

# Bis[ $\mu$ -4,4',6,6'-tetrachloro-2,2'-(piperazine-1,4-diylidimethylene)-diphenolato]dicopper(II)

Koji Kubono,\* Chisato Noshita, Keita Tani and Kunihiro Yokoi

Division of Natural Sciences, Osaka Kyoiku University, Kashiwara, Osaka 582-8582, Japan

Correspondence e-mail: kubono@cc.osaka-kyoiku.ac.jp

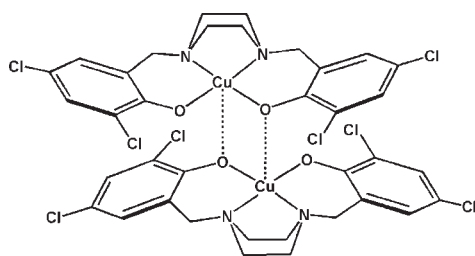
Received 5 November 2009; accepted 20 November 2009

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.041;  $wR$  factor = 0.119; data-to-parameter ratio = 18.9.

In the centrosymmetric dinuclear  $\text{Cu}^{\text{II}}$  title complex,  $[\text{Cu}_2(\text{C}_{18}\text{H}_{16}\text{Cl}_4\text{N}_2\text{O}_2)_2]$ , the  $\text{Cu}^{\text{II}}$  atom adopts a square-pyramidal geometry with a tetradentate ligand in the basal plane. The apical site is occupied by a phenolate O atom from an adjacent ligand, forming a dimer. The molecular structure is stabilized by intramolecular  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{Cl}$  hydrogen bonds.

## Related literature

For the synthesis and the monoclinic and orthorhombic polymorphs of a tetrachloro-2,2'-(piperazine-1,4-diylidimethylene)diphenol, see: Kubono & Yokoi (2007). For related structures, see: Butcher *et al.* (2007); Kubono *et al.* (2003); Massoud & Mautner (2004); Weinberger *et al.* (2000).



## Experimental

### Crystal data

$[\text{Cu}_2(\text{C}_{18}\text{H}_{16}\text{Cl}_4\text{N}_2\text{O}_2)_2]$	$V = 4023.9(7)$ Å <sup>3</sup>
$M_r = 995.36$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 20.1772(18)$ Å	$\mu = 1.63$ mm <sup>-1</sup>
$b = 15.3901(18)$ Å	$T = 296$ K
$c = 15.1397(14)$ Å	$0.20 \times 0.08 \times 0.07$ mm
$\beta = 121.140(6)^\circ$	

### Data collection

Rigaku AFC-7R diffractometer	2574 reflections with $I > 2\sigma(I)$
Absorption correction: $\psi$ scan	$R_{\text{int}} = 0.046$
(North <i>et al.</i> , 1968)	3 standard reflections
$T_{\text{min}} = 0.855$ , $T_{\text{max}} = 0.892$	every 150 reflections
4759 measured reflections	intensity decay: 0.7%
4634 independent reflections	

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	245 parameters
$wR(F^2) = 0.119$	H-atom parameters constrained
$S = 0.99$	$\Delta\rho_{\text{max}} = 0.37$ e Å <sup>-3</sup>
4634 reflections	$\Delta\rho_{\text{min}} = -0.39$ e Å <sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	1.913 (2)	Cu1—N1	2.026 (4)
Cu1—O2	1.955 (2)	Cu1—N2	2.033 (3)
Cu1—O2 <sup>i</sup>	2.381 (3)		
O1—Cu1—O2	97.69 (11)	O2—Cu1—N2	92.90 (12)
O1—Cu1—O2 <sup>i</sup>	96.68 (12)	O2 <sup>i</sup> —Cu1—N1	104.18 (13)
O1—Cu1—N1	93.97 (12)	O2 <sup>i</sup> —Cu1—N2	97.64 (12)
O2—Cu1—O2 <sup>i</sup>	85.84 (11)	N1—Cu1—N2	73.22 (13)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
C11—H12 $\cdots$ Cl4 <sup>i</sup>	0.97	2.76	3.544 (5)	138
C12—H14 $\cdots$ O1 <sup>i</sup>	0.97	2.19	3.112 (6)	159

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

Data collection: *WinAFC* (Rigaku/MS, 2006); cell refinement: *WinAFC*; data reduction: *CrystalStructure* (Rigaku/MS, 2006); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *CrystalStructure*.

