

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Tetrakis(μ_3 -2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]-6-nitrophenolato)tetracopper(II)

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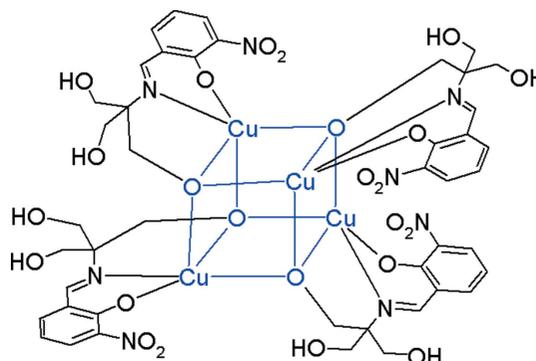
Received 11 December 2013; accepted 13 January 2014

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.012$ Å; R factor = 0.075; wR factor = 0.184; data-to-parameter ratio = 18.4.

The title cluster, $[\text{Cu}_4(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_6)_4]$, was obtained from the $\text{Cu}^0\text{-FeCl}_2\cdot 4\text{H}_2\text{O}\text{-H}_4\text{L}\text{-Et}_3\text{N}\text{-DMF}$ reaction system (in air), where H_4L is 2-hydroxymethyl-2[[2-(2-hydroxy-3-nitrophenyl)methylidene]amino]propane-1,3-diol and DMF is dimethylformamide. The asymmetric unit consists of one Cu^{2+} ion and one dianionic ligand; a $\bar{4}$ symmetry element generates the cluster, which contains a $\{\text{Cu}_4\text{O}_4\}$ cubane-like core. The metal ion has an elongated square-based pyramidal CuNO_4 coordination geometry with the N atom in a basal site. An intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond is observed. The solvent molecules were found to be highly disordered and their contribution to the scattering was removed with the SQUEEZE procedure in *PLATON* [Spek (2009). *Acta Cryst. D* **65**, 148–155], which indicated a solvent cavity of volume 3131 Å³ containing approximately 749 electrons. These solvent molecules are not considered in the given chemical formula.

Related literature

For general background to direct synthesis (DS), see: Kokozay & Shevchenko (2005). For related structures, see: Dey *et al.* (2002); Dong *et al.* (2007); Guo *et al.* (2008). For successful realisation of DS, see: Chygorin *et al.* (2012); Nesterov *et al.* (2012).



Experimental

Crystal data

$[\text{Cu}_4(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_6)_4]$
 $M_r = 1327.06$
 Tetragonal, $I4_1/a$
 $a = 20.5587$ (14) Å
 $c = 18.010$ (2) Å
 $V = 7612.0$ (11) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.17$ mm⁻¹
 $T = 173$ K
 $0.40 \times 0.40 \times 0.30$ mm

Data collection

Agilent Xcalibur Sapphire3
 diffractometer
 Absorption correction: multi-scan
 (*CrysAlis PRO*; Agilent, 2012)
 $T_{\text{min}} = 0.653$, $T_{\text{max}} = 0.721$

3349 measured reflections
 3349 independent reflections
 1395 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.075$
 $wR(F^2) = 0.184$
 $S = 0.80$
 3349 reflections

182 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.94$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.57$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cu1—O1	1.892 (5)	Cu1—O6	1.954 (4)
Cu1—O6 ⁱ	1.940 (5)	Cu1—O6 ⁱⁱ	2.524 (5)
Cu1—N1	1.952 (6)		

Symmetry codes: (i) $-y + \frac{5}{4}, x + \frac{1}{4}, -z + \frac{1}{4}$; (ii) $-x + 1, -y + \frac{3}{2}, z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O4}-\text{H4A}\cdots\text{O4}^{\text{ii}}$	0.78	1.96	2.729 (9)	171

Symmetry code: (ii) $-x + 1, -y + \frac{3}{2}, z$.

Data collection: *CrysAlis CCD* (Agilent, 2012); cell refinement: *CrysAlis RED* (Agilent, 2012); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *OLEX2* (Dolomanov *et al.*, 2009); molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF* (Westrip, 2010).

This work was partly supported by the State Fund for Fundamental Research of Ukraine (project 54.3/005).

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7174).

