Aqua[4-(hydroxyiminomethyl)pyridine-κN^1](pyridine-2,6-dicarboxylato-$\kappa^3 O^2,N,O^6$)copper(II)

E. M. Mutambi

University of Bristol, Bristol, England BS8 1TS, England

Correspondence e-mail: emutambi@yahoo.com

In the title compound, [Cu(C₇H₃NO₄)(C₆H₆N₂O)(H₂O)], the coordination geometry of the Cu^{II} atom can be described as distorted square pyramidal. The basal plane is defined by one N atom and two O atoms from the deprotonated pyridine-2,6-dicarboxylate ligand, and a pyridyl N atom from the 4-pyridyl aldoxime ligand. The apical position is occupied by a water molecule. O—H···O hydrogen bonds lead to the formation of a two-dimensional network.

Related literature

For related literature, see: Blake *et al.* (2002); Germán-Acacio *et al.* (2007); Ucar *et al.* (2007); Xie *et al.* (2004).

Experimental

Crystal data

[Cu(C₇H₃NO₄)(C₆H₆N₂O)(H₂O)]	γ = 69.739 (1)°
M_r = 368.79	V = 659.91 (4) Å³
Triclinic, $P\bar{1}$	Z = 2
a = 6.7826 (2) Å	Mo $K\alpha$ radiation
b = 7.1858 (3) Å	μ = 1.69 mm⁻¹
c = 14.8746 (6) Å	T = 120 (2) K
α = 76.154 (2)°	0.16 × 0.14 × 0.04 mm
β = 87.152 (1)°	

Data collection

Bruker–Nonius APEXII CCD diffractometer	12553 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	2951 independent reflections
T_{min} = 0.763, T_{max} = 0.925	2814 reflections with $I > 2\sigma(I)$
	R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039	209 parameters
$wR(F^2)$ = 0.103	H-atom parameters constrained
S = 1.10	$\Delta\rho_{max}$ = 0.49 e Å⁻³
2951 reflections	$\Delta\rho_{min}$ = −0.47 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.903 (2)	Cu1—O3	2.0574 (18)
Cu1—N2	1.957 (2)	Cu1—O5	2.2273 (18)
Cu1—O2	2.0018 (18)		
N1—Cu1—N2	168.18 (9)	O2—Cu1—O3	159.29 (8)
N1—Cu1—O2	81.66 (8)	N1—Cu1—O5	91.57 (8)
N2—Cu1—O2	97.18 (8)	N2—Cu1—O5	100.24 (8)
N1—Cu1—O3	79.84 (8)	O2—Cu1—O5	96.71 (7)
N2—Cu1—O3	99.02 (8)	O3—Cu1—O5	93.03 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5C···O1ⁱ	0.84	1.93	2.769 (3)	180
O5—H5B···O4ⁱⁱ	0.83	2.07	2.836 (3)	155
O5—H5B···O6ⁱⁱⁱ	0.83	2.51	2.939 (3)	113
O6—H6···O3ⁱᵛ	0.84	1.89	2.725 (3)	173

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2141).

References

Blake, A. J., Felloni, M., Hubberstey, P., Wilson, C. & Schröder, M. (2002). *Acta Cryst.* E**58**, m43–m46.

Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Germán-Acacio, J. M., Hernández-Ortega, S. & Valdés-Martínez, J. (2007). *Acta Cryst.* E**63**, m1057–m1058.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Ucar, I., Karabulut, B., Bulut, A. & Büyükgüngör, O. (2007). *J. Mol. Struct.* **834–836**, 336–344.

Xie, C., Zhang, B., Liu, X., Wang, X., Kou, H., Shen, G. & Shen, D. (2004). *Inorg. Chem. Commun.* **7**, 1037–1040.

supporting information

Aqua[4-(hydroxyiminomethyl)pyridine-*κN*^{1}](pyridine-2,6-dicarboxylato-*κ*^{3}*O*^{2},*N*,*O*^{6})copper(II)

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S1. Comment

In the design and synthesis of polymeric complexes, various bridging and chelating ligands have been used extensively. Coordination bonds and hydrogen bonds are the major interactions in these assemblies (Xie *et al.*, 2004). Pyridine-2,6-di-carboxylic acid (H$_2$pydc) is an efficient ligand with three coordinating sites. H$_2$pydc coordinates with transition metals in different ways to form various coordination geometries. The relative positions of the coordinating atoms (O and N) determine the type of coordination that will be seen in the molecular structure. The interest in this ligand centers on the versatile yet unpredictable manner in which it coordinates to a wide variety of metals due to its rigid and planar nature (Ucar *et al.*, 2007). This paper aims to report one of the rare coordination modes that can be exhibited by copper(II) when coordinated by H$_2$pydc, 4-pyridyl aldoxime and H$_2$O.

