

# Crystal structure of bis( $\mu_2$ -tetrabromophthalato- $\kappa^2O^1:O^2$ )bis[aqua( $N,N,N',N'$ -tetramethylethane-1,2-diamine- $\kappa^2N,N'$ )-copper(II)]

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In the title complex,  $[\text{Cu}_2(\text{C}_8\text{Br}_4\text{O}_4)_2(\text{C}_6\text{H}_{16}\text{N}_2)_2(\text{H}_2\text{O})_2]$ , the  $\text{Cu}^{\text{II}}$  cation is chelated by a tetramethylethane-1,2-diamine ligand and coordinated by a water molecule as well as bridged by two tetrabromophthalate anions in a distorted  $\text{O}_3\text{N}_2$  trigonal-bipyramidal geometry. The two symmetry-related tetrabromophthalate anions bridge the two  $\text{Cu}^{\text{II}}$  cations, forming a centrosymmetric dinuclear complex in which the  $\text{Cu}\cdots\text{Cu}$  separation is 5.054 (2) Å. Intramolecular classic  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds and weak  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds occur in the dinuclear molecule. In the crystal, the molecules are linked by weak  $\text{C}-\text{H}\cdots\text{Br}$  and  $\text{C}-\text{H}\cdots\text{O}$  interactions into supramolecular chains propagating along the  $b$ -axis direction.

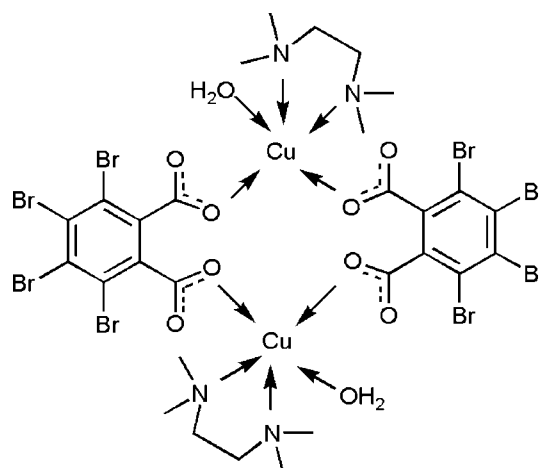
**Keywords:** crystal structure; copper(II) complex; tetramethylethane-1,2-diamine; tetrabromophthalate anion; hydrogen bonding.

**CCDC reference:** 1418832

## 1. Related literature

For the crystal structures of related copper(II) complexes with tetramethylethylen-1,2-diamine and carboxylate ligands; see: Ene *et al.* (2009); Dorazco-González *et al.* (2013); Liang *et al.* (2004). For the synthesis of coordination compounds with one-dimensional polymeric structures, see: Hong & You (2004); Colacio *et al.* (2009); Rodpun *et al.* (2015); Yang *et al.* (2002). For their magnetic properties, see: Ene *et al.* (2009); Kozlevčar *et al.* (2004). For supramolecular polymorphism, see: Dorazco-González *et al.* (2013); Stibrany *et al.* (2009); Aakeröy *et al.*

(2003); Valdés-Martínez *et al.* (1993); Julve *et al.* (1984). For molecular recognition and sensing; see: Dorazco-González & Yatsimirsky (2010); Mendy *et al.* (2010).



## 2. Experimental

### 2.1. Crystal data

$[\text{Cu}_2(\text{C}_8\text{Br}_4\text{O}_4)_2(\text{C}_6\text{H}_{16}\text{N}_2)_2(\text{H}_2\text{O})_2]$   
 $M_r = 1354.97$   
 Monoclinic,  $P2_1/n$   
 $a = 9.0961$  (2) Å  
 $b = 9.2281$  (2) Å  
 $c = 24.4026$  (7) Å  
 $\beta = 95.4910$  (6)°  
 $V = 2038.95$  (9) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 8.94$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.25 \times 0.15 \times 0.08$  mm