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supporting information

Acta Cryst. (2014). E70, m54–m55 [doi:10.1107/S1600536814000798]

Tetrakis(μ_3 -2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]-6-nitrophenolato)tetracopper(II)

Eduard N. Chygorin, Yuri O. Smal, Vladimir N. Kokozay and Irina V. Omelchenko

S1. Comment

In last few decades polynuclear complexes have been in focus of intense interest due to their relevance to the active sites of metalloenzymes, and their potential applications as magnetic materials. Thus development of synthetic approaches that could lead to new polynuclear compounds or improve their yields is quite important. Our research group is interested in employment of so-called "direct synthesis" (DS), a serendipitous self-assembling approach based on utilization of metal powders as starting materials to construct coordination compounds both homo- and heterometallic ones. Recently we have shown its ability to produce Co/Fe complexes with Schiff base ligand (Chygorin *et al.*, 2012; Nesterov *et al.*, 2012). It should be noted that outcome of DS is not highly predictable and sometimes we can isolated homometallic or mononuclear complexes only. Such a case was observed in the investigated system: $\text{Cu}^0\text{-FeCl}_2\cdot 4\text{H}_2\text{O-H}_4\text{L-Et}_3\text{N-dmf}$, where H_4L is 2-hydroxymethyl-2-[[2-(2-hydroxy-3-nitrophenyl)methylene]amino]propane-1,3-diol (Fig. 1). The Schiff base ligand, that is obtained by condensation of the salicylaldehyde derivative and tris(hydroxymethyl)aminomethane is typical hydroxy-rich ligand, which can coordinate to several metal centers and accepts various coordination modes, and thus it is an attractive ligand system for serendipitous self-assembling. Despite of this fact this Schiff base ligand has received little attention to date [only 35 hits were found by searching *via* CSD (<http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi?>)]. Herein we report the synthesis of a new tetranuclear cubane complex starting from potentially polydentate hydroxyl-rich ligand.

The reaction of copper powder with iron(II) chloride in dmf solution of the tetrapodal Schiff base ligand, formed *in situ*, in basic medium with free access of air leads to the isolation of the homometallic cubane complex $[\text{Cu}_4(\text{C}_{11}\text{H}_{12}\text{O}_6\text{N}_2)_4]$. The Schiff base ligand H_4L was obtained by condensation of 3-nitro-salicylaldehyde and tris(hydroxymethyl)aminomethane (Fig. 1). The molar ratio of starting materials (Cu^0 : FeCl_2 : Schiff base ligand) was taken 1:1:2. The reaction was carried out in air with heating and stirring till total dissolution of metal powder was observed.

Tetranuclear molecular complex (Fig. 2) consists of the discrete $[\text{Cu}_4(\text{H}_2\text{L})_4]$ moiety with a $\{\text{Cu}_4\text{O}_4\}$ cubane-like core. Eight alternately arranged metal centers and oxygen atoms from methoxy groups form a distorted $\{\text{Cu}_4\text{O}_4\}$ cube with local S_4 -symmetry. Each of four ligands coordinates in a tridentate mode as an $(\text{H}_2\text{L})^{2-}$ dianion, with the phenoxyl and one of the alkoxyl groups deprotonated. The NO_2 donor set from one ligand molecule together with O-atom from methoxy arm of another ligand forms distorted square coordination polyhedra around each metal center (with RMS deviation of atoms from square plane of 0.135 Å). Coordination lengths vary in the range of 1.892 - 1.955 Å, and $X\text{-Cu-Y}$ angles vary in the range of 84.8 - 94.9° that is comparable with the known literature data. The oxygen atom of the methoxy group of the third ligand molecule coordinates on this metal atom with Cu-O length of 2.524 Å, so that can be treated as additional coordination. In crystal, weak $\text{C4-H4B}\cdots\text{O2}'$ hydrogen bonds (1.25 - y,x - 0.25, z - 0.25; $\text{H}\cdots\text{O}'$ 2.51 Å, $\text{C-H}\cdots\text{O}'$ 153°) form three-dimensional-connected network with channels along (111) crystallographic direction. Minimal channel

dimension is about 6.74 Å (O5···O5' distance). The crystal packing diagram is shown in Fig. 3.