The structure of the title compound is shown in Fig. 1. The molecule is approximately planar and the increased co-planarity is due to the resonance between the pyridine rings, which leads to the formation of square-pyramidal geometry (Fig. 1). The elongated square-pyramidal geometry of the structure (Table 1) is typical of Jahn-Teller-distorted copper(II) (Blake *et al.*, 2002). The structure shows hydrogen-bonding interactions, which enhance the formation of two-dimensional network of the structure (Germán-Acacio *et al.*, 2007). Bond lengths and angles are in the range expected for heteroaromatic-oximes and pryridne dicarboxylates. The hydrogen-bonding interactions are presented in Fig. 2. All the hydrogen-bonding donors and acceptors are involved in O—H···O hydrogen bonds (Table 2), which organize the molecules into a two-dimensional network (Fig. 3).

S2. Experimental

An aqueous solution of Cu(CH$_3$COO)$_2$.6H$_2$O (0.290 g, 1 mmol), KOH (0.220 g, 2 mmol) and H$_2$pydc (0.360 g, 2 mmol) in a 1:2:2 molar ratio was refluxed for 2 h and the resultant reaction mixture was reduced to less than 50 ml. After one day, the grown crystals of K$_2$[Cu(C$_7$H$_3$NO$_4$)$_2$] were filtered out and dried in air. Equimolar amounts of K$_2$[Cu(C$_7$H$_3$NO$_4$)$_2$] and 4-pyridyl aldoxime were dissolved in water in small vials, respectively, and then mixed together. The solution was left at room temperature in a vapour diffusion setup with ethanol. Blue crystals of the title compound were obtained after 3 weeks.

S3. Refinement

H atoms bonded to O atoms were located in a difference map and fixed in the refinements with U_{iso}(H) = 1.5U_{eq}(O). Other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å and with U_{iso}(H) = 1.2U_{eq}(C).
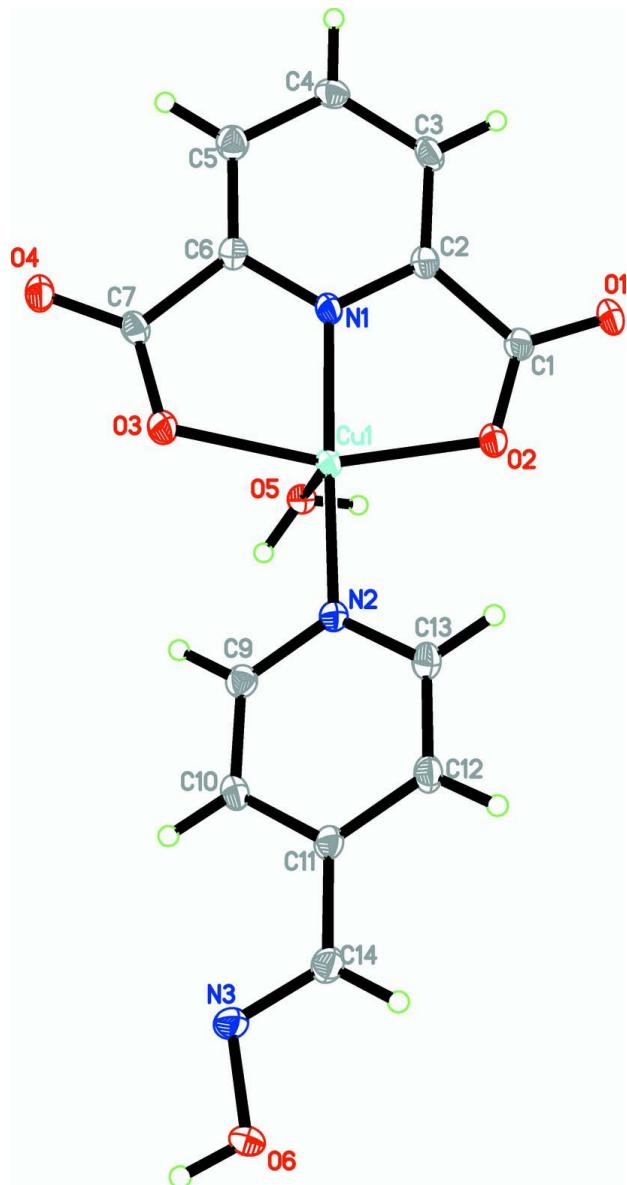
Figure 1

