



ISSN 1600-5368

# Crystal structure of *trans*-aqua(perchlorato- $\kappa$ O)-bis(propane-1,3-diamine- $\kappa^2N,N'$ )copper(II) perchlorate

J. Govindaraj,<sup>a</sup> K. Rajkumar,<sup>b</sup> A. S. Ganeshraja,<sup>b</sup> K. Anbalagan<sup>b</sup> and A. SubbiahPandi<sup>c,\*</sup>

Received 13 October 2014

Accepted 25 October 2014

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

**Keywords:** crystal structure; propane-1,3-diamine; copper(II) complex

**CCDC reference:** 1031014

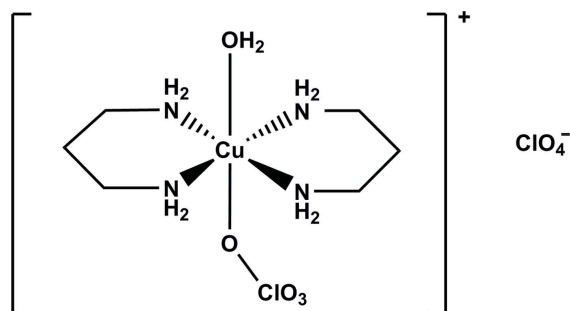
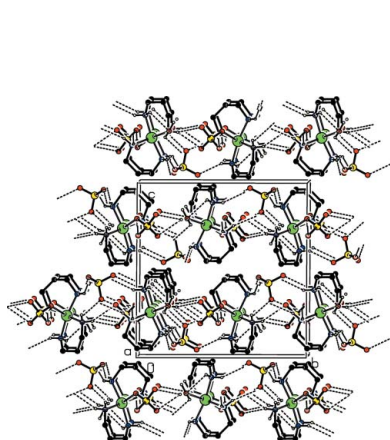
**Supporting information:** this article has supporting information at journals.iucr.org/e

<sup>a</sup>Department of Physics, Pachaiyappa's College for Men, Kanchipuram 631 501, India, <sup>b</sup>Department of Chemistry, Pondicherry University, Pondicherry 605 014, India, and <sup>c</sup>Department of Physics, Presidency College (Autonomous), Chennai 600 005, India. \*Correspondence e-mail: aspandian59@gmail.com

In the title compound,  $[\text{Cu}(\text{ClO}_4)(\text{C}_3\text{H}_{10}\text{N}_2)_2(\text{H}_2\text{O})]\text{ClO}_4$ , the  $\text{Cu}^{\text{II}}$  atom has a distorted octahedral coordination sphere and is coordinated by the N atoms of two propane-1,3-diamine ligands in the equatorial plane. The axial positions are occupied by a water O atom and an O atom of a disordered perchlorate anion [occupancy ratio 0.631 (9):0.369 (9)]. In the crystal, the various components are linked *via*  $\text{O}-\text{H}\cdots\text{O}$ ,  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds, forming sheets lying parallel to (001).

## 1. Chemical context

There have been numerous reports of bis(propane-1,3-diamine)copper(II) complexes, essentially with the copper atom coordinated by the N atoms of the ligands in the equatorial plane of the copper octahedral coordination sphere and with two identical O-containing ligands in the axial positions, for example, *trans*-diaquabis(propane-1,3-diamine- $\kappa^2N,N'$ )copper(II) dithionate (Kim *et al.*, 2003) and bis[aqua(1,3-diaminopropane- $\kappa^2N,N'$ )]copper(II) difluoride (Emsley *et al.*, 1988). In order to further develop the coordination chemistry of such copper complexes, we report herein on the synthesis and crystal structure of the title complex, which has two different ligands in the axial positions of the octahedral coordination sphere of the copper atom.



## 2. Structural commentary

The molecular structure of the title complex is illustrated in Fig. 1. The  $\text{Cu}^{\text{II}}$  atom has a distorted octahedral coordination sphere, reflecting the characteristic Jahn–Teller distortion. It is coordinated by the N atoms of two propane-1,3-diamine ligands in the equatorial plane with  $\text{Cu}-\text{N}$  bond lengths varying between 2.003 (4)–2.023 (3) Å. The axial positions are