### 2.2. Data collection

Bruker APEXII CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2012)  
 $T_{\text{min}} = 0.442$ ,  $T_{\text{max}} = 0.745$   
 17394 measured reflections  
 3739 independent reflections  
 3547 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.019$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$   
 $wR(F^2) = 0.039$   
 $S = 1.07$   
 3739 reflections  
 245 parameters  
 2 restraints  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.80$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.41$  e Å<sup>-3</sup>

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O5}-\text{H5A}\cdots\text{O2}$	0.81 (2)	1.87 (2)	2.649 (2)	161 (2)
$\text{O5}-\text{H5B}\cdots\text{O4}^{\text{i}}$	0.82 (2)	1.83 (2)	2.630 (2)	167 (3)
$\text{C10}-\text{H10A}\cdots\text{Br4}^{\text{ii}}$	0.99	2.84	3.729 (3)	150
$\text{C11}-\text{H11C}\cdots\text{O4}$	0.98	2.40	3.376 (3)	179
$\text{C13}-\text{H13A}\cdots\text{O4}^{\text{iii}}$	0.98	2.58	3.506 (3)	158

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

Data collection: APEX2 (Bruker, 2012); cell refinement: SAINT (Bruker, 2012); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick 2008); program(s) used to refine

structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: XU5866).

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### References

- Aakeröy, C. B., Beatty, A. M., Desper, J., O'Shea, M. & Valdés-Martínez, J. (2003). *Dalton Trans.* pp. 3956–3962.
- Bruker (2012). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc. Madison, Wisconsin, USA.
- Colacio, E., Aouryaghal, H., Mota, A. J., Cano, J., Sillanpää, R. & Rodríguez-Diéguez, A. (2009). *CrystEngComm*, **11**, 2054–2064.
- Dorazco-González, A., Martínez-Vargas, S., Hernández-Ortega, S. & Valdés-Martínez, J. (2013). *CrystEngComm*, **15**, 5961–5968.
- Dorazco-González, A. & Yatsimirsky, A. K. (2010). *Inorg. Chim. Acta*, **363**, 270–274.
- Ene, C. D., Madalan, A. M., Maxim, C., Jurca, B., Avarvari, N. & Andruh, M. (2009). *J. Am. Chem. Soc.* **131**, 4586–4587.
- Hong, C. S. & You, Y. S. (2004). *Polyhedron*, **23**, 3043–3050.
- Julve, M., Faus, J., Verdaguer, M. & Gleizes, A. (1984). *J. Am. Chem. Soc.* **106**, 8306–8308.
- Kozlevčar, B., Leban, I., Petrič, M., Petriček, S., Roubeau, O., Reedijk, J. & Šegedin, P. (2004). *Inorg. Chim. Acta*, **357**, 4220–4230.
- Liang, M., Liao, D.-Z., Jiang, Z.-H., Yan, S.-P. & Cheng, P. (2004). *Inorg. Chem. Commun.* **7**, 173–175.
- Mendy, J. S., Saeed, M. A., Fronczek, F. R., Powell, D. R. & Hossain, A. (2010). *Inorg. Chem.* **49**, 7223–7225.
- Rodpun, K., Blackman, A. G., Gardiner, M. G., Tan, E. W., Meledandri, C. J. & Lucas, N. T. (2015). *CrystEngComm*, **17**, 2974–2988.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Stibrany, R. T. (2009). *J. Chem. Crystallogr.* **39**, 719–722.
- Valdés-Martínez, J., Cervantes-Lee, F. & ter Haar, L. W. (1993). *J. Appl. Phys.* **74**, 1918–1921.
- Yang, S.-Y., Long, L.-S., Wu, Z.-Y., Zhan, M.-X., Huang, R.-B. & Zheng, L.-S. (2002). *Transition Met. Chem.* **27**, 546–549.

