



# Crystal structure of *catena*-poly[diammonium [di- $\mu$ -oxalato-cuprate(II)]]

Diane A. Dickie<sup>a</sup> and Richard A. Kemp<sup>a,b\*</sup>

<sup>a</sup>Department of Chemistry and Chemical Biology, MSC03 2060, 1 University of New Mexico, Albuquerque, NM 87131, USA, and <sup>b</sup>Advanced Materials Laboratory, Sandia National Laboratories, 1001 University Blvd SE, Albuquerque, NM 87106, USA. \*Correspondence e-mail: rakemp@unm.edu

Received 27 October 2016  
Accepted 4 November 2016

Edited by T. J. Prior, University of Hull, England

**Keywords:** crystal structure; copper; oxalate; hydrogen bonding; ammonium.

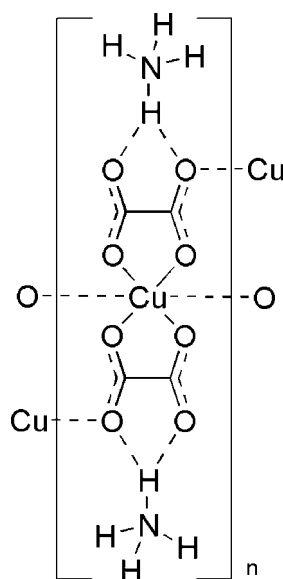
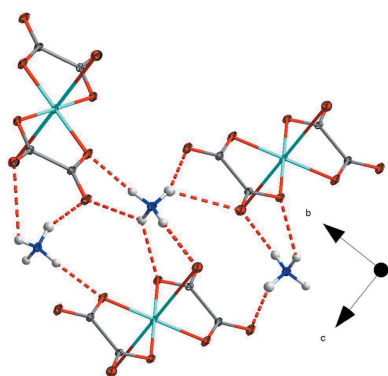
**CCDC reference:** 1515161

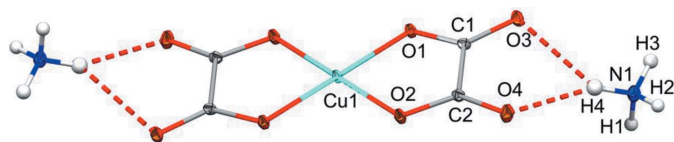
**Supporting information:** this article has supporting information at journals.iucr.org/e

The structure of the title compound,  $\{(\text{NH}_4)_2[\text{Cu}(\text{C}_2\text{O}_4)_2]\}_n$ , at 100 K has monoclinic ( $P2_1/c$ ) symmetry with the  $\text{Cu}^{\text{II}}$  atom on an inversion center. The compound has a polymeric structure due to long  $\text{Cu}\cdots\text{O}$  interactions which create  $[\text{Cu}(\text{C}_2\text{O}_4)_2]$  chains along the  $a$  axis. The structure also displays intermolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonding, which links these chains into a three-dimensional network.

## 1. Chemical context

Metal oxalate salts are ubiquitous in nature (Baran, 2014) and are also of great interest to synthetic chemists and materials scientists because they often display unusual magnetic and conductive properties (Nenwa *et al.*, 2015; Robinson *et al.*, 2015; Zhang *et al.*, 2012; Clemente-León *et al.*, 2011; Gruselle *et al.*, 2006). Other areas of study for metal oxalates include, but are not limited to, metallogels (Feldner *et al.*, 2016), coordination polymers and networks (Guo *et al.*, 2016; Mizzi & LaDuca, 2016; Yeşilel *et al.*, 2010), and precursors for nanomaterials and metallic inks (Yadav *et al.*, 2013; Cheng *et al.*, 2016). The properties of metal oxalates are often tuned by using a combination of different cations. These may be simply metal cations, but often they are more complex, such as quaternary nitrogen cations. Surprisingly, the structure of the simplest of the  $(\text{NR}_4)_2[\text{Cu}(\text{C}_2\text{O}_4)_2]$  family,  $(\text{NH}_4)_2[\text{Cu}(\text{C}_2\text{O}_4)_2]$ , has not previously been reported.





**Figure 1**

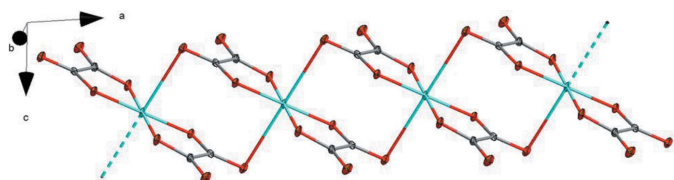
The molecular structure of the title compound, with non-H atoms shown as displacement ellipsoids at the 50% probability level.