S2. Experimental

Tris(hydroxymethyl)aminomethane (0.303 g, 2.5 mmol), 3-Nitrosalicylaldehyde (0.418 g, 2.5 mmol), and triethylamine (0.35 ml, 2.5 mmol) were dissolved in dmf (25 ml) in this order, forming an orange solution and magnetically stirred at 60–70°C (15 min). Then, copper powder (0.079 g, 1.25 mmol) and FeCl₂·4H₂O (0.248 g, 1.25 mmol) were successfully added to the hot orange solution with stirring about 3 h. Brown blocks were isolated by adding diethylether to the dark orange-brown solution after 2 days. Yield: 0.4 g, 48%. The compound is sparingly soluble in dmsol and dmf, and it is stable in air.

S3. Refinement

All H atoms were placed in idealized positions (C–H = 0.95 – 0.99 Å, O–H = 0.84 Å) and constrained to ride on their parent atoms, with $U_{\text{iso}} = 1.2\text{Ueq}$ (except $U_{\text{iso}} = 1.5\text{Ueq}$ for hydroxyl groups). Hydrogen atom of the hydroxyl group O4–H4 was disordered over two sites with equal occupancy factors of 0.50 in order to fit the intramolecular hydrogen bond O4–H4A···O4'. Several isolated electron density peaks were located during the refinement, whose were believe to be a solvent molecules. Large displacement parameters were observed modeling the disordered oxygen, carbon, and sulfur atoms. SQUEEZE procedure of *PLATON* indicated a solvent cavity of volume 3131 Å³ centered at (0,0,0), containing approximately 749 electrons. In the final refinement, this contribution was removed from the intensity data that produced better refinement results. The hydroxyl group O5–H5A located near the void was believed to be H-bonded with one of the removed solvent molecules. Several reflections with great differences between calculated and observed F^2 were omitted during the refinement. These reflections were believed to arise because of little impurities of the crystal under study.

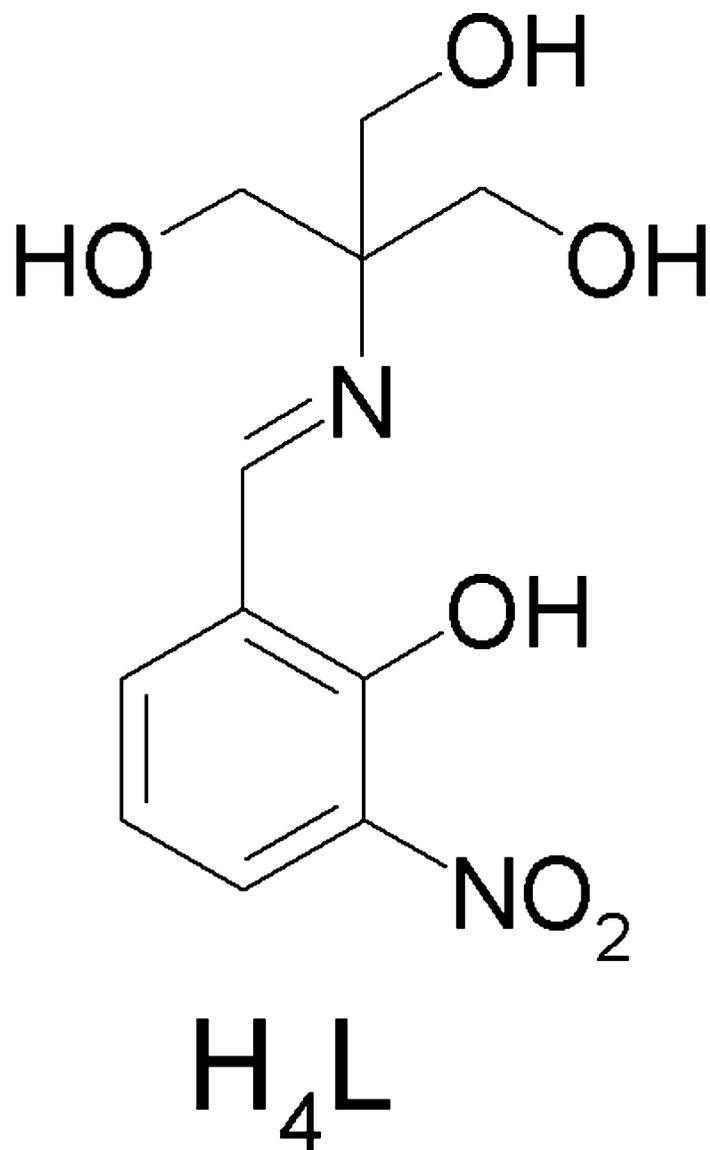


Figure 1

Schiff base ligand: the product of condensation of 3-nitro-salicylaldehyde and tris(hydroxymethyl)aminomethane.

