

# Crystal structure of *catena*-poly[[bis(acetato- $\kappa$ O)-copper(II)]-bis[ $\mu$ -4-(1*H*-imidazol-1-yl)phenol]- $\kappa^2$ N<sup>3</sup>:O; $\kappa^2$ O:N<sup>3</sup>]

Mehmet Poyraz<sup>a\*</sup> and Musa Sari<sup>b</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science and Arts, Afyon Kocatepe University, TR-03200 Afyonkarahisar, Turkey, and <sup>b</sup>Department of Physics Education, Gazi University, Beşevler, TR-06500 Ankara, Turkey. \*Correspondence e-mail: poyraz@aku.edu.tr

Received 4 December 2016

Accepted 16 January 2017

Edited by M. Weil, Vienna University of  
Technology, Austria

**Keywords:** crystal structure; polymeric structure; hydrogen bonds; copper(II); acetate; imidazole;  $\pi$ - $\pi$  stacking.

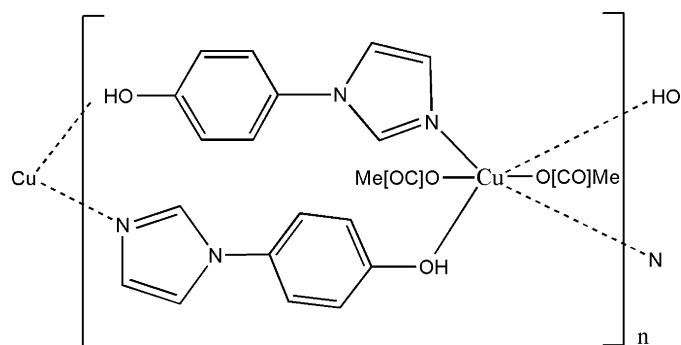
**CCDC reference:** 1520352

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

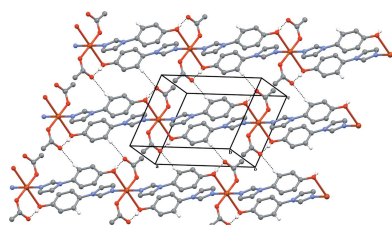
In the title compound,  $[\text{Cu}(\text{CH}_3\text{COO})_2(\text{C}_9\text{H}_8\text{N}_2\text{O})_2]_n$ , the  $\text{Cu}^{\text{II}}$  ion resides on a centre of inversion, displaying a tetragonally distorted octahedral coordination environment defined by two pairs of N and O atoms of symmetry-related 4-(1*H*-imidazol-1-yl)phenol ligands and the O atoms of two symmetry-related acetate ligands. The bridging mode of the 4-(1*H*-imidazol-1-yl)phenol ligands is associated with a very long  $\text{Cu}\cdots\text{O}$  interactions involving the phenol O atom of the heterocyclic ligand, which creates chains extending parallel to [100]. In the crystal, the chains are arranged in a distorted hexagonal rod packing and are linked *via*  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds and by  $\pi$ - $\pi$  stacking interactions involving centrosymmetrically related pairs of imidazole and phenol rings.

## 1. Chemical context

Coordination polymers have been investigated as materials with interesting properties such as magnetism (Zhu *et al.*, 2010), luminescence (Cui *et al.*, 2012), catalysis (Wang *et al.*, 2011) or absorption (Zhang *et al.*, 2017). Some coordination polymers are also known to show photocatalytic activity with respect to the decomposition of organic dyes (Yang *et al.*, 2010; Yin *et al.*, 2015).



In the past few years, metal complexes with ligands derived from imidazole have attracted much attention, not only for their fascinating crystal structures, but also for their interesting applications related to antifungal (Rezaei *et al.*, 2011), pesticidal (Stenersen *et al.*, 2004) and plant-growth regulatory properties (Choi *et al.*, 2010), or drugs in general (Lednicer *et al.*, 1998; Adams *et al.*, 2001). Most of these compounds exhibit typical molecular structures whereas the number of imidazole-based coordination polymers (Martins *et al.*, 2010; Masciocchi *et al.*, 2001; Stamatatos *et al.*, 2009) is much lower, probably due to the difficulty of growing single crystals.