## 2. Structural commentary

The title compound crystallizes in the monoclinic space group  $P2_1/c$  with the copper atom on an inversion center (Fig. 1). As is true for all but one copper oxalate complex (Gu & Xue, 2007) found in the CSD (Version 5.37, May 2016 update; Groom *et al.*, 2016), the copper atom is chelated by oxygen atoms from the adjacent carbon atoms to form a five membered ring, rather than oxygen atoms from the same carbon. The coordination environment of copper is nearly perfectly square planar, with the O1—Cu1—O2 bond angle measuring  $85.44(3)^\circ$  within the asymmetric unit, and  $94.56(3)^\circ$  across the inversion center. Within the plane of the oxalate ligand, O1 and O2 form bonds to Cu1 measuring  $1.9326(7)$  and  $1.9301(7)$  Å, respectively. O3 interacts weakly, at a distance of  $2.7057(8)$  Å, with the symmetry-related Cu atoms above and below the ligand plane, giving an elongated octahedron. O4 has no bonding interactions with Cu, but does engage in hydrogen bonding with the ammonium cation (see below). The different ways that the oxygen atoms do or do not interact with copper is reflected in the C—O bonds. The two oxygen atoms that are strongly bound to copper, O1 and O2, have slightly longer bonds to carbon of  $1.2798(11)$  and  $1.2895(12)$  Å for C1—O1 and C2—O2, respectively. The weakly interacting O3 and non-bonded O4 have shorter C—O bonds of  $1.2355(12)$  and  $1.2249(12)$  Å for C1—O3 and C2—O4, respectively.

## 3. Supramolecular features

As noted above, the coordination sphere of the copper atoms is completed by a long interaction of  $2.7057(8)$  Å between O3 and Cu1 in the planes above and below the ligand, giving rise to polymeric copper oxalate chains along the  $a$  axis (Fig. 2). These chains do not interact directly with one another. Instead, they are linked into a three-dimensional network by partly bifurcated N—H...O hydrogen bonds (Fig. 3) between



**Figure 2**

A single chain of the copper oxalate complex with the ammonium cation omitted.

**Table 1**

Hydrogen-bond geometry (Å, °).

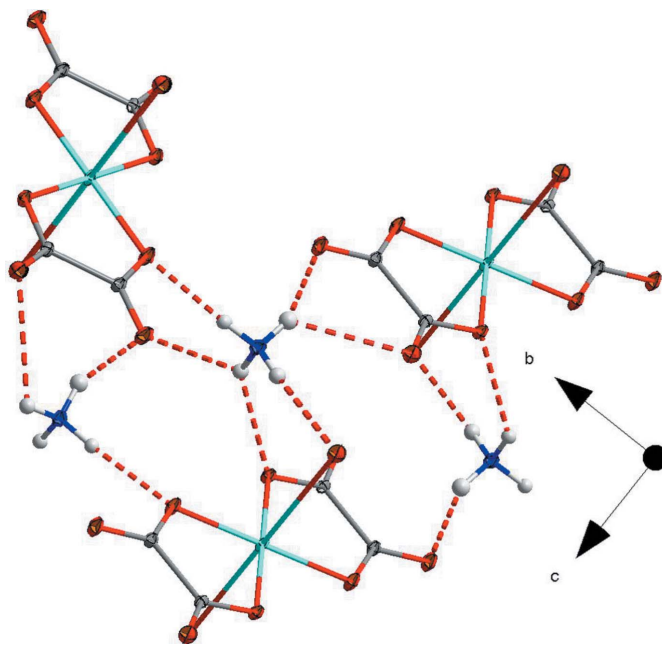
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1...O1 <sup>i</sup>	0.824 (17)	2.230 (17)	2.8667 (11)	134.2 (16)
N1—H1...O4 <sup>ii</sup>	0.824 (17)	2.475 (17)	3.0503 (12)	127.8 (15)
N1—H2...O2 <sup>iii</sup>	0.865 (18)	1.991 (18)	2.8507 (11)	172.5 (16)
N1—H3...O3 <sup>iv</sup>	0.854 (19)	2.053 (19)	2.8884 (11)	165.7 (17)
N1—H4...O3	0.85 (2)	2.43 (2)	3.0015 (11)	124.7 (16)
N1—H4...O4	0.85 (2)	2.04 (2)	2.8330 (12)	155.1 (18)

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

all four protons of the ammonium cation and the oxalate oxygen atoms indicated by the symmetry operations in Table 1.