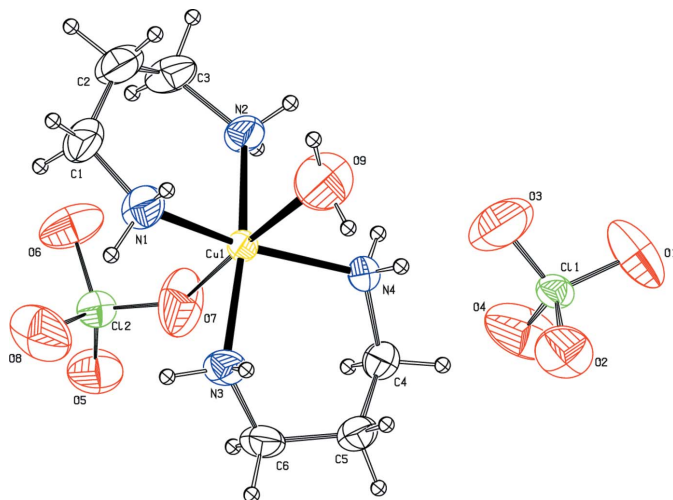


Figure 1

The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 30% probability level. The minor components of the disordered coordinating perchlorate anion have been omitted for clarity.

occupied by the water O9 atom and by atom O7 of a disordered perchlorate anion [occupancy ratio 0.631 (9):0.369 (9)], with Cu—O bond lengths of 2.585 (6) and 2.680 (10) Å, respectively.

### 3. Supramolecular features

In the crystal, the various components are linked *via* O—H···O, N—H···O and C—H···O hydrogen bonds forming sheets lying parallel to (001); see Table 1 and Fig. 2.

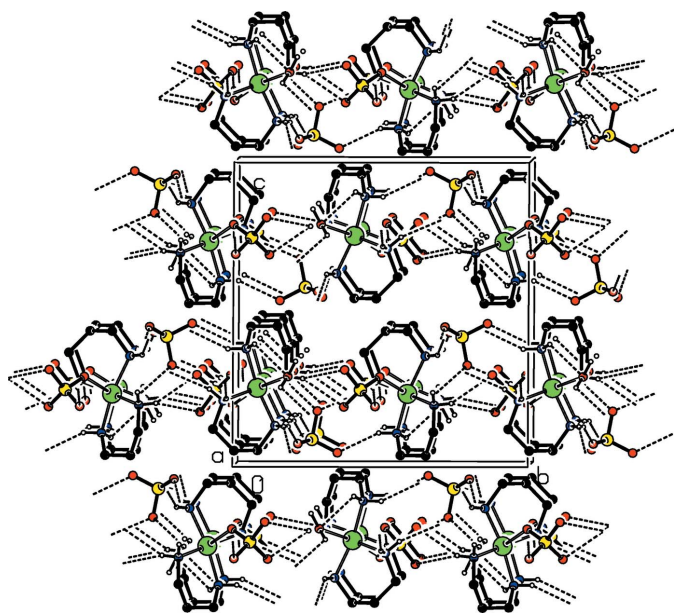


Figure 2

A view along the *a* axis of the crystal structure of the title compound. O—H···O and N—H···O hydrogen bonds are shown as dashed lines (see Table 1 for details; the minor components of the disordered coordinating perchlorate anion and the C-bound H atoms have been omitted for clarity).

Table 1

Hydrogen-bond geometry (Å, °).

| <i>D</i> —H··· <i>A</i>    | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| O9—H9B···O3 <sup>i</sup>   | 0.90 (2)    | 2.38 (11)     | 2.917 (9)             | 118 (9)                 |
| N1—H1C···O1                | 0.90        | 2.22          | 3.040 (7)             | 151                     |
| N1—H1D···O1 <sup>ii</sup>  | 0.90        | 2.69          | 3.511 (8)             | 151                     |
| N1—H1D···O9                | 0.90        | 2.41          | 2.927 (8)             | 117                     |
| N2—H2C···O5 <sup>iii</sup> | 0.90        | 2.58          | 3.443 (12)            | 162                     |
| N2—H2C···O8 <sup>iii</sup> | 0.90        | 2.42          | 3.183 (10)            | 143                     |
| N2—H2C···O5 <sup>iv</sup>  | 0.90        | 2.39          | 3.23 (3)              | 156                     |
| N2—H2D···O3 <sup>iii</sup> | 0.90        | 2.70          | 3.449 (11)            | 141                     |
| N3—H3C···O6 <sup>iv</sup>  | 0.90        | 2.15          | 3.014 (9)             | 160                     |
| N3—H3C···O7 <sup>iv</sup>  | 0.90        | 2.36          | 3.246 (17)            | 169                     |
| N3—H3D···O3                | 0.90        | 2.28          | 3.137 (8)             | 160                     |
| N4—H4C···O2 <sup>iii</sup> | 0.90        | 2.35          | 3.127 (6)             | 144                     |
| N4—H4D···O4 <sup>i</sup>   | 0.90        | 2.45          | 3.223 (7)             | 145                     |
| C4—H4A···O5 <sup>v</sup>   | 0.97        | 2.47          | 3.264 (14)            | 139                     |
| C5—H5B···O4 <sup>i</sup>   | 0.97        | 2.63          | 3.368 (7)             | 133                     |