**Table 1**  
Selected geometric parameters (Å, °).

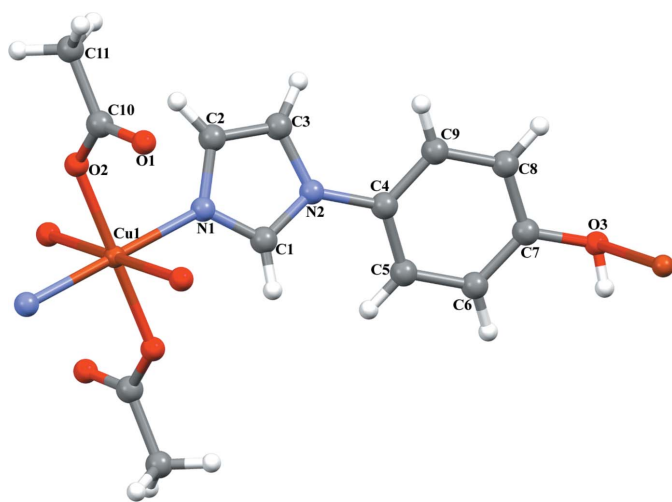
N1—Cu1	2.003 (2)	O3—Cu1 <sup>i</sup>	2.739 (2)
Cu1—O2	1.9322 (18)		
O2—Cu1—N1	90.56 (8)	N1—Cu1—O3 <sup>iii</sup>	91.31 (7)
N1—Cu1—N1 <sup>ii</sup>	180.0	O2—Cu1—O3 <sup>iv</sup>	86.94 (7)
O2—Cu1—O3 <sup>iii</sup>	93.06 (7)	N1—Cu1—O3 <sup>iv</sup>	88.69 (7)

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

In this communication we report on the synthesis and crystal structure of a copper(II) coordination polymer,  $[\text{Cu}(\text{CH}_3\text{COO})_2(\text{C}_9\text{H}_8\text{N}_2\text{O})_2]_n$ , comprising 4-(1*H*-imidazol-1-yl)-phenol and acetate ligands.

## 2. Structural commentary

The asymmetric unit of the title compound comprises of one Cu<sup>II</sup> atom, one 4-(1*H*-imidazol-1-yl)-phenol ligand and one acetate group, with the Cu<sup>II</sup> atom situated on a crystallographic inversion centre. The distorted octahedral coordination environment of the Cu<sup>II</sup> atom is defined by two symmetry-related pairs of imidazole N atoms and phenol O atoms from the heterocyclic ligands and by two O atoms of a symmetry-related pair of monodentate acetate ligands (Fig. 1). The Cu—O(acetate) [1.9322 (18) Å] and Cu—N(imidazole) [2.003 (2) Å] bonds are arranged in the equatorial plane and are within normal lengths (Ding *et al.*, 2005; Song *et al.*, 2008; Yun *et al.*, 2008; Yu & Deng, 2011). The equatorial bond angles are in the range 86.94 (7)–93.06 (7)° in the Cu1N<sub>2</sub>O<sub>4</sub> polyhedron (Table 1). The bond involving the phenolic O3 atom is very weak, with a distance of Cu···O = 2.739 (2) Å, completing the tetragonally distorted octahedron. The *N,O*-bridging character of the 4-(1*H*-imidazol-1-yl)-phenol ligand leads to the formation of chains extending parallel to [100],



**Figure 1**  
The coordination environment of the Cu<sup>II</sup> atom in the title compound. Displacement ellipsoids are drawn at the 30% probability level; non-labelled atoms are related to labelled atoms by  $(-x + 1, -y + 1, -z)$ .