This study was supported financially in part by Grants-in-Aid (No. 20550075) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FK2007).

## References

- Altomare, A., Casciarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Butcher, R. J., Pourian, M. & Jasinski, J. P. (2007). *Acta Cryst.* **E63**, m1913–m1914.
- Kubono, K., Hirayama, N., Kokusen, H. & Yokoi, K. (2003). *Anal. Sci.* **19**, 645–646.
- Kubono, K. & Yokoi, K. (2007). *Acta Cryst.* **C63**, o535–o537.
- Massoud, S. S. & Mautner, F. A. (2004). *Inorg. Chem. Commun.* **7**, 559–562.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

# metal-organic compounds

---

Rigaku/MSK (2006). *WinAFC* and *CrystalStructure*. Rigaku/MSK, The Woodlands, Texas, USA.  
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.  
Weinberger, P., Costisor, O., Tudose, R., Baumgartner, O. & Linert, W. (2000). *J. Mol. Struct.* **519**, 21–31.

**supplementary materials**

*Acta Cryst.* (2009). E65, m1685-m1686 [ doi:10.1107/S1600536809049800 ]

## Bis[ $\mu$ -4,4',6,6'-tetrachloro-2,2'-(piperazine-1,4-diyl dimethylene)diphenolato]dicopper(II)

K. Kubono, C. Noshita, K. Tani and K. Yokoi

### Comment

Recently, we have reported the crystal structure of tetrachloro-2,2'-(piperazine-1,4-diyl dimethylene)diphenol, H<sub>2</sub>Cl<sub>2</sub>bpi (Kubono & Yokoi, 2007). As a continuation of this work on the structural characterization of piperazinediphenol compounds, the title dinuclear Cu<sup>II</sup> complex (Fig. 1) is reported here. The Cu<sup>II</sup> atom has a square-pyramidal coordination geometry with the basal plane comprised of two phenolate O and two tertiary alkyl N atoms from a piperazinediphenol ligand. The apical site is occupied by a phenolate O atom from an adjacent ligand generated by inversion operation, building a centrosymmetric dimer. The Cu...Cu distance within the dimer is 3.1883 (10) Å. The dihedral angle between the benzene rings (C1–C6 and C13–C18) is 87.96 (16) °. The coordination bond lengths and angles (Table 1) are comparable to those observed in related complexes (Butcher *et al.*, 2007; Kubono *et al.*, 2003; Massoud *et al.*, 2004; Weinberger *et al.*, 2000). The molecular structure complex is stabilized by intramolecular C—H...O and C—H...Cl hydrogen bonds (Table 2).

### Experimental

H<sub>2</sub>Cl<sub>2</sub>bpi (0.109 g, 0.25 mmol) was dissolved in 30 ml hot chloroform. Then 30 ml of a methanol solution of copper acetate monohydrate (0.0499 g, 0.25 mmol) were added to this solution. The mixture was stirred for 20 min at 340 K. After a few days at room temperature, dark-green crystals of (I) were obtained. Yield 24.4%. Analysis calculated for C<sub>36</sub>H<sub>32</sub>Cl<sub>8</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>4</sub>: C 43.44, H 3.24, N 5.63%; found: C 43.05, H 3.22, N 5.53%.

### Refinement

All H atoms were placed at idealized positions and refined as a riding atoms, with C—H = 0.93–0.97 Å and  $U_{iso}(H) = 1.2 U_{eq}(C)$ .

### Figures

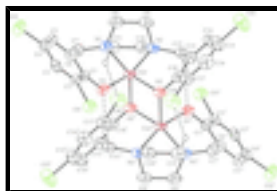


Fig. 1. The molecule of the title complex showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. Only the H atoms involved in the hydrogen bonds are represented by circles of arbitrary size. [Symmetry code: (i) 1/2 - x, 1/2 - y, -z.]