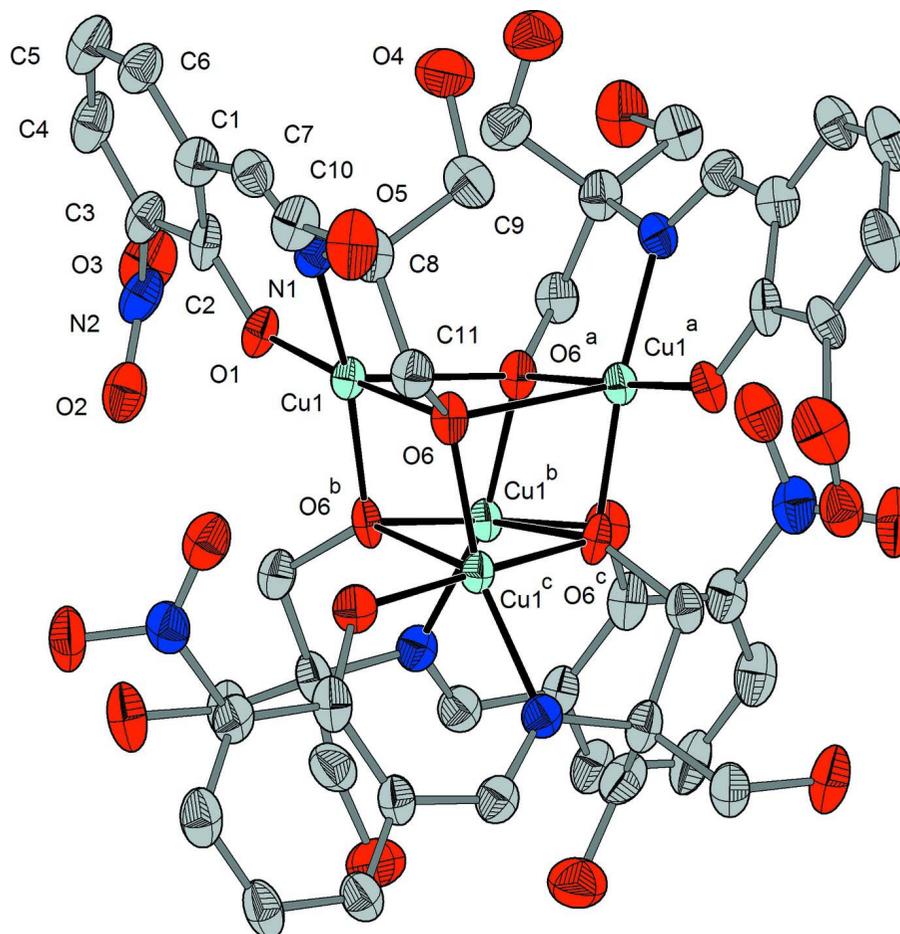


Figure 2

View of cubane tetranuclear complex $[\text{Cu}_4(\text{C}_{11}\text{H}_{12}\text{O}_6\text{N}_2)_4]$ (H atoms are omitted for clarity, the non-hydrogen atoms are shown as 30% thermal ellipsoids). Symmetry transformation used to generate equivalent atoms: $^a 1 - x, 1.5 - y, z$; $^b x + 0.25, 1.25 - y, 0.25 - z$; $^c 1.25 - x, y - 0.25, 0.25 - z$.