**Table 2**  
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5···O1 <sup>v</sup>	0.95	2.44	3.356 (3)	161
O3—H3A···O1 <sup>iii</sup>	0.84	1.80	2.637 (3)	172

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

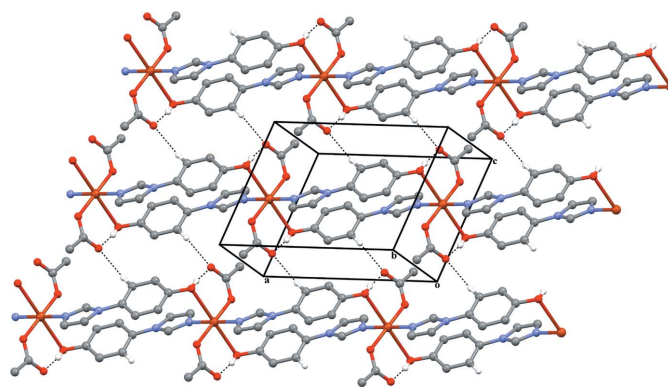
whereby the ligands are oriented in an antiparallel fashion within a chain. The dihedral angle between the imidazole group (N1,N2,C1–C3) and the phenyl ring (C4–C9) is 24.07 (2)°. An intrachain hydrogen bond between the phenol OH group (O3) and the non-coordinating carboxylate O atom (O1) of the acetate ligand is present (Table 2, Fig. 2).

## 3. Supramolecular features

In the crystal, the chains are aligned in a distorted hexagonal rod packing perpendicular to the chain direction. Chains are linked through intermolecular C—H···O interactions between a phenyl CH group and the non-coordinating carboxylate O atom (O1) that consequently acts as a double acceptor atom (Fig. 2, Table 2). Additional  $\pi$ – $\pi$  stacking interactions involving centrosymmetrically related pairs of imidazole and phenol rings, with the shortest distance between an N atom and a C atom being 3.372 (2) Å, are also present. The interplanar angle between the two rings is 24.1 (1)°.

## 4. Database survey

The literature about one-dimensional inorganic–organic coordination polymers based on copper(II) complexes with Cu<sup>II</sup> either in a square-pyramidal or a distorted octahedral coordination environment is vast. Just to take very recent examples, three such structures have been reported (Hazra *et al.*, 2017; Puchonová *et al.*, 2017; Shaabani *et al.*, 2017). Nevertheless, there is only limited research on 4-(1*H*-imidazol-1-yl)-phenol as a ligand (Maher *et al.*, 1994; Wei *et al.*, 2007; Yurdakul & Badođlu, 2015). To the best of our know-



**Figure 2**  
The crystal structure of the title compound showing the formation of chains extending parallel to [100]. Hydrogen-bonding interactions are shown as dashed lines.

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	[Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> O) <sub>2</sub> ]
<i>M<sub>r</sub></i>	501.99
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.2029 (15), 15.089 (2), 7.7814 (11)
$\beta$ (°)	111.545 (4)
<i>V</i> (Å <sup>3</sup> )	1114.2 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.03
Crystal size (mm)	0.11 × 0.09 × 0.07
Data collection	
Diffraction	Broker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2013)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.895, 0.931
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	40729, 2784, 2156
<i>R<sub>int</sub></i>	0.051
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.667
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>	0.041, 0.100, 1.15
No. of reflections	2784
No. of parameters	153
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.26, -0.30

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *pubCIF* (Westrip, 2010).

ledge, only one discrete copper(II) complex of 4-(1*H*-imidazol-1-yl)-phenol (Yu & Deng, 2011) has been reported. In this regard, the title compound is the first Cu<sup>II</sup> coordination polymer with 4-(1*H*-imidazol-1-yl)-phenol.

## 5. Synthesis and crystallization

4-(1*H*-Imidazol-1-yl)phenol (0.0480 g, 0.3 mmol) was dissolved in 5 ml ethanol, a water solution (5 ml) of Na<sub>2</sub>CO<sub>3</sub> (0.0318 g, 0.3 mmol) was slowly added, and an ethanol solution (5 ml) of Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (0.0349 g, 0.15 mmol) was added slowly with stirring for 30 min. To the formed cloudy suspension, an aqueous solution of acetic acid (0.3 mmol) was added. The resulting solution turned to a transparent blue colour. After stirring for three h, the solution was allowed to evaporate at room temperature. A number of blue single crystals were obtained after a few days.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C-bound H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with distances in the range 0.93–0.96 Å and with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) or 1.5*U*<sub>eq</sub>(C) for methyl atoms. The H atom of the phenol OH group was located in a difference

map and was constrained at a distance of O—H = 0.84 Å and with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O).

