



Received 10 September 2015

Accepted 16 September 2015

Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; Cu^{II} cubane-type complex; Schiff base ligand; *o*-vanillin; tris(hydroxymethyl)aminomethane; hydrogen bonding

CCDC reference: 1424781

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

Crystal structure of tetrakis(μ_3 -2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]-6-methoxyphenolato)tetrakis[aquacopper(II)]: a redetermination at 200 K

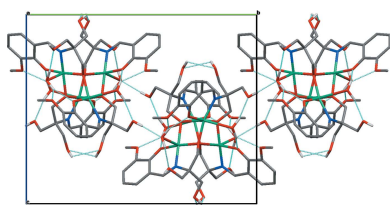
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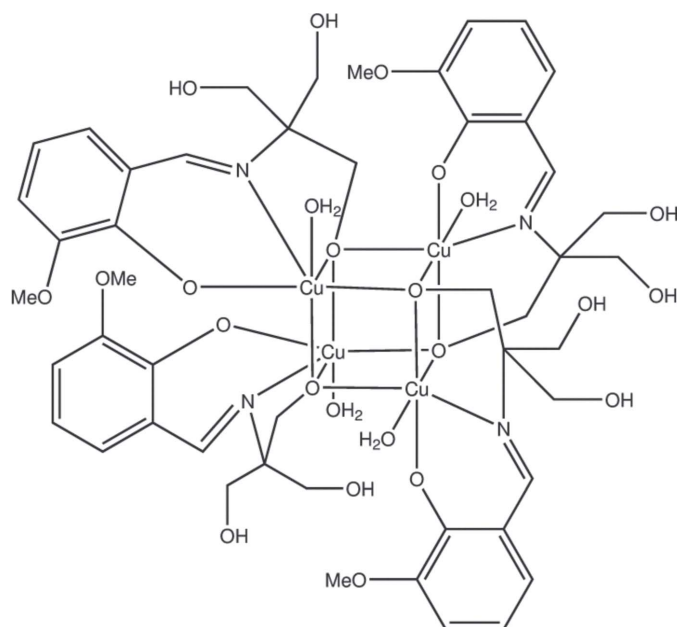
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The crystal structure of the tetranuclear title compound, [Cu₄(C₁₂H₁₅NO₅)₄·(H₂O)₄], has been previously reported by Back, Oliveira, Canabarro & Iglesias [*Z. Anorg. Allg. Chem.* (2015), **641**, 941–947], based on room-temperature data. In the previously published structure, no standard uncertainties are recorded for the deprotonated hydroxymethyl group and water molecule O atoms coordinating to the metal atom indicating that they were not refined; furthermore, the H atoms of some OH groups and water molecules have not been positioned accurately. Since the current structure was determined at a lower temperature, all atoms, including the H atoms of these hydroxy groups and the water molecule, have been determined more accurately resulting in improved standard uncertainties in the bond lengths and angles. Diffraction data were collected at 200 K, rather than the more usual 100 K, due to apparent disordering at lower temperatures. In addition, it is now possible to report intra- and intermolecular O—H···O interactions. In the title complex molecule, which has crystallographic $\bar{4}$ symmetry, the Cu^{II} ions are coordinated by the tridentate Schiff base ligands and water molecules, forming a tetranuclear Cu₄O₄ cubane-like core. The Cu^{II} ion adopts a CuNO₅ elongated octahedral environment. The coordination environment of Cu^{II} at 200 K displays a small contraction of the Cu—N/O bonds, compared with the room-temperature structure. In the crystal lattice, the neutral clusters are linked by intermolecular O—H···O hydrogen bonds into a one-dimensional hydrogen-bonding network propagating along the *b* axis.

