17—C18 | 1.387 (7) |
| N1—C7 | 1.480 (5) | C17—H17A | 0.9300 |
| N1—H1A | 0.8600 | C18—C19 | 1.368 (7) |
| N2—C22 | 1.344 (6) | C18—H18A | 0.9300 |
| N2—C23 | 1.476 (5) | C19—C20 | 1.389 (7) |
| N2—H2A | 0.8600 | C19—C22 | 1.516 (6) |
| N3—C17 | 1.315 (7) | C20—C21 | 1.375 (6) |
| N3—C21 | 1.350 (6) | C20—H20A | 0.9300 |
| N4—C1 | 1.328 (6) | C21—H21A | 0.9300 |
| N4—C5 | 1.353 (6) | C23—C26 | 1.534 (6) |
| C1—C2 | 1.387 (6) | C23—C25 | 1.536 (6) |
| C1—H1B | 0.9300 | C23—C24 | 1.539 (6) |
| C2—C3 | 1.392 (6) | C24—C30 | 1.535 (6) |
| C2—H2B | 0.9300 | C24—H24A | 0.9700 |
| C3—C4 | 1.386 (6) | C24—H24B | 0.9700 |
| C3—C6 | 1.519 (5) | C25—C28 | 1.536 (6) |
| C4—C5 | 1.390 (6) | C25—H25A | 0.9700 |
| C4—H4A | 0.9300 | C25—H25B | 0.9700 |
| C5—H5A | 0.9300 | C26—C32 | 1.542 (6) |
| C7—C10 | 1.528 (6) | C26—H26A | 0.9700 |

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| C7—C8 | 1.534 (6) | C26—H26B | 0.9700 |
| C7—C9 | 1.534 (6) | C27—C32 | 1.532 (7) |
| C8—C12 | 1.539 (6) | C27—C28 | 1.543 (7) |
| C8—H8A | 0.9700 | C27—H27A | 0.9700 |
| C8—H8B | 0.9700 | C27—H27B | 0.9700 |
| C9—C14 | 1.534 (6) | C28—C29 | 1.535 (7) |
| C9—H9A | 0.9700 | C28—H28A | 0.9800 |
| C9—H9B | 0.9700 | C29—C30 | 1.535 (7) |
| C10—C16 | 1.530 (6) | C29—H29A | 0.9700 |
| C10—H10A | 0.9700 | C29—H29B | 0.9700 |
| C10—H10B | 0.9700 | C30—C31 | 1.548 (8) |
| C11—C16 | 1.524 (7) | C30—H30A | 0.9800 |
| C11—C12 | 1.543 (7) | C31—C32 | 1.519 (7) |
| C11—H11A | 0.9700 | C31—H31A | 0.9700 |
| C11—H11B | 0.9700 | C31—H31B | 0.9700 |
| C12—C13 | 1.530 (7) | C32—H32A | 0.9800 |
| C12—H12A | 0.9800 | O1W—H1WA | 0.8258 |
| C13—C14 | 1.538 (7) | O1W—H1WB | 0.8262 |
| C13—H13A | 0.9700 | | |

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|---|---|---|---|
| N3—Cu1—N4 | 167.22 (17) | C16—C15—H15A | 109.7 |
| N3—Cu1—Cl1 | 88.13 (12) | C14—C15—H15A | 109.7 |
| N4—Cu1—Cl1 | 90.06 (12) | C16—C15—H15B | 109.7 |
| N3—Cu1—Cl2$^{i}$ | 87.18 (12) | C14—C15—H15B | 109.7 |
| N4—Cu1—Cl2$^{i}$ | 89.94 (12) | H15A—C15—H15B | 108.2 |
| Cl1—Cu1—Cl2$^{i}$ | 158.66 (6) | C15—C16—C11 | 109.7 (4) |
| N3—Cu1—Cl2 | 96.71 (12) | C15—C16—C10 | 110.0 (4) |
| N4—Cu1—Cl2 | 95.73 (12) | C11—C16—C10 | 109.7 (4) |
| Cl1—Cu1—Cl2 | 111.32 (7) | C15—C16—H16A | 109.1 |
| Cl2$^{i}$—Cu1—Cl2 | 89.91 (5) | C11—C16—H16A | 109.1 |
| Cu1$^{i}$—Cl2—Cu1 | 90.09 (5) | C10—C16—H16A | 109.1 |
| C6—N1—C7 | 124.3 (4) | N3—C17—C18 | 123.6 (5) |
| C6—N1—H1A | 117.9 | N3—C17—H17A | 118.2 |
| C7—N1—H1A | 117.8 | C18—C17—H17A | 118.2 |
| C22—N2—C23 | 124.6 (4) | C19—C18—C17 | 118.8 (5) |
| C22—N2—H2A | 117.7 | C19—C18—H18A | 120.6 |
| C23—N2—H2A | 117.7 | C17—C18—H18A | 120.6 |
| C17—N3—C21 | 118.0 (4) | C18—C19—C20 | 118.0 (4) |
| C17—N3—Cu1 | 117.1 (3) | C18—C19—C22 | 122.0 (5) |
| C21—N3—Cu1 | 124.9 (3) | C20—C19—C22 | 119.7 (4) |
| C1—N4—C5 | 118.3 (4) | C21—C20—C19 | 119.8 (5) |
| C1—N4—Cu1 | 117.8 (3) | C21—C20—H20A | 120.1 |
| C5—N4—Cu1 | 123.9 (3) | C19—C20—H20A | 120.1 |
| N4—C1—C2 | 123.4 (4) | N3—C21—C20 | 121.6 (5) |
| N4—C1—H1B | 118.3 | N3—C21—H21A | 119.2 |
| C2—C1—H1B | 118.3 | C20—C21—H21A | 119.2 |
| C1—C2—C3 | 118.8 (4) | O1—C22—N2 | 125.3 (4) |
| C1—C2—H2B | 120.6 | O1—C22—C19 | 118.4 (4) |

