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

# Tetrakis[(3-hydroxypropyl)dimethylammonium] tetra-$\mu$-acetato-$\kappa^8O$:$O'$-bis[chloridocuprate(II)](*Cu—Cu*) dichloride

**Muhammad Shahid,[a] Muhammad Mazhar,[a]* Matthias Zeller[b] and Allen D. Hunter[b]**

[a]Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan, and [b]STaRBURSTT-Cyberdiffraction Consortium at YSU, and Department of Chemistry, Youngstown State University, 1 University Plaza, Youngstown, Ohio 44555-3663, USA
Correspondence e-mail: mazhar42pk@yahoo.com

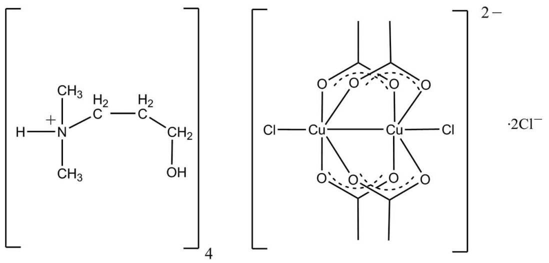
Received 31 January 2009; accepted 23 February 2009

Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.004 Å; disorder in solvent or counterion; $R$ factor = 0.036; $wR$ factor = 0.094; data-to-parameter ratio = 21.4.

The title compound $(C_5H_{14}NO)_4[Cu_2(CH_3COO)_4Cl_2]Cl_2$, consists of a pair of Cu$^{II}$ ions bridged by four acetate groups, resulting in a $Cu_2(CH_3COO)_4$ unit, four (3-hydroxypropyl)dimethylammonium cations (two crystallographically independent pairs) and two chloride anions. The Cu atoms at both termini are bonded to chloride anions. The latter are hydrogen bonded to one of the two pairs of crystallographically independent (3-hydroxypropyl)dimethylammonium cations. The $Cu_2(CH_3COO)_4$ unit is located on a crystallographic inversion center, and the geometry around each metal center is close to octahedral. The Cl—Cu—Cu angles are nearly linear [177.48 (2)°] and the Cu—O bond lengths are in the range 1.9712 (18)–1.9809 (19) Å. The Cu$\cdots$Cu separation between the two acetate-bridged Cu$^{II}$ centers is 2.6793 (8) Å. The packing of the crystal structure is dominated by N—H$\cdots$Cl hydrogen bonding between the ammonium groups and the chloride anions, as well as by O—H$\cdots$O and O—H$\cdots$Cl hydrogen bonds. One of the 3-hydroxypropyldimethylammonium cations shows orientational disorder with an occupancy ratio of 0.812 (4): 0.188 (4).

## Related literature

For the structure of binuclear copper(II) complexes, see: Ackermann *et al.* (2000); Shahid, Mazhar, Helliwell *et al.* (2008). For reports on the X-ray diffraction analysis of cupric acetate hydrate, $Cu_2(CH_3COO)_4(H_2O)_2$, see: Van Niekerk & Schoening (1953); de Meester *et al.* (1973); Nieger (2001); Ferguson & Glidewell (2003); Steed *et al.* (1998); Vives *et al.* (2003); Golzar Hossain (2007); Mahmoudkhani & Langer (1998). For the neutron-diffraction analysis of the same compound, see: Brown & Chidambaram (1973). For details concerning the geometric parameters of organo-copper complexes, see: Shahid, Mazhar, Malik *et al.* (2008); Shahid *et al.* (2009); Zhang *et al.* (2004).



## Experimental

### *Crystal data*

$(C_5H_{14}NO)_4[Cu_2(C_2H_3O_2)_4Cl_2]Cl_2$
$M_r$ = 921.74
Monoclinic, $P2_1/c$
$a$ = 11.438 (3) Å
$b$ = 11.266 (3) Å
$c$ = 16.876 (4) Å
$\beta$ = 97.940 (5)°
$V$ = 2153.8 (9) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 1.29 mm$^{-1}$
$T$ = 100 K
0.39 × 0.33 × 0.30 mm

### *Data collection*

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (TWINABS; Sheldrick, 2007)
$T_{min}$ = 0.562, $T_{max}$ = 0.679
19624 measured reflections
5259 independent reflections
4776 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.094
$S$ = 1.02
5259 reflections
246 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.67 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.66 e Å$^{-3}$

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| N1—H1$\cdots$Cl2 | 0.93 | 2.15 | 3.072 (3) | 169 |
| N1$B$—H1$B\cdots$Cl1$^{i}$ | 0.93 | 2.53 | 3.404 (13) | 156 |
| N2—H2$\cdots$Cl1 | 0.93 | 2.16 | 3.074 (2) | 166 |
| O5—H5$\cdots$O6$^{ii}$ | 0.837 (19) | 1.99 (2) | 2.810 (3) | 166 (4) |
| O6—H6$\cdots$Cl2$^{iii}$ | 0.84 | 2.25 | 3.082 (2) | 173 |

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* and *CELL* NOW (Sheldrick, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

MS is grateful to the Higher Education Commission of Pakistan and the Pakistan Science Foundation Islamabad, Pakistan for financial support *via* its PhD program. The X-ray diffractometer at Youngstown State University was funded by

NSF Grant 0087210, Ohio Board of Regents Grant CAP-491, and by Youngstown State University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2095).

## References

Ackermann, H., Neumüller, B. & Dehnicke, K. (2000). *Z. Anorg. Allg. Chem.* **626**, 1712-1714.

Brown, G. M. & Chidambaram, R. (1973). *Acta Cryst.* B**29**, 2393–2403.

Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Ferguson, G. & Glidewell, C. (2003). *Acta Cryst.* E**59**, m710–m712.

Golzar Hossain, G. M. (2007). Private communication (refcode CUAQAC27). CCDC, Cambridge, England.

Mahmoudkhani, A. H. & Langer, V. (1998). Private communication (refcode CUAQAC01). CCDC, Cambridge, England.

Meester, P. de, Fletcher, S. R. & Skapski, A. C. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2575–2578.

Nieger, M. (2001). Private communication (refcode CUAQAC05). CCDC, Cambridge, England.

Shahid, M., Mazhar, M., Helliwell, M., Akhtar, J. & Ahmad, K. (2008). *Acta Cryst.* E**64**, m1139–m1140.