1. Chemical context

During the last few years, we have been exploring the chemistry of transition metal complexes of Schiff base ligands with the aim of preparing heterometallic polynuclear compounds with diverse potential advantages. In these studies, we continued to apply the *direct synthesis of coordination compounds* based on spontaneous self-assembly, in which one of the metals is introduced as a powder (zerovalent state) and oxidized during the synthesis (typically by dioxygen from the air) (Pryma *et al.*, 2003; Nesterova *et al.*, 2008; Nesterov *et al.*, 2012). The main advantage of this approach is the generation of building blocks *in situ*, in one reaction vessel, thus eliminating separate steps in building-block construction. Reactions of a metal powder and another metal salt in air with a solution containing a pre-formed Schiff base ligand have yielded a number of novel Co/Fe and Cu/Fe compounds (Chygorin *et al.*, 2015; Nesterova *et al.*, 2013).





The title compound was prepared in studies of the coordination behavior of the versatile multidentate Schiff base ligand 2-[[2-(2-hydroxy-3-methoxyphenyl)methylene]amino]-2-(hydroxymethyl)-1,3-propanediol (H_4L) (Odabaşoğlu *et al.*, 2003) which results from the condensation between *o*-vanillin and tris(hydroxymethyl)aminomethane. In the syntheses, the condensation reaction was utilized without isolation of the resulting Schiff base. In an attempt to prepare a heterometallic assembly we reacted Cu powder and $Zn(CH_3COO)_2$ with a methanol solution of the Schiff base in a 1:1:2 molar ratio. However, the isolated green microcrystalline product was identified crystallographically to be the tetranuclear Cu^{II}

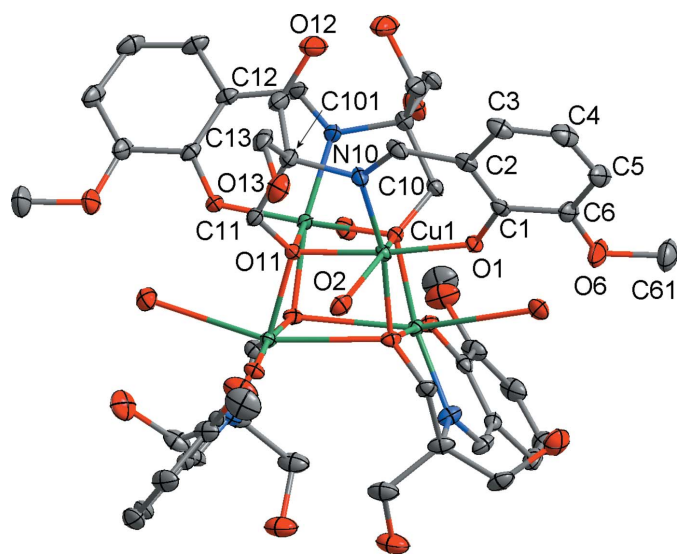


Figure 1
The molecular structure of the title complex, showing the atom-numbering scheme. Non-H atoms are shown with displacement ellipsoids at the 50% probability level. H atoms are not shown.

Table 1
Selected bond lengths (Å).

Cu1—O1	1.912 (4)	Cu1—O2	2.738 (5)
Cu1—O11	1.941 (4)	Cu1—O11 ⁱ	1.968 (3)
Cu1—N10	1.953 (5)	Cu1—O11 ⁱⁱ	2.547 (4)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O12—H12 \cdots O12 ⁱⁱ	0.84	2.37	2.736 (12)	107
O13—H13 \cdots O2 ⁱⁱⁱ	0.84	1.91	2.700 (6)	156
O2—H2A $O\cdots$ O1 ^{iv}	0.93 (5)	1.92 (4)	2.791 (6)	155 (8)
O2—H2A $O\cdots$ O6 ^{iv}	0.93 (5)	2.23 (7)	2.853 (7)	124 (6)
O2—H2B $O\cdots$ O13	0.96 (5)	1.95 (3)	2.892 (7)	165 (6)

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

Schiff base complex $Cu_4(H_2L)_4(H_2O)_4$ (**1**) of a hetero-cubane type.