## Bis[ $\mu$ -4,4',6,6'-tetrachloro-2,2'-(piperazine-1,4-diyl dimethylene)diphenolato]dicopper(II)

### Crystal data

[Cu<sub>2</sub>(C<sub>18</sub>H<sub>16</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]

$F(000) = 2008.00$

# supplementary materials

---

$$M_r = 995.36$$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$$a = 20.1772\ (18)\ \text{\AA}$$

$$b = 15.3901\ (18)\ \text{\AA}$$

$$c = 15.1397\ (14)\ \text{\AA}$$

$$\beta = 121.140\ (6)^\circ$$

$$V = 4023.9\ (7)\ \text{\AA}^3$$

$$Z = 4$$

$$D_x = 1.643\ \text{Mg m}^{-3}$$

Mo  $K\alpha$  radiation,  $\lambda = 0.71069\ \text{\AA}$

Cell parameters from 25 reflections

$$\theta = 13.4\text{--}14.9^\circ$$

$$\mu = 1.63\ \text{mm}^{-1}$$

$$T = 296\ \text{K}$$

Column, dark-green

$$0.20 \times 0.08 \times 0.07\ \text{mm}$$

## Data collection

Rigaku AFC-7R  
diffractometer

$\omega$ -2 $\theta$  scans

Absorption correction:  $\psi$  scan  
(North *et al.*, 1968)

$$T_{\min} = 0.855, T_{\max} = 0.892$$

4759 measured reflections

4634 independent reflections

2574 reflections with  $I > 2\sigma(I)$

$$R_{\text{int}} = 0.046$$

$$\theta_{\max} = 27.5^\circ$$

$$h = 0 \rightarrow 26$$

$$k = 0 \rightarrow 19$$

$$l = -19 \rightarrow 16$$

3 standard reflections every 150 reflections

intensity decay: 0.7%

## Refinement

Refinement on  $F^2$

$$R[F^2 > 2\sigma(F^2)] = 0.041$$

$$wR(F^2) = 0.119$$

$$S = 0.99$$

4634 reflections

245 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.37\ \text{e \AA}^{-3}$$

$$\Delta\rho_{\min} = -0.39\ \text{e \AA}^{-3}$$

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

$x$

$y$

$z$

$U_{\text{iso}}^*/U_{\text{eq}}$

Cu1	0.23572 (3)	0.25394 (3)	0.09411 (4)	0.03688 (13)
Cl1	0.42437 (6)	0.45428 (7)	0.29614 (8)	0.0506 (2)
Cl2	0.41605 (8)	0.34818 (11)	0.62836 (9)	0.0812 (4)
Cl3	-0.07156 (8)	0.53920 (10)	-0.17092 (12)	0.0863 (4)
Cl4	0.23821 (7)	0.53026 (7)	0.00693 (10)	0.0645 (3)
O1	0.33424 (16)	0.29710 (19)	0.1996 (2)	0.0490 (7)
O2	0.21681 (15)	0.33844 (16)	-0.01288 (19)	0.0391 (6)
N1	0.22348 (19)	0.1741 (2)	0.1911 (2)	0.0421 (7)
N2	0.12414 (18)	0.2118 (2)	0.0166 (2)	0.0381 (7)
C1	0.3513 (2)	0.3070 (2)	0.2952 (2)	0.0384 (8)
C2	0.3933 (2)	0.3796 (2)	0.3535 (2)	0.0356 (8)
C3	0.4129 (2)	0.3920 (2)	0.4540 (3)	0.0427 (9)
C4	0.3895 (2)	0.3322 (3)	0.4996 (3)	0.0497 (10)
C5	0.3496 (2)	0.2591 (2)	0.4474 (3)	0.0498 (10)
C6	0.3311 (2)	0.2455 (2)	0.3472 (3)	0.0421 (8)
C7	0.2937 (2)	0.1606 (2)	0.2929 (3)	0.0494 (10)
C8	0.1593 (2)	0.2145 (3)	0.1957 (3)	0.0550 (11)
C9	0.0965 (2)	0.2379 (2)	0.0862 (3)	0.0498 (10)
C10	0.1323 (2)	0.1156 (2)	0.0214 (3)	0.0493 (10)
C11	0.1958 (2)	0.0924 (2)	0.1308 (3)	0.0509 (10)
C12	0.0751 (2)	0.2445 (2)	-0.0894 (3)	0.0440 (9)
C13	0.0784 (2)	0.3422 (2)	-0.0909 (3)	0.0435 (9)
C14	0.0111 (2)	0.3904 (3)	-0.1272 (3)	0.0548 (11)
C15	0.0140 (2)	0.4794 (3)	-0.1254 (3)	0.0582 (11)
C16	0.0832 (2)	0.5220 (3)	-0.0846 (3)	0.0588 (12)
C17	0.1506 (2)	0.4743 (2)	-0.0473 (3)	0.0474 (9)
C18	0.1510 (2)	0.3828 (2)	-0.0497 (3)	0.0393 (8)
H1	0.4417	0.4403	0.4907	0.051*
H2	0.3350	0.2185	0.4797	0.060*
H3	0.3308	0.1272	0.2844	0.059*
H4	0.2805	0.1271	0.3359	0.059*
H5	0.1772	0.2662	0.2383	0.066*
H6	0.1391	0.1743	0.2255	0.066*
H7	0.0488	0.2076	0.0675	0.060*
H8	0.0865	0.2999	0.0808	0.060*
H9	0.1462	0.0957	-0.0277	0.059*
H10	0.0839	0.0884	0.0049	0.059*
H11	0.1756	0.0535	0.1618	0.061*
H12	0.2381	0.0634	0.1300	0.061*
H13	0.0221	0.2259	-0.1168	0.053*
H14	0.0929	0.2206	-0.1329	0.053*
H15	-0.0361	0.3622	-0.1529	0.066*
H16	0.0849	0.5824	-0.0820	0.070*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0394 (2)	0.0371 (2)	0.0428 (2)	-0.0113 (2)	0.0273 (2)	-0.0080 (2)