Molecular structure of the title compound, showing the coordination geometry. Displacement ellipsoids are drawn at the 50% probability level.
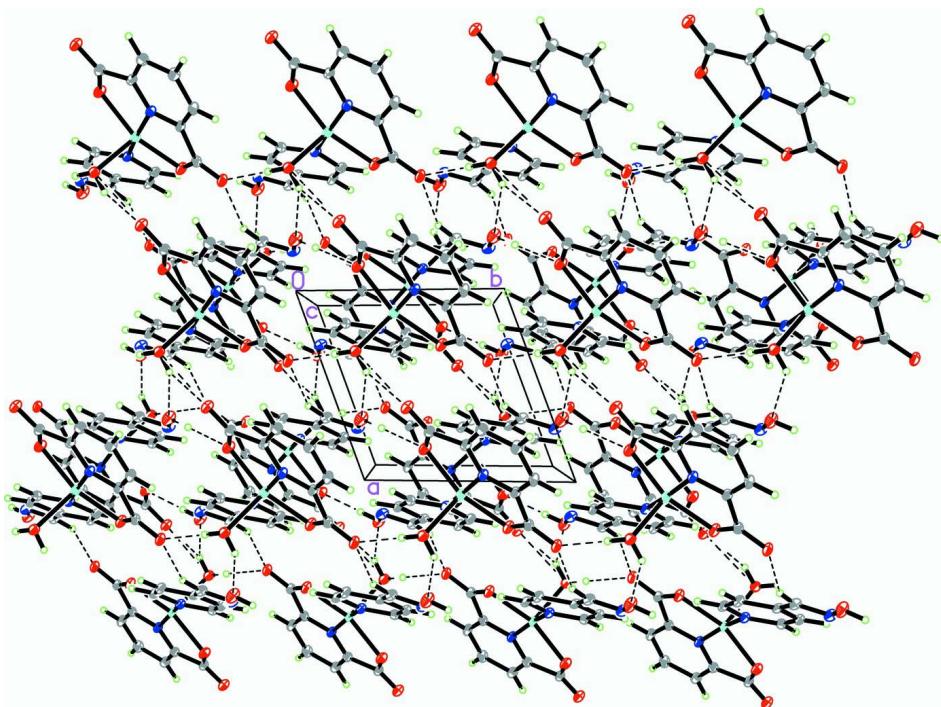
Figure 2