Shahid, M., Mazhar, M., Malik, M. A., 'O Brien, P. & Raftery, J. (2008). *Polyhedron*, **27**, 3337–3342.

Shahid, M., Mazhar, M., O'Brien, P., Afzaal, M. & Raftery, J. (2009). *Acta Cryst.* E**65**, m163–m164.

Sheldrick, G. M. (2005). *CELL NOW*. University of Göttingen, Germany, and Bruker AXS Inc, Madison, Wisconsin, USA.

Sheldrick, G. M. (2007). *TWINABS*. University of Göttingen, Germany, and Bruker AXS Inc, Madison, Wisconsin, USA.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Steed, J. W., McCool, B. J. & Junk, P. C. (1998). *J. Chem. Soc. Dalton Trans.* pp. 3417–3423.

Van Niekerk, J. N. & Schoening, F. R. L. (1953). *Nature (London)*, **171**, 36–37.

Vives, G., Mason, S. A., Prince, P. D., Junk, P. C. & Steed, J. W. (2003). *Cryst. Growth Des.* **3**, 699–704.

Zhang, Y.-L., Chen, S.-W., Liu, W.-S. & Wang, D.-Q. (2004). *Acta Cryst.* E**60**, m196–m197.

**m346** Shahid *et al.* • $(C_5H_{14}NO)_4[Cu_2(C_2H_3O_2)_4Cl_2]Cl_2$ *Acta Cryst.* (2009). E**65**, m345–m346

# supporting information

*Acta Cryst.* (2009). E**65**, m345–m346    [doi:10.1107/S160053680900662X]

## Tetrakis[(3-hydroxypropyl)dimethylammonium] tetra-$\mu$-acetato-$\kappa^8O$:$O'$-bis-[chloridocuprate(II)](*Cu*—*Cu*) dichloride

**Muhammad Shahid, Muhammad Mazhar, Matthias Zeller and Allen D. Hunter**

### S1. Comment

In relation to our previous work on the structural chemistry of copper complexes (Shahid, Mazhar, Helliwell *et al.*, 2008) we described here the crystal structure of the title compound. It consists of a centrosymmetric acetate bridged $Cu_2(CH_3COO)_4$ moiety with chloride anions at both termini, four (dimethylammonium)propanol cations and two chloride anions.

In the title compound (Fig. 1) the two metal centers are related by a crystallographic inversion cernter; each has a coordination environment close to octahedral, with a $CuO_4CuCl$ set of ligating atoms, composed of four oxygen atoms of four bridging acetate groups, a terminal chloride atom and the second copper atom. The equatorial plane is made up of atoms O1, O2, O3 and O4 of the four bridging acetate ligands connecting both copper atoms, while the chloride ion Cl1 links to Cu1 in the axial position of the octahedron. The inversion related copper atoms are linked by a Cu—Cu bond thus completing the octahedral coordination of each copper center. The *trans* angles in the equatorial plane deviate slightly from the ideal value of 180°, and the Cu—O bond lengths fall in the range of 1.9712 (18)–1.9809 (19) Å. These values are in good agreement with the values reported for $Cu_2(CH_3COO)_4(H_2O)_2$ (Van Niekerk & Schoening,1953), and in more accurate structure determinations of this compound (Meester *et al.*, 1973; Nieger, 2001; Ferguson & Glidewell, 2003; Steed *et al.*, 1998; Vives *et al.*, 2003; Golzar Hossain, 2007; Mahmoudkhani & Langer, 1998) and for similar complexes (Shahid, Mazhar, Malik *et al.*, 2008; Shahid *et al.*, 2009; Zhang *et al.*, 2004). They indicate a slightly distorted octahedral geometry around both copper centers in the complex. The length of the central Cu—Cu bond of 2.6793 (8) Å is significantly longer than the value reported for dinuclear copper (II) acetate monohydrate by X-ray diffraction (see above) as well as by neutron diffraction analysis (Brown & Chidambaram, 1973), but it does agree well with that of the only other structurally determined tetra-$\mu$-acetato-$k^8O$:$O'$-dicuprate(II) with two terminal chloride ligands, which was reported by Ackermann *et al.* (2000) as 2.687 Å.

In the crystal structure the terminal chlorides are hydrogen bonded to one of crystallography independent (dimethylammonium)propanol cations (Fig. 2 and Table 1). The other crystallographically indepenent dimethyl(3-hydroxypropyl) ammonium ion is disordered over two positions, with both moieties being approximate mirror images of each other (see refinement section for details). This disorder results in a significantlty different hydrogen bonding environment for the two moieties. The dominant orientation exhibits an N—H···Cl hydrogen bond of *ca* 2.15 Å between H1 and Cl2. The less prevalent moiety shows a much weaker bond with an N1B—H1B···Cl1$^i$ bond distance of 2.53 Å (symmetry operator (i): -*x* + 1, *y* - 1/2, -*z* + 3/2). The packing of the crystal structure is dominated by hydrogen bonding between the ammonium N—H units and the chloride (Cl2) anions, as well as O—H···O and O—H···Cl hydrogen bonds (Fig. 3 and Table 1).

## S2. Experimental

*N*,*N*-Dimethylaminopropanol (dmapH) (0.76 g, 7.43 mmol) and acetic acid (0.45 g, 7.43 mmol) were added to a stirred suspension of $Cu(CH_3COO)_2.H_2O$ (0.74 g, 3.72 mmol) and anhydrous $CuCl_2$ (0.50 g, 3.72 mmol) in 30 ml tetrahydrofuran (THF). After two hours stirring, the mixture was vacuum evaporated to dryness and the solid was redissolved in a minimum amount of THF to give green block-shaped crystals at room temperature after 10 days.

## S3. Refinement

The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell Now (Sheldrick, 2005). The twin operation was found to be a two fold rotation around the *a* axis. The two components were integrated using Saint implemented in Apex2, resulting in a total of 19624 reflections. 1995 reflections (1332 unique ones) involved component 1 only (mean I/sigma = 16.7), 1945 reflections (1310 unique ones) involved component 2 only (mean I/sigma = 5.6), and 15684 reflections (6317 unique ones) involved both components (mean I/sigma = 10.8). The exact twin matrix identified by the integration program was found to be 1.00091 0.00101 0.00457, 0.00080 - 1.00000 - 0.00090, -0.39803 0.00179 - 1.00091.