## supplementary materials

---

C11	0.0544 (6)	0.0427 (5)	0.0575 (6)	-0.0089 (4)	0.0308 (5)	-0.0021 (4)
C12	0.0865 (9)	0.1165 (12)	0.0375 (6)	0.0042 (8)	0.0298 (6)	-0.0045 (7)
C13	0.0662 (8)	0.0757 (9)	0.0988 (11)	0.0224 (7)	0.0297 (7)	-0.0121 (8)
C14	0.0670 (7)	0.0423 (6)	0.0935 (9)	-0.0160 (5)	0.0482 (7)	-0.0237 (6)
O1	0.0489 (16)	0.0635 (19)	0.0403 (15)	-0.0248 (14)	0.0272 (13)	-0.0149 (14)
O2	0.0414 (14)	0.0367 (14)	0.0448 (15)	-0.0073 (12)	0.0263 (12)	-0.0059 (12)
N1	0.0474 (19)	0.0402 (19)	0.0470 (19)	-0.0135 (14)	0.0304 (16)	-0.0111 (15)
N2	0.0384 (17)	0.0362 (16)	0.0497 (19)	-0.0090 (14)	0.0298 (16)	-0.0095 (15)
C1	0.0337 (19)	0.045 (2)	0.037 (2)	-0.0012 (16)	0.0183 (16)	-0.0034 (17)
C2	0.0314 (18)	0.0345 (19)	0.038 (2)	0.0022 (15)	0.0159 (16)	-0.0009 (16)
C3	0.037 (2)	0.039 (2)	0.043 (2)	0.0103 (17)	0.0138 (18)	-0.0039 (18)
C4	0.046 (2)	0.064 (2)	0.035 (2)	0.015 (2)	0.0181 (19)	0.003 (2)
C5	0.046 (2)	0.060 (2)	0.046 (2)	0.005 (2)	0.025 (2)	0.011 (2)
C6	0.043 (2)	0.042 (2)	0.045 (2)	-0.0020 (19)	0.0247 (18)	-0.0021 (19)
C7	0.058 (2)	0.040 (2)	0.055 (2)	-0.0046 (19)	0.032 (2)	0.0053 (19)
C8	0.054 (2)	0.068 (3)	0.059 (2)	-0.009 (2)	0.041 (2)	-0.012 (2)
C9	0.049 (2)	0.050 (2)	0.068 (2)	-0.004 (2)	0.043 (2)	-0.011 (2)
C10	0.045 (2)	0.040 (2)	0.066 (2)	-0.0138 (18)	0.031 (2)	-0.016 (2)
C11	0.064 (2)	0.031 (2)	0.066 (2)	-0.0147 (19)	0.039 (2)	-0.0104 (19)
C12	0.038 (2)	0.045 (2)	0.051 (2)	-0.0141 (19)	0.0248 (18)	-0.017 (2)
C13	0.042 (2)	0.046 (2)	0.040 (2)	-0.0026 (18)	0.0205 (18)	-0.0064 (18)
C14	0.040 (2)	0.063 (3)	0.057 (2)	-0.006 (2)	0.022 (2)	-0.014 (2)
C15	0.055 (2)	0.056 (2)	0.055 (2)	0.012 (2)	0.023 (2)	-0.007 (2)
C16	0.072 (3)	0.039 (2)	0.069 (3)	-0.001 (2)	0.038 (2)	-0.009 (2)
C17	0.050 (2)	0.043 (2)	0.055 (2)	-0.0035 (19)	0.031 (2)	-0.011 (2)
C18	0.045 (2)	0.036 (2)	0.040 (2)	-0.0041 (17)	0.0241 (18)	-0.0073 (17)