Packing diagram viewed down the *c*-axis, showing hydrogen bonds (dashed lines).
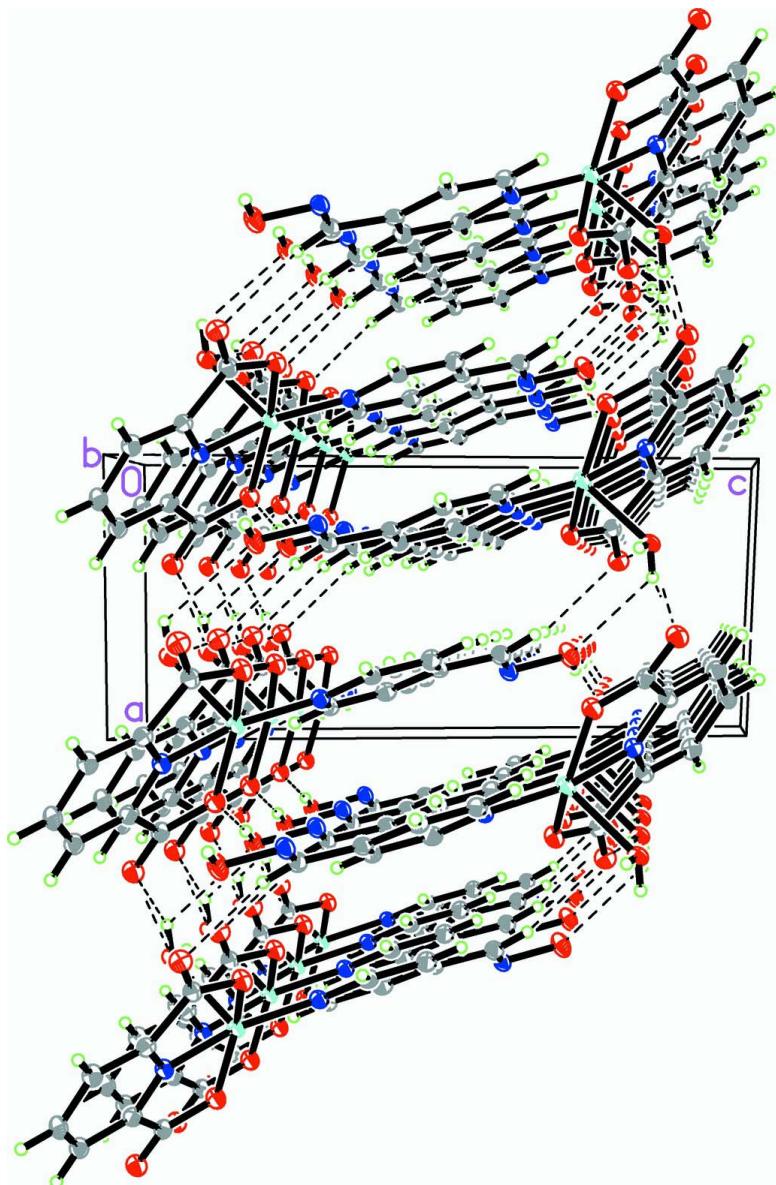
Figure 3

View of a two-dimensional hydrogen-bonded layer along the *c*-axis. Hydrogen bonds are shown as dashed lines.

Aqua[4-(hydroxyiminomethyl)pyridine-*κN*¹](pyridine-2,6-dicarboxylato- *κ³O²,N,O⁶*)copper(II)

Crystal data

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$M_r = 368.79$	$V = 659.91\,(4)$ Å³
Triclinic, $P\bar{1}$	$Z = 2$
Hall symbol: -P 1	$F(000) = 374$
$a = 6.7826\,(2)$ Å	$D_x = 1.848$ Mg m⁻³
$b = 7.1858\,(3)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$c = 14.8746\,(6)$ Å	Cell parameters from 18028 reflections
$\alpha = 76.154\,(2)°$	$\theta = 2.9–27.5°$
$\beta = 87.152\,(1)°$	$\mu = 1.69$ mm⁻¹

T = 120 K

Plate, blue

0.16 × 0.14 × 0.04 mm

Data collection

Bruker–Nonius APEXII CCD diffractometer	T_{min} = 0.763, T_{max} = 0.925
Radiation source: Bruker-Nonius FR591 rotating anode	12553 measured reflections
	2951 independent reflections
10cm confocal mirrors monochromator	2814 reflections with $I > 2\sigma(I)$
Detector resolution: 4096x4096 pixels / 62x62mm pixels mm⁻¹	R_{int} = 0.055
	θ_{max} = 27.4°, θ_{min} = 3.1°
φ and ω scans	h = 0→8
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	k = −8→9
	l = −18→19

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)]$ = 0.039	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.103	
S = 1.10	H-atom parameters constrained
2951 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 1.382P]$ where $P = (F_o^2 + 2F_c^2)/3$
209 parameters	
0 restraints	$(\Delta/\sigma)_{max}$ = 0.001
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max}$ = 0.49 e Å⁻³
	$\Delta\rho_{min}$ = −0.47 e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.89909 (5)	0.56560 (4)	0.26849 (2)	0.01368 (12)
C1	0.7448 (4)	0.2868 (4)	0.22309 (17)	0.0146 (5)
C2	0.9262 (4)	0.2935 (4)	0.15912 (17)	0.0140 (5)
C3	1.0017 (4)	0.1862 (4)	0.09243 (18)	0.0165 (5)
H3	0.9379	0.0962	0.0797	0.020*
C4	1.1751 (4)	0.2134 (4)	0.04381 (18)	0.0176 (5)
H4	1.2321	0.1389	−0.0019	0.021*
C5	1.2656 (4)	0.3486 (4)	0.06166 (18)	0.0170 (5)
H5	1.3821	0.3693	0.0281	0.020*
C6	1.1803 (4)	0.4515 (4)	0.12958 (17)	0.0147 (5)
C7	1.2478 (4)	0.6059 (4)	0.16230 (17)	0.0145 (5)
N2	0.8203 (3)	0.6662 (3)	0.38093 (15)	0.0140 (4)
C9	0.8504 (4)	0.8386 (4)	0.38654 (18)	0.0149 (5)
H9	0.9058	0.9087	0.3349	0.018*
C10	0.8047 (4)	0.9181 (4)	0.46359 (18)	0.0152 (5)
H10	0.8249	1.0422	0.4642	0.018*
C11	0.7280 (4)	0.8137 (4)	0.54125 (17)	0.0145 (5)
C12	0.6947 (4)	0.6355 (4)	0.53510 (18)	0.0164 (5)
H12	0.6404	0.5619	0.5859	0.020*
C13	0.7416 (4)	0.5671 (4)	0.45432 (18)	0.0161 (5)
H13	0.7174	0.4465	0.4506	0.019*
C14	0.6845 (4)	0.8833 (4)	0.62729 (18)	0.0169 (5)