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

### 4. Synthesis and crystallization

The complex was prepared by mixing copper(II) perchlorate hexahydrate with 1,3-diaminopropane in a (1:2) molar ratio. Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (3.7 g, 1 M) was dissolved in 15 ml of warm water. After an hour, about 10 ml of an ethanol solution of 1,3-diaminopropane (1.48 g, 2M) was added dropwise with continuous stirring. This solution was then filtered to remove

Table 2

Experimental details.

|  |   |
|--|---|
| Crystal data   |   |
| Chemical formula   | [Cu(ClO <sub>4</sub> ) <sub>2</sub> (C <sub>3</sub> H <sub>10</sub> N <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O)]ClO <sub>4</sub> |
| <i>M<sub>r</sub></i>   | 428.72  |
| Crystal system, space group  | Monoclinic, <i>P</i> <sub>2</sub> /c  |
| Temperature (K)  | 293   |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)   | 7.8563 (4), 14.2936 (6), 14.8769 (7)  |
| $\beta$ (°)  | 100.022 (5)   |
| <i>V</i> (Å <sup>3</sup> )   | 1645.11 (13)  |
| <i>Z</i>   | 4   |
| Radiation type   | Mo <i>K</i> $\alpha$  |
| $\mu$ (mm <sup>-1</sup> )  | 1.70  |
| Crystal size (mm)  | 0.30 × 0.30 × 0.25  |
| Data collection  |   |
| Diffractometer   | Oxford Diffraction Xcalibur with an Eos detector  |
| Absorption correction  | Multi-scan ( <i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)  |
| <i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>  | 0.607, 0.654  |
| No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections                             | 7573, 2900, 2353  |
| <i>R<sub>int</sub></i>   | 0.032   |
| (sin $\theta$ /λ) <sub>max</sub> (Å <sup>-1</sup> )  | 0.595   |
| Refinement   |   |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.046, 0.127, 1.06  |
| No. of reflections   | 2900  |
| No. of parameters  | 242   |
| No. of restraints  | 109   |
| H-atom treatment   | H atoms treated by a mixture of independent and constrained refinement  |
| $\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )                                     | 0.60, -0.42   |

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

any impurities and the solution was kept over  $P_2O_5$  in a desiccator. Finally, violet–purple-coloured crystals suitable for X-ray diffraction analysis were harvested and washed repeatedly with cold water (yield 70%).

## 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The water H atoms were located in a difference Fourier map and refined with a distance restraint,  $O-H = 0.90$  (2) Å, and with  $U_{iso}(H) = 1.5U_{eq}(O)$ . The N- and C-bound H atoms were positioned geometrically and allowed to ride on their parent atoms, with  $N-H = 0.90$  and  $C-H = 0.97$  Å, and with  $U_{iso}(H) = 1.2U_{eq}(N,C)$ . The disordered coordinating perchlorate anion, involving atom Cl2, was refined with an occupancy ratio of 0.631 (9):0.369 (9).

## Acknowledgements

JG and ASP are grateful to the CSIR, New Delhi [Lr: No. 01 (2570)/12/EMR-II/3.4.2012] for financial support through a major research project. The authors thank the Department of Chemistry, Pondicherry University, for the single-crystal XRD instrumentation facility.

## References

- Emsley, J., Arif, M., Bates, P. A. & Hursthouse, M. B. (1988). *Inorg. Chim. Acta*, **154**, 17–20.
- Kim, Y., Skelton, B. W. & White, A. H. (2003). *Acta Cryst. C* **59**, m546–m548.
- Oxford Diffraction (2009). *CrysAlis CCD*, *CrysAlis RED* and *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst. D* **65**, 148–155.