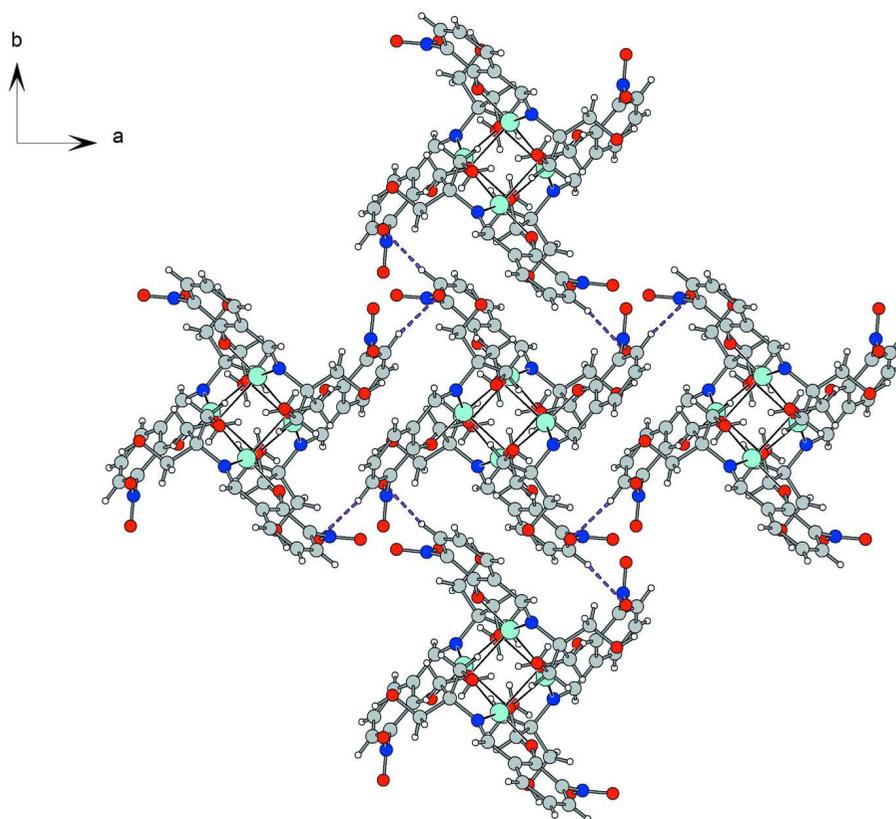


Figure 3

The crystal-packing diagram along the (001) direction.

Tetrakis(μ_3 -2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]-6-nitrophenolato)tetracopper(II)

Crystal data

[Cu₄(C₁₁H₁₂N₂O₆)₄]

$M_r = 1327.06$

Tetragonal, $I4_1/a$

Hall symbol: $-I\ 4ad$

$a = 20.5587$ (14) Å

$c = 18.010$ (2) Å

$V = 7612.0$ (11) Å³

$Z = 4$

$F(000) = 2704$

$D_x = 1.158$ Mg m⁻³

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

Cell parameters from 462 reflections

$\theta = 3.0$ – 25.0°

$\mu = 1.17$ mm⁻¹

$T = 173$ K

Block, brown

$0.40 \times 0.40 \times 0.30$ mm

Data collection

Agilent Xcalibur Sapphire3
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1827 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Agilent, 2012)

$T_{\min} = 0.653$, $T_{\max} = 0.721$

3349 measured reflections

3349 independent reflections

1395 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.000$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 3.2^\circ$