### *Geometric parameters (Å, °)*

Cu1—O1	1.913 (2)	C10—C11	1.523 (5)
Cu1—O2	1.955 (2)	C12—C13	1.505 (5)
Cu1—O2 <sup>i</sup>	2.381 (3)	C13—C14	1.387 (6)
Cu1—N1	2.026 (4)	C13—C18	1.408 (5)
Cu1—N2	2.033 (3)	C14—C15	1.371 (6)
C11—C2	1.740 (4)	C15—C16	1.368 (7)
C12—C4	1.751 (4)	C16—C17	1.383 (6)
C13—C15	1.752 (5)	C17—C18	1.409 (5)
C14—C17	1.744 (4)	C3—H1	0.930
O1—C1	1.313 (5)	C5—H2	0.930
O2—C18	1.332 (4)	C7—H3	0.970
N1—C7	1.472 (4)	C7—H4	0.970
N1—C8	1.470 (7)	C8—H5	0.970
N1—C11	1.484 (5)	C8—H6	0.970
N2—C9	1.479 (7)	C9—H7	0.970
N2—C10	1.487 (4)	C9—H8	0.970
N2—C12	1.472 (4)	C10—H9	0.970
C1—C2	1.406 (4)	C10—H10	0.970
C1—C6	1.419 (6)	C11—H11	0.970
C2—C3	1.373 (6)	C11—H12	0.970

C3—C4	1.372 (7)	C12—H13	0.970
C4—C5	1.373 (5)	C12—H14	0.970
C5—C6	1.378 (6)	C14—H15	0.930
C6—C7	1.519 (5)	C16—H16	0.930
C8—C9	1.521 (5)		
O1—Cu1—O2	97.69 (11)	C13—C14—C15	120.3 (4)
O1—Cu1—O2 <sup>i</sup>	96.68 (12)	C13—C15—C14	119.7 (3)
O1—Cu1—N1	93.97 (12)	C13—C15—C16	119.6 (3)
O1—Cu1—N2	162.75 (17)	C14—C15—C16	120.7 (4)
O2—Cu1—O2 <sup>i</sup>	85.84 (11)	C15—C16—C17	119.2 (4)
O2—Cu1—N1	163.66 (13)	C14—C17—C16	118.3 (3)
O2—Cu1—N2	92.90 (12)	C14—C17—C18	119.2 (3)
O2 <sup>i</sup> —Cu1—N1	104.18 (13)	C16—C17—C18	122.5 (4)
O2 <sup>i</sup> —Cu1—N2	97.64 (12)	O2—C18—C13	122.8 (3)
N1—Cu1—N2	73.22 (13)	O2—C18—C17	121.3 (3)
Cu1—O1—C1	121.8 (3)	C13—C18—C17	115.9 (3)
Cu1—O2—Cu1 <sup>i</sup>	94.16 (10)	C2—C3—H1	120.4
Cu1—O2—C18	114.4 (3)	C4—C3—H1	120.4
Cu1 <sup>i</sup> —O2—C18	132.1 (2)	C4—C5—H2	119.9
Cu1—N1—C7	115.6 (3)	C6—C5—H2	119.9
Cu1—N1—C8	102.7 (2)	N1—C7—H3	109.1
Cu1—N1—C11	102.5 (2)	N1—C7—H4	109.1
C7—N1—C8	113.9 (3)	C6—C7—H3	109.1
C7—N1—C11	112.1 (2)	C6—C7—H4	109.1
C8—N1—C11	109.0 (3)	H3—C7—H4	107.8
Cu1—N2—C9	102.5 (2)	N1—C8—H5	110.1
Cu1—N2—C10	103.1 (2)	N1—C8—H6	110.1
Cu1—N2—C12	116.0 (2)	C9—C8—H5	110.1
C9—N2—C10	107.9 (3)	C9—C8—H6	110.1
C9—N2—C12	113.3 (3)	H5—C8—H6	108.4
C10—N2—C12	112.8 (3)	N2—C9—H7	110.2
O1—C1—C2	120.9 (4)	N2—C9—H8	110.2
O1—C1—C6	123.2 (3)	C8—C9—H7	110.2
C2—C1—C6	115.8 (3)	C8—C9—H8	110.2
C11—C2—C1	117.9 (3)	H7—C9—H8	108.5
C11—C2—C3	119.3 (2)	N2—C10—H9	110.3
C1—C2—C3	122.7 (4)	N2—C10—H10	110.3
C2—C3—C4	119.2 (3)	C11—C10—H9	110.3
C12—C4—C3	118.7 (3)	C11—C10—H10	110.3
C12—C4—C5	120.4 (4)	H9—C10—H10	108.5
C3—C4—C5	120.8 (4)	N1—C11—H11	110.1
C4—C5—C6	120.2 (4)	N1—C11—H12	110.1
C1—C6—C5	121.2 (3)	C10—C11—H11	110.1
C1—C6—C7	118.5 (4)	C10—C11—H12	110.1
C5—C6—C7	120.2 (4)	H11—C11—H12	108.4
N1—C7—C6	112.6 (3)	N2—C12—H13	109.6
N1—C8—C9	107.8 (4)	N2—C12—H14	109.6