The crystal structure of (**1**) has been reported previously at room temperature by Back *et al.* (2015) (refcode IGOSUU). In that report of the structure, no standard uncertainties are recorded for the oxygen atoms of the deprotonated hydroxymethyl group, O2, and the water molecule coordinating to the metal atom, O6, indicating that they were not refined. The hydrogen atoms of some OH groups and water molecules have also not been positioned accurately. It is clear from the *checkCIF* output that at least one of the water molecule hydrogen atoms, H6B, and one OH hydrogen atom, H4, are incorrectly positioned. Since the present structure was determined at a lower temperature, all atoms, including these hydrogen atoms, have been determined more accurately, resulting in improved standard uncertainties in the bond lengths and angles.

2. Structural commentary

The neutral $[Cu_4(C_{12}H_{15}NO_5)_4(H_2O)_4]$ molecule of (**1**) has crystallographic $\bar{4}$ inversion symmetry. The Cu^{II} ions are coordinated by the tridentate Schiff base ligands and water molecules, forming a tetranuclear Cu_4O_4 cubane-like configuration. The ligand acts in a chelating-bridging mode *via* phenoxo-, alkoxo-O and imine-N atoms. The two hydroxymethyl groups remain protonated. The coordination about the Cu^{II} atom is distorted octahedral as a result of a significant Jahn–Teller distortion, the two axial distances Cu1—O2 2.738 (5) Å (to the water molecule) and the bridging bond, Cu1—O11 2.547 (4) Å, being significantly longer than the remainder which lie in the range 1.912 (4)–1.968 (3) Å (Fig. 1, Table 1). The *trans* angles at the metal atom lie in the range 159.30 (12)–171.70 (15)°, while the *cis* ones vary from 73.02 (12) to 116.70 (16)°. The Cu \cdots Cu distances within the Cu_4O_4 core are 3.1724 (8) and 3.4474 (8) Å.

There are intramolecular O2—H2A $O\cdots$ O13 hydrogen bonds between a hydrogen atom of the water molecule and

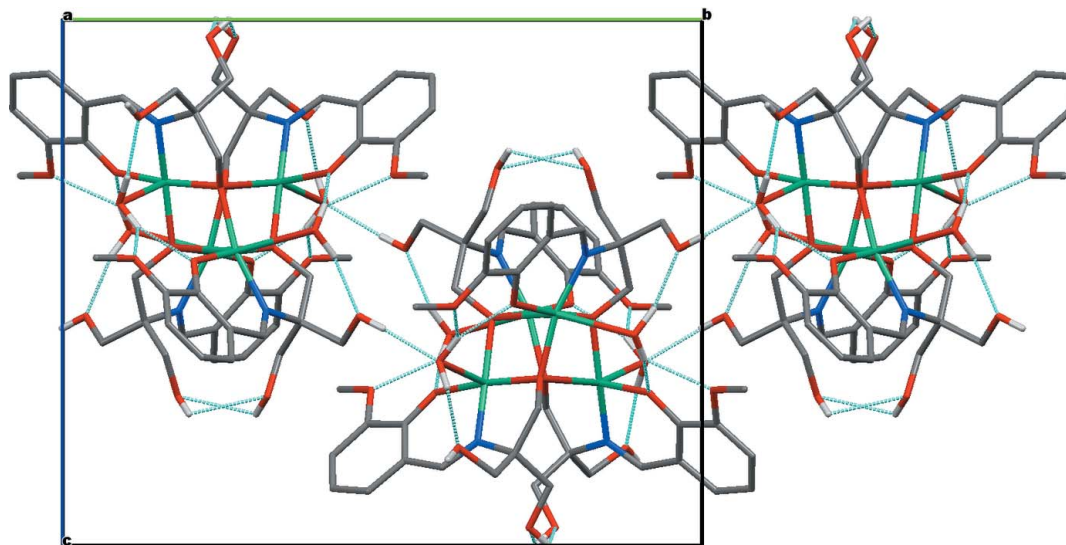


Figure 2
Part of the crystal structure with intra- and intermolecular hydrogen bonds shown as blue dashed lines. C–H hydrogens have been omitted for clarity.

the oxygen atom of one hydroxymethyl group. A further intramolecular hydrogen bond involves the other hydroxymethyl group (O12). Bifurcated intermolecular hydrogen bonds are also present, involving the remaining hydrogen atom of water molecule and the phenolic and methoxy oxygen atoms. These hydrogen-bond contacts are of weak-to-moderate strength [2.736 (12)–2.892 (7) Å], Table 2.