The data were corrected for absorption using Twinabs, and the structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones) below a *d*-spacing threshold of 3/4, resulting in a BASF value of 0.118 (6). The $R_{\rm int}$ value given is for all reflections before the cutoff at d = 0.75 and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions [Twinabs (Sheldrick, 2007)].

One of the 3-dimethylamine-propan-1-ol ligands shows orientational disorder with an occupancy ratio of 0.812 (4) to 0.188 (4), with both moieties being approximate mirror images of each other. Atoms N1, C5 and C6, which significantely overlap with their equivalent counterparts, were constrained to have the same ADPs as their equivalent partners in the minor moiety. No restraints were applied for non-hydrogen atoms.

The hydroxyl hydrogen atom bonded to O5 did not show any visible disorder [despite being part of the disordered dimethyl(3-hydroxypropyl)ammonium group] and was freely refined with an O—H distance restraint of 0.837 (19) Å. The C—H and N—H atoms were placed in calculated positions and treated as riding atoms: N-H = 0.93 Å, C-H = 0.98 - 0.99 Å, with $U_{\rm iso}$(H) = k × $U_{\rm eq}$(parent atom), where k is 1.2 for C-methylene and N-ammonium, and 1.5 for C-methyl and O-hydroxyl.

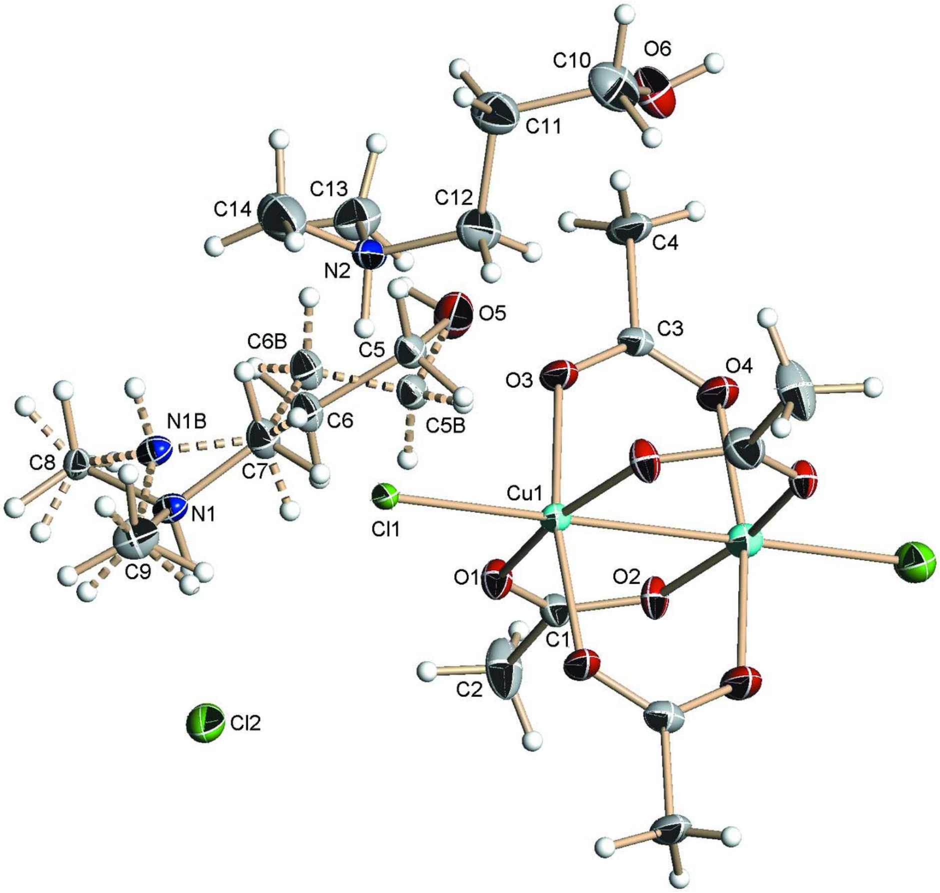


**Figure 1**

Molecular structure of the title compound showing the atom-labelling scheme and displacement ellipsoids (50% probability level). Minor moiety atoms of the disordered (dimethylammonium)propanol cation have been omitted for clarity.

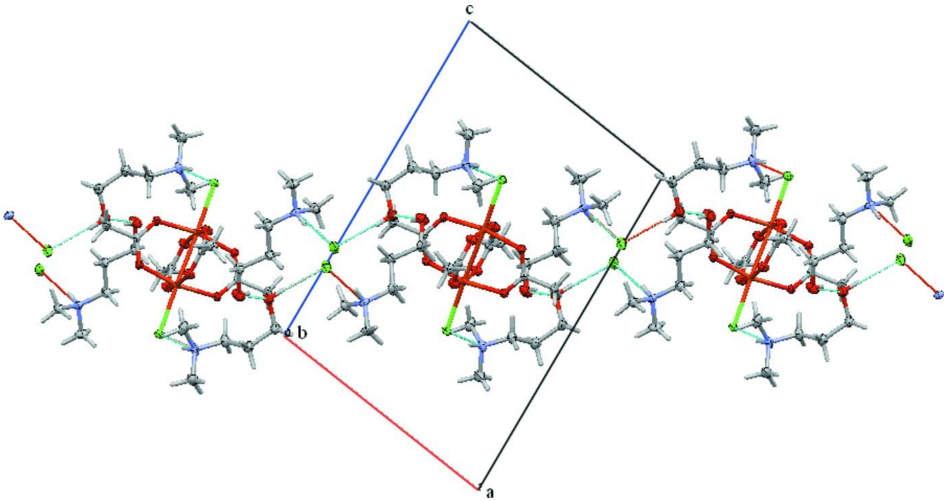


**Figure 2**

View along the *a* axis of the title compound, showing one of the H-bonded planes. H-bonding interactions are indicated by dashed blue lines.