## supporting information

*Acta Cryst.* (2014). E70, 438–440 [doi:10.1107/S1600536814023496]

## Crystal structure of *trans*-aqua(perchlorato- $\kappa$ O)bis(propane-1,3-diamine- $\kappa^2$ N,N')copper(II) perchlorate

J. Govindaraj, K. Rajkumar, A. S. Ganeshraja, K. Anbalagan and A. SubbiahPandi

### Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis CCD* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

### *trans*-Aqua(perchlorato- $\kappa$ O)bis(propane-1,3-diamine- $\kappa^2$ N,N')copper(II) perchlorate

#### Crystal data

[Cu(ClO<sub>4</sub>)(C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)]ClO<sub>4</sub>

$M_r = 428.72$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.8563$  (4) Å

$b = 14.2936$  (6) Å

$c = 14.8769$  (7) Å

$\beta = 100.022$  (5)°

$V = 1645.11$  (13) Å<sup>3</sup>

$Z = 4$

$F(000) = 884$

$D_x = 1.731$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2353 reflections

$\theta = 3.8$ – $25.0$ °

$\mu = 1.70$  mm<sup>-1</sup>

$T = 293$  K

Block, violet-purple

$0.30 \times 0.30 \times 0.25$  mm

#### Data collection

Oxford diffraction Xcalibur

diffractometer with an Eos detector

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  and  $\phi$  scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.607$ ,  $T_{\max} = 0.654$

7573 measured reflections

2900 independent reflections

2353 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 25.0$ °,  $\theta_{\min} = 3.8$ °

$h = -9 \rightarrow 9$

$k = -16 \rightarrow 16$

$l = -17 \rightarrow 16$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.127$

$S = 1.06$

2900 reflections

242 parameters

109 restraints

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

$$w = 1/[\sigma^2(F_o^2) + (0.0667P)^2 + 1.2858P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$

$$\Delta\rho_{\max} = 0.60 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$$

### 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 ( $\text{\AA}^2$ )

|     | <i>x</i>    | <i>y</i>    | <i>z</i>   | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-------------|-------------|------------|----------------------------------|-----------|
| C1  | 0.2060 (10) | 0.0648 (5)  | 0.4655 (4) | 0.0879 (19)                      |           |
| H1A | 0.2841      | 0.0599      | 0.5234     | 0.105*                           |           |
| H1B | 0.1231      | 0.0142      | 0.4630     | 0.105*                           |           |
| C2  | 0.1130 (10) | 0.1523 (5)  | 0.4648 (4) | 0.099 (2)                        |           |
| H2A | 0.0517      | 0.1508      | 0.5160     | 0.119*                           |           |
| H2B | 0.1985      | 0.2017      | 0.4771     | 0.119*                           |           |
| C3  | −0.0098 (8) | 0.1800 (5)  | 0.3854 (4) | 0.0846 (17)                      |           |
| H3A | −0.0506     | 0.2423      | 0.3965     | 0.101*                           |           |
| H3B | −0.1084     | 0.1383      | 0.3802     | 0.101*                           |           |
| C4  | 0.1631 (8)  | 0.0875 (3)  | 0.0573 (3) | 0.0667 (14)                      |           |
| H4A | 0.1641      | 0.1259      | 0.0037     | 0.080*                           |           |
| H4B | 0.0489      | 0.0602      | 0.0524     | 0.080*                           |           |
| C5  | 0.2934 (7)  | 0.0105 (3)  | 0.0589 (3) | 0.0659 (13)                      |           |
| H5A | 0.2758      | −0.0197     | −0.0004    | 0.079*                           |           |
| H5B | 0.4083      | 0.0376      | 0.0693     | 0.079*                           |           |
| C6  | 0.2841 (8)  | −0.0610 (3) | 0.1296 (3) | 0.0700 (14)                      |           |
| H6A | 0.1671      | −0.0851     | 0.1218     | 0.084*                           |           |
| H6B | 0.3597      | −0.1126     | 0.1208     | 0.084*                           |           |
| N1  | 0.3041 (7)  | 0.0504 (4)  | 0.3943 (3) | 0.0860 (15)                      |           |
| H1C | 0.3285      | −0.0111     | 0.3940     | 0.103*                           |           |
| H1D | 0.4054      | 0.0803      | 0.4113     | 0.103*                           |           |
| N2  | 0.0484 (6)  | 0.1812 (3)  | 0.2978 (3) | 0.0705 (12)                      |           |
| H2C | 0.0951      | 0.2380      | 0.2925     | 0.085*                           |           |
| H2D | −0.0471     | 0.1780      | 0.2546     | 0.085*                           |           |
| N3  | 0.3333 (6)  | −0.0259 (3) | 0.2235 (3) | 0.0678 (11)                      |           |
| H3C | 0.4473      | −0.0136     | 0.2325     | 0.081*                           |           |
| H3D | 0.3180      | −0.0730     | 0.2614     | 0.081*                           |           |
| N4  | 0.1967 (6)  | 0.1474 (2)  | 0.1393 (2) | 0.0573 (10)                      |           |
| H4C | 0.1117      | 0.1902      | 0.1342     | 0.069*                           |           |
| H4D | 0.2958      | 0.1786      | 0.1382     | 0.069*                           |           |
| O1  | 0.3452 (8)  | −0.1512 (3) | 0.4593 (5) | 0.149 (2)                        |           |
| O2  | 0.1810 (6)  | −0.2818 (4) | 0.4266 (4) | 0.1161 (16)                      |           |