## supporting information

*Acta Cryst.* (2015). E71, m171–m172 [doi:10.1107/S2056989015015194]

## Crystal structure of bis( $\mu_2$ -tetrabromophthalato- $\kappa^2O^1:O^2$ )bis[aqua(*N,N,N',N'*-tetramethylethane-1,2-diamine- $\kappa^2N,N'$ )]copper(II)

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### S1. Introduction

The self-assembly of metal complexes with benzene-multicarboxylate ligands remains an active area in coordination chemistry especially with copper due to the very wide structural diversity and interesting properties in magnetism, host-guest systems, porous material (Ene *et al.*, 2009; Dorazco-González *et al.*, 2013; Liang *et al.*, 2004). Dinuclear copper(II) compounds have been used in magnetism, as biomimetic active sites in bioinorganic chemistry and in the design and synthesis of metallic networks (Lu *et al.*, 2004). Herein we present a dinuclear copper complex synthesised by self-assembly between copper perchlorate, a aliphatic diamine (tmen) and a bulky benzendicarboxylate (tetrabromophthalate). The title compound represents the first example of copper complex with tetrabromophthalate.

### S2. Experimental

Compound. Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1 mmol, 0.037 g) was added directly to a solution of tmen (0.1 mmol) in methanol-water solution 1:1 (8 mL). Then the dianion of tetrabromophthalic acid (0.1 mmol, 0.055 g) in methanol-water solution 1:1 again (12 mL) was slowly added with stirring at room temperature, and a slight warming at 50 °C for 3 minutes.

#### S2.1. Synthesis and crystallization

Blue deep suitable crystals for diffraction X-ray were grown directly from solution by slow evaporation during 5 days. IR(KBr pellet), 3012 (w), 2971 (w), 2947 (w), 1741 (s), 1606 (m), 1396 (m), 1504 (w), 1459 (w), 1371 (s), 1315 (m), 1213 (m), 1096 (w), 1018 (w), 951 (w), 867 (w), 805 (w), 765 (w), 733 (w), 558 (w), 525 (w).

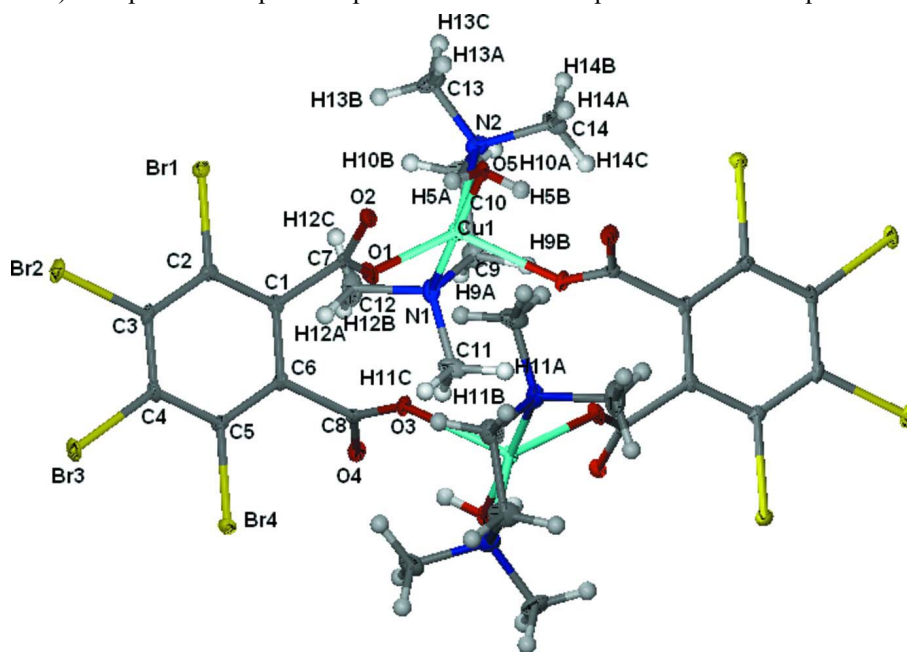
#### S2.2. Refinement

Water H atoms were placed in a difference Fourier map and positional parameters were refined,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . Other H atoms were placed in calculated positions with C—H = 0.98–0.99 Å and refined in riding mode,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for methylene H atoms and  $1.5U_{\text{eq}}(\text{C})$  for methyl H atoms.