## Acknowledgements

The authors acknowledge Scientific and Technological Research Application and Research Center, Sinop University, Turkey, for the use of the Bruker D8 QUEST diffractometer and Dr Onur Şahin for help and guidance.

## References

- Adams, J. L., Boehm, J. C., Gallagher, T. F., Kassis, S., Webb, E. F., Hall, R., Sorenson, M., Garigipati, R., Griswold, D. E. & Lee, J. C. (2001). *Bioorg. Med. Chem. Lett.* **11**, 2867–2870.
- Bruker (2013). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Choi, J. H., Abe, N., Tanaka, H., Fushimi, K., Nishina, Y., Morita, A., Kiriwa, Y., Motohashi, R., Hashizume, D., Koshino, H. & Kawagishi, H. (2010). *J. Agric. Food Chem.* **58**, 9956–9959.
- Cui, Y. J., Yue, Y. F., Qian, G. D. & Chen, B. L. (2012). *Chem. Rev.* **112**, 1126–1162.
- Ding, C.-F., Zhang, S.-S., Tian, B.-Q., Li, X.-M., Xu, H. & Ouyang, P.-K. (2005). *Acta Cryst.* **E61**, m235–m236.
- Hazra, S., Martins, L. M. D. R. S., Guedes da Silva, M. F. C. & Pombeiro, A. J. L. (2017). *Inorg. Chim. Acta*, **455**, 549–556.
- Lednicer, D. (1998). *Drugs Based on Five-Membered Heterocycles*, in *Strategies for Organic Drug Synthesis and Design*. New York: Wiley.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Maher, J. P., McCleverty, J. A., Ward, M. D. & Wlodarczyk, A. (1994). *J. Chem. Soc. Dalton Trans.* pp. 143–147.
- Martins, G. A. V., Byrne, P. J., Allan, P., Teat, S. J., Slawin, A. M. Z., Li, Y. & Morris, R. E. (2010). *Dalton Trans.* **39**, 1758–1762.
- Masciocchi, N., Bruni, S., Cariati, E., Cariati, F., Galli, S. & Sironi, A. (2001). *Inorg. Chem.* **40**, 5897–5905.
- Puchoňová, M., Švorec, J., Švorc, Ľ., Pavlik, J., Mazúr, M., Dlháň, Ľ., Růžičková, Z., Moncol, J. & Valigura, D. (2017). *Inorg. Chim. Acta*, **455**, 298–306.
- Rezaei, Z., Khabnadideh, S., Zomorodian, K., Pakshir, K., Kashi, G., Sanagoei, N. & Gholami, S. (2011). *Arch. Pharm. Pharm. Med. Chem.* **344**, 658–665.
- Shaabani, B., Rad-Yousefnia, N., Zahedi, M., Ertan, Ş., Blake, G. R. & Zakerhamidi, M. S. (2017). *Inorg. Chim. Acta*, **455**, 158–165.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Song, W.-D., Huang, X.-H. & Wang, H. (2008). *Acta Cryst.* **E64**, m764.
- Stamatatos, T. C., Perlepes, S. P., Raptopoulou, C. P., Terzis, A., Patrickios, C. S., Tasiopoulos, A. J. & Boudalis, A. K. (2009). *Dalton Trans.* pp. 3354–3362.
- Stenersen, J. (2004). In *Chemical Pesticides Mode of Action and Toxicology*. Boca Raton: CRC Press.
- Wang, S. J., Li, L., Zhang, J. Y., Yuan, X. C. & Su, C. Y. (2011). *J. Mater. Chem.* **21**, 7098–7104.
- Wei, R. G., Adler, M., Davey, D., Ho, E., Mohan, R., Polokoff, R., Tseng, J.-L., Whitlow, M., Xu, W., Yuan, S. & Phillips, G. (2007). *Bioorg. Med. Chem. Lett.* **17**, 2499–2504.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yang, H. X., Liu, T. F., Cao, M. N., Li, H. F., Gao, S. Y. & Cao, R. (2010). *Chem. Commun.* **46**, 2429–2431.
- Yin, W.-Y., Huang, Z.-L., Tang, X.-Y., Wang, J., Cheng, H.-J., Ma, Y.-S., Yuan, R.-X. & Liu, D. (2015). *New J. Chem.* **39**, 7130–7139.
- Yu, R.-J. & Deng, B. (2011). *Acta Cryst.* **E67**, m1253.
- Yun, R., Ying, W., Qi, B., Fan, X. & Wu, H. (2008). *Acta Cryst.* **E64**, m1529.