|     |               |              |             |            |           |
|-----|---------------|--------------|-------------|------------|-----------|
| O3  | 0.3230 (12)   | −0.2194 (6)  | 0.3219 (5)  | 0.185 (3)  |           |
| O4  | 0.4749 (7)    | −0.2926 (4)  | 0.4506 (5)  | 0.156 (3)  |           |
| Cl1 | 0.33528 (15)  | −0.23745 (7) | 0.41570 (8) | 0.0557 (3) |           |
| Cl2 | −0.18163 (15) | −0.06425 (9) | 0.24310 (7) | 0.0576 (3) |           |
| Cu1 | 0.21563 (6)   | 0.08711 (3)  | 0.26368 (3) | 0.0411 (2) |           |
| O5  | −0.2890 (12)  | −0.1162 (7)  | 0.1754 (6)  | 0.102 (3)  | 0.631 (9) |
| O6  | −0.2845 (9)   | −0.0126 (8)  | 0.2958 (6)  | 0.109 (3)  | 0.631 (9) |
| O7  | −0.0828 (12)  | −0.0013 (7)  | 0.2023 (6)  | 0.133 (4)  | 0.631 (9) |
| O8  | −0.0665 (16)  | −0.1226 (7)  | 0.3013 (6)  | 0.142 (4)  | 0.631 (9) |
| O5′ | −0.188 (3)    | −0.1082 (17) | 0.1585 (9)  | 0.156 (9)  | 0.369 (9) |
| O6′ | −0.0084 (12)  | −0.0497 (11) | 0.2830 (12) | 0.117 (5)  | 0.369 (9) |
| O7′ | −0.2628 (19)  | 0.0227 (8)   | 0.2243 (14) | 0.131 (6)  | 0.369 (9) |
| O8′ | −0.258 (2)    | −0.1212 (13) | 0.2983 (10) | 0.138 (6)  | 0.369 (9) |
| O9  | 0.4814 (7)    | 0.1951 (5)   | 0.3062 (4)  | 0.133 (2)  |           |
| H9B | 0.557 (10)    | 0.173 (8)    | 0.272 (6)   | 0.200*     |           |
| H9A | 0.536 (11)    | 0.222 (7)    | 0.357 (4)   | 0.200*     |           |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$    | $U^{13}$    | $U^{23}$     |
|-----|------------|------------|------------|-------------|-------------|--------------|
| C1  | 0.121 (5)  | 0.097 (4)  | 0.048 (3)  | 0.019 (4)   | 0.022 (3)   | 0.011 (3)    |
| C2  | 0.141 (6)  | 0.105 (5)  | 0.058 (3)  | 0.035 (5)   | 0.032 (4)   | −0.006 (3)   |
| C3  | 0.081 (4)  | 0.101 (4)  | 0.076 (4)  | 0.024 (3)   | 0.026 (3)   | −0.019 (3)   |
| C4  | 0.092 (4)  | 0.062 (3)  | 0.045 (2)  | 0.005 (3)   | 0.009 (3)   | 0.003 (2)    |
