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A copper complex of an unusual hydroxy–carboxylate ligand: [Cu(bpy)($C_4H_4O_6$)]

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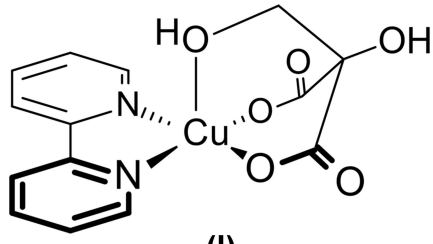
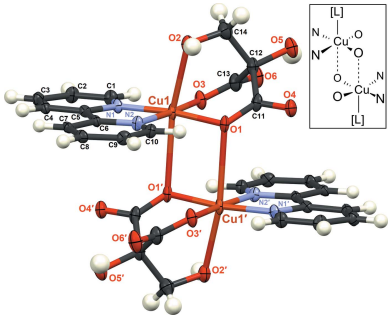
A copper(II) complex, (2,2′-bipyridine-κ^2N,N')[2-hydroxy-2-(hydroxymethyl-κO)propanedioato-κ^2O^1,O^3]copper(II), [Cu($C_4H_4O_6$)($C_{10}H_8N_2$)], containing the unusual anionic chelating ligand 2-(hydroxymethyl)tartronate, has been synthesized. [Cu(bpy)$_2$(NO_3)](NO_3) was mixed with ascorbic acid and Dabco (1,4-diazabicyclo[2.2.2]octane) in DMF (dimethylformamide) solution in the presence of air to produce the title compound. The structure consists of square-pyramidal complexes that are joined by Cu···O contacts [2.703 (2) Å] into centrosymmetric dimers. The $C_4H_4O_6^{2-}$ ligand, which occupies three coordination sites at Cu, has previously been identified as an oxidation product of ascorbate ion.

1. Chemical context

Copper complexes have drawn recent attention owing to applications in redox reactions (Zubair *et al.*, 2019; Maity *et al.*, 2010; Wang *et al.*, 2006) and oxygen transport (Sheykhi *et al.*, 2018; Liu *et al.*, 2016; Tadsanaprasittipol *et al.*, 1998; Kato *et al.*, 2016). The 2,2′-bipyridine ligand has been used in a variety of supramolecular architectures (Fei *et al.*, 2013; John *et al.*, 2004; Seco *et al.*, 2000; Barquín *et al.*, 2010; Yuan *et al.*, 2008).



(I)



As a common reducing reagent, ascorbic acid has also been investigated in complex synthesis and redox reactions (Creutz, 1981; Niemelä, 1987; Sorouraddin *et al.*, 2000). For example, we have recently observed that mixtures of Cu complexes and ascorbate react with O_2 to produce Cu^{II} oxalate complexes (Khamespanah *et al.*, 2021). However, to our knowledge, the particular degradation product of ascorbic acid observed here, 2-(hydroxymethyl)tartronic acid [2-(hydroxymethyl)-2-hydroxy-1,3-propanedioic acid], has been reported only a few times. It was identified by mass spectrometry as a product of oxidation of ascorbic acid (Niemelä, 1987; Löwendahl & Petersson, 1976) and two carbohydrates (Löwendahl *et al.*, 1975*a*,*b*). We have now isolated compound (I), a copper(II) complex of the 2-(hydroxymethyl)tartronate anion (see Scheme), and its crystal structure is reported here.

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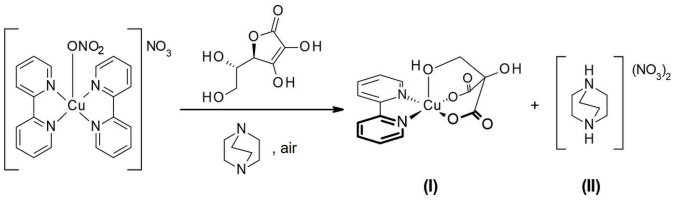

Figure 1
Preparation of the title compound, Cu(bpy)($C_4H_4O_6$) (I), with [DabcoH$_2$](NO_3)$_2$ (II) as byproduct.

The preparation of the title complex is shown in Fig. 1. A solution of [(bpy)$_2$Cu(ONO_2)]NO_3 and Dabco (1,4-diazabicyclo[2.2.2]octane) turned from blue to dark brown on addition of ascorbic acid, suggesting reduction of Cu^{II} to Cu^{I}. The solution was then exposed to air. It turned green over a period of several days, and the title compound (I) could be crystallized (Fig. 2).