The title compound appears to be a new solvatomorph of the blue copper(II) complex with the same ligand, $[\text{Cu}_4(\text{C}_{12}\text{H}_{15}\text{NO}_5)_4(\text{H}_2\text{O})] \cdot 3.75\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (refcode SUGKUC; Tabassum & Usman, 2015). Monoclinic SUGKUC crystallizes in the $P2_1/n$ space group and has no crystallographically imposed symmetry. It is also a cubane-type complex but with some of the coordinating water molecules replaced by other solvents. The bond lengths and angles of (**1**) are comparable to those in the Ni^{II} analogue (refcode ZEHGUQ; Guo *et al.*, 2008) and a Cu^{II} complex with a similar ligand (refcode AFIMUY; Dong *et al.*, 2007). The ligand of the latter does not have the methoxy group and the copper atom is five-coordinate, the structure lacking the coordinating water molecule of (**1**).

3. Supramolecular features

Interactions between $[\text{Cu}_4(\text{H}_2\text{L})_4(\text{H}_2\text{O})_4]$ molecules in the crystal lattice are weak, the closest $\text{Cu} \cdots \text{Cu}$ inter-cluster separation exceeds 8.43 Å. The hydrogen on the hydroxymethyl group (O13) is involved in an intermolecular hydrogen bond to the water molecule on the cluster related by a crystallographic twofold axis (Table 2), forming a hydrogen-bonded polymer propagating along the *b* axis (Fig. 2). No π - π stacking is observed.

4. Database survey

In the solid state, the H_4L ligand adopts the keto–amine tautomeric form, with the formal aryl–OH H atom relocated

to the N atom, and the NH group and phenolic O atom forming a strong intramolecular $\text{N}—\text{H} \cdots \text{O}$ hydrogen bond (Odabaşoğlu *et al.*, 2003). Crystal structures of about 30 metal complexes of this ligand are found in the Cambridge Database (CSD Version 5.36 with one update; Groom & Allen, 2014). These comprise five homometallic mononuclear Mn, Ni and Mo complexes, polynuclear Co_2 , V_2 , Cu_4 , Mn_4 , Ni_4 , Ln_9 and Ln_{10} assemblies and heterometallic $1s$ – $3d$ and $3d$ – $4f$ clusters of 4–20 nuclearity. The ligand molecules exist in either doubly or triply deprotonated forms and adopt a chelating-bridging mode, forming five- and six-membered rings. Obviously, the H_4L ligand favours formation of polynuclear paramagnetic clusters due to the presence of the tripodal alcohol functionality. At the same time, the lack of heterometallic structures with two kinds of $3d$ metal supported by H_4L is also evident. This perhaps explains the failure of the preparation of a Cu/Zn compound in the present study.

5. Synthesis and crystallization

2-Hydroxy-3-methoxy-benzaldehyde (0.30 g, 2 mmol), tris-(hydroxymethyl)aminomethane (0.24 g, 2 mmol), $\text{N}(\text{Et})_3$ (0.3 ml, 2 mmol) were added to methanol (20 ml) and stirred magnetically for 30 min. Next copper powder (0.06 g, 1 mmol) and $\text{Zn}(\text{CH}_3\text{COO})_2$ (0.19 g, 1 mmol) were added to the yellow solution and the mixture was heated to 323 K under stirring until total dissolution of the copper powder was observed (1 h). The resulting green solution was filtered and allowed to stand at room temperature. Dark-green rhombic prisms of the title compound were formed in several days. They were collected by filter-suction, washed with dry Pr^iOH and finally dried *in vacuo* (yield: 59% based on copper).