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|---|---|---|---|
| C3—C2—H2B | 120.6 | N2—C22—C19 | 116.2 (4) |
| C4—C3—C2 | 118.0 (4) | N2—C23—C26 | 109.8 (4) |
| C4—C3—C6 | 126.2 (4) | N2—C23—C25 | 108.0 (3) |
| C2—C3—C6 | 115.7 (4) | C26—C23—C25 | 109.5 (4) |
| C3—C4—C5 | 119.8 (4) | N2—C23—C24 | 110.9 (4) |
| C3—C4—H4A | 120.1 | C26—C23—C24 | 110.2 (4) |
| C5—C4—H4A | 120.1 | C25—C23—C24 | 108.4 (4) |
| N4—C5—C4 | 121.6 (4) | C30—C24—C23 | 109.5 (4) |
| N4—C5—H5A | 119.2 | C30—C24—H24A | 109.8 |
| C4—C5—H5A | 119.2 | C23—C24—H24A | 109.8 |
| O2—C6—N1 | 124.1 (4) | C30—C24—H24B | 109.8 |
| O2—C6—C3 | 119.4 (4) | C23—C24—H24B | 109.8 |
| N1—C6—C3 | 116.4 (4) | H24A—C24—H24B | 108.2 |
| N1—C7—C10 | 111.2 (4) | C23—C25—C28 | 109.9 (4) |
| N1—C7—C8 | 107.4 (3) | C23—C25—H25A | 109.7 |
| C10—C7—C8 | 109.5 (4) | C28—C25—H25A | 109.7 |
| N1—C7—C9 | 110.7 (3) | C23—C25—H25B | 109.7 |
| C10—C7—C9 | 109.8 (4) | C28—C25—H25B | 109.7 |
| C8—C7—C9 | 108.1 (4) | H25A—C25—H25B | 108.2 |
| C7—C8—C12 | 110.0 (3) | C23—C26—C32 | 109.4 (4) |
| C7—C8—H8A | 109.7 | C23—C26—H26A | 109.8 |
| C12—C8—H8A | 109.7 | C32—C26—H26A | 109.8 |
| C7—C8—H8B | 109.7 | C23—C26—H26B | 109.8 |
| C12—C8—H8B | 109.7 | C32—C26—H26B | 109.8 |
| H8A—C8—H8B | 108.2 | H26A—C26—H26B | 108.2 |
| C14—C9—C7 | 109.9 (3) | C32—C27—C28 | 109.3 (4) |
| C14—C9—H9A | 109.7 | C32—C27—H27A | 109.8 |
| C7—C9—H9A | 109.7 | C28—C27—H27A | 109.8 |
| C14—C9—H9B | 109.7 | C32—C27—H27B | 109.8 |
| C7—C9—H9B | 109.7 | C28—C27—H27B | 109.8 |
| H9A—C9—H9B | 108.2 | H27A—C27—H27B | 108.3 |
| C7—C10—C16 | 109.5 (4) | C29—C28—C25 | 110.0 (4) |
| C7—C10—H10A | 109.8 | C29—C28—C27 | 109.2 (4) |
| C16—C10—H10A | 109.8 | C25—C28—C27 | 109.0 (4) |
| C7—C10—H10B | 109.8 | C29—C28—H28A | 109.6 |
| C16—C10—H10B | 109.8 | C25—C28—H28A | 109.6 |
| H10A—C10—H10B | 108.2 | C27—C28—H28A | 109.6 |
| C16—C11—C12 | 109.6 (4) | C28—C29—C30 | 109.5 (4) |
| C16—C11—H11A | 109.8 | C28—C29—H29A | 109.8 |
| C12—C11—H11A | 109.8 | C30—C29—H29A | 109.8 |
| C16—C11—H11B | 109.8 | C28—C29—H29B | 109.8 |
| C12—C11—H11B | 109.8 | C30—C29—H29B | 109.8 |
| H11A—C11—H11B | 108.2 | H29A—C29—H29B | 108.2 |
| C13—C12—C8 | 110.1 (4) | C29—C30—C24 | 109.8 (4) |
| C13—C12—C11 | 108.8 (4) | C29—C30—C31 | 108.9 (4) |
| C8—C12—C11 | 108.9 (4) | C24—C30—C31 | 109.3 (4) |
| C13—C12—H12A | 109.7 | C29—C30—H30A | 109.6 |
| C8—C12—H12A | 109.7 | C24—C30—H30A | 109.6 |