### S3. Results and discussion

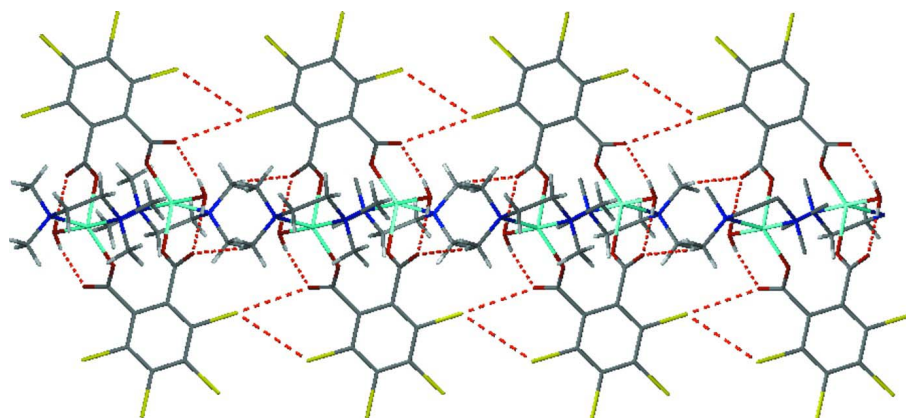
The reaction between the aqua-complex [Cu(tmen)(H<sub>2</sub>O)<sub>x</sub>](ClO<sub>4</sub>)<sub>2</sub> and potassium salt of tetrabromophthalate in mixture ethanol gives the title compound in good yield (>94 %) as blue suitable crystals for X ray diffraction. The single-crystal X-ray analysis reveals that the compound is a neutral dinuclear centro-symmetric copper (II) complex which crystallizes in monoclinic crystal system, space group P21/n (Figure 1). The asymmetric unit contains a five-coordinate copper atom [Cu(N<sub>2</sub>O<sub>3</sub>)] with two sites occupied by diamine and three sites by oxygen atoms from two carboxylate groups and one molecule of water. The Addison tau-parameter has been used to describe the distortion around coordination geometry,  $\tau =$  (difference between two largest angles/60 for five-coordinated metal centers allows the distinction between trigonal-

bipyramidal (ideally  $\tau = 1$ ) and square-pyramidal (ideally  $\tau = 0$ ). In this context, the coordination geometry of complex is distorted trigonal-bypiramide,  $\tau = 0.68$ . The distance Cu  $\cdots$  Cu is 5.054 (2) Å and a macrocycle is formed by 14 atoms containing two TBr-phthalate-bridge ligands. The combination of copper(II) with multi-carboxylic acids has formed one of the largest subgroups in metal-organic compounds and despite this there are few examples of coordination complex with 1,2,3,4,-tetrahalogenated benzenes among these only with tetrachlorophthalate have been reported (Hong & You, 2004; Yang *et al.*, 2002). The present compound represents the first example with tetrabromophthalate.



**Figure 1**

The structure with displacement ellipsoids drawn at the 30% probability level and H atoms shown as small spheres of arbitrary radii.



**Figure 2**

View of interactions in the crystal.