In this procedure, Dabco also crystallizes, in its doubly protonated form as colorless [DabcoH$_2$](NO_3)$_2$ (II). We could not isolate the title compound (I) when Dabco was omitted from the reaction mixture. We determined the structure of (II) as well (Gao *et al.*, 2020). Although this structure was reported previously by Knope & Cahill (2007), the new structure provides improved resolution.

2. Structural commentary

The Cu atom in (I) adopts a square-pyramidal geometry, with coordination to two bpy N atoms and three O atoms from the 2-(hydroxymethyl)tartronate anion ($C_4H_4O_6^{2-}$).

The two inversion-related complexes in the unit cell make a dimer *via* two Cu···O contacts: Cu1···O1′ = 2.703 (2) Å. This kind of dimerization (see inset in Fig. 2) is commonly observed in 4- and 5-coordinate Cu^{II} complexes. It is discussed further in the *Database survey* section.

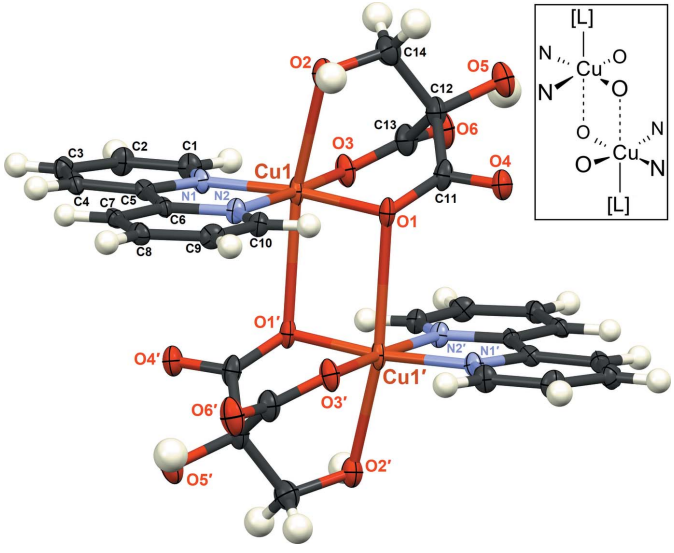

Figure 2
Crystal structure of (I). Ellipsoids are drawn at the 50% probability level; hydrogen atoms are displayed but not labeled. Primed and unprimed atoms are related by an inversion center, which brings the two square-pyramidal Cu(bpy)($C_4H_4O_6$) moieties into contact [Cu···O1′ = 2.703 (2) Å]. The inset is a schematic illustration of the dimerization.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O4^{i}	0.88 (2)	1.85 (2)	2.723 (3)	169 (4)
O5—H5O···O6	0.93 (2)	1.80 (3)	2.549 (3)	136 (3)

Symmetry code: (i) $-x+2, -y+1, -z+1$.

3. Supramolecular features

The structure of (I) includes two O—H···O hydrogen bonds, one intramolecular and one intermolecular; see Table 1. The intermolecular hydrogen bonds form centrosymmetric hydrogen-bonded dimers with graph set $R_2^2(12)$ (Etter *et al.*, 1990). These dimers are linked into chains in the [100] direction, as illustrated in Fig. 3.

4. Database survey

A survey of the Cambridge Structural Database (Version 5.40; Groom *et al.*, 2016) yielded four five-coordinate Cu^{II} complexes with 2,2′-bipyridine, one alcohol, and two carboxylate ligands [CSD refcodes DAXVED (Antolini *et al.*, 1984), SEKXAI (Devereux *et al.*, 2006), TERTEQ (Ma *et al.*, 2006), and VAJTIL (Zhang *et al.*, 2010)]. The Cu atoms in these structures have a square-pyramidal geometry, with the alcohol ligand in the apical position, as in (I), with the following average angles and distances: N—Cu—N, 81.3 (10)°; Cu—N, 2.004 (13) Å; Cu—O(carboxylate), 1.949 (15) Å; and Cu—O(alcohol), 2.32 (6) Å. These are similar to values in (I):