| C5  | 0.073 (3)  | 0.067 (3)  | 0.064 (3)  | −0.004 (3)  | 0.028 (3)   | −0.013 (2)   |
| C6  | 0.081 (4)  | 0.054 (3)  | 0.076 (3)  | 0.015 (3)   | 0.017 (3)   | −0.014 (2)   |
| N1  | 0.115 (4)  | 0.086 (3)  | 0.056 (2)  | 0.043 (3)   | 0.013 (3)   | 0.019 (2)    |
| N2  | 0.088 (3)  | 0.066 (3)  | 0.063 (2)  | 0.036 (2)   | 0.028 (2)   | 0.0098 (19)  |
| N3  | 0.078 (3)  | 0.060 (2)  | 0.064 (2)  | 0.031 (2)   | 0.010 (2)   | 0.0014 (19)  |
| N4  | 0.080 (3)  | 0.045 (2)  | 0.049 (2)  | 0.0049 (19) | 0.0173 (19) | 0.0063 (15)  |
| O1  | 0.138 (5)  | 0.072 (3)  | 0.221 (6)  | 0.001 (3)   | −0.014 (4)  | −0.046 (4)   |
| O2  | 0.078 (3)  | 0.114 (3)  | 0.163 (5)  | −0.024 (3)  | 0.039 (3)   | 0.001 (3)    |
| O3  | 0.245 (9)  | 0.197 (7)  | 0.139 (5)  | 0.046 (6)   | 0.107 (6)   | 0.062 (5)    |
| O4  | 0.080 (3)  | 0.107 (4)  | 0.276 (8)  | 0.042 (3)   | 0.021 (4)   | 0.059 (5)    |
| Cl1 | 0.0524 (6) | 0.0451 (6) | 0.0733 (7) | 0.0054 (5)  | 0.0212 (6)  | 0.0074 (5)   |
| Cl2 | 0.0526 (6) | 0.0603 (7) | 0.0599 (7) | −0.0013 (5) | 0.0092 (5)  | −0.0059 (5)  |
| Cu1 | 0.0435 (3) | 0.0393 (3) | 0.0415 (3) | 0.0075 (2)  | 0.0096 (2)  | 0.00435 (19) |
| O5  | 0.104 (6)  | 0.099 (5)  | 0.097 (6)  | −0.017 (5)  | 0.002 (5)   | −0.030 (5)   |
| O6  | 0.069 (4)  | 0.162 (9)  | 0.098 (5)  | 0.007 (5)   | 0.019 (4)   | −0.049 (6)   |
| O7  | 0.109 (7)  | 0.167 (8)  | 0.127 (7)  | −0.064 (6)  | 0.037 (6)   | 0.023 (6)    |
| O8  | 0.185 (10) | 0.101 (6)  | 0.117 (6)  | 0.043 (7)   | −0.040 (7)  | 0.016 (5)    |
| O5′ | 0.23 (2)   | 0.172 (15) | 0.059 (8)  | 0.010 (18)  | 0.020 (12)  | −0.023 (9)   |
| O6′ | 0.045 (6)  | 0.115 (11) | 0.184 (14) | −0.002 (7)  | −0.002 (7)  | 0.008 (10)   |
| O7′ | 0.108 (11) | 0.064 (7)  | 0.203 (16) | 0.002 (7)   | −0.022 (12) | −0.012 (9)   |
| O8′ | 0.128 (12) | 0.182 (15) | 0.109 (10) | −0.019 (12) | 0.036 (9)   | 0.044 (10)   |
| O9  | 0.118 (4)  | 0.150 (5)  | 0.133 (5)  | −0.054 (4)  | 0.024 (4)   | −0.030 (4)   |