Yurdakul, S. & Badođlu, S. (2015). *Spectrochim. Acta Part A*, **150**, 614–622.

Zhang, X., Wu, X. X., Guo, J. Z., Huo, J. H. & Ding, B. (2017). *J. Mol. Struct.* **1127**, 183–190.

Zhu, X., Zhao, J. W., Li, B. L., Song, Y., Zhang, Y. M. & Zhang, Y. (2010). *Inorg. Chem.* **49**, 1266–1270.

## supporting information

*Acta Cryst.* (2017). E73, 209-212 [https://doi.org/10.1107/S2056989017000780]

## Crystal structure of *catena*-poly[[bis(acetato- $\kappa$ O)copper(II)]-bis[ $\mu$ -4-(1*H*-imidazol-1-yl)phenol]- $\kappa^2$ N<sup>3</sup>:O; $\kappa^2$ O:N<sup>3</sup>]

Mehmet Poyraz and Musa Sari

### Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINTE* (Bruker, 2013); data reduction: *SAINTE* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

*catena*-Poly[[bis(acetato- $\kappa$ O)copper(II)]-bis[ $\mu$ -4-(1*H*-imidazol-1-yl)phenol]- $\kappa^2$ N<sup>3</sup>:O; $\kappa^2$ O:N<sup>3</sup>]

### Crystal data

[Cu(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>9</sub>H<sub>8</sub>N<sub>2</sub>O)<sub>2</sub>]

$M_r = 501.99$

Monoclinic,  $P2_1/c$

$a = 10.2029$  (15) Å

$b = 15.089$  (2) Å

$c = 7.7814$  (11) Å

$\beta = 111.545$  (4)°

$V = 1114.2$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 518$

$D_x = 1.496$  Mg m<sup>-3</sup>

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

Cell parameters from 9911 reflections

$\theta = 3.2$ – $28.0$ °

$\mu = 1.03$  mm<sup>-1</sup>

$T = 296$  K

Block, blue

$0.11 \times 0.09 \times 0.07$  mm

### Data collection

Bruker APEXII CCD  
diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Bruker, 2013)