## 4. Database survey

There are three published reports of hydrated ammonium copper oxalate but to the best of our knowledge, the anhydrous title compound has not been reported previously. The earliest report, for  $(\text{NH}_4)_{4n}[\text{Cu}_2(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$  (Viswamitra, 1962) was reinterpreted (Novosad *et al.*, 2000) as a polymeric complex with the repeat unit consisting of two  $[\text{Cu}(\text{C}_2\text{O}_4)_2]$  moieties. One copper atom forms long Cu—O bonds to the next unit, similar to the way in which the title compound forms its chains, while the other is capped by two water molecules. A different hydrate,  $(\text{NH}_4)_8[\text{Cu}_4(\text{C}_2\text{O}_4)_8(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}]$ , has also been reported (Kadir *et al.*, 2006), but it does not feature chains of polymeric copper oxalate. Instead, it exists as a discrete water-capped tetramer. In each case, these hydrates also display hydrogen bonding between the oxalate, ammonium and water molecules. Besides the



**Figure 3**

Packing viewed along the  $a$  axis, showing the polymeric complex formed by hydrogen bonding between the ammonium cations and oxalate ligands.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	(NH <sub>4</sub> ) <sub>2</sub> [Cu(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ]
<i>M<sub>r</sub></i>	275.66
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.8564 (2), 13.5188 (5), 6.7205 (3)
$\beta$ (°)	96.992 (2)
<i>V</i> (Å <sup>3</sup> )	437.94 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	2.53
Crystal size (mm)	0.43 × 0.28 × 0.28
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2015)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.41, 0.54
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	8277, 1672, 1537
<i>R</i> <sub>int</sub>	0.017
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.769
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.018, 0.051, 1.08
No. of reflections	1672
No. of parameters	86
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.37, -0.51

Computer programs: *BIS* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 1999) and *publCIF* (Westrip, 2010).

simple hydrates, structures of ammonium copper oxalates with polyoxidometalates based on tungsten (Reinoso *et al.*, 2005, 2007) or molybdenum (Li *et al.*, 2011) have been reported.

## 5. Synthesis and crystallization

A solution of bis(diisopropylphosphanyl)amine (0.25 g, 1.0 mmol) in 1 mL MeOH was added to a slurry of copper(II) oxalate hemihydrate (0.15 g, 1.0 mmol) in 1 mL MeOH. The mixture was heated to reflux for 5 min and then allowed to cool to room temperature. After three days, the blue supernatant solution was decanted from an insoluble powder and cooled to 248 K. Block-like blue crystals of the title compound were isolated after six weeks. The mechanism by which bis(diisopropylphosphanyl)amine decomposes into ammonium is under investigation.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

## Acknowledgements

This work was supported financially by the National Science Foundation (grant CHE12-13529). The Bruker X-ray diffractometer was purchased by a National Science Foundation CRIF:MU award to the University of New Mexico (CHE04-43580). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94-AL85000.