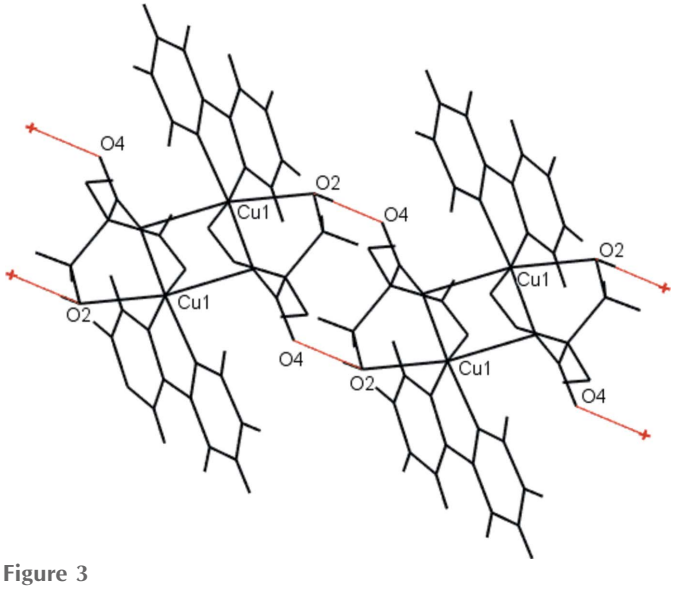

Figure 3
Packing structure of (I), showing the intermolecular O2—H2O···O4 hydrogen bonds.

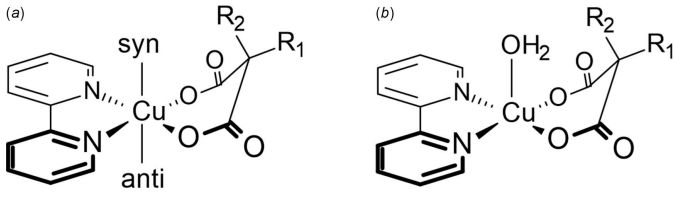

Figure 4
Generalized structures of [Cu(bpy)(malonate)] complexes: (*a*) showing the typical bending of the malonate ligand, with *syn* and *anti* coordination sites; (*b*) an example with H_2O in the *syn* position, as can occur when R_2 is small.

N—Cu—N, 81.35 (9)°; Cu—N, 1.985 (2), 1.990 (2) Å; Cu—O, 1.9587 (19), 1.935 (2), and 2.384 (2) Å, respectively.

Another group of structures closely related to (I) is Cu(bpy)(malonate) (malonate = 1,3-propanedioate); see Fig. 4. There are 14 such structures in the CSD, in all of which [as in (I)] the malonate C—O bonds are bent significantly out of the CuN_2O_2 coordination plane. Of these, seven [FIXDUM (Cui *et al.*, 2005), SAYCUQ (Gasque *et al.*, 1998), TIPZAT02 (Cernak, 2016), UNOJOY, UNOJUE, UNOKAL (Jaramillo-García *et al.*, 2016), and XECFOC (Manochitra *et al.*, 2012)] are monomeric, with R_2 = H and syn H_2O ligands [Fig. 4(*b*)]. This arrangement is similar to that observed in the Cu(bpy)($C_4H_4O_6$) moiety of (I), except that (I) contains an apical alcohol ligand rather than H_2O. Because the alcohol in (I) is part of a small chelate ring, its coordination is bent slightly away from perpendicularity to the CuO_2N_2 plane [N1—Cu1—O2 104.04 (9), N2—Cu1—O2 91.77 (9)°]; the average N—Cu—OH_2 angle in the above seven published structures is 93 (3)°.

In four structures [PUJJUC (Ghosh *et al.*, 2020), CIJNEQ (Dey *et al.*, 2013), MEHYON (Guan *et al.*, 1998*a*,*b*), and WAHVOR (Pasán *et al.*, 2004)], bulky R_2 groups prevent *syn* coordination, and there are *anti* H_2O ligands. In four structures [PUJJUC (Ghosh *et al.*, 2020), CELSIW01 (Reinoso *et al.*, 2007), CIJNEQ (Dey *et al.*, 2013), and PESBAR (Baldomá *et al.*, 2006)], dimers form as illustrated in Fig. 2, with Cu···O distances ranging from 2.315 (2) to 2.494 (3) Å. (Note: PUJJUC and CIJNEQ each contain two molecules in the asymmetric unit, one a five-coordinate monomer and the other a dimer of four-coordinate complexes.) As far as we are aware, the present complex [Cu(bpy)($C_4H_4O_6$)] (I) is the only example of a Cu(bpy)(malonate) in which a five-coordinate species dimerizes. Our structure shows a considerably larger Cu···O distance in its dimers than the above four published examples. This is likely because of the apical alcohol ligand in (I): a five-coordinate species is less likely to form strong Cu···O associations than a four-coordinate species.