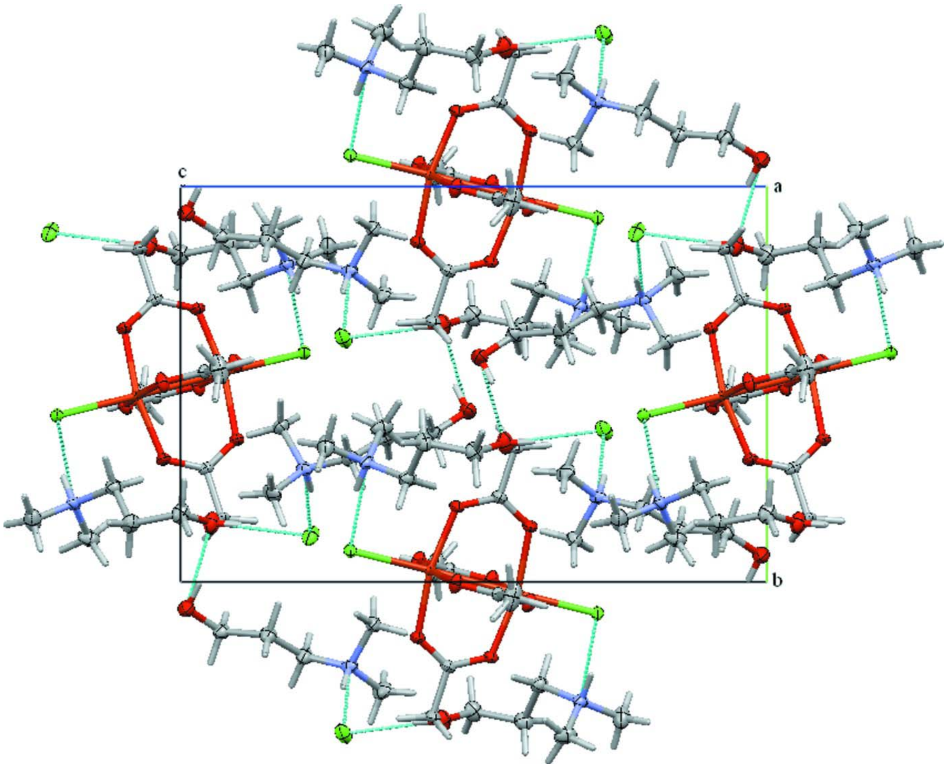


**Figure 3**

View of the title compound down the *b* axis (perpendicular to one of the hydrogen bonded planes). H-bonding interactions are indicated by dashed blue lines.

## Tetrakis[(3-hydroxypropyl)dimethylammonium] tetra-$\mu$-acetato- $\kappa^8O$:$O'$-bis[chloridocuprate(II)](*Cu*—*Cu*) dichloride

*Crystal data*

$(C_5H_{14}NO)_4[Cu_2(C_2H_3O_2)_4Cl_2]Cl_2$
$M_r = 921.74$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 11.438$ (3) Å
$b = 11.266$ (3) Å
$c = 16.876$ (4) Å
$\beta = 97.940$ (5)°
$V = 2153.8$ (9) Å$^3$
$Z = 2$

$F(000) = 972$
$D_x = 1.421$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2075 reflections
$\theta = 2.7$–30.4°
$\mu = 1.29$ mm$^{-1}$
$T = 100$ K
Block, green
0.39 × 0.33 × 0.30 mm

*Data collection*

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (TWINABS; Sheldrick, 2007)
$T_{\min} = 0.562$, $T_{\max} = 0.679$

19624 measured reflections
5259 independent reflections
4776 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.030$
$\theta_{\max} = 28.3°$, $\theta_{\min} = 1.8°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 22$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.094$
$S = 1.02$
5259 reflections
246 parameters
1 restraint
3 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 2.2181P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.67$ e Å$^{-3}$
$\Delta\rho_{min} = -0.66$ 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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| C1 | 0.7197 (2) | 0.9685 (2) | 0.54155 (15) | 0.0174 (5) | |
| C2 | 0.8514 (3) | 0.9625 (4) | 0.5660 (2) | 0.0406 (9) | |
| H2A | 0.8854 | 0.9046 | 0.5323 | 0.061* | |
| H2B | 0.8683 | 0.9382 | 0.6221 | 0.061* | |
| H2C | 0.8860 | 1.0408 | 0.5593 | 0.061* | |
| C3 | 0.4643 (2) | 0.7863 (2) | 0.45644 (15) | 0.0166 (5) | |
| C4 | 0.4394 (3) | 0.6600 (2) | 0.42948 (17) | 0.0239 (5) | |
| H4A | 0.4418 | 0.6541 | 0.3718 | 0.036* | |
| H4B | 0.3610 | 0.6366 | 0.4411 | 0.036* | |
| H4C | 0.4991 | 0.6073 | 0.4580 | 0.036* | |
| N1 | 0.7861 (2) | 0.7142 (2) | 0.78810 (17) | 0.0189 (6) | 0.812 (4) |
| H1 | 0.8449 | 0.7666 | 0.7777 | 0.023* | 0.812 (4) |
| C5 | 0.7036 (4) | 0.6247 (3) | 0.5698 (2) | 0.0245 (8) | 0.812 (4) |
| H5A | 0.6312 | 0.5809 | 0.5778 | 0.029* | 0.812 (4) |
| H5B | 0.6797 | 0.7055 | 0.5511 | 0.029* | 0.812 (4) |
| C6 | 0.7825 (4) | 0.6345 (4) | 0.6499 (2) | 0.0252 (8) | 0.812 (4) |
| H6A | 0.8115 | 0.5548 | 0.6677 | 0.030* | 0.812 (4) |
| H6B | 0.8517 | 0.6849 | 0.6440 | 0.030* | 0.812 (4) |
| N1B | 0.7363 (11) | 0.6648 (11) | 0.7942 (7) | 0.0189 (6) | 0.188 (4) |
| H1B | 0.6773 | 0.6120 | 0.8038 | 0.023* | 0.188 (4) |
| C6B | 0.7335 (17) | 0.6065 (17) | 0.6489 (11) | 0.0252 (8) | 0.188 (4) |
| H6B1 | 0.6645 | 0.5527 | 0.6406 | 0.030* | 0.188 (4) |
| H6B2 | 0.8028 | 0.5573 | 0.6695 | 0.030* | 0.188 (4) |
| C5B | 0.7530 (17) | 0.6512 (16) | 0.5689 (11) | 0.0245 (8) | 0.188 (4) |