$T_{\min} = 0.895$ ,  $T_{\max} = 0.931$

40729 measured reflections

2784 independent reflections

2156 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.051$

$\theta_{\max} = 28.3$ °,  $\theta_{\min} = 3.1$ °

$h = -13 \rightarrow 13$

$k = -20 \rightarrow 20$

$l = -10 \rightarrow 10$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

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

$wR(F^2) = 0.100$

$S = 1.15$

2784 reflections

153 parameters

0 restraints

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2 + 1.2448P]$

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

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

$\Delta\rho_{\max} = 0.26$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.30$  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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7431 (2)	0.55700 (18)	0.5692 (3)	0.0350 (5)
H1	0.7461	0.5059	0.6420	0.042*
C2	0.7933 (4)	0.6526 (2)	0.4009 (5)	0.0601 (9)
H2	0.8394	0.6819	0.3308	0.072*
C3	0.6778 (4)	0.6824 (2)	0.4266 (5)	0.0656 (10)
H3	0.6285	0.7359	0.3794	0.079*
C4	0.5265 (2)	0.62360 (16)	0.5918 (3)	0.0333 (5)
C5	0.5302 (3)	0.57796 (19)	0.7472 (4)	0.0408 (6)
H5	0.6125	0.5463	0.8195	0.049*
C6	0.4129 (3)	0.5787 (2)	0.7968 (4)	0.0430 (6)
H6	0.4149	0.5470	0.9033	0.052*
C7	0.2929 (2)	0.62494 (18)	0.6930 (3)	0.0370 (6)
C8	0.2926 (3)	0.67390 (18)	0.5434 (4)	0.0419 (6)
H8	0.2126	0.7087	0.4760	0.050*
C9	0.4084 (3)	0.67258 (18)	0.4912 (4)	0.0403 (6)
H9	0.4069	0.7053	0.3861	0.048*
C10	0.9356 (3)	0.56669 (19)	0.1300 (3)	0.0402 (6)
C11	0.9592 (4)	0.6405 (2)	0.0154 (4)	0.0617 (9)
H11A	0.9094	0.6273	-0.1159	0.093*
H11B	1.0603	0.6463	0.0408	0.093*
H11C	0.9234	0.6961	0.0464	0.093*
N1	0.8345 (2)	0.57396 (15)	0.4905 (3)	0.0368 (5)
N2	0.6450 (2)	0.62096 (14)	0.5338 (3)	0.0362 (5)
Cu1	1.0000	0.5000	0.5000	0.03750 (14)
O1	0.8401 (2)	0.51168 (15)	0.0597 (3)	0.0528 (5)
O2	1.01849 (18)	0.56716 (14)	0.2987 (2)	0.0455 (5)
O3	0.17326 (19)	0.62330 (15)	0.7320 (3)	0.0502 (5)
H3A	0.1775	0.5811	0.8043	0.075*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0274 (11)	0.0431 (14)	0.0347 (12)	-0.0002 (10)	0.0115 (9)	0.0037 (10)
C2	0.073 (2)	0.0432 (17)	0.089 (2)	0.0039 (15)	0.060 (2)	0.0134 (16)
C3	0.079 (2)	0.0395 (17)	0.104 (3)	0.0157 (16)	0.064 (2)	0.0252 (17)
C4	0.0288 (11)	0.0337 (12)	0.0384 (13)	-0.0008 (9)	0.0135 (10)	-0.0017 (10)
C5	0.0271 (12)	0.0540 (17)	0.0403 (13)	0.0071 (11)	0.0111 (10)	0.0107 (12)
C6	0.0345 (13)	0.0601 (18)	0.0369 (13)	0.0048 (12)	0.0161 (11)	0.0117 (12)
C7	0.0282 (11)	0.0441 (14)	0.0403 (13)	0.0003 (10)	0.0144 (10)	-0.0056 (11)

C8	0.0333 (13)	0.0411 (15)	0.0494 (15)	0.0096 (11)	0.0129 (11)	0.0067 (12)
C9	0.0380 (13)	0.0397 (14)	0.0440 (14)	0.0047 (11)	0.0159 (11)	0.0092 (11)
C10	0.0364 (13)	0.0524 (16)	0.0369 (13)	0.0142 (12)	0.0195 (11)	0.0071 (12)
C11	0.082 (2)	0.056 (2)	0.0539 (18)	0.0127 (17)	0.0328 (17)	0.0158 (15)
N1	0.0313 (10)	0.0428 (12)	0.0393 (11)	-0.0035 (9)	0.0165 (9)	-0.0029 (9)
N2	0.0333 (10)	0.0357 (11)	0.0435 (11)	0.0015 (9)	0.0187 (9)	0.0027 (9)
Cu1	0.0246 (2)	0.0589 (3)	0.0293 (2)	0.0002 (2)	0.01022 (15)	0.0018 (2)
O1	0.0430 (10)	0.0701 (14)	0.0416 (10)	0.0012 (10)	0.0112 (8)	0.0052 (10)
O2	0.0316 (9)	0.0717 (14)	0.0350 (9)	0.0000 (9)	0.0141 (8)	0.0087 (9)
O3	0.0339 (9)	0.0667 (14)	0.0571 (12)	0.0073 (9)	0.0253 (9)	0.0065 (10)