*Geometric parameters (Å, °)*

|            |           |             |            |
|------------|-----------|-------------|------------|
| C1—N1      | 1.429 (7) | N2—H2C      | 0.9000     |
| C1—C2      | 1.447 (8) | N2—H2D      | 0.9000     |
| C1—H1A     | 0.9700    | N3—Cu1      | 2.003 (4)  |
| C1—H1B     | 0.9700    | N3—H3C      | 0.9000     |
| C2—C3      | 1.445 (9) | N3—H3D      | 0.9000     |
| C2—H2A     | 0.9700    | N4—Cu1      | 2.023 (3)  |
| C2—H2B     | 0.9700    | N4—H4C      | 0.9000     |
| C3—N2      | 1.454 (6) | N4—H4D      | 0.9000     |
| C3—H3A     | 0.9700    | O1—Cl1      | 1.388 (5)  |
| C3—H3B     | 0.9700    | O2—Cl1      | 1.402 (4)  |
| C4—N4      | 1.476 (6) | O3—Cl1      | 1.406 (6)  |
| C4—C5      | 1.500 (7) | O4—Cl1      | 1.377 (5)  |
| C4—H4A     | 0.9700    | Cl2—O8'     | 1.368 (11) |
| C4—H4B     | 0.9700    | Cl2—O7      | 1.395 (7)  |
| C5—C6      | 1.478 (7) | Cl2—O5'     | 1.399 (12) |
| C5—H5A     | 0.9700    | Cl2—O6'     | 1.402 (9)  |
| C5—H5B     | 0.9700    | Cl2—O7'     | 1.403 (10) |
| C6—N3      | 1.471 (6) | Cl2—O5      | 1.408 (7)  |
| C6—H6A     | 0.9700    | Cl2—O8      | 1.411 (7)  |
| C6—H6B     | 0.9700    | Cl2—O6      | 1.425 (6)  |
| N1—Cu1     | 2.015 (4) | O9—H9B      | 0.90 (2)   |
| N1—H1C     | 0.9000    | O9—H9A      | 0.89 (2)   |
| N1—H1D     | 0.9000    | Cu1—O9      | 2.585 (6)  |
| N2—Cu1     | 2.006 (4) | Cu1—O7      | 2.680 (1)  |
|            |           |             |            |
| N1—C1—C2   | 117.2 (5) | C6—N3—H3D   | 107.3      |
| N1—C1—H1A  | 108.0     | Cu1—N3—H3D  | 107.3      |
| C2—C1—H1A  | 108.0     | H3C—N3—H3D  | 106.9      |
| N1—C1—H1B  | 108.0     | C4—N4—Cu1   | 118.9 (3)  |
| C2—C1—H1B  | 108.0     | C4—N4—H4C   | 107.6      |
| H1A—C1—H1B | 107.3     | Cu1—N4—H4C  | 107.6      |
| C3—C2—C1   | 120.5 (5) | C4—N4—H4D   | 107.6      |
| C3—C2—H2A  | 107.2     | Cu1—N4—H4D  | 107.6      |
| C1—C2—H2A  | 107.2     | H4C—N4—H4D  | 107.0      |
| C3—C2—H2B  | 107.2     | O4—Cl1—O1   | 110.8 (4)  |
| C1—C2—H2B  | 107.2     | O4—Cl1—O2   | 110.2 (3)  |
| H2A—C2—H2B | 106.8     | O1—Cl1—O2   | 109.1 (4)  |
| C2—C3—N2   | 117.8 (5) | O4—Cl1—O3   | 113.1 (5)  |
| C2—C3—H3A  | 107.9     | O1—Cl1—O3   | 106.8 (5)  |
| N2—C3—H3A  | 107.9     | O2—Cl1—O3   | 106.6 (5)  |
| C2—C3—H3B  | 107.9     | O8'—Cl2—O7  | 169.0 (9)  |
| N2—C3—H3B  | 107.9     | O8'—Cl2—O5' | 108.7 (11) |
| H3A—C3—H3B | 107.2     | O7—Cl2—O5'  | 80.5 (10)  |
| N4—C4—C5   | 112.9 (4) | O8'—Cl2—O6' | 109.2 (10) |
| N4—C4—H4A  | 109.0     | O7—Cl2—O6'  | 61.0 (7)   |
| C5—C4—H4A  | 109.0     | O5'—Cl2—O6' | 109.2 (10) |