The IR spectrum of (**1**) in the range 4000–400 cm^{-1} shows all the characteristic Schiff base ligand frequencies: $\nu(\text{OH})$, $\nu(\text{CH})$ and $\nu(\text{C}=\text{N})$ at 3400, 3066–2840, and 1604 cm^{-1} , respectively. A strong peak at 1628 cm^{-1} that is due to the

Table 3
Experimental details.

Crystal data	
Chemical formula	[Cu ₄ (C ₁₂ H ₁₅ NO ₅) ₄ (H ₂ O) ₄]
<i>M_r</i>	1339.22
Crystal system, space group	Tetragonal, <i>I</i> ₄ / <i>a</i>
Temperature (K)	200
<i>a</i> , <i>c</i> (Å)	18.7108 (3), 15.3800 (3)
<i>V</i> (Å ³)	5384.4 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.65
Crystal size (mm)	0.39 × 0.23 × 0.17
Data collection	
Diffractometer	Oxford Diffraction Xcalibur
Absorption correction	Analytical (<i>CrysAlis CCD</i> and <i>CrysAlis RED</i> ; Agilent, 2013)
<i>T</i> _{min} , <i>T</i> _{max}	0.687, 0.843
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	25330, 3247, 2942
<i>R</i> _{int}	0.044
(sin θ/λ) _{max} (Å ⁻¹)	0.660
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.076, 0.195, 1.12
No. of reflections	3247
No. of parameters	188
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.58, -0.98

Computer programs: *CrysAlis CCD* (Agilent, 2013), *SIR92* (Altomare *et al.*, 1994), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999) and *WinGX* (Farrugia, 2012).

bending of H₂O molecule provides evidence of the presence of water in (**1**).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Diffraction data were collected at 200 K, rather than the more usual 100 K, due to apparent disordering at lower temperatures. Water molecule hydrogen atoms were refined with geometries restrained to ideal values; the OH hydrogen atoms H12 and H13 were refined using a riding model. All hydrogen atoms bound to carbon were included in calculated positions and refined using a riding model with isotropic displacement parameters based on those

of the parent atom [C–H = 0.95 Å, *U*_{iso}(H) = 1.2*U*_{eq}(C) for CH and CH₂, 1.5*U*_{eq}(C) for CH₃]. Anisotropic displacement parameters were employed for the non-hydrogen atoms.

Acknowledgements

The authors acknowledge the facilities, scientific and technical assistance of the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy, Characterization & Analysis, the University of Western Australia, a facility funded by the University, State and Commonwealth Governments.

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supporting information

Acta Cryst. (2015). E71, 1203-1206 [doi:10.1107/S2056989015017314]

Crystal structure of tetrakis(μ_3 -2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]-6-methoxyphenolato)tetrakis[aquacopper(II)]: a redetermination at 200 K

Elena A. Buvaylo, Olga Yu. Vassilyeva and Brian W. Skelton

Computing details

Data collection: *CrysAlis CCD* (Agilent, 2013); cell refinement: *CrysAlis CCD* (Agilent, 2013); data reduction: *CrysAlis CCD* (Agilent, 2013); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Tetrakis(μ_3 -2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]-6-methoxyphenolato)tetrakis[aquacopper(II)]

Crystal data

[Cu₄(C₁₂H₁₅NO₅)₄(H₂O)₄]

$M_r = 1339.22$

Tetragonal, $I4_1/a$

Hall symbol: -I 4ad

$a = 18.7108$ (3) Å

$c = 15.3800$ (3) Å

$V = 5384.4$ (2) Å³

$Z = 4$

$F(000) = 2768$

$D_x = 1.652$ Mg m⁻³

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

Cell parameters from 7964 reflections

$\theta = 2.8$ – 28.9°

$\mu = 1.65$ mm⁻¹

$T = 200$ K

Prism, dark green

$0.39 \times 0.23 \times 0.17$ mm

Data collection

Oxford Diffraction Xcalibur
diffractometer

Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator

Detector resolution: 16.0009 pixels mm⁻¹

ω scans

Absorption correction: analytical
(*CrysAlis CCD* and *CrysAlis RED*; Agilent,
2013)