## References

- Baran, E. J. (2014). *J. Coord. Chem.* **67**, 3734–3768.
- Brandenburg (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2015). *BIS*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cheng, G., Si, C., Zhang, J., Wang, Y., Yang, W., Dong, C. & Zhang, Z. (2016). *J. Power Sources*, **312**, 184–191.
- Clemente-León, M., Coronado, E., Martí-Gastaldo, C. & Romero, F. M. (2011). *Chem. Soc. Rev.* **40**, 473–497.
- Feldner, T., Häring, M., Saha, S., Esquena, J., Banerjee, R. & Díaz, D. D. (2016). *Chem. Mater.* **28**, 3210–3217.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Gruselle, M., Train, C., Boubekeur, K., Gredin, P. & Ovanesyan, N. (2006). *Coord. Chem. Rev.* **250**, 2491–2500.
- Gu, X. & Xue, D. (2007). *Cryst. Growth Des.* **7**, 1726–1732.
- Guo, F., Chen, C., Wang, K., Zhang, Q. & Lin, Z. (2016). *Inorg. Chem.* **55**, 7817–7819.
- Kadir, K., Mohammad Ahmed, T., Noreús, D. & Eriksson, L. (2006). *Acta Cryst.* **E62**, m1139–m1141.
- Li, J., Liu, Y., Luo, J., Zhao, J. W., Ma, P. T. & Niu, J. Y. (2011). *Russ. J. Coord. Chem.* **37**, 849–853.
- Mizzi, J. E. & LaDuca, R. L. (2016). *Inorg. Chem. Commun.* **70**, 4–6.
- Nenwa, J., Djomo, E. D., Nfor, E. N., Djonwouo, P. L., Mbarki, M. & Fokwa, B. P. T. (2015). *Polyhedron*, **99**, 26–33.
- Novosad, J., Messimeri, A. C., Papadimitriou, C. D., Veltsistas, P. G. & Woollins, J. D. (2000). *Transition Met. Chem.* **25**, 664–669.
- Reinoso, S., Vitoria, P., Gutiérrez-Zorrilla, J. M., Lezama, L., Madariaga, J. M., San Felices, L. & Iturrospe, A. (2007). *Inorg. Chem.* **46**, 4010–4021.
- Reinoso, S., Vitoria, P., Gutiérrez-Zorrilla, J. M., Lezama, L., San Felices, L. & Beitia, J. I. (2005). *Inorg. Chem.* **44**, 9731–9742.
- Robinson, M. E., Mizzi, J. E., Staples, R. J. & LaDuca, R. L. (2015). *Cryst. Growth Des.* **15**, 2260–2271.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Viswamitra, M. A. (1962). *J. Chem. Phys.* **37**, 1408–1414.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yadav, G. G., David, A., Favaloro, T., Yang, H., Shakouri, A., Caruthers, J. & Wu, Y. (2013). *J. Mater. Chem. A*, **1**, 11901–11908.
- Yeşilel, O. Z., Erer, H., Odabaşoğlu, M. & Büyükgüngör, O. (2010). *J. Inorg. Organomet. Polym.* **20**, 78–82.
- Zhang, B., Zhang, Y. & Zhu, D. (2012). *Dalton Trans.* **41**, 8509–8511.

## supporting information

*Acta Cryst.* (2016). E72, 1780-1782 [https://doi.org/10.1107/S2056989016017631]

Crystal structure of *catena*-poly[diammonium [di- $\mu$ -oxalato-cuprate(II)]]

Diane A. Dickie and Richard A. Kemp

## Computing details

Data collection: *BIS* (Bruker, 2015); cell refinement: *SAINTE* (Bruker, 2015); data reduction: *SAINTE* (Bruker, 2015); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

*catena*-Poly[diammonium [di- $\mu$ -oxalato-cuprate(II)]]

## Crystal data

$2(\text{H}_4\text{N}^+)\cdot\text{C}_4\text{CuO}_8^{2-}$

$M_r = 275.66$

Monoclinic,  $P2_1/c$

$a = 4.8564$  (2) Å

$b = 13.5188$  (5) Å

$c = 6.7205$  (3) Å

$\beta = 96.992$  (2)°

$V = 437.94$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 278$

$D_x = 2.090$  Mg m<sup>-3</sup>

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

Cell parameters from 5449 reflections

$\theta = 3.0\text{--}33.1^\circ$

$\mu = 2.53$  mm<sup>-1</sup>

$T = 100$  K

Block, blue

$0.43 \times 0.28 \times 0.28$  mm

## Data collection

Bruker Kappa APEXII CCD  
diffractometer

Radiation source: fine-focus tube

Graphite monochromator

Detector resolution: 8.3333 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2015)

$T_{\min} = 0.41$ ,  $T_{\max} = 0.54$

8277 measured reflections

1672 independent reflections

1537 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 33.2^\circ$ ,  $\theta_{\min} = 3.0^\circ$

$h = -7 \rightarrow 7$

$k = -20 \rightarrow 18$

$l = -9 \rightarrow 10$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.018$

$wR(F^2) = 0.051$

$S = 1.08$

1672 reflections

86 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2 + 0.1971P]$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.37$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.51$  e Å<sup>-3</sup>