5. Synthesis and crystallization

General procedures. Reagents were used as received, from Sigma–Aldrich. FTIR spectra were recorded on a Bruker Tensor 27 spectrometer in attenuated total reflectance mode.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_4H_4O_6)(C_{10}H_8N_2)]$
M_r	367.80
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	90
a, b, c (Å)	7.6516 (5), 9.9272 (6), 10.0722 (6)
α, β, γ (°)	95.204 (4), 107.729 (4), 111.462 (4)
V (Å^3)	660.34 (7)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.69
Crystal size (mm)	0.15 × 0.09 × 0.07
Data collection	
Diffractometer	Bruker Kappa APEXII DUO CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.838, 0.891
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18442, 4041, 2675
R_{int}	0.063
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.105, 1.02
No. of reflections	4041
No. of parameters	214
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.74, −0.56

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2014/7* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020), and *publCIF* (Westrip, 2010).

Synthesis of Cu(bpy)($C_4H_4O_6$). To a mixture of $[Cu(bpy)_2(NO_3)](NO_3)$ (Marjani *et al.*, 2005) (25.5 mg, 0.075 mmol, in 2 mL of DMF) and Dabco (8.4 mg, 0.075 mmol, in 1 mL of DMF), ascorbic acid (13.2 mg, 0.075 mmol, in 1 mL of DMF) was added. The mixture turned to dark brownish-red. It was stirred for two days in air, during which time it turned green, and filtered. The filtrate was used for vapor diffusion with diethyl ether. Crystals of Cu(bpy)($C_4H_4O_6$) [(I), blue] and $[DabcoH_2](NO_3)_2$ [(II), colorless] formed, which were suitable for X-ray analysis.

Cu(bpy)($C_4H_4O_6$). FTIR (cm^{-1}) 3036*m*, 2853*w*, 1704*s*, 1667*m*, 1612*m*, 1412*m*, 1391*m*, 1362*m*, 1312*m*, 1204*s*, 1149*s*, 1055*m*, 1036*m*, 778*m*, 732*m*, 639*w*.

6. Refinement

Crystal data, data collection, and structure refinement are summarized in Table 2. All H atoms were visible in difference-Fourier maps. Coordinates of those on O were refined with O—H distances restrained to 0.88 (2) Å. Those on C were positioned geometrically (C—H = 0.95 Å for aromatic C, 0.99 Å for CH_2) and treated as riding. Displacement parameters for H were assigned as U_{eq}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(O).

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supporting information

Acta Cryst. (2021). E**77**, 282-285 [https://doi.org/10.1107/S2056989021001286]

A copper complex of an unusual hydroxy–carboxylate ligand: [Cu(bpy)($C_4H_4O_6$)]

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(2,2′-Bipyridine-κ^2N,N')[2-hydroxy-2-(hydroxymethyl-κO)propanedioato-κ^2O^1,O^3]copper(II)

Crystal data

$[Cu(C_4H_4O_6)(C_{10}H_8N_2)]$
M_r = 367.80
Triclinic, $P\overline{1}$
a = 7.6516 (5) Å
b = 9.9272 (6) Å
c = 10.0722 (6) Å
α = 95.204 (4)°
β = 107.729 (4)°
γ = 111.462 (4)°
V = 660.34 (7) Å^3
Z = 2
$F(000)$ = 374
D_x = 1.850 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3354 reflections
θ = 2.2–29.3°
μ = 1.69 mm^{-1}
T = 90 K
Fragment, light blue
0.15 × 0.09 × 0.07 mm