*Geometric parameters (Å, °)*

C1—N1	1.315 (3)	C8—C9	1.383 (4)
C1—N2	1.345 (3)	C8—Cu1 <sup>i</sup>	3.895 (3)
C1—Cu1	2.989 (2)	C8—H8	0.9500
C1—H1	0.9500	C9—H9	0.9500
C2—C3	1.343 (4)	C10—O1	1.244 (3)
C2—N1	1.361 (4)	C10—O2	1.274 (3)
C2—Cu1	3.024 (3)	C10—C11	1.501 (4)
C2—H2	0.9500	C10—Cu1	2.888 (3)
C3—N2	1.369 (4)	C11—H11A	0.9800
C3—H3	0.9500	C11—H11B	0.9800
C4—C5	1.380 (3)	C11—H11C	0.9800
C4—C9	1.385 (3)	N1—Cu1	2.003 (2)
C4—N2	1.438 (3)	Cu1—O2 <sup>ii</sup>	1.9322 (18)
C5—C6	1.386 (3)	Cu1—O2	1.9322 (18)
C5—H5	0.9500	Cu1—N1 <sup>ii</sup>	2.003 (2)
C6—C7	1.383 (4)	Cu1—O3 <sup>iii</sup>	2.739 (2)
C6—H6	0.9500	Cu1—O3 <sup>iv</sup>	2.739 (2)
C7—O3	1.363 (3)	O3—Cu1 <sup>i</sup>	2.739 (2)
C7—C8	1.377 (4)	O3—H3A	0.8400
C7—Cu1 <sup>i</sup>	3.383 (2)		
N1—C1—N2	111.5 (2)	O1—C10—O2	125.0 (3)
N2—C1—Cu1	143.71 (17)	O1—C10—C11	120.3 (3)
N1—C1—H1	124.2	O2—C10—C11	114.7 (3)
N2—C1—H1	124.2	O1—C10—Cu1	93.50 (16)
Cu1—C1—H1	92.1	C11—C10—Cu1	145.5 (2)
C3—C2—N1	109.8 (3)	C10—C11—H11A	109.5
C3—C2—Cu1	141.7 (2)	C10—C11—H11B	109.5
C3—C2—H2	125.1	H11A—C11—H11B	109.5
N1—C2—H2	125.1	C10—C11—H11C	109.5
Cu1—C2—H2	93.2	H11A—C11—H11C	109.5
C2—C3—N2	106.8 (3)	H11B—C11—H11C	109.5
C2—C3—H3	126.6	C1—N1—C2	105.7 (2)
N2—C3—H3	126.6	C1—N1—Cu1	127.34 (18)
C5—C4—C9	120.0 (2)	C2—N1—Cu1	127.00 (18)