**Bis( $\mu_2$ -tetrabromophthalato- $\kappa^2O^1:O^2$ )bis[aqua( $N,N,N',N'$ -tetramethylethane-1,2-diamine- $\kappa^2N,N'$ )copper(II)]***Crystal data*[Cu<sub>2</sub>(C<sub>8</sub>Br<sub>4</sub>O<sub>4</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] $M_r = 1354.97$ Monoclinic,  $P2_1/n$  $a = 9.0961$  (2) Å $b = 9.2281$  (2) Å $c = 24.4026$  (7) Å $\beta = 95.4910$  (6)° $V = 2038.95$  (9) Å<sup>3</sup> $Z = 2$  $F(000) = 1300$  $D_x = 2.207$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9880 reflections

 $\theta = 2.4$ – $25.7$ ° $\mu = 8.94$  mm<sup>-1</sup> $T = 100$  K

Prism, blue

 $0.25 \times 0.15 \times 0.08$  mm*Data collection*

Bruker APEXII CCD

diffractometer

Radiation source: Incoatec ImuS

Mirrors monochromator

 $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2012)

 $T_{\min} = 0.442$ ,  $T_{\max} = 0.745$ 

17394 measured reflections

3739 independent reflections

3547 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.019$  $\theta_{\max} = 25.4$ °,  $\theta_{\min} = 2.3$ ° $h = -10$ → $10$  $k = -11$ → $11$  $l = -29$ → $29$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.016$  $wR(F^2) = 0.039$  $S = 1.07$ 

3739 reflections

245 parameters

2 restraints

Hydrogen site location: inferred from

neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0162P)^2 + 2.4857P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.002$  $\Delta\rho_{\max} = 0.80$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.41$  e Å<sup>-3</sup>*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.34950 (2)	0.30336 (3)	0.71377 (2)	0.01607 (6)
Br2	0.62992 (3)	0.47283 (3)	0.78249 (2)	0.02118 (6)
Br3	0.95418 (3)	0.47738 (3)	0.73268 (2)	0.01934 (6)
Br4	1.00627 (2)	0.27574 (3)	0.62483 (2)	0.01671 (6)
Cu1	0.32727 (3)	-0.12890 (3)	0.55897 (2)	0.01122 (6)
O1	0.45257 (16)	0.02014 (16)	0.59851 (6)	0.0143 (3)
O2	0.32220 (16)	0.22748 (16)	0.58559 (6)	0.0135 (3)
O3	0.65378 (16)	0.19336 (16)	0.52428 (6)	0.0132 (3)
O4	0.79787 (17)	0.02815 (16)	0.57131 (6)	0.0144 (3)