$h = -16 \rightarrow 17$

$k = 0 \rightarrow 24$

$l = 0 \rightarrow 21$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.075$
 $wR(F^2) = 0.184$
 $S = 0.80$
 3349 reflections
 182 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.060P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.94 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.57 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.48941 (4)	0.66864 (4)	0.06731 (4)	0.0396 (3)	
O1	0.5536 (2)	0.6041 (2)	0.0524 (3)	0.0451 (13)	
N1	0.4460 (3)	0.6539 (3)	-0.0276 (3)	0.0406 (16)	
C1	0.5204 (4)	0.5693 (4)	-0.0716 (4)	0.047 (2)	
N2	0.6541 (4)	0.5153 (3)	0.0538 (4)	0.0542 (19)	
O2	0.6303 (3)	0.5101 (3)	0.1159 (3)	0.0611 (17)	
C2	0.5608 (4)	0.5690 (4)	-0.0063 (5)	0.047 (2)	
O3	0.7144 (3)	0.5100 (3)	0.0436 (3)	0.0751 (19)	
C3	0.6141 (4)	0.5230 (4)	-0.0096 (5)	0.050 (2)	
O4	0.4358 (3)	0.7332 (3)	-0.1606 (3)	0.0761 (19)	
H4A	0.4728	0.7401	-0.1646	0.114*	0.50
H4C	0.4145	0.7014	-0.1769	0.114*	0.50
C4	0.6276 (4)	0.4875 (4)	-0.0723 (5)	0.061 (2)	
H4B	0.6644	0.4596	-0.0728	0.073*	
O5	0.2776 (3)	0.7029 (3)	-0.0736 (4)	0.0732 (18)	
H5A	0.2430	0.6816	-0.0784	0.110*	
C5	0.5890 (4)	0.4913 (4)	-0.1342 (5)	0.061 (3)	
H5B	0.5991	0.4672	-0.1777	0.073*	
O6	0.4282 (2)	0.7408 (2)	0.0779 (2)	0.0369 (12)	
C6	0.5353 (4)	0.5310 (4)	-0.1317 (4)	0.052 (2)	
H6A	0.5071	0.5320	-0.1735	0.063*	
C7	0.4659 (4)	0.6122 (4)	-0.0773 (4)	0.048 (2)	
H7A	0.4416	0.6101	-0.1220	0.057*	
C8	0.3906 (4)	0.6972 (4)	-0.0412 (4)	0.047 (2)	
C9	0.4121 (4)	0.7530 (4)	-0.0911 (4)	0.057 (2)	

H9A	0.3747	0.7826	-0.0989	0.069*
H9B	0.4465	0.7780	-0.0653	0.069*
C10	0.3319 (4)	0.6594 (4)	-0.0737 (5)	0.058 (2)
H10A	0.3415	0.6448	-0.1249	0.069*
H10B	0.3223	0.6206	-0.0430	0.069*
C11	0.3712 (4)	0.7262 (4)	0.0359 (4)	0.0436 (19)
H11A	0.3454	0.7663	0.0285	0.052*
H11B	0.3440	0.6945	0.0633	0.052*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0337 (6)	0.0344 (6)	0.0509 (5)	0.0009 (5)	-0.0021 (5)	-0.0018 (4)
O1	0.044 (3)	0.029 (3)	0.062 (3)	-0.005 (3)	-0.002 (3)	-0.015 (3)
N1	0.039 (4)	0.037 (4)	0.046 (3)	-0.005 (3)	-0.001 (3)	-0.006 (3)
C1	0.032 (5)	0.046 (5)	0.064 (5)	0.001 (4)	0.007 (4)	-0.004 (5)
N2	0.053 (5)	0.038 (4)	0.071 (5)	0.012 (4)	-0.004 (4)	-0.017 (4)
O2	0.059 (4)	0.040 (4)	0.084 (4)	0.008 (3)	-0.019 (4)	-0.004 (3)
C2	0.034 (5)	0.022 (4)	0.084 (6)	-0.001 (4)	0.003 (5)	-0.009 (4)
O3	0.032 (4)	0.077 (5)	0.116 (5)	0.013 (3)	-0.001 (3)	-0.026 (4)
C3	0.039 (5)	0.041 (5)	0.071 (5)	-0.023 (4)	-0.002 (5)	-0.018 (5)
O4	0.082 (5)	0.088 (5)	0.059 (3)	-0.014 (4)	0.006 (3)	0.006 (3)
C4	0.039 (5)	0.045 (6)	0.098 (6)	-0.004 (5)	0.005 (5)	-0.024 (5)
O5	0.038 (4)	0.065 (4)	0.116 (5)	0.001 (3)	-0.020 (4)	0.000 (4)
C5	0.037 (5)	0.051 (6)	0.094 (6)	-0.004 (5)	0.020 (5)	-0.033 (5)
O6	0.019 (3)	0.029 (3)	0.063 (3)	0.002 (2)	-0.007 (2)	0.004 (2)
C6	0.040 (5)	0.054 (6)	0.062 (5)	-0.012 (5)	0.005 (4)	-0.016 (5)
C7	0.044 (5)	0.048 (5)	0.051 (5)	-0.013 (4)	-0.001 (4)	0.010 (4)
C8	0.032 (5)	0.043 (5)	0.067 (5)	0.005 (4)	-0.013 (4)	0.004 (4)
C9	0.048 (6)	0.063 (6)	0.062 (5)	-0.010 (5)	-0.017 (4)	0.010 (5)
C10	0.041 (5)	0.061 (6)	0.071 (5)	0.005 (5)	0.000 (5)	-0.007 (5)
C11	0.030 (5)	0.041 (5)	0.059 (4)	0.000 (4)	0.003 (4)	-0.002 (4)