$T_{\min} = 0.687$, $T_{\max} = 0.843$

25330 measured reflections

3247 independent reflections

2942 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 28.0^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -23 \rightarrow 24$

$k = -23 \rightarrow 24$

$l = -19 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.076$

$wR(F^2) = 0.195$

$S = 1.12$

3247 reflections

188 parameters

4 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0811P)^2 + 52.6317P]$

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

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

$\Delta\rho_{\max} = 1.58$ e Å⁻³

$\Delta\rho_{\min} = -0.98$ e Å⁻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. Diffraction data were collected at 200 K, rather than the more usual 100 K, due to apparent disordering at lower temperatures. Water molecule hydrogen atoms were refined with geometries restrained to ideal values.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.47922 (3)	0.66025 (3)	0.69100 (4)	0.0279 (2)
C1	0.5392 (3)	0.5347 (3)	0.7698 (3)	0.0355 (11)
O1	0.5448 (2)	0.58332 (19)	0.7095 (2)	0.0350 (8)
C2	0.4880 (3)	0.5355 (3)	0.8386 (4)	0.0384 (12)
C3	0.4858 (4)	0.4778 (4)	0.8971 (4)	0.0533 (16)
H3	0.4506	0.4777	0.9416	0.064*
C4	0.5322 (5)	0.4225 (4)	0.8922 (5)	0.063 (2)
H4	0.5285	0.3839	0.9322	0.076*
C5	0.5845 (5)	0.4218 (3)	0.8297 (5)	0.062 (2)
H5	0.6179	0.3836	0.8277	0.075*
C6	0.5887 (4)	0.4770 (3)	0.7690 (4)	0.0531 (16)
O6	0.6377 (4)	0.4824 (3)	0.7043 (4)	0.0781 (18)
C61	0.6974 (6)	0.4339 (5)	0.7031 (7)	0.094 (3)
H61A	0.7184	0.4311	0.7614	0.14*
H61B	0.7334	0.4512	0.6619	0.14*
H61C	0.681	0.3863	0.6852	0.14*
C10	0.4376 (3)	0.5937 (4)	0.8514 (4)	0.0453 (14)
H10	0.4063	0.5904	0.8999	0.054*
N10	0.4318 (2)	0.6488 (3)	0.8033 (3)	0.0416 (11)
C101	0.3781 (4)	0.7071 (4)	0.8247 (4)	0.0492 (15)
C11	0.3629 (3)	0.7439 (3)	0.7393 (4)	0.0384 (12)
H11A	0.3232	0.7186	0.7099	0.046*
H11B	0.3468	0.7933	0.7513	0.046*
O11	0.42189 (18)	0.7465 (2)	0.6827 (2)	0.0322 (7)
C12	0.4105 (5)	0.7622 (4)	0.8871 (5)	0.065 (2)
H12A	0.4533	0.7841	0.8601	0.078*
H12B	0.3753	0.8006	0.8984	0.078*
O12	0.4299 (3)	0.7293 (3)	0.9664 (3)	0.0827 (18)
H12	0.4473	0.76	1.0001	0.124*
C13	0.3123 (4)	0.6764 (4)	0.8649 (4)	0.0551 (17)
H13A	0.3232	0.6592	0.9243	0.066*
H13B	0.2751	0.7139	0.8694	0.066*
O13	0.2862 (3)	0.6191 (3)	0.8141 (4)	0.0724 (16)
H13	0.2492	0.6023	0.8374	0.109*
O2	0.3560 (3)	0.5887 (2)	0.6505 (3)	0.0497 (10)
H2AO	0.341 (4)	0.618 (4)	0.605 (3)	0.075*
H2BO	0.326 (4)	0.601 (4)	0.699 (3)	0.075*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0264 (3)	0.0308 (3)	0.0265 (3)	−0.0006 (2)	−0.0008 (2)	0.0045 (2)
C1	0.044 (3)	0.030 (2)	0.033 (3)	−0.003 (2)	−0.013 (2)	0.0002 (19)
O1	0.0390 (19)	0.0342 (18)	0.0317 (17)	0.0055 (15)	0.0023 (15)	0.0060 (14)
C2	0.039 (3)	0.042 (3)	0.034 (3)	−0.010 (2)	−0.008 (2)	0.008 (2)
C3	0.062 (4)	0.051 (4)	0.046 (3)	−0.017 (3)	−0.009 (3)	0.019 (3)
C4	0.094 (6)	0.042 (3)	0.053 (4)	−0.008 (4)	−0.012 (4)	0.015 (3)
C5	0.101 (6)	0.033 (3)	0.052 (4)	0.015 (3)	−0.012 (4)	0.000 (3)
C6	0.082 (5)	0.033 (3)	0.044 (3)	0.014 (3)	−0.004 (3)	−0.004 (2)
O6	0.105 (4)	0.057 (3)	0.073 (3)	0.044 (3)	0.023 (3)	0.012 (3)
C61	0.101 (7)	0.074 (6)	0.106 (8)	0.046 (5)	0.016 (6)	0.006 (5)
C10	0.033 (3)	0.067 (4)	0.036 (3)	0.000 (3)	0.002 (2)	0.019 (3)
N10	0.033 (2)	0.054 (3)	0.038 (2)	0.011 (2)	0.0041 (19)	0.013 (2)
C101	0.055 (4)	0.054 (4)	0.039 (3)	0.020 (3)	0.009 (3)	0.002 (3)
C11	0.039 (3)	0.040 (3)	0.037 (3)	0.006 (2)	0.009 (2)	−0.005 (2)
O11	0.0298 (17)	0.0392 (19)	0.0274 (17)	0.0051 (14)	−0.0015 (13)	0.0032 (14)
C12	0.095 (6)	0.057 (4)	0.042 (4)	0.026 (4)	0.006 (4)	−0.004 (3)
O12	0.126 (5)	0.081 (4)	0.041 (3)	0.019 (4)	−0.006 (3)	−0.003 (3)
C13	0.060 (4)	0.058 (4)	0.047 (3)	0.015 (3)	0.025 (3)	0.003 (3)
O13	0.049 (3)	0.083 (4)	0.085 (4)	0.002 (3)	0.027 (3)	−0.004 (3)
O2	0.060 (3)	0.037 (2)	0.053 (3)	−0.0002 (19)	0.005 (2)	−0.0109 (19)