O5	0.17319 (17)	0.01324 (17)	0.53376 (6)	0.0133 (3)
H5A	0.205 (3)	0.091 (2)	0.5454 (10)	0.016*
H5B	0.179 (3)	0.014 (3)	0.5006 (7)	0.016*
N1	0.4780 (2)	-0.2831 (2)	0.58485 (7)	0.0153 (4)
N2	0.1667 (2)	-0.2787 (2)	0.57861 (8)	0.0180 (4)
C1	0.5567 (2)	0.2309 (2)	0.63834 (8)	0.0102 (4)
C2	0.5382 (2)	0.3046 (2)	0.68693 (8)	0.0108 (4)
C3	0.6563 (2)	0.3755 (2)	0.71631 (8)	0.0119 (4)
C4	0.7951 (2)	0.3723 (2)	0.69622 (8)	0.0123 (4)
C5	0.8155 (2)	0.2926 (2)	0.64905 (8)	0.0114 (4)
C6	0.6979 (2)	0.2221 (2)	0.62005 (8)	0.0101 (4)
C7	0.4303 (2)	0.1547 (2)	0.60456 (8)	0.0104 (4)
C8	0.7190 (2)	0.1388 (2)	0.56745 (8)	0.0112 (4)
C9	0.3941 (3)	-0.4200 (2)	0.57551 (10)	0.0206 (5)
H9A	0.4525	-0.5017	0.5925	0.025*
H9B	0.3757	-0.4388	0.5355	0.025*
C10	0.2483 (3)	-0.4091 (3)	0.60056 (11)	0.0267 (6)
H10A	0.1885	-0.4970	0.5915	0.032*
H10B	0.2665	-0.4022	0.6411	0.032*
C11	0.6075 (3)	-0.2849 (3)	0.55284 (11)	0.0221 (5)
H11A	0.5747	-0.2979	0.5137	0.033*
H11B	0.6728	-0.3651	0.5655	0.033*
H11C	0.6611	-0.1931	0.5581	0.033*
C12	0.5316 (3)	-0.2652 (3)	0.64386 (10)	0.0295 (6)
H12A	0.5925	-0.1776	0.6485	0.044*
H12B	0.5908	-0.3497	0.6564	0.044*
H12C	0.4470	-0.2564	0.6657	0.044*
C13	0.0750 (3)	-0.2171 (3)	0.61946 (10)	0.0270 (6)
H13A	0.0211	-0.1327	0.6036	0.040*
H13B	0.1384	-0.1874	0.6523	0.040*
H13C	0.0045	-0.2903	0.6297	0.040*
C14	0.0693 (3)	-0.3163 (3)	0.52836 (10)	0.0244 (5)
H14A	0.0251	-0.2277	0.5119	0.037*
H14B	-0.0091	-0.3815	0.5381	0.037*
H14C	0.1275	-0.3644	0.5019	0.037*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.01284 (11)	0.02352 (12)	0.01199 (11)	0.00231 (9)	0.00185 (8)	-0.00263 (9)
Br2	0.02459 (13)	0.02531 (13)	0.01399 (11)	-0.00390 (10)	0.00359 (9)	-0.01160 (9)
Br3	0.02013 (12)	0.02323 (13)	0.01411 (11)	-0.01075 (9)	-0.00115 (8)	-0.00597 (9)
Br4	0.01220 (11)	0.02355 (13)	0.01461 (11)	-0.00571 (9)	0.00253 (8)	-0.00292 (9)
Cu1	0.01308 (13)	0.00842 (13)	0.01167 (13)	-0.00056 (10)	-0.00133 (10)	-0.00121 (10)
O1	0.0144 (8)	0.0097 (8)	0.0178 (8)	-0.0008 (6)	-0.0039 (6)	-0.0018 (6)
O2	0.0123 (8)	0.0125 (8)	0.0151 (8)	0.0011 (6)	-0.0019 (6)	-0.0023 (6)
O3	0.0172 (8)	0.0142 (8)	0.0080 (7)	0.0012 (6)	0.0002 (6)	-0.0017 (6)
O4	0.0168 (8)	0.0129 (8)	0.0130 (7)	0.0032 (6)	-0.0005 (6)	-0.0012 (6)