Geometric parameters (Å, °)

Cu1—O1	1.892 (5)	C4—C5	1.371 (11)
Cu1—O6 ⁱ	1.940 (5)	C4—H4B	0.9500
Cu1—N1	1.952 (6)	O5—C10	1.430 (9)
Cu1—O6	1.954 (4)	O5—H5A	0.8400
Cu1—O6 ⁱⁱ	2.524 (5)	C5—C6	1.374 (11)
O1—C2	1.288 (8)	C5—H5B	0.9500
N1—C7	1.304 (9)	O6—C11	1.428 (8)
N1—C8	1.467 (9)	O6—Cu1 ⁱⁱⁱ	1.940 (5)
C1—C6	1.373 (10)	C6—H6A	0.9500
C1—C7	1.428 (10)	C7—H7A	0.9500
C1—C2	1.440 (10)	C8—C9	1.524 (10)
N2—O2	1.224 (8)	C8—C10	1.551 (10)
N2—O3	1.259 (8)	C8—C11	1.562 (10)

N2—C3	1.417 (10)	C9—H9A	0.9900
C2—C3	1.449 (10)	C9—H9B	0.9900
C3—C4	1.373 (10)	C10—H10A	0.9900
O4—C9	1.403 (9)	C10—H10B	0.9900
O4—H4A	0.7773	C11—H11A	0.9900
O4—H4C	0.8400	C11—H11B	0.9900
O1—Cu1—O6 ⁱ	93.6 (2)	C6—C5—H5B	120.9
O1—Cu1—N1	94.9 (2)	C11—O6—Cu1 ⁱⁱⁱ	118.5 (4)
O6 ⁱ —Cu1—N1	164.4 (2)	C11—O6—Cu1	108.5 (4)
O1—Cu1—O6	174.8 (2)	Cu1 ⁱⁱⁱ —O6—Cu1	108.6 (2)
O6 ⁱ —Cu1—O6	87.9 (2)	C1—C6—C5	123.1 (8)
O1—Cu1—O6 ⁱⁱ	93.45 (18)	C1—C6—H6A	118.5
O6 ⁱ —Cu1—O6 ⁱⁱ	73.19 (17)	C5—C6—H6A	118.5
N1—Cu1—O6 ⁱⁱ	119.2 (2)	N1—C7—C1	127.0 (7)
O6—Cu1—O6 ⁱⁱ	82.22 (17)	N1—C7—H7A	116.5
N1—Cu1—O6	84.8 (2)	C1—C7—H7A	116.5
C2—O1—Cu1	126.0 (5)	N1—C8—C9	109.3 (6)
C7—N1—C8	121.9 (6)	N1—C8—C10	111.3 (6)
C7—N1—Cu1	124.0 (5)	C9—C8—C10	112.3 (6)
C8—N1—Cu1	114.0 (5)	N1—C8—C11	106.4 (6)
C6—C1—C7	118.2 (8)	C9—C8—C11	108.1 (7)
C6—C1—C2	120.9 (8)	C10—C8—C11	109.2 (6)
C7—C1—C2	120.8 (7)	O4—C9—C8	114.1 (7)
O2—N2—O3	121.3 (7)	O4—C9—H9A	108.7
O2—N2—C3	120.9 (7)	C8—C9—H9A	108.7
O3—N2—C3	117.6 (7)	O4—C9—H9B	108.7
O1—C2—C1	127.1 (7)	C8—C9—H9B	108.7
O1—C2—C3	119.0 (7)	H9A—C9—H9B	107.6
C1—C2—C3	113.9 (7)	O5—C10—C8	107.0 (6)
C4—C3—N2	119.1 (8)	O5—C10—H10A	110.3
C4—C3—C2	122.3 (8)	C8—C10—H10A	110.3
N2—C3—C2	118.6 (7)	O5—C10—H10B	110.3
C9—O4—H4A	111.7	C8—C10—H10B	110.3
C9—O4—H4C	110.9	H10A—C10—H10B	108.6
H4A—O4—H4C	128.4	O6—C11—C8	110.0 (6)
C5—C4—C3	121.4 (8)	O6—C11—H11A	109.7
C5—C4—H4B	119.3	C8—C11—H11A	109.7
C3—C4—H4B	119.3	O6—C11—H11B	109.7
C10—O5—H5A	109.5	C8—C11—H11B	109.7
C4—C5—C6	118.2 (8)	H11A—C11—H11B	108.2
C4—C5—H5B	120.9		
O6 ⁱ —Cu1—O1—C2	170.0 (6)	O6 ⁱ —Cu1—O6—C11	-139.6 (4)
N1—Cu1—O1—C2	3.0 (6)	N1—Cu1—O6—C11	26.7 (4)
O6—Cu1—O1—C2	-84 (2)	O1—Cu1—O6—Cu1 ⁱⁱⁱ	-116 (2)
O6 ⁱⁱ —Cu1—O1—C2	-116.7 (6)	O6 ⁱ —Cu1—O6—Cu1 ⁱⁱⁱ	-9.5 (2)
O1—Cu1—N1—C7	-2.5 (6)	N1—Cu1—O6—Cu1 ⁱⁱⁱ	156.7 (3)