| | | | | | |
|---|---|---|---|---|---|
| H5B1 | 0.6895 | 0.7086 | 0.5505 | 0.029* | 0.188 (4) |
| H5B2 | 0.8286 | 0.6952 | 0.5752 | 0.029* | 0.188 (4) |
| C7 | 0.7144 (3) | 0.6879 (3) | 0.71129 (18) | 0.0278 (6) | |
| H7C | 0.7609 | 0.7597 | 0.7025 | 0.033* | 0.188 (4) |
| H7D | 0.6304 | 0.7114 | 0.7001 | 0.033* | 0.188 (4) |
| H7A | 0.6777 | 0.7626 | 0.6892 | 0.033* | 0.812 (4) |
| H7B | 0.6499 | 0.6333 | 0.7206 | 0.033* | 0.812 (4) |
| C8 | 0.8470 (2) | 0.6073 (2) | 0.82870 (17) | 0.0235 (5) | |
| H8D | 0.8953 | 0.5912 | 0.7862 | 0.035* | 0.188 (4) |
| H8E | 0.8293 | 0.5324 | 0.8541 | 0.035* | 0.188 (4) |
| H8F | 0.8904 | 0.6598 | 0.8688 | 0.035* | 0.188 (4) |
| H8A | 0.9118 | 0.5819 | 0.8001 | 0.035* | 0.812 (4) |
| H8B | 0.7904 | 0.5422 | 0.8295 | 0.035* | 0.812 (4) |
| H8C | 0.8788 | 0.6291 | 0.8838 | 0.035* | 0.812 (4) |
| C9 | 0.7160 (3) | 0.7754 (3) | 0.84400 (19) | 0.0300 (6) | |
| H9D | 0.6966 | 0.8432 | 0.8082 | 0.045* | 0.188 (4) |
| H9E | 0.7878 | 0.7930 | 0.8809 | 0.045* | 0.188 (4) |
| H9F | 0.6506 | 0.7606 | 0.8746 | 0.045* | 0.188 (4) |
| H9A | 0.6952 | 0.8553 | 0.8238 | 0.045* | 0.812 (4) |
| H9B | 0.7625 | 0.7810 | 0.8973 | 0.045* | 0.812 (4) |
| H9C | 0.6436 | 0.7302 | 0.8474 | 0.045* | 0.812 (4) |
| C10 | 0.0463 (3) | 0.6724 (3) | 0.49916 (18) | 0.0293 (6) | |
| H10A | −0.0239 | 0.6212 | 0.4849 | 0.035* | |
| H10B | 0.0207 | 0.7563 | 0.4940 | 0.035* | |
| C11 | 0.1022 (3) | 0.6472 (3) | 0.58522 (18) | 0.0283 (6) | |
| H11A | 0.0406 | 0.6491 | 0.6210 | 0.034* | |
| H11B | 0.1380 | 0.5670 | 0.5883 | 0.034* | |
| C12 | 0.1966 (3) | 0.7392 (3) | 0.61261 (18) | 0.0267 (6) | |
| H12A | 0.2394 | 0.7589 | 0.5672 | 0.032* | |
| H12B | 0.1578 | 0.8125 | 0.6281 | 0.032* | |
| C13 | 0.3698 (3) | 0.6112 (3) | 0.6563 (2) | 0.0321 (7) | |
| H13A | 0.4199 | 0.5798 | 0.7034 | 0.048* | |
| H13B | 0.4192 | 0.6507 | 0.6212 | 0.048* | |
| H13C | 0.3265 | 0.5459 | 0.6272 | 0.048* | |
| C14 | 0.2309 (3) | 0.6569 (3) | 0.75181 (19) | 0.0360 (7) | |
| H14A | 0.1747 | 0.7164 | 0.7658 | 0.054* | |
| H14B | 0.2929 | 0.6449 | 0.7973 | 0.054* | |
| H14C | 0.1895 | 0.5818 | 0.7386 | 0.054* | |
| Cl1 | 0.44011 (5) | 0.92078 (5) | 0.71072 (4) | 0.01876 (13) | |
| Cl2 | 0.99391 (6) | 0.88351 (7) | 0.77784 (4) | 0.03015 (16) | |
| Cu1 | 0.48200 (3) | 0.97068 (2) | 0.574297 (18) | 0.01280 (8) | |
| N2 | 0.2843 (2) | 0.6984 (2) | 0.68207 (14) | 0.0217 (5) | |
| H2 | 0.3285 | 0.7651 | 0.6994 | 0.026* | |
| O1 | 0.65475 (16) | 0.94688 (18) | 0.59419 (11) | 0.0222 (4) | |
| O2 | 0.68435 (16) | 0.99580 (19) | 0.46970 (11) | 0.0226 (4) | |
| O3 | 0.45992 (18) | 0.80971 (15) | 0.52892 (11) | 0.0217 (4) | |
| O4 | 0.48787 (17) | 0.85928 (15) | 0.40413 (11) | 0.0215 (4) | |
| O5 | 0.7561 (2) | 0.5676 (2) | 0.50998 (13) | 0.0322 (5) | |