Geometric parameters (Å, °)

Cu1—O1	1.912 (4)	C61—H61C	0.98
Cu1—O11	1.941 (4)	C10—N10	1.273 (7)
Cu1—N10	1.953 (5)	C10—H10	0.95
Cu1—O2	2.738 (5)	N10—C101	1.519 (7)
Cu1—O11 ⁱ	1.968 (3)	C101—C13	1.494 (9)
Cu1—O11 ⁱⁱ	2.547 (4)	C101—C11	1.510 (8)
C1—O1	1.303 (6)	C101—C12	1.533 (11)
C1—C6	1.422 (8)	C11—O11	1.407 (6)
C1—C2	1.427 (8)	C11—H11A	0.99
C2—C3	1.406 (8)	C11—H11B	0.99
C2—C10	1.455 (9)	O11—Cu1 ⁱⁱⁱ	1.968 (3)
C3—C4	1.353 (11)	C12—O12	1.414 (9)
C3—H3	0.95	C12—H12A	0.99
C4—C5	1.373 (11)	C12—H12B	0.99
C4—H4	0.95	O12—H12	0.84
C5—C6	1.394 (9)	C13—O13	1.413 (9)
C5—H5	0.95	C13—H13A	0.99
C6—O6	1.356 (9)	C13—H13B	0.99
O6—C61	1.439 (9)	O13—H13	0.84
C61—H61A	0.98	O2—H2AO	0.93 (5)
C61—H61B	0.98	O2—H2BO	0.96 (5)