O6 ⁱ —Cu1—N1—C7	-125.4 (8)	C7—C1—C6—C5	175.5 (7)
O6—Cu1—N1—C7	172.3 (6)	C2—C1—C6—C5	-0.9 (12)
O6 ⁱⁱ —Cu1—N1—C7	94.2 (6)	C4—C5—C6—C1	3.4 (13)
O1—Cu1—N1—C8	-178.6 (5)	C8—N1—C7—C1	177.6 (7)
O6 ⁱ —Cu1—N1—C8	58.5 (11)	Cu1—N1—C7—C1	1.8 (11)
O6—Cu1—N1—C8	-3.8 (5)	C6—C1—C7—N1	-177.0 (7)
O6 ⁱⁱ —Cu1—N1—C8	-81.9 (5)	C2—C1—C7—N1	-0.6 (12)
Cu1—O1—C2—C1	-2.8 (11)	C7—N1—C8—C9	-77.3 (8)
Cu1—O1—C2—C3	178.0 (5)	Cu1—N1—C8—C9	98.9 (6)
C6—C1—C2—O1	177.4 (7)	C7—N1—C8—C10	47.3 (9)
C7—C1—C2—O1	1.0 (12)	Cu1—N1—C8—C10	-136.5 (5)
C6—C1—C2—C3	-3.4 (11)	C7—N1—C8—C11	166.2 (6)
C7—C1—C2—C3	-179.7 (7)	Cu1—N1—C8—C11	-17.6 (7)
O2—N2—C3—C4	-135.5 (8)	N1—C8—C9—O4	59.8 (8)
O3—N2—C3—C4	40.2 (11)	C10—C8—C9—O4	-64.2 (9)
O2—N2—C3—C2	45.5 (10)	C11—C8—C9—O4	175.3 (6)
O3—N2—C3—C2	-138.8 (8)	N1—C8—C10—O5	170.8 (6)
O1—C2—C3—C4	-175.1 (7)	C9—C8—C10—O5	-66.3 (8)
C1—C2—C3—C4	5.5 (11)	C11—C8—C10—O5	53.6 (8)
O1—C2—C3—N2	3.8 (11)	Cu1 ⁱⁱⁱ —O6—C11—C8	-167.6 (4)
C1—C2—C3—N2	-175.5 (7)	Cu1—O6—C11—C8	-43.2 (6)
N2—C3—C4—C5	177.6 (8)	N1—C8—C11—O6	39.5 (8)
C2—C3—C4—C5	-3.5 (13)	C9—C8—C11—O6	-77.8 (7)
C3—C4—C5—C6	-1.2 (13)	C10—C8—C11—O6	159.8 (6)
O1—Cu1—O6—C11	114 (2)		

Symmetry codes: (i) $-y+5/4, x+1/4, -z+1/4$; (ii) $-x+1, -y+3/2, z$; (iii) $y-1/4, -x+5/4, -z+1/4$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4A \cdots O4 ⁱⁱ	0.78	1.96	2.729 (9)	171

Symmetry code: (ii) $-x+1, -y+3/2, z$.