| | | | | |
|---|---|---|---|---|
| H5 | 0.787 (4) | 0.506 (3) | 0.531 (2) | 0.048* |
| O6 | 0.13091 (19) | 0.6490 (2) | 0.44697 (13) | 0.0319 (5) |
| H6 | 0.0969 | 0.6451 | 0.3996 | 0.048* |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0166 (11) | 0.0172 (11) | 0.0174 (12) | 0.0003 (9) | −0.0008 (9) | −0.0002 (9) |
| C2 | 0.0172 (13) | 0.074 (3) | 0.0297 (16) | 0.0020 (15) | 0.0012 (12) | 0.0113 (17) |
| C3 | 0.0147 (10) | 0.0146 (10) | 0.0202 (12) | −0.0002 (9) | 0.0012 (9) | −0.0039 (9) |
| C4 | 0.0353 (15) | 0.0133 (11) | 0.0241 (13) | −0.0064 (10) | 0.0076 (12) | −0.0036 (10) |
| N1 | 0.0184 (13) | 0.0156 (13) | 0.0238 (13) | −0.0010 (10) | 0.0070 (11) | −0.0008 (11) |
| C5 | 0.024 (2) | 0.0215 (17) | 0.0265 (16) | 0.0052 (15) | −0.0011 (17) | −0.0015 (14) |
| C6 | 0.022 (2) | 0.0281 (19) | 0.0245 (16) | 0.0078 (16) | −0.0001 (16) | −0.0018 (14) |
| N1B | 0.0184 (13) | 0.0156 (13) | 0.0238 (13) | −0.0010 (10) | 0.0070 (11) | −0.0008 (11) |
| C6B | 0.022 (2) | 0.0281 (19) | 0.0245 (16) | 0.0078 (16) | −0.0001 (16) | −0.0018 (14) |
| C5B | 0.024 (2) | 0.0215 (17) | 0.0265 (16) | 0.0052 (15) | −0.0011 (17) | −0.0015 (14) |
| C7 | 0.0301 (15) | 0.0265 (14) | 0.0254 (15) | 0.0084 (11) | −0.0015 (12) | −0.0017 (12) |
| C8 | 0.0252 (13) | 0.0225 (13) | 0.0223 (13) | 0.0028 (11) | 0.0012 (11) | 0.0018 (11) |
| C9 | 0.0338 (15) | 0.0266 (14) | 0.0325 (16) | 0.0026 (12) | 0.0145 (13) | −0.0064 (12) |
| C10 | 0.0205 (13) | 0.0357 (15) | 0.0301 (15) | 0.0026 (11) | −0.0019 (11) | −0.0038 (13) |
| C11 | 0.0247 (13) | 0.0304 (14) | 0.0296 (15) | −0.0043 (11) | 0.0031 (11) | −0.0016 (12) |
| C12 | 0.0274 (14) | 0.0220 (13) | 0.0288 (15) | 0.0013 (11) | −0.0033 (12) | 0.0007 (11) |
| C13 | 0.0256 (14) | 0.0264 (14) | 0.0431 (18) | 0.0033 (12) | 0.0003 (13) | 0.0048 (13) |
| C14 | 0.0360 (17) | 0.0467 (19) | 0.0249 (15) | −0.0124 (15) | 0.0024 (13) | 0.0013 (14) |
| Cl1 | 0.0248 (3) | 0.0182 (3) | 0.0133 (3) | −0.0063 (2) | 0.0026 (2) | −0.0005 (2) |
| Cl2 | 0.0299 (3) | 0.0342 (4) | 0.0242 (3) | −0.0153 (3) | −0.0042 (3) | 0.0082 (3) |
| Cu1 | 0.01441 (13) | 0.01100 (13) | 0.01291 (14) | −0.00040 (10) | 0.00160 (11) | −0.00054 (10) |
| N2 | 0.0254 (11) | 0.0159 (10) | 0.0215 (11) | −0.0030 (9) | −0.0048 (9) | 0.0011 (9) |
| O1 | 0.0167 (8) | 0.0294 (10) | 0.0202 (9) | 0.0011 (7) | 0.0020 (7) | 0.0052 (8) |
| O2 | 0.0158 (8) | 0.0337 (10) | 0.0180 (9) | 0.0035 (8) | 0.0010 (7) | 0.0050 (8) |
| O3 | 0.0331 (10) | 0.0135 (8) | 0.0189 (9) | −0.0045 (7) | 0.0054 (8) | −0.0026 (7) |
| O4 | 0.0332 (10) | 0.0129 (8) | 0.0187 (9) | −0.0031 (7) | 0.0043 (8) | −0.0020 (7) |
| O5 | 0.0470 (13) | 0.0255 (11) | 0.0234 (11) | 0.0082 (10) | 0.0022 (10) | −0.0015 (9) |
| O6 | 0.0281 (10) | 0.0425 (13) | 0.0235 (10) | 0.0065 (10) | −0.0021 (8) | −0.0025 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—O1 | 1.258 (3) | C8—H8F | 0.9800 |
| C1—O2 | 1.262 (3) | C8—H8A | 0.9804 |
| C1—C2 | 1.506 (4) | C8—H8B | 0.9801 |
| C2—H2A | 0.9800 | C8—H8C | 0.9821 |
| C2—H2B | 0.9800 | C9—H9D | 0.9800 |
| C2—H2C | 0.9800 | C9—H9E | 0.9800 |
| C3—O3 | 1.259 (3) | C9—H9F | 0.9800 |
| C3—O4 | 1.262 (3) | C9—H9A | 0.9799 |
| C3—C4 | 1.509 (3) | C9—H9B | 0.9824 |
| C4—H4A | 0.9800 | C9—H9C | 0.9805 |

| | | | |
|---|---|---|---|
| C4—H4B | 0.9800 | C10—O6 | 1.421 (4) |
| C4—H4C | 0.9800 | C10—C11 | 1.531 (4) |
| N1—C7 | 1.465 (4) | C10—H10A | 0.9900 |
| N1—C9 | 1.489 (4) | C10—H10B | 0.9900 |
| N1—C8 | 1.508 (4) | C11—C12 | 1.522 (4) |
| N1—H1 | 0.9300 | C11—H11A | 0.9900 |
| C5—O5 | 1.399 (4) | C11—H11B | 0.9900 |
| C5—C6 | 1.522 (6) | C12—N2 | 1.506 (4) |
| C5—H5A | 0.9900 | C12—H12A | 0.9900 |
| C5—H5B | 0.9900 | C12—H12B | 0.9900 |
| C6—C7 | 1.505 (5) | C13—N2 | 1.493 (4) |
| C6—H6A | 0.9900 | C13—H13A | 0.9800 |
| C6—H6B | 0.9900 | C13—H13B | 0.9800 |
| N1B—C7 | 1.412 (13) | C13—H13C | 0.9800 |
| N1B—C8 | 1.469 (12) | C14—N2 | 1.475 (4) |
| N1B—C9 | 1.538 (12) | C14—H14A | 0.9800 |
| N1B—H1B | 0.9300 | C14—H14B | 0.9800 |
| C6B—C7 | 1.435 (18) | C14—H14C | 0.9800 |
| C6B—C5B | 1.49 (3) | Cl1—Cu1 | 2.4800 (9) |
| C6B—H6B1 | 0.9900 | Cu1—O3 | 1.9712 (18) |
| C6B—H6B2 | 0.9900 | Cu1—O4$^{i}$ | 1.9714 (18) |
| C5B—O5 | 1.374 (18) | Cu1—O1 | 1.9762 (19) |
| C5B—H5B1 | 0.9900 | Cu1—O2$^{i}$ | 1.9809 (19) |
| C5B—H5B2 | 0.9900 | Cu1—Cu1$^{i}$ | 2.6793 (8) |
| C7—H7C | 0.9900 | N2—H2 | 0.9300 |
| C7—H7D | 0.9900 | O2—Cu1$^{i}$ | 1.9809 (19) |
| C7—H7A | 0.9902 | O4—Cu1$^{i}$ | 1.9714 (18) |
| C7—H7B | 0.9902 | O5—H5 | 0.837 (19) |
| C8—H8D | 0.9800 | O6—H6 | 0.8400 |
| C8—H8E | 0.9800 | | |