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| C11—C12—H12A | 109.7 | C31—C30—H30A | 109.6 |
| C12—C13—C14 | 108.9 (4) | C32—C31—C30 | 109.9 (4) |
| C12—C13—H13A | 109.9 | C32—C31—H31A | 109.7 |
| C14—C13—H13A | 109.9 | C30—C31—H31A | 109.7 |
| C12—C13—H13B | 109.9 | C32—C31—H31B | 109.7 |
| C14—C13—H13B | 109.9 | C30—C31—H31B | 109.7 |
| H13A—C13—H13B | 108.3 | H31A—C31—H31B | 108.2 |
| C9—C14—C15 | 109.4 (4) | C31—C32—C27 | 110.5 (4) |
| C9—C14—C13 | 109.4 (4) | C31—C32—C26 | 108.9 (4) |
| C15—C14—C13 | 109.4 (4) | C27—C32—C26 | 109.3 (4) |
| C9—C14—H14A | 109.5 | C31—C32—H32A | 109.3 |
| C15—C14—H14A | 109.5 | C27—C32—H32A | 109.3 |
| C13—C14—H14A | 109.5 | C26—C32—H32A | 109.3 |
| C16—C15—C14 | 109.7 (4) | H1WA—O1W—H1WB | 109.6 |

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|---|---|---|---|
| N3—Cu1—Cl2—Cu1$^{i}$ | −87.15 (12) | C12—C13—C14—C9 | −59.6 (5) |
| N4—Cu1—Cl2—Cu1$^{i}$ | 89.93 (12) | C12—C13—C14—C15 | 60.3 (5) |
| Cl1—Cu1—Cl2—Cu1$^{i}$ | −177.76 (5) | C9—C14—C15—C16 | 59.7 (5) |
| Cl2$^{i}$—Cu1—Cl2—Cu1$^{i}$ | 0.000 (2) | C13—C14—C15—C16 | −60.2 (5) |
| N4—Cu1—N3—C17 | −7.0 (9) | C14—C15—C16—C11 | 60.1 (5) |
| Cl1—Cu1—N3—C17 | −89.0 (4) | C14—C15—C16—C10 | −60.6 (5) |
| Cl2$^{i}$—Cu1—N3—C17 | 70.1 (4) | C12—C11—C16—C15 | −60.4 (5) |
| Cl2—Cu1—N3—C17 | 159.7 (4) | C12—C11—C16—C10 | 60.5 (5) |
| N4—Cu1—N3—C21 | 175.6 (6) | C7—C10—C16—C15 | 60.2 (5) |
| Cl1—Cu1—N3—C21 | 93.6 (4) | C7—C10—C16—C11 | −60.6 (5) |
| Cl2$^{i}$—Cu1—N3—C21 | −107.2 (4) | C21—N3—C17—C18 | 0.4 (8) |
| Cl2—Cu1—N3—C21 | −17.7 (4) | Cu1—N3—C17—C18 | −177.2 (5) |
| N3—Cu1—N4—C1 | 16.7 (9) | N3—C17—C18—C19 | 2.1 (9) |
| Cl1—Cu1—N4—C1 | 98.5 (4) | C17—C18—C19—C20 | −3.2 (8) |
| Cl2$^{i}$—Cu1—N4—C1 | −60.2 (3) | C17—C18—C19—C22 | 170.9 (5) |
| Cl2—Cu1—N4—C1 | −150.1 (3) | C18—C19—C20—C21 | 1.9 (8) |
| N3—Cu1—N4—C5 | −160.5 (6) | C22—C19—C20—C21 | −172.4 (4) |
| Cl1—Cu1—N4—C5 | −78.8 (4) | C17—N3—C21—C20 | −1.8 (7) |
| Cl2$^{i}$—Cu1—N4—C5 | 122.6 (4) | Cu1—N3—C21—C20 | 175.6 (4) |
| Cl2—Cu1—N4—C5 | 32.7 (4) | C19—C20—C21—N3 | 0.7 (8) |
| C5—N4—C1—C2 | 0.5 (7) | C23—N2—C22—O1 | 5.3 (9) |
| Cu1—N4—C1—C2 | −176.9 (4) | C23—N2—C22—C19 | −172.0 (5) |
| N4—C1—C2—C3 | −1.8 (8) | C18—C19—C22—O1 | −127.1 (6) |
| C1—C2—C3—C4 | 1.0 (7) | C20—C19—C22—O1 | 46.9 (8) |
| C1—C2—C3—C6 | 178.9 (4) | C18—C19—C22—N2 | 50.4 (7) |
| C2—C3—C4—C5 | 0.8 (7) | C20—C19—C22—N2 | −135.6 (5) |
| C6—C3—C4—C5 | −176.8 (4) | C22—N2—C23—C26 | 61.0 (6) |
| C1—N4—C5—C4 | 1.4 (7) | C22—N2—C23—C25 | −179.7 (5) |
| Cu1—N4—C5—C4 | 178.6 (3) | C22—N2—C23—C24 | −61.0 (6) |
| C3—C4—C5—N4 | −2.1 (7) | N2—C23—C24—C30 | −179.4 (4) |
| C7—N1—C6—O2 | 0.7 (7) | C26—C23—C24—C30 | 58.8 (5) |
| C7—N1—C6—C3 | 177.9 (4) | C25—C23—C24—C30 | −61.0 (5) |
| C4—C3—C6—O2 | 162.0 (5) | N2—C23—C25—C28 | −179.4 (4) |