O5	0.0160 (8)	0.0127 (8)	0.0109 (7)	-0.0013 (6)	-0.0006 (6)	-0.0043 (6)
N1	0.0210 (10)	0.0108 (9)	0.0136 (9)	-0.0004 (8)	-0.0011 (7)	0.0003 (7)
N2	0.0196 (10)	0.0167 (10)	0.0185 (10)	-0.0029 (8)	0.0052 (8)	0.0036 (8)
C1	0.0138 (10)	0.0060 (10)	0.0103 (10)	0.0006 (8)	-0.0015 (8)	0.0030 (8)
C2	0.0125 (10)	0.0084 (10)	0.0116 (10)	0.0017 (8)	0.0023 (8)	0.0020 (8)
C3	0.0190 (11)	0.0095 (10)	0.0070 (10)	0.0005 (9)	0.0003 (8)	-0.0012 (8)
C4	0.0160 (11)	0.0100 (10)	0.0100 (10)	-0.0037 (9)	-0.0040 (8)	0.0007 (8)
C5	0.0131 (10)	0.0115 (10)	0.0100 (10)	-0.0017 (8)	0.0032 (8)	0.0027 (8)
C6	0.0148 (11)	0.0084 (10)	0.0069 (10)	0.0001 (8)	-0.0003 (8)	0.0031 (8)
C7	0.0122 (10)	0.0117 (11)	0.0074 (9)	-0.0017 (8)	0.0022 (8)	-0.0004 (8)
C8	0.0104 (10)	0.0117 (11)	0.0116 (10)	-0.0047 (9)	0.0025 (8)	-0.0009 (8)
C9	0.0255 (13)	0.0097 (11)	0.0260 (13)	-0.0008 (10)	0.0003 (10)	0.0021 (9)
C10	0.0288 (14)	0.0165 (12)	0.0357 (15)	-0.0019 (11)	0.0077 (11)	0.0117 (11)
C11	0.0169 (12)	0.0180 (12)	0.0311 (14)	0.0039 (10)	0.0009 (10)	0.0069 (10)
C12	0.0426 (16)	0.0238 (14)	0.0194 (13)	0.0077 (12)	-0.0113 (11)	0.0013 (10)
C13	0.0276 (14)	0.0328 (15)	0.0228 (13)	0.0022 (12)	0.0140 (11)	0.0060 (11)
C14	0.0196 (12)	0.0228 (13)	0.0307 (14)	-0.0104 (10)	0.0010 (10)	-0.0042 (11)

*Geometric parameters (Å, °)*

Br1—C2	1.895 (2)	N1—C9	1.482 (3)
Br2—C3	1.883 (2)	N1—C12	1.485 (3)
Br3—C4	1.892 (2)	N2—C13	1.473 (3)
Br4—C5	1.893 (2)	N2—C14	1.484 (3)
Cu1—O5	1.9744 (16)	N2—C10	1.487 (3)
Cu1—O1	1.9776 (15)	C1—C2	1.391 (3)
Cu1—N1	2.0340 (19)	C1—C6	1.402 (3)
Cu1—N2	2.0995 (19)	C1—C7	1.521 (3)
Cu1—O3 <sup>i</sup>	2.1396 (14)	C2—C3	1.396 (3)
O1—C7	1.269 (3)	C3—C4	1.398 (3)
O2—C7	1.243 (3)	C4—C5	1.393 (3)
O3—C8	1.263 (3)	C5—C6	1.387 (3)
O3—Cu1 <sup>i</sup>	2.1396 (14)	C6—C8	1.524 (3)
O4—C8	1.246 (3)	C9—C10	1.516 (3)
N1—C11	1.475 (3)		
O5—Cu1—O1	92.80 (6)	C2—C1—C7	122.73 (19)
O5—Cu1—N1	177.14 (7)	C6—C1—C7	117.98 (18)
O1—Cu1—N1	89.71 (7)	C1—C2—C3	121.13 (19)
O5—Cu1—N2	91.13 (7)	C1—C2—Br1	118.64 (16)
O1—Cu1—N2	136.68 (7)	C3—C2—Br1	120.21 (16)
N1—Cu1—N2	86.10 (8)	C2—C3—C4	119.12 (19)
O5—Cu1—O3 <sup>i</sup>	90.46 (6)	C2—C3—Br2	120.61 (16)
O1—Cu1—O3 <sup>i</sup>	124.17 (6)	C4—C3—Br2	120.27 (15)
N1—Cu1—O3 <sup>i</sup>	89.26 (7)	C5—C4—C3	119.80 (19)
N2—Cu1—O3 <sup>i</sup>	98.90 (7)	C5—C4—Br3	120.18 (16)
C7—O1—Cu1	130.25 (14)	C3—C4—Br3	120.02 (15)
C8—O3—Cu1 <sup>i</sup>	127.37 (14)	C6—C5—C4	120.80 (19)