O1—Cu1—O11	171.70 (15)	H61A—C61—H61B	109.5
O1—Cu1—N10	94.41 (17)	O6—C61—H61C	109.5
O11—Cu1—N10	84.16 (17)	H61A—C61—H61C	109.5
N10—Cu1—O2	76.41 (16)	H61B—C61—H61C	109.5
O11—Cu1—O2	85.77 (14)	N10—C10—C2	125.6 (5)
O1—Cu1—O2	101.89 (14)	N10—C10—H10	117.2
O1—Cu1—O11 ⁱ	94.54 (15)	C2—C10—H10	117.2
O11—Cu1—O11 ⁱ	88.41 (16)	C10—N10—C101	120.8 (5)
N10—Cu1—O11 ⁱ	166.34 (18)	C10—N10—Cu1	124.3 (4)
O2—Cu1—O11 ⁱⁱ	159.30 (12)	C101—N10—Cu1	114.4 (3)
O1—Cu1—O11 ⁱ	94.54 (15)	C13—C101—C11	112.3 (6)
O11—Cu1—O11 ⁱ	88.44 (16)	C13—C101—N10	111.0 (5)
O1—Cu1—O11 ⁱⁱ	93.29 (13)	C11—C101—N10	105.3 (4)
N10—Cu1—O11 ⁱⁱ	116.70 (16)	C13—C101—C12	109.1 (6)
O11—Cu1—O11 ⁱⁱ	80.15 (13)	C11—C101—C12	108.2 (6)
O11 ⁱ —Cu1—O11 ⁱⁱ	73.02 (12)	N10—C101—C12	110.9 (5)
O2—Cu1—O11 ⁱ	91.64 (15)	O11—C11—C101	113.9 (5)
O2—Cu1—O11 ⁱⁱ	159.32 (12)	O11—C11—H11A	108.8
O1—C1—C6	118.1 (5)	C101—C11—H11A	108.8
O1—C1—C2	125.1 (5)	O11—C11—H11B	108.8
C6—C1—C2	116.8 (5)	C101—C11—H11B	108.8
C1—O1—Cu1	125.5 (3)	H11A—C11—H11B	107.7
C3—C2—C1	119.2 (6)	C11—O11—Cu1	111.4 (3)
C3—C2—C10	118.0 (6)	C11—O11—Cu1 ⁱⁱⁱ	121.3 (3)
C1—C2—C10	122.9 (5)	Cu1—O11—Cu1 ⁱⁱⁱ	108.47 (17)
C4—C3—C2	122.2 (7)	O12—C12—C101	110.4 (6)
C4—C3—H3	118.9	O12—C12—H12A	109.6
C2—C3—H3	118.9	C101—C12—H12A	109.6
C3—C4—C5	120.2 (6)	O12—C12—H12B	109.6
C3—C4—H4	119.9	C101—C12—H12B	109.6
C5—C4—H4	119.9	H12A—C12—H12B	108.1
C4—C5—C6	120.2 (7)	C12—O12—H12	109.5
C4—C5—H5	119.9	O13—C13—C101	110.4 (5)
C6—C5—H5	119.9	O13—C13—H13A	109.6
O6—C6—C5	125.7 (6)	C101—C13—H13A	109.6
O6—C6—C1	113.0 (5)	O13—C13—H13B	109.6
C5—C6—C1	121.3 (7)	C101—C13—H13B	109.6
C6—O6—C61	119.2 (6)	H13A—C13—H13B	108.1
O6—C61—H61A	109.5	C13—O13—H13	109.5
O6—C61—H61B	109.5	H2AO—O2—H2BO	105 (3)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O12—H12 \cdots O12 ⁱⁱ	0.84	2.37	2.736 (12)	107
O13—H13 \cdots O2 ^{iv}	0.84	1.91	2.700 (6)	156

O2—H2AO···O1 ⁱⁱⁱ	0.93 (5)	1.92 (4)	2.791 (6)	155 (8)
O2—H2AO···O6 ⁱⁱⁱ	0.93 (5)	2.23 (7)	2.853 (7)	124 (6)
O2—H2BO···O13	0.96 (5)	1.95 (3)	2.892 (7)	165 (6)

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