C5—C4—N2	120.4 (2)	C1—N2—C3	106.3 (2)
C9—C4—N2	119.6 (2)	C1—N2—C4	127.2 (2)
C4—C5—C6	119.4 (2)	C3—N2—C4	126.5 (2)
C4—C5—H5	120.3	O2 <sup>ii</sup> —Cu1—O2	180.0
C6—C5—H5	120.3	O2 <sup>ii</sup> —Cu1—N1	89.44 (8)
C7—C6—C5	120.7 (2)	O2—Cu1—N1	90.56 (8)
C7—C6—H6	119.6	O2 <sup>ii</sup> —Cu1—N1 <sup>ii</sup>	90.56 (8)
C5—C6—H6	119.6	O2—Cu1—N1 <sup>ii</sup>	89.44 (8)
O3—C7—C8	118.3 (2)	N1—Cu1—N1 <sup>ii</sup>	180.0
O3—C7—C6	122.3 (2)	O2 <sup>ii</sup> —Cu1—O3 <sup>iii</sup>	86.94 (7)
C8—C7—C6	119.4 (2)	O2—Cu1—O3 <sup>iii</sup>	93.06 (7)
O3—C7—Cu1 <sup>i</sup>	51.02 (13)	N1—Cu1—O3 <sup>iii</sup>	91.31 (7)
C8—C7—Cu1 <sup>i</sup>	101.33 (16)	N1 <sup>ii</sup> —Cu1—O3 <sup>iii</sup>	88.69 (7)
C6—C7—Cu1 <sup>i</sup>	115.23 (18)	O2 <sup>ii</sup> —Cu1—O3 <sup>iv</sup>	93.06 (7)
C7—C8—C9	120.2 (2)	O2—Cu1—O3 <sup>iv</sup>	86.94 (7)
C7—C8—Cu1 <sup>i</sup>	58.39 (14)	N1—Cu1—O3 <sup>iv</sup>	88.69 (7)
C9—C8—Cu1 <sup>i</sup>	132.43 (19)	N1 <sup>ii</sup> —Cu1—O3 <sup>iv</sup>	91.31 (7)
C7—C8—H8	119.9	O3 <sup>iii</sup> —Cu1—O3 <sup>iv</sup>	180.00 (7)
C9—C8—H8	119.9	C10—O1—Cu1	63.78 (14)
Cu1 <sup>i</sup> —C8—H8	81.3	C10—O2—Cu1	127.36 (18)
C8—C9—C4	120.1 (2)	C7—O3—Cu1 <sup>i</sup>	106.23 (16)
C8—C9—H9	120.0	C7—O3—H3A	109.5
C4—C9—H9	120.0	Cu1 <sup>i</sup> —O3—H3A	77.8
N1—C2—C3—N2	-0.4 (4)	C3—C2—N1—C1	0.1 (4)
Cu1—C2—C3—N2	-0.5 (6)	Cu1—C2—N1—C1	179.9 (3)
C9—C4—C5—C6	2.6 (4)	C3—C2—N1—Cu1	-179.8 (2)
N2—C4—C5—C6	-177.6 (3)	N1—C1—N2—C3	-0.4 (3)
C4—C5—C6—C7	-0.3 (4)	Cu1—C1—N2—C3	-0.5 (4)
C5—C6—C7—O3	176.5 (3)	N1—C1—N2—C4	177.9 (2)
C5—C6—C7—C8	-2.9 (4)	Cu1—C1—N2—C4	177.83 (19)
C5—C6—C7—Cu1 <sup>i</sup>	118.1 (3)	C2—C3—N2—C1	0.5 (4)
O3—C7—C8—C9	-175.6 (3)	C2—C3—N2—C4	-177.9 (3)
C6—C7—C8—C9	3.8 (4)	C5—C4—N2—C1	25.2 (4)
Cu1 <sup>i</sup> —C7—C8—C9	-123.9 (2)	C9—C4—N2—C1	-155.1 (3)
O3—C7—C8—Cu1 <sup>i</sup>	-51.63 (19)	C5—C4—N2—C3	-156.8 (3)
C6—C7—C8—Cu1 <sup>i</sup>	127.7 (3)	C9—C4—N2—C3	23.0 (4)
C7—C8—C9—C4	-1.5 (4)	O2—C10—O1—Cu1	6.7 (2)
Cu1 <sup>i</sup> —C8—C9—C4	-74.7 (3)	C11—C10—O1—Cu1	-172.5 (3)
C5—C4—C9—C8	-1.7 (4)	O1—C10—O2—Cu1	-12.6 (4)
N2—C4—C9—C8	178.5 (2)	C11—C10—O2—Cu1	166.60 (19)
N2—C1—N1—C2	0.2 (3)	C8—C7—O3—Cu1 <sup>i</sup>	81.4 (3)
Cu1—C1—N1—C2	-179.9 (3)	C6—C7—O3—Cu1 <sup>i</sup>	-97.9 (3)
N2—C1—N1—Cu1	-179.88 (16)		

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



*Hydrogen-bond geometry (Å, °)*

<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>
C5—H5 $\cdots$ O1 <sup>v</sup>	0.95	2.44	3.356 (3)	161
O3—H3A $\cdots$ O1 <sup>iii</sup>	0.84	1.80	2.637 (3)	172

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