C11—N1—C9	109.53 (18)	C6—C5—Br4	119.17 (16)
C11—N1—C12	108.07 (19)	C4—C5—Br4	120.01 (16)
C9—N1—C12	111.12 (19)	C5—C6—C1	119.73 (19)
C11—N1—Cu1	113.14 (14)	C5—C6—C8	120.89 (19)
C9—N1—Cu1	103.09 (14)	C1—C6—C8	119.35 (18)
C12—N1—Cu1	111.86 (15)	O2—C7—O1	127.93 (19)
C13—N2—C14	108.52 (19)	O2—C7—C1	118.85 (18)
C13—N2—C10	111.32 (19)	O1—C7—C1	113.20 (18)
C14—N2—C10	110.3 (2)	O4—C8—O3	127.65 (19)
C13—N2—Cu1	110.61 (15)	O4—C8—C6	117.88 (18)
C14—N2—Cu1	109.81 (14)	O3—C8—C6	114.47 (18)
C10—N2—Cu1	106.31 (14)	N1—C9—C10	109.8 (2)
C2—C1—C6	119.26 (19)	N2—C10—C9	109.52 (19)
C6—C1—C2—C3	3.0 (3)	C2—C1—C6—C8	178.75 (18)
C7—C1—C2—C3	-178.78 (19)	C7—C1—C6—C8	0.5 (3)
C6—C1—C2—Br1	-175.50 (15)	Cu1—O1—C7—O2	-1.5 (3)
C7—C1—C2—Br1	2.7 (3)	Cu1—O1—C7—C1	-179.92 (13)
C1—C2—C3—C4	0.2 (3)	C2—C1—C7—O2	60.4 (3)
Br1—C2—C3—C4	178.71 (15)	C6—C1—C7—O2	-121.4 (2)
C1—C2—C3—Br2	-179.24 (15)	C2—C1—C7—O1	-121.0 (2)
Br1—C2—C3—Br2	-0.7 (2)	C6—C1—C7—O1	57.2 (2)
C2—C3—C4—C5	-3.3 (3)	Cu1 <sup>i</sup> —O3—C8—O4	-6.9 (3)
Br2—C3—C4—C5	176.09 (16)	Cu1 <sup>i</sup> —O3—C8—C6	172.16 (13)
C2—C3—C4—Br3	176.10 (15)	C5—C6—C8—O4	66.3 (3)
Br2—C3—C4—Br3	-4.5 (2)	C1—C6—C8—O4	-115.6 (2)
C3—C4—C5—C6	3.3 (3)	C5—C6—C8—O3	-112.8 (2)
Br3—C4—C5—C6	-176.16 (16)	C1—C6—C8—O3	65.3 (3)
C3—C4—C5—Br4	-175.18 (16)	C11—N1—C9—C10	-170.79 (19)
Br3—C4—C5—Br4	5.4 (2)	C12—N1—C9—C10	69.9 (2)
C4—C5—C6—C1	0.0 (3)	Cu1—N1—C9—C10	-50.1 (2)
Br4—C5—C6—C1	178.46 (15)	C13—N2—C10—C9	-148.7 (2)
C4—C5—C6—C8	178.09 (19)	C14—N2—C10—C9	90.8 (2)
Br4—C5—C6—C8	-3.4 (3)	Cu1—N2—C10—C9	-28.2 (2)
C2—C1—C6—C5	-3.1 (3)	N1—C9—C10—N2	54.4 (3)
C7—C1—C6—C5	178.62 (18)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5A <sup>i</sup> ···O2	0.81 (2)	1.87 (2)	2.649 (2)	161 (2)
O5—H5B <sup>i</sup> ···O4 <sup>i</sup>	0.82 (2)	1.83 (2)	2.630 (2)	167 (3)
C10—H10A <sup>i</sup> ···Br4 <sup>ii</sup>	0.99	2.84	3.729 (3)	150
C11—H11C <sup>i</sup> ···O4	0.98	2.40	3.376 (3)	179
C13—H13A <sup>i</sup> ···O4 <sup>iii</sup>	0.98	2.58	3.506 (3)	158

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