| | | | |
|---|---|---|---|
| O1—C1—O2 | 125.7 (2) | H8A—C8—H8B | 109.5 |
| O1—C1—C2 | 117.6 (2) | N1—C8—H8C | 108.5 |
| O2—C1—C2 | 116.7 (2) | H8A—C8—H8C | 109.4 |
| C1—C2—H2A | 109.5 | H8B—C8—H8C | 109.5 |
| C1—C2—H2B | 109.5 | N1B—C9—H9D | 109.5 |
| H2A—C2—H2B | 109.5 | N1B—C9—H9E | 109.5 |
| C1—C2—H2C | 109.5 | H9D—C9—H9E | 109.5 |
| H2A—C2—H2C | 109.5 | N1B—C9—H9F | 109.5 |
| H2B—C2—H2C | 109.5 | H9D—C9—H9F | 109.5 |
| O3—C3—O4 | 125.7 (2) | H9E—C9—H9F | 109.5 |
| O3—C3—C4 | 117.3 (2) | N1—C9—H9A | 109.4 |
| O4—C3—C4 | 116.9 (2) | N1—C9—H9B | 109.8 |
| C3—C4—H4A | 109.5 | H9A—C9—H9B | 109.5 |
| C3—C4—H4B | 109.5 | N1—C9—H9C | 109.2 |
| H4A—C4—H4B | 109.5 | H9D—C9—H9C | 108.7 |
| C3—C4—H4C | 109.5 | H9A—C9—H9C | 109.4 |
| H4A—C4—H4C | 109.5 | H9B—C9—H9C | 109.5 |

| | | | |
|---|---|---|---|
| H4B—C4—H4C | 109.5 | O6—C10—C11 | 108.8 (2) |
| C7—N1—C9 | 111.7 (2) | O6—C10—H10A | 109.9 |
| C7—N1—C8 | 114.1 (2) | C11—C10—H10A | 109.9 |
| C9—N1—C8 | 109.8 (2) | O6—C10—H10B | 109.9 |
| C7—N1—H1 | 107.0 | C11—C10—H10B | 109.9 |
| C9—N1—H1 | 107.0 | H10A—C10—H10B | 108.3 |
| C8—N1—H1 | 107.0 | C12—C11—C10 | 110.4 (2) |
| O5—C5—C6 | 114.4 (3) | C12—C11—H11A | 109.6 |
| O5—C5—H5A | 108.6 | C10—C11—H11A | 109.6 |
| C6—C5—H5A | 108.6 | C12—C11—H11B | 109.6 |
| O5—C5—H5B | 108.6 | C10—C11—H11B | 109.6 |
| C6—C5—H5B | 108.6 | H11A—C11—H11B | 108.1 |
| H5A—C5—H5B | 107.6 | N2—C12—C11 | 113.4 (2) |
| C7—C6—C5 | 110.0 (3) | N2—C12—H12A | 108.9 |
| C7—C6—H6A | 109.7 | C11—C12—H12A | 108.9 |
| C5—C6—H6A | 109.7 | N2—C12—H12B | 108.9 |
| C7—C6—H6B | 109.7 | C11—C12—H12B | 108.9 |
| C5—C6—H6B | 109.7 | H12A—C12—H12B | 107.7 |
| H6A—C6—H6B | 108.2 | N2—C13—H13A | 109.5 |
| C7—N1B—C8 | 119.9 (8) | N2—C13—H13B | 109.5 |
| C7—N1B—C9 | 111.9 (8) | H13A—C13—H13B | 109.5 |
| C8—N1B—C9 | 109.2 (8) | N2—C13—H13C | 109.5 |
| C7—N1B—H1B | 104.8 | H13A—C13—H13C | 109.5 |
| C8—N1B—H1B | 104.8 | H13B—C13—H13C | 109.5 |
| C9—N1B—H1B | 104.8 | N2—C14—H14A | 109.5 |
| C7—C6B—C5B | 120.5 (15) | N2—C14—H14B | 109.5 |
| C7—C6B—H6B1 | 107.2 | H14A—C14—H14B | 109.5 |
| C5B—C6B—H6B1 | 107.2 | N2—C14—H14C | 109.5 |
| C7—C6B—H6B2 | 107.2 | H14A—C14—H14C | 109.5 |
| C5B—C6B—H6B2 | 107.2 | H14B—C14—H14C | 109.5 |
| H6B1—C6B—H6B2 | 106.8 | O3—Cu1—O4$^{i}$ | 167.29 (7) |
| O5—C5B—C6B | 116.6 (15) | O3—Cu1—O1 | 90.72 (8) |
| O5—C5B—H5B1 | 108.1 | O4$^{i}$—Cu1—O1 | 87.44 (8) |
| C6B—C5B—H5B1 | 108.1 | O3—Cu1—O2$^{i}$ | 87.99 (9) |
| O5—C5B—H5B2 | 108.1 | O4$^{i}$—Cu1—O2$^{i}$ | 91.05 (9) |
| C6B—C5B—H5B2 | 108.1 | O1—Cu1—O2$^{i}$ | 167.32 (8) |
| H5B1—C5B—H5B2 | 107.3 | O3—Cu1—Cl1 | 96.96 (6) |
| N1B—C7—C6B | 125.9 (9) | O4$^{i}$—Cu1—Cl1 | 95.74 (6) |
| N1—C7—C6 | 114.3 (3) | O1—Cu1—Cl1 | 97.38 (6) |
| N1B—C7—H7C | 105.9 | O2$^{i}$—Cu1—Cl1 | 95.30 (6) |
| C6B—C7—H7C | 105.9 | O3—Cu1—Cu1$^{i}$ | 83.76 (6) |
| N1B—C7—H7D | 105.9 | O4$^{i}$—Cu1—Cu1$^{i}$ | 83.56 (6) |
| C6B—C7—H7D | 105.9 | O1—Cu1—Cu1$^{i}$ | 85.02 (6) |
| H7C—C7—H7D | 106.2 | O2$^{i}$—Cu1—Cu1$^{i}$ | 82.30 (6) |
| N1—C7—H7A | 108.5 | Cl1—Cu1—Cu1$^{i}$ | 177.48 (2) |
| C6—C7—H7A | 108.3 | C14—N2—C13 | 112.6 (2) |
| N1—C7—H7B | 108.9 | C14—N2—C12 | 114.4 (2) |
| C6—C7—H7B | 109.2 | C13—N2—C12 | 111.5 (2) |