H14	0.6167	0.8189	0.6759	0.020*
N1	1.0162 (3)	0.4206 (3)	0.17580 (15)	0.0138 (4)
N3	0.7389 (3)	1.0317 (4)	0.63636 (15)	0.0172 (4)
O1	0.6349 (3)	0.1882 (3)	0.21279 (13)	0.0174 (4)
O2	0.7219 (3)	0.3883 (3)	0.28564 (13)	0.0167 (4)
O3	1.1531 (3)	0.6594 (3)	0.23461 (13)	0.0175 (4)
O4	1.3813 (3)	0.6698 (3)	0.12037 (13)	0.0187 (4)
O5	0.6858 (3)	0.8261 (3)	0.16420 (12)	0.0159 (4)
H5C	0.6703	0.9360	0.1789	0.024*
H5B	0.5729	0.8094	0.1586	0.024*
O6	0.6877 (3)	1.0704 (3)	0.72334 (13)	0.0215 (4)
H6	0.7376	1.1574	0.7314	0.032*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01538 (18)	0.01586 (18)	0.01443 (18)	−0.00932 (13)	0.00346 (12)	−0.00687 (12)
C1	0.0162 (12)	0.0134 (11)	0.0143 (11)	−0.0060 (9)	0.0011 (9)	−0.0022 (9)
C2	0.0149 (11)	0.0129 (11)	0.0144 (11)	−0.0061 (9)	0.0004 (9)	−0.0016 (9)
C3	0.0206 (12)	0.0160 (12)	0.0177 (12)	−0.0105 (10)	0.0004 (10)	−0.0063 (10)
C4	0.0225 (13)	0.0182 (12)	0.0156 (12)	−0.0084 (10)	0.0035 (10)	−0.0086 (10)
C5	0.0179 (12)	0.0186 (12)	0.0160 (12)	−0.0079 (10)	0.0005 (9)	−0.0043 (10)
C6	0.0147 (11)	0.0154 (11)	0.0151 (11)	−0.0071 (9)	0.0008 (9)	−0.0028 (9)
C7	0.0166 (12)	0.0152 (11)	0.0139 (11)	−0.0079 (9)	−0.0011 (9)	−0.0039 (9)
N2	0.0138 (10)	0.0160 (10)	0.0149 (10)	−0.0075 (8)	0.0024 (8)	−0.0056 (8)
C9	0.0136 (11)	0.0145 (11)	0.0161 (12)	−0.0045 (9)	0.0008 (9)	−0.0031 (9)
C10	0.0145 (11)	0.0145 (11)	0.0184 (12)	−0.0073 (9)	−0.0003 (9)	−0.0037 (9)
C11	0.0115 (11)	0.0181 (12)	0.0158 (12)	−0.0071 (9)	0.0009 (9)	−0.0050 (9)
C12	0.0168 (12)	0.0194 (12)	0.0167 (12)	−0.0110 (10)	0.0010 (9)	−0.0038 (10)
C13	0.0144 (11)	0.0181 (12)	0.0182 (12)	−0.0087 (10)	0.0004 (9)	−0.0037 (10)
C14	0.0156 (12)	0.0215 (12)	0.0159 (12)	−0.0091 (10)	0.0018 (9)	−0.0048 (10)
N1	0.0157 (10)	0.0154 (10)	0.0142 (10)	−0.0090 (8)	0.0017 (8)	−0.0054 (8)
N3	0.0170 (10)	0.0240 (11)	0.0152 (10)	−0.0099 (9)	0.0035 (8)	−0.0092 (9)
O1	0.0198 (9)	0.0155 (8)	0.0211 (9)	−0.0109 (7)	0.0014 (7)	−0.0051 (7)
O2	0.0199 (9)	0.0189 (9)	0.0168 (9)	−0.0124 (7)	0.0041 (7)	−0.0066 (7)
O3	0.0184 (9)	0.0222 (9)	0.0178 (9)	−0.0119 (7)	0.0030 (7)	−0.0088 (7)
O4	0.0192 (9)	0.0222 (9)	0.0201 (9)	−0.0129 (8)	0.0035 (7)	−0.0069 (7)
O5	0.0147 (8)	0.0166 (8)	0.0188 (9)	−0.0069 (7)	0.0031 (7)	−0.0072 (7)
O6	0.0280 (10)	0.0280 (10)	0.0190 (9)	−0.0173 (9)	0.0085 (8)	−0.0150 (8)