Data collection

Bruker Kappa APEXII DUO CCD diffractometer
Radiation source: fine-focus sealed tube
TRIUMPH curved graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.838, T_{max} = 0.891
18442 measured reflections
4041 independent reflections
2675 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 30.6°, θ_{min} = 2.2°
h = −10→10
k = −14→14
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.105
S = 1.02
4041 reflections
214 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.3982P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.74$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.60628 (6)	0.63056 (4)	0.41304 (4)	0.01841 (12)
O1	0.7261 (3)	0.5158 (2)	0.52799 (19)	0.0200 (5)
O2	0.9188 (3)	0.7153 (3)	0.3763 (2)	0.0247 (5)
H2O	0.931 (6)	0.635 (3)	0.346 (4)	0.037*
O3	0.7221 (3)	0.7944 (2)	0.5778 (2)	0.0241 (5)
O4	0.9916 (3)	0.5149 (2)	0.6990 (2)	0.0239 (5)
O5	1.2089 (3)	0.8062 (3)	0.7594 (2)	0.0296 (5)
H5O	1.178 (6)	0.869 (4)	0.813 (3)	0.044*
O6	0.9741 (4)	0.9263 (3)	0.7840 (2)	0.0337 (6)
N1	0.4537 (4)	0.7282 (3)	0.2933 (2)	0.0170 (5)
N2	0.4699 (4)	0.4750 (3)	0.2317 (2)	0.0166 (5)
C1	0.4522 (5)	0.8585 (3)	0.3373 (3)	0.0201 (6)
H1	0.5308	0.9116	0.4337	0.024*
C2	0.3410 (5)	0.9188 (3)	0.2483 (3)	0.0217 (7)
H2	0.3409	1.0109	0.2833	0.026*
C3	0.2293 (4)	0.8435 (3)	0.1071 (3)	0.0195 (6)
H3	0.1527	0.8836	0.0433	0.023*
C4	0.2309 (4)	0.7080 (3)	0.0597 (3)	0.0180 (6)
H4	0.1567	0.6548	−0.0372	0.022*
C5	0.3422 (4)	0.6519 (3)	0.1558 (3)	0.0142 (6)
C6	0.3512 (4)	0.5078 (3)	0.1208 (3)	0.0142 (6)
C7	0.2500 (4)	0.4119 (3)	−0.0127 (3)	0.0155 (6)
H7	0.1676	0.4365	−0.0892	0.019*
C8	0.2703 (4)	0.2792 (3)	−0.0335 (3)	0.0180 (6)
H8	0.2000	0.2107	−0.1239	0.022*
C9	0.3938 (5)	0.2480 (3)	0.0789 (3)	0.0191 (6)
H9	0.4109	0.1583	0.0665	0.023*
C10	0.4924 (4)	0.3482 (3)	0.2098 (3)	0.0180 (6)
H10	0.5788	0.3267	0.2866	0.022*
C11	0.9051 (5)	0.5800 (3)	0.6238 (3)	0.0217 (7)
C12	1.0222 (5)	0.7493 (4)	0.6426 (3)	0.0247 (7)
C13	0.8962 (5)	0.8297 (4)	0.6718 (3)	0.0258 (7)
C14	1.0784 (5)	0.7878 (4)	0.5103 (3)	0.0284 (7)
H14A	1.1263	0.8965	0.5195	0.034*
H14B	1.1917	0.7614	0.5117	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0245 (2)	0.0195 (2)	0.00897 (15)	0.01379 (17)	−0.00134 (13)	−0.00131 (13)
O1	0.0255 (12)	0.0221 (12)	0.0104 (9)	0.0137 (10)	−0.0002 (8)	0.0018 (8)
O2	0.0272 (12)	0.0276 (13)	0.0172 (10)	0.0135 (11)	0.0035 (9)	0.0032 (9)
O3	0.0257 (12)	0.0268 (13)	0.0147 (10)	0.0143 (11)	−0.0012 (9)	−0.0040 (9)
O4	0.0247 (12)	0.0272 (12)	0.0202 (10)	0.0155 (10)	0.0031 (9)	0.0053 (9)
O5	0.0283 (13)	0.0337 (14)	0.0213 (11)	0.0169 (11)	−0.0006 (9)	−0.0024 (10)
O6	0.0366 (14)	0.0325 (14)	0.0221 (11)	0.0185 (12)	−0.0035 (10)	−0.0070 (10)
N1	0.0182 (13)	0.0181 (13)	0.0128 (10)	0.0084 (11)	0.0030 (9)	0.0005 (10)
N2	0.0212 (13)	0.0163 (13)	0.0129 (11)	0.0104 (11)	0.0045 (10)	0.0013 (10)
C1	0.0244 (17)	0.0168 (15)	0.0183 (13)	0.0108 (13)	0.0051 (12)	−0.0005 (12)
C2	0.0279 (18)	0.0163 (16)	0.0237 (15)	0.0138 (14)	0.0079 (13)	0.0037 (12)
C3	0.0195 (16)	0.0195 (16)	0.0223 (14)	0.0123 (13)	0.0052 (12)	0.0071 (12)
C4	0.0149 (15)	0.0242 (17)	0.0143 (13)	0.0095 (13)	0.0034 (11)	0.0031 (12)
C5	0.0136 (14)	0.0142 (14)	0.0145 (12)	0.0063 (12)	0.0046 (10)	0.0005 (11)
C6	0.0125 (14)	0.0167 (15)	0.0113 (12)	0.0060 (12)	0.0022 (10)	0.0019 (11)
C7	0.0116 (14)	0.0165 (15)	0.0140 (12)	0.0038 (12)	0.0020 (10)	0.0005 (11)
C8	0.0173 (15)	0.0170 (15)	0.0142 (12)	0.0039 (12)	0.0040 (11)	−0.0016 (11)
C9	0.0241 (16)	0.0142 (15)	0.0214 (14)	0.0101 (13)	0.0092 (12)	0.0022 (12)
C10	0.0202 (16)	0.0201 (16)	0.0155 (13)	0.0108 (13)	0.0056 (11)	0.0044 (12)
C11	0.0310 (18)	0.0229 (17)	0.0115 (12)	0.0158 (15)	0.0035 (12)	0.0006 (12)
C12	0.0257 (17)	0.0276 (18)	0.0162 (13)	0.0123 (15)	0.0010 (12)	0.0019 (13)
C13	0.0288 (18)	0.0260 (18)	0.0209 (15)	0.0149 (15)	0.0036 (13)	0.0015 (14)
C14	0.0271 (18)	0.0294 (19)	0.0235 (15)	0.0108 (16)	0.0049 (13)	0.0008 (14)