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0	0.5	0	0.00661 (5)
O1	0.32614 (14)	0.44779 (5)	0.15885 (10)	0.00795 (12)
O2	0.15437 (14)	0.62834 (5)	0.07337 (11)	0.00968 (13)
O3	0.72392 (16)	0.50253 (5)	0.32622 (12)	0.01101 (14)
O4	0.52948 (15)	0.69388 (5)	0.25066 (12)	0.01245 (14)
C1	0.4930 (2)	0.51573 (7)	0.23064 (14)	0.00716 (15)
C2	0.39072 (19)	0.62308 (7)	0.18343 (14)	0.00800 (15)
N1	0.95132 (18)	0.67395 (6)	0.57854 (13)	0.00966 (14)
H1	0.840 (3)	0.6723 (13)	0.662 (3)	0.020 (4)*
H2	1.027 (3)	0.7319 (13)	0.582 (3)	0.019 (4)*
H3	1.072 (4)	0.6285 (14)	0.607 (3)	0.023 (4)*
H4	0.849 (4)	0.6643 (14)	0.468 (3)	0.029 (5)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.00454 (8)	0.00426 (8)	0.01054 (8)	−0.00002 (5)	−0.00113 (5)	0.00048 (5)
O1	0.0065 (3)	0.0063 (3)	0.0106 (3)	0.0002 (2)	−0.0011 (2)	0.0008 (2)
O2	0.0068 (3)	0.0060 (3)	0.0153 (3)	0.0005 (2)	−0.0026 (2)	−0.0002 (2)
O3	0.0084 (3)	0.0099 (3)	0.0136 (3)	0.0011 (2)	−0.0033 (2)	−0.0005 (2)
O4	0.0125 (3)	0.0075 (3)	0.0160 (3)	−0.0016 (2)	−0.0035 (2)	−0.0014 (2)
C1	0.0071 (3)	0.0064 (3)	0.0081 (3)	0.0007 (3)	0.0013 (3)	0.0003 (3)
C2	0.0074 (3)	0.0070 (4)	0.0094 (3)	0.0009 (3)	0.0005 (3)	0.0000 (3)
N1	0.0100 (3)	0.0075 (3)	0.0110 (3)	−0.0017 (3)	−0.0007 (3)	0.0004 (3)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

Cu1—O2 <sup>i</sup>	1.9301 (7)	O4—C2	1.2249 (12)
Cu1—O2	1.9301 (7)	C1—C2	1.5541 (13)
Cu1—O1 <sup>i</sup>	1.9326 (7)	N1—H1	0.824 (17)
Cu1—O1	1.9326 (7)	N1—H2	0.865 (18)
O1—C1	1.2798 (11)	N1—H3	0.854 (19)
O2—C2	1.2895 (12)	N1—H4	0.85 (2)
O3—C1	1.2355 (12)		
O2 <sup>i</sup> —Cu1—O2	180.00 (4)	O1—C1—C2	114.91 (8)
O2 <sup>i</sup> —Cu1—O1 <sup>i</sup>	85.44 (3)	O4—C2—O2	125.44 (9)
O2—Cu1—O1 <sup>i</sup>	94.56 (3)	O4—C2—C1	120.44 (8)
O2 <sup>i</sup> —Cu1—O1	94.57 (3)	O2—C2—C1	114.12 (8)

O2—Cu1—O1	85.43 (3)	H1—N1—H2	108.8 (16)
O1 <sup>i</sup> —Cu1—O1	180.0	H1—N1—H3	108.4 (16)
C1—O1—Cu1	112.64 (6)	H2—N1—H3	111.5 (16)
C2—O2—Cu1	112.83 (6)	H1—N1—H4	103.3 (16)
O3—C1—O1	125.83 (9)	H2—N1—H4	111.1 (16)
O3—C1—C2	119.23 (8)	H3—N1—H4	113.3 (17)
Cu1—O1—C1—O3	-175.08 (8)	O3—C1—C2—O4	-4.51 (14)
Cu1—O1—C1—C2	2.83 (9)	O1—C1—C2—O4	177.43 (9)
Cu1—O2—C2—O4	-179.39 (8)	O3—C1—C2—O2	176.24 (9)
Cu1—O2—C2—C1	-0.18 (10)	O1—C1—C2—O2	-1.82 (12)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O1 <sup>ii</sup>	0.824 (17)	2.230 (17)	2.8667 (11)	134.2 (16)
N1—H1 $\cdots$ O4 <sup>iii</sup>	0.824 (17)	2.475 (17)	3.0503 (12)	127.8 (15)
N1—H2 $\cdots$ O2 <sup>iv</sup>	0.865 (18)	1.991 (18)	2.8507 (11)	172.5 (16)
N1—H3 $\cdots$ O3 <sup>v</sup>	0.854 (19)	2.053 (19)	2.8884 (11)	165.7 (17)
N1—H4 $\cdots$ O3	0.85 (2)	2.43 (2)	3.0015 (11)	124.7 (16)
N1—H4 $\cdots$ O4	0.85 (2)	2.04 (2)	2.8330 (12)	155.1 (18)

Symmetry codes: (ii)  $-x+1, -y+1, -z+1$ ; (iii)  $x, -y+3/2, z+1/2$ ; (iv)  $x+1, -y+3/2, z+1/2$ ; (v)  $-x+2, -y+1, -z+1$ .