Geometric parameters (Å, º)

Cu1—N1	1.903 (2)	C7—O3	1.295 (3)
Cu1—N2	1.957 (2)	N2—C9	1.345 (3)
Cu1—O2	2.0018 (18)	N2—C13	1.348 (3)
Cu1—O3	2.0574 (18)	C9—C10	1.375 (4)
Cu1—O5	2.2273 (18)	C9—H9	0.9500
C1—O1	1.229 (3)	C10—C11	1.401 (3)

C1—O2	1.286 (3)	C10—H10	0.9500
C1—C2	1.524 (3)	C11—C12	1.399 (3)
C2—N1	1.334 (3)	C11—C14	1.463 (4)
C2—C3	1.372 (4)	C12—C13	1.387 (4)
C3—C4	1.397 (4)	C12—H12	0.9500
C3—H3	0.9500	C13—H13	0.9500
C4—C5	1.394 (4)	C14—N3	1.280 (3)
C4—H4	0.9500	C14—H14	0.9500
C5—C6	1.380 (4)	N3—O6	1.390 (3)
C5—H5	0.9500	O5—H5C	0.8400
C6—N1	1.335 (3)	O5—H5B	0.8263
C6—C7	1.520 (3)	O6—H6	0.8400
C7—O4	1.231 (3)		
N1—Cu1—N2	168.18 (9)	C9—N2—C13	118.4 (2)
N1—Cu1—O2	81.66 (8)	C9—N2—Cu1	118.92 (17)
N2—Cu1—O2	97.18 (8)	C13—N2—Cu1	122.68 (18)
N1—Cu1—O3	79.84 (8)	N2—C9—C10	123.0 (2)
N2—Cu1—O3	99.02 (8)	N2—C9—H9	118.5
O2—Cu1—O3	159.29 (8)	C10—C9—H9	118.5
N1—Cu1—O5	91.57 (8)	C9—C10—C11	119.2 (2)
N2—Cu1—O5	100.24 (8)	C9—C10—H10	120.4
O2—Cu1—O5	96.71 (7)	C11—C10—H10	120.4
O3—Cu1—O5	93.03 (7)	C12—C11—C10	117.8 (2)
O1—C1—O2	125.2 (2)	C12—C11—C14	119.7 (2)
O1—C1—C2	119.9 (2)	C10—C11—C14	122.5 (2)
O2—C1—C2	114.9 (2)	C13—C12—C11	119.5 (2)
N1—C2—C3	120.4 (2)	C13—C12—H12	120.2
N1—C2—C1	111.3 (2)	C11—C12—H12	120.2
C3—C2—C1	128.3 (2)	N2—C13—C12	122.1 (2)
C2—C3—C4	118.0 (2)	N2—C13—H13	119.0
C2—C3—H3	121.0	C12—C13—H13	119.0
C4—C3—H3	121.0	N3—C14—C11	119.3 (2)
C5—C4—C3	120.7 (2)	N3—C14—H14	120.4
C5—C4—H4	119.7	C11—C14—H14	120.4
C3—C4—H4	119.7	C2—N1—C6	122.9 (2)
C6—C5—C4	117.9 (2)	C2—N1—Cu1	117.51 (17)
C6—C5—H5	121.1	C6—N1—Cu1	119.60 (17)
C4—C5—H5	121.1	C14—N3—O6	110.1 (2)
N1—C6—C5	120.2 (2)	C1—O2—Cu1	113.75 (16)
N1—C6—C7	111.4 (2)	C7—O3—Cu1	113.79 (16)
C5—C6—C7	128.5 (2)	Cu1—O5—H5C	109.5
O4—C7—O3	125.6 (2)	Cu1—O5—H5B	110.7
O4—C7—C6	120.1 (2)	H5C—O5—H5B	112.6
O3—C7—C6	114.3 (2)	N3—O6—H6	109.5
O1—C1—C2—N1	174.9 (2)	C12—C11—C14—N3	171.6 (2)
O2—C1—C2—N1	−5.5 (3)	C10—C11—C14—N3	−7.7 (4)