Geometric parameters (Å, º)

Cu1—O3	1.935 (2)	C2—H2	0.9500
Cu1—O1	1.9587 (19)	C3—C4	1.391 (4)
Cu1—N1	1.985 (2)	C3—H3	0.9500
Cu1—N2	1.990 (2)	C4—C5	1.383 (4)
Cu1—O2	2.384 (2)	C4—H4	0.9500
O1—C11	1.288 (3)	C5—C6	1.474 (4)
O2—C14	1.417 (4)	C6—C7	1.381 (4)
O2—H2O	0.880 (18)	C7—C8	1.387 (4)
O3—C13	1.275 (4)	C7—H7	0.9500
O4—C11	1.236 (3)	C8—C9	1.377 (4)
O5—C12	1.417 (4)	C8—H8	0.9500
O5—H5O	0.929 (18)	C9—C10	1.380 (4)
O6—C13	1.236 (4)	C9—H9	0.9500
N1—C1	1.334 (4)	C10—H10	0.9500
N1—C5	1.355 (3)	C11—C12	1.549 (5)
N2—C10	1.339 (4)	C12—C13	1.532 (4)
N2—C6	1.358 (3)	C12—C14	1.558 (4)
C1—C2	1.375 (4)	C14—H14A	0.9900
C1—H1	0.9500	C14—H14B	0.9900