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| C2—C3—C6—O2 | −15.7 (6) | C26—C23—C25—C28 | −59.8 (5) |
| C4—C3—C6—N1 | −15.3 (7) | C24—C23—C25—C28 | 60.5 (5) |
| C2—C3—C6—N1 | 167.1 (4) | N2—C23—C26—C32 | 178.0 (4) |
| C6—N1—C7—C10 | 65.9 (5) | C25—C23—C26—C32 | 59.6 (5) |
| C6—N1—C7—C8 | −174.3 (4) | C24—C23—C26—C32 | −59.6 (5) |
| C6—N1—C7—C9 | −56.5 (6) | C23—C25—C28—C29 | −59.7 (5) |
| N1—C7—C8—C12 | 179.5 (4) | C23—C25—C28—C27 | 60.0 (5) |
| C10—C7—C8—C12 | −59.6 (5) | C32—C27—C28—C29 | 59.7 (5) |
| C9—C7—C8—C12 | 60.0 (5) | C32—C27—C28—C25 | −60.5 (5) |
| N1—C7—C9—C14 | −178.4 (4) | C25—C28—C29—C30 | 58.4 (5) |
| C10—C7—C9—C14 | 58.4 (5) | C27—C28—C29—C30 | −61.1 (5) |
| C8—C7—C9—C14 | −61.0 (5) | C28—C29—C30—C24 | −59.1 (6) |
| N1—C7—C10—C16 | 178.4 (4) | C28—C29—C30—C31 | 60.6 (5) |
| C8—C7—C10—C16 | 59.8 (5) | C23—C24—C30—C29 | 60.8 (5) |
| C9—C7—C10—C16 | −58.7 (5) | C23—C24—C30—C31 | −58.5 (5) |
| C7—C8—C12—C13 | −60.1 (5) | C29—C30—C31—C32 | −59.4 (5) |
| C7—C8—C12—C11 | 59.1 (5) | C24—C30—C31—C32 | 60.5 (5) |
| C16—C11—C12—C13 | 60.5 (5) | C30—C31—C32—C27 | 59.1 (5) |
| C16—C11—C12—C8 | −59.5 (5) | C30—C31—C32—C26 | −61.1 (5) |
| C8—C12—C13—C14 | 59.0 (5) | C28—C27—C32—C31 | −59.1 (5) |
| C11—C12—C13—C14 | −60.3 (5) | C28—C27—C32—C26 | 60.8 (5) |
| C7—C9—C14—C15 | −58.5 (5) | C23—C26—C32—C31 | 60.5 (5) |
| C7—C9—C14—C13 | 61.4 (5) | C23—C26—C32—C27 | −60.4 (5) |

Symmetry code: (i) −*x*, −*y*+1, −*z*+1.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*A*···O1$^{i}$ | 0.86 | 2.35 | 2.969 (5) | 129 |
| N2—H2*A*···Cl1$^{ii}$ | 0.86 | 2.66 | 3.499 (4) | 165 |
| O1*W*—H1*WA*···O1*W*$^{iii}$ | 0.83 | 2.22 | 3.00 (4) | 159 |

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