O1—C1—C2—C3	−6.4 (4)	C3—C2—N1—C6	0.4 (4)
O2—C1—C2—C3	173.2 (2)	C1—C2—N1—C6	179.2 (2)
N1—C2—C3—C4	0.5 (4)	C3—C2—N1—Cu1	179.26 (19)
C1—C2—C3—C4	−178.1 (2)	C1—C2—N1—Cu1	−1.9 (3)
C2—C3—C4—C5	−1.2 (4)	C5—C6—N1—C2	−0.6 (4)
C3—C4—C5—C6	1.0 (4)	C7—C6—N1—C2	179.3 (2)
C4—C5—C6—N1	−0.1 (4)	C5—C6—N1—Cu1	−179.45 (19)
C4—C5—C6—C7	−179.9 (2)	C7—C6—N1—Cu1	0.4 (3)
N1—C6—C7—O4	−171.9 (2)	N2—Cu1—N1—C2	90.7 (4)
C5—C6—C7—O4	7.9 (4)	O2—Cu1—N1—C2	5.49 (18)
N1—C6—C7—O3	7.7 (3)	O3—Cu1—N1—C2	176.1 (2)
C5—C6—C7—O3	−172.5 (2)	O5—Cu1—N1—C2	−91.07 (19)
N1—Cu1—N2—C9	116.4 (4)	N2—Cu1—N1—C6	−90.4 (4)
O2—Cu1—N2—C9	−160.01 (19)	O2—Cu1—N1—C6	−175.6 (2)
O3—Cu1—N2—C9	32.9 (2)	O3—Cu1—N1—C6	−4.92 (19)
O5—Cu1—N2—C9	−61.82 (19)	O5—Cu1—N1—C6	87.88 (19)
N1—Cu1—N2—C13	−61.9 (5)	C11—C14—N3—O6	−178.7 (2)
O2—Cu1—N2—C13	21.7 (2)	O1—C1—O2—Cu1	−170.6 (2)
O3—Cu1—N2—C13	−145.3 (2)	C2—C1—O2—Cu1	9.9 (3)
O5—Cu1—N2—C13	119.9 (2)	N1—Cu1—O2—C1	−8.63 (17)
C13—N2—C9—C10	0.0 (4)	N2—Cu1—O2—C1	−176.76 (17)
Cu1—N2—C9—C10	−178.33 (19)	O3—Cu1—O2—C1	−35.5 (3)
N2—C9—C10—C11	1.6 (4)	O5—Cu1—O2—C1	81.98 (17)
C9—C10—C11—C12	−2.2 (4)	O4—C7—O3—Cu1	168.1 (2)
C9—C10—C11—C14	177.2 (2)	C6—C7—O3—Cu1	−11.5 (3)
C10—C11—C12—C13	1.1 (4)	N1—Cu1—O3—C7	9.31 (17)
C14—C11—C12—C13	−178.3 (2)	N2—Cu1—O3—C7	177.38 (17)
C9—N2—C13—C12	−1.1 (4)	O2—Cu1—O3—C7	36.3 (3)
Cu1—N2—C13—C12	177.19 (19)	O5—Cu1—O3—C7	−81.74 (18)
C11—C12—C13—N2	0.5 (4)		

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O5—H5C⋯O1[i]	0.84	1.93	2.769 (3)	180
O5—H5B⋯O4[ii]	0.83	2.07	2.836 (3)	155
O5—H5B⋯O6[iii]	0.83	2.51	2.939 (3)	113
O6—H6⋯O3[iv]	0.84	1.89	2.725 (3)	173

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