## supplementary materials

---

N2—C9—C8	107.7 (3)	C13—C12—H13	109.6
N2—C10—C11	107.3 (3)	C13—C12—H14	109.6
N1—C11—C10	107.9 (3)	H13—C12—H14	108.1
N2—C12—C13	110.3 (2)	C13—C14—H15	119.8
C12—C13—C14	119.9 (3)	C15—C14—H15	119.8
C12—C13—C18	118.8 (3)	C15—C16—H16	120.4
C14—C13—C18	121.2 (3)	C17—C16—H16	120.4
O1—Cu1—O2—Cu1 <sup>i</sup>	96.20 (12)	C8—N1—C7—C6	-66.1 (5)
O1—Cu1—O2—C18	-123.4 (2)	C7—N1—C11—C10	-170.3 (4)
O2—Cu1—O1—C1	134.9 (2)	C11—N1—C7—C6	169.5 (4)
O1—Cu1—O2 <sup>i</sup> —Cu1 <sup>i</sup>	-97.27 (11)	C8—N1—C11—C10	62.6 (5)
O1—Cu1—O2 <sup>i</sup> —C18 <sup>i</sup>	31.3 (3)	C11—N1—C8—C9	-63.2 (4)
O2 <sup>i</sup> —Cu1—O1—C1	-138.5 (2)	Cu1—N2—C9—C8	-44.0 (3)
O1—Cu1—N1—C7	-12.9 (3)	Cu1—N2—C10—C11	43.3 (4)
O1—Cu1—N1—C8	111.7 (2)	Cu1—N2—C12—C13	-53.1 (4)
O1—Cu1—N1—C11	-135.2 (2)	C9—N2—C10—C11	-64.7 (4)
N1—Cu1—O1—C1	-33.7 (3)	C10—N2—C9—C8	64.4 (3)
O1—Cu1—N2—C9	12.7 (5)	C9—N2—C12—C13	65.1 (4)
O1—Cu1—N2—C10	-99.3 (4)	C12—N2—C9—C8	-169.8 (3)
O1—Cu1—N2—C12	136.8 (4)	C10—N2—C12—C13	-171.8 (4)
N2—Cu1—O1—C1	7.5 (5)	C12—N2—C10—C11	169.2 (4)
O2—Cu1—O2 <sup>i</sup> —C18 <sup>i</sup>	128.6 (3)	O1—C1—C2—C11	-1.8 (5)
O2 <sup>i</sup> —Cu1—O2—C18	140.4 (2)	O1—C1—C2—C3	-179.4 (3)
O2—Cu1—N1—C7	-148.4 (3)	O1—C1—C6—C5	-179.4 (3)
O2—Cu1—N1—C8	-23.8 (5)	O1—C1—C6—C7	5.2 (5)
O2—Cu1—N1—C11	89.3 (5)	C2—C1—C6—C5	2.3 (5)
N1—Cu1—O2—Cu1 <sup>i</sup>	-128.7 (4)	C2—C1—C6—C7	-173.1 (3)
N1—Cu1—O2—C18	11.7 (5)	C6—C1—C2—C11	176.5 (2)
O2—Cu1—N2—C9	-115.2 (2)	C6—C1—C2—C3	-1.0 (5)
O2—Cu1—N2—C10	132.8 (3)	C11—C2—C3—C4	-178.9 (3)
O2—Cu1—N2—C12	8.9 (3)	C1—C2—C3—C4	-1.3 (6)
N2—Cu1—O2—Cu1 <sup>i</sup>	-97.46 (12)	C2—C3—C4—C12	179.2 (3)
N2—Cu1—O2—C18	43.0 (2)	C2—C3—C4—C5	2.5 (6)
O2 <sup>i</sup> —Cu1—N1—C7	85.0 (3)	C12—C4—C5—C6	-177.9 (3)
O2 <sup>i</sup> —Cu1—N1—C8	-150.4 (2)	C3—C4—C5—C6	-1.3 (6)
O2 <sup>i</sup> —Cu1—N1—C11	-37.3 (2)	C4—C5—C6—C1	-1.2 (6)
N1—Cu1—O2 <sup>i</sup> —Cu1 <sup>i</sup>	166.91 (10)	C4—C5—C6—C7	174.1 (4)
N1—Cu1—O2 <sup>i</sup> —C18 <sup>i</sup>	-64.5 (3)	C1—C6—C7—N1	-55.4 (6)
O2 <sup>i</sup> —Cu1—N2—C9	158.6 (2)	C5—C6—C7—N1	129.1 (4)
O2 <sup>i</sup> —Cu1—N2—C10	46.6 (3)	N1—C8—C9—N2	-0.5 (4)
O2 <sup>i</sup> —Cu1—N2—C12	-77.3 (2)	N2—C10—C11—N1	1.5 (6)
N2—Cu1—O2 <sup>i</sup> —Cu1 <sup>i</sup>	92.37 (12)	N2—C12—C13—C14	-120.3 (4)
N2—Cu1—O2 <sup>i</sup> —C18 <sup>i</sup>	-139.0 (3)	N2—C12—C13—C18	56.3 (6)
N1—Cu1—N2—C9	56.1 (2)	C12—C13—C14—C15	177.7 (4)
N1—Cu1—N2—C10	-56.0 (3)	C12—C13—C18—O2	2.5 (7)