C2—C3	1.383 (4)		
O3—Cu1—O1	91.06 (8)	N1—C5—C6	114.2 (2)
O3—Cu1—N1	91.97 (9)	C4—C5—C6	124.4 (2)
O1—Cu1—N1	173.29 (10)	N2—C6—C7	121.5 (3)
O3—Cu1—N2	173.32 (9)	N2—C6—C5	114.4 (2)
O1—Cu1—N2	95.56 (9)	C7—C6—C5	124.1 (2)
N1—Cu1—N2	81.35 (9)	C6—C7—C8	119.1 (3)
O3—Cu1—O2	90.05 (9)	C6—C7—H7	120.4
O1—Cu1—O2	81.94 (8)	C8—C7—H7	120.4
N1—Cu1—O2	104.04 (9)	C9—C8—C7	119.0 (3)
N2—Cu1—O2	91.77 (9)	C9—C8—H8	120.5
C11—O1—Cu1	120.61 (19)	C7—C8—H8	120.5
C14—O2—Cu1	108.93 (18)	C8—C9—C10	119.5 (3)
C14—O2—H2O	106 (2)	C8—C9—H9	120.3
Cu1—O2—H2O	106 (2)	C10—C9—H9	120.3
C13—O3—Cu1	121.7 (2)	N2—C10—C9	121.9 (3)
C12—O5—H5O	96 (2)	N2—C10—H10	119.1
C1—N1—C5	119.1 (2)	C9—C10—H10	119.1
C1—N1—Cu1	125.71 (19)	O4—C11—O1	124.3 (3)
C5—N1—Cu1	115.18 (19)	O4—C11—C12	117.9 (3)
C10—N2—C6	119.0 (2)	O1—C11—C12	117.8 (2)
C10—N2—Cu1	126.08 (19)	O5—C12—C13	108.3 (2)
C6—N2—Cu1	114.81 (18)	O5—C12—C11	111.3 (2)
N1—C1—C2	122.5 (3)	C13—C12—C11	109.2 (3)
N1—C1—H1	118.8	O5—C12—C14	105.0 (3)
C2—C1—H1	118.8	C13—C12—C14	110.5 (3)
C1—C2—C3	119.0 (3)	C11—C12—C14	112.4 (2)
C1—C2—H2	120.5	O6—C13—O3	125.2 (3)
C3—C2—H2	120.5	O6—C13—C12	117.0 (3)
C2—C3—C4	119.0 (3)	O3—C13—C12	117.8 (3)
C2—C3—H3	120.5	O2—C14—C12	114.7 (3)
C4—C3—H3	120.5	O2—C14—H14A	108.6
C5—C4—C3	119.0 (3)	C12—C14—H14A	108.6
C5—C4—H4	120.5	O2—C14—H14B	108.6
C3—C4—H4	120.5	C12—C14—H14B	108.6
N1—C5—C4	121.4 (3)	H14A—C14—H14B	107.6
C5—N1—C1—C2	0.1 (5)	C6—N2—C10—C9	−2.0 (4)
Cu1—N1—C1—C2	−179.4 (2)	Cu1—N2—C10—C9	−178.8 (2)
N1—C1—C2—C3	−1.3 (5)	C8—C9—C10—N2	0.8 (5)
C1—C2—C3—C4	0.8 (5)	Cu1—O1—C11—O4	−179.0 (2)
C2—C3—C4—C5	0.8 (4)	Cu1—O1—C11—C12	−1.0 (4)
C1—N1—C5—C4	1.5 (4)	O4—C11—C12—O5	−6.9 (4)
Cu1—N1—C5—C4	−178.9 (2)	O1—C11—C12—O5	175.0 (2)
C1—N1—C5—C6	−178.4 (3)	O4—C11—C12—C13	−126.3 (3)
Cu1—N1—C5—C6	1.2 (3)	O1—C11—C12—C13	55.6 (3)
C3—C4—C5—N1	−2.0 (4)	O4—C11—C12—C14	110.7 (3)

C3—C4—C5—C6	177.9 (3)	O1—C11—C12—C14	−67.4 (4)
C10—N2—C6—C7	1.6 (4)	Cu1—O3—C13—O6	−175.1 (3)
Cu1—N2—C6—C7	178.7 (2)	Cu1—O3—C13—C12	6.5 (4)
C10—N2—C6—C5	−178.2 (3)	O5—C12—C13—O6	1.0 (4)
Cu1—N2—C6—C5	−1.1 (3)	C11—C12—C13—O6	122.3 (3)
N1—C5—C6—N2	−0.1 (4)	C14—C12—C13—O6	−113.5 (3)
C4—C5—C6—N2	−179.9 (3)	O5—C12—C13—O3	179.6 (3)
N1—C5—C6—C7	−179.9 (3)	C11—C12—C13—O3	−59.1 (4)
C4—C5—C6—C7	0.3 (5)	C14—C12—C13—O3	65.1 (4)
N2—C6—C7—C8	0.0 (4)	Cu1—O2—C14—C12	19.3 (3)
C5—C6—C7—C8	179.8 (3)	O5—C12—C14—O2	167.8 (3)
C6—C7—C8—C9	−1.2 (4)	C13—C12—C14—O2	−75.7 (3)
C7—C8—C9—C10	0.8 (4)	C11—C12—C14—O2	46.6 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O4^{i}	0.88 (2)	1.85 (2)	2.723 (3)	169 (4)
O5—H5*O*···O6	0.93 (2)	1.80 (3)	2.549 (3)	136 (3)

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.