|              |            |              |            |
|--------------|------------|--------------|------------|
| N4—C4—H4B    | 109.0      | O8'—Cl2—O7'  | 114.5 (10) |
| C5—C4—H4B    | 109.0      | O7—Cl2—O7'   | 67.0 (8)   |
| H4A—C4—H4B   | 107.8      | O5'—Cl2—O7'  | 105.9 (13) |
| C6—C5—C4     | 113.7 (4)  | O6'—Cl2—O7'  | 109.1 (8)  |
| C6—C5—H5A    | 108.8      | O8'—Cl2—O5   | 81.0 (9)   |
| C4—C5—H5A    | 108.8      | O7—Cl2—O5    | 109.8 (6)  |
| C6—C5—H5B    | 108.8      | O5'—Cl2—O5   | 36.4 (9)   |
| C4—C5—H5B    | 108.8      | O6'—Cl2—O5   | 142.9 (7)  |
| H5A—C5—H5B   | 107.7      | O7'—Cl2—O5   | 97.5 (8)   |
| N3—C6—C5     | 113.7 (4)  | O8'—Cl2—O8   | 65.3 (8)   |
| N3—C6—H6A    | 108.8      | O7—Cl2—O8    | 107.6 (6)  |
| C5—C6—H6A    | 108.8      | O5'—Cl2—O8   | 101.9 (11) |
| N3—C6—H6B    | 108.8      | O6'—Cl2—O8   | 50.0 (7)   |
| C5—C6—H6B    | 108.8      | O7'—Cl2—O8   | 150.1 (8)  |
| H6A—C6—H6B   | 107.7      | O5—Cl2—O8    | 111.6 (6)  |
| C1—N1—Cu1    | 122.5 (4)  | O8'—Cl2—O6   | 68.1 (8)   |
| C1—N1—H1C    | 106.7      | O7—Cl2—O6    | 108.5 (6)  |
| Cu1—N1—H1C   | 106.7      | O5'—Cl2—O6   | 142.2 (11) |
| C1—N1—H1D    | 106.7      | O6'—Cl2—O6   | 106.9 (7)  |
| Cu1—N1—H1D   | 106.7      | O7'—Cl2—O6   | 50.9 (8)   |
| H1C—N1—H1D   | 106.6      | O5—Cl2—O6    | 109.9 (5)  |
| C3—N2—Cu1    | 122.8 (3)  | O8—Cl2—O6    | 109.5 (6)  |
| C3—N2—H2C    | 106.6      | N3—Cu1—N2    | 166.5 (2)  |
| Cu1—N2—H2C   | 106.6      | N3—Cu1—N1    | 88.76 (17) |
| C3—N2—H2D    | 106.6      | N2—Cu1—N1    | 93.53 (17) |
| Cu1—N2—H2D   | 106.6      | N3—Cu1—N4    | 91.99 (15) |
| H2C—N2—H2D   | 106.6      | N2—Cu1—N4    | 89.94 (15) |
| C6—N3—Cu1    | 120.0 (3)  | N1—Cu1—N4    | 161.9 (2)  |
| C6—N3—H3C    | 107.3      | H9B—O9—H9A   | 111 (3)    |
| Cu1—N3—H3C   | 107.3      |              |            |
| N1—C1—C2—C3  | 56.0 (10)  | C6—N3—Cu1—N4 | −35.4 (4)  |
| C1—C2—C3—N2  | −53.1 (10) | C3—N2—Cu1—N3 | 79.8 (9)   |
| N4—C4—C5—C6  | 67.7 (6)   | C3—N2—Cu1—N1 | −19.6 (5)  |
| C4—C5—C6—N3  | −66.7 (6)  | C3—N2—Cu1—N4 | 178.1 (5)  |
| C2—C1—N1—Cu1 | −41.1 (9)  | C1—N1—Cu1—N3 | −144.4 (5) |
| C2—C3—N2—Cu1 | 35.8 (8)   | C1—N1—Cu1—N2 | 22.4 (5)   |
| C5—C6—N3—Cu1 | 54.2 (6)   | C1—N1—Cu1—N4 | 123.0 (6)  |
| C5—C4—N4—Cu1 | −55.5 (5)  | C4—N4—Cu1—N3 | 36.2 (4)   |
| C6—N3—Cu1—N2 | 62.7 (8)   | C4—N4—Cu1—N2 | −130.4 (4) |
| C6—N3—Cu1—N1 | 162.7 (4)  | C4—N4—Cu1—N1 | 128.3 (6)  |

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

| $D\cdots H\cdots A$              | $D\cdots H$ | $H\cdots A$ | $D\cdots A$ | $D\cdots H\cdots A$ |
|----------------------------------|-------------|-------------|-------------|---------------------|
| O9—H9B $\cdots$ O3 <sup>i</sup>  | 0.90 (2)    | 2.38 (11)   | 2.917 (9)   | 118 (9)             |
| N1—H1C $\cdots$ O1               | 0.90        | 2.22        | 3.040 (7)   | 151                 |
| N1—H1D $\cdots$ O1 <sup>ii</sup> | 0.90        | 2.69        | 3.511 (8)   | 151                 |



---

|                             |      |      |            |     |
|-----------------------------|------|------|------------|-----|
| N1—H1D···O9                 | 0.90 | 2.41 | 2.927 (8)  | 117 |
| N2—H2C···O5 <sup>iii</sup>  | 0.90 | 2.58 | 3.443 (12) | 162 |
| N2—H2C···O8 <sup>iii</sup>  | 0.90 | 2.42 | 3.183 (10) | 143 |
| N2—H2C···O5 <sup>riii</sup> | 0.90 | 2.39 | 3.23 (3)   | 156 |
| N2—H2D···O3 <sup>iii</sup>  | 0.90 | 2.70 | 3.449 (11) | 141 |
| N3—H3C···O6 <sup>iv</sup>   | 0.90 | 2.15 | 3.014 (9)  | 160 |
| N3—H3C···O7 <sup>riv</sup>  | 0.90 | 2.36 | 3.246 (17) | 169 |
| N3—H3D···O3                 | 0.90 | 2.28 | 3.137 (8)  | 160 |
| N4—H4C···O2 <sup>iii</sup>  | 0.90 | 2.35 | 3.127 (6)  | 144 |
| N4—H4D···O4 <sup>i</sup>    | 0.90 | 2.45 | 3.223 (7)  | 145 |
| C4—H4A···O5 <sup>rv</sup>   | 0.97 | 2.47 | 3.264 (14) | 139 |
| C5—H5B···O4 <sup>i</sup>    | 0.97 | 2.63 | 3.368 (7)  | 133 |

---

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