N1—Cu1—N2—C12	-179.9 (2)	C12—C13—C18—C17	-176.0 (4)
N2—Cu1—N1—C7	178.8 (3)	C14—C13—C18—O2	179.0 (4)
N2—Cu1—N1—C8	-56.5 (2)	C14—C13—C18—C17	0.5 (7)
N2—Cu1—N1—C11	56.5 (2)	C18—C13—C14—C15	1.1 (8)
Cu1—O1—C1—C2	-140.0 (3)	C13—C14—C15—C13	-179.6 (4)
Cu1—O1—C1—C6	41.7 (5)	C13—C14—C15—C16	-2.2 (8)
Cu1—O2—C18—C13	-54.9 (5)	C13—C15—C16—C17	179.0 (4)
Cu1—O2—C18—C17	123.5 (4)	C14—C15—C16—C17	1.6 (9)
Cu1 <sup>i</sup> —O2—C18—C13	66.2 (6)	C15—C16—C17—C14	-178.5 (4)
Cu1 <sup>i</sup> —O2—C18—C17	-115.3 (4)	C15—C16—C17—C18	0.2 (6)
Cu1—N1—C7—C6	52.4 (5)	C14—C17—C18—O2	-1.0 (7)
Cu1—N1—C8—C9	45.0 (3)	C14—C17—C18—C13	177.5 (3)
Cu1—N1—C11—C10	-45.7 (4)	C16—C17—C18—O2	-179.7 (5)
C7—N1—C8—C9	170.8 (3)	C16—C17—C18—C13	-1.2 (7)

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

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

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C11—H12 $\cdots$ C14 <sup>i</sup>	0.97	2.76	3.544 (5)	138
C12—H14 $\cdots$ O1 <sup>i</sup>	0.97	2.19	3.112 (6)	159

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

Fig. 1