| | | | |
|---|---|---|---|
| H7A—C7—H7B | 107.6 | C14—N2—H2 | 105.9 |
| N1B—C8—H8D | 109.5 | C13—N2—H2 | 105.9 |
| N1B—C8—H8E | 109.5 | C12—N2—H2 | 105.9 |
| H8D—C8—H8E | 109.5 | C1—O1—Cu1 | 121.88 (17) |
| N1B—C8—H8F | 109.5 | C1—O2—Cu1$^{i}$ | 124.78 (16) |
| H8D—C8—H8F | 109.5 | C3—O3—Cu1 | 123.36 (16) |
| H8E—C8—H8F | 109.5 | C3—O4—Cu1$^{i}$ | 123.53 (16) |
| N1—C8—H8A | 110.0 | C5B—O5—H5 | 109 (3) |
| N1—C8—H8B | 109.8 | C5—O5—H5 | 106 (3) |
| H8D—C8—H8B | 108.2 | C10—O6—H6 | 109.5 |

| | | | |
|---|---|---|---|
| O5—C5—C6—C7 | −175.3 (3) | C7—N1B—C9—N1 | −67.1 (9) |
| C7—C6B—C5B—O5 | −172.2 (12) | C8—N1B—C9—N1 | 68.0 (9) |
| C8—N1B—C7—C6B | 45.4 (17) | O6—C10—C11—C12 | 69.3 (3) |
| C9—N1B—C7—C6B | 175.1 (11) | C10—C11—C12—N2 | −159.0 (2) |
| C8—N1B—C7—N1 | −66.4 (10) | C11—C12—N2—C14 | −53.9 (3) |
| C9—N1B—C7—N1 | 63.3 (8) | C11—C12—N2—C13 | 75.3 (3) |
| C8—N1B—C7—C6 | 14.5 (14) | O2—C1—O1—Cu1 | −7.1 (4) |
| C9—N1B—C7—C6 | 144.3 (5) | C2—C1—O1—Cu1 | 172.3 (2) |
| C5B—C6B—C7—N1B | −155.9 (14) | O3—Cu1—O1—C1 | 86.9 (2) |
| C5B—C6B—C7—N1 | −114.2 (15) | O4$^{i}$—Cu1—O1—C1 | −80.6 (2) |
| C5B—C6B—C7—C6 | −59.1 (19) | O2$^{i}$—Cu1—O1—C1 | 2.8 (5) |
| C9—N1—C7—N1B | −67.2 (9) | Cl1—Cu1—O1—C1 | −176.03 (19) |
| C8—N1—C7—N1B | 57.9 (9) | Cu1$^{i}$—Cu1—O1—C1 | 3.18 (19) |
| C9—N1—C7—C6B | −162.1 (11) | O1—C1—O2—Cu1$^{i}$ | 7.4 (4) |
| C8—N1—C7—C6B | −37.0 (12) | C2—C1—O2—Cu1$^{i}$ | −172.0 (2) |
| C9—N1—C7—C6 | 175.5 (3) | O4—C3—O3—Cu1 | 3.2 (4) |
| C8—N1—C7—C6 | −59.4 (4) | C4—C3—O3—Cu1 | −176.89 (18) |
| C5—C6—C7—N1B | 151.0 (7) | O4$^{i}$—Cu1—O3—C3 | −5.5 (5) |
| C5—C6—C7—C6B | 49.7 (18) | O1—Cu1—O3—C3 | −87.0 (2) |
| C5—C6—C7—N1 | −173.2 (3) | O2$^{i}$—Cu1—O3—C3 | 80.3 (2) |
| C7—N1B—C8—N1 | 66.6 (10) | Cl1—Cu1—O3—C3 | 175.4 (2) |
| C9—N1B—C8—N1 | −64.3 (8) | Cu1$^{i}$—Cu1—O3—C3 | −2.1 (2) |
| C7—N1—C8—N1B | −57.1 (9) | O3—C3—O4—Cu1$^{i}$ | −2.1 (4) |
| C9—N1—C8—N1B | 69.1 (9) | C4—C3—O4—Cu1$^{i}$ | 177.95 (17) |
| C7—N1—C9—N1B | 62.5 (9) | C6B—C5B—O5—C5 | 54.7 (17) |
| C8—N1—C9—N1B | −65.1 (9) | C6—C5—O5—C5B | −51.9 (17) |

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

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1···Cl2 | 0.93 | 2.15 | 3.072 (3) | 169 |
| N1*B*—H1*B*···Cl1$^{ii}$ | 0.93 | 2.53 | 3.404 (13) | 156 |
| N2—H2···Cl1 | 0.93 | 2.16 | 3.074 (2) | 166 |

| | | | | |
|---|---|---|---|---|
| O5—H5···O6$^{iii}$ | 0.84 (2) | 1.99 (2) | 2.810 (3) | 166 (4) |
| O6—H6···Cl2$^{iv}$ | 0.84 | 2.25 | 3.082 (2) | 173 |

Symmetry codes: (ii) −*x*+1, *y*−1/2, −*z*+3/2; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*−1, −*y*+3/2, *z*−1/2.