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(Metformin-κ^2N,N')(salicylato-κ^2O,O')copper(II) trihydrate

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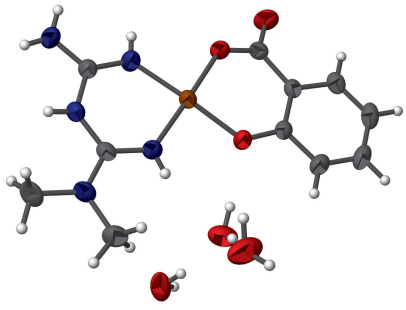
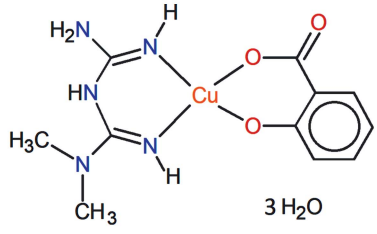
The hydrous title complex [systematic name: (1,1-dimethylbiguanide-κ^2N^2,N^4)(2-oxidobenzoato-κ^2O,O')copper(II) trihydrate], $[Cu(C_7H_4O_3)(C_4H_{11}N_5)]\cdot 3H_2O$, was synthesized electrolytically from an ethanolic solution of metformin hydrochloride, acetylsalicylic acid, Pepto-Bismol and a copper sacrificial anode. Diffraction data were collected at 0.56 Å resolution, allowing the accurate determination of H-atom positions in the neutral metformin ligand. Both imine groups in metformin have very similar N=C bond lengths, 1.2978 (17) and 1.3033 (17) Å, and the salicylate dianion behaves as a chelating ligand. The coordination sphere of the copper(II) cation deviates marginally from a square-planar arrangement. In the crystal, short Cu···Cu separations of 3.5476 (3) Å are observed, along with classical hydrogen-bonding interactions.

3D view



Chemical scheme



Structure description

In the past few years, metformin hydrochloride (1,1-dimethylbiguanide hydrochloride; Niranjana Devi *et al.*, 2017) has been the most commonly used drug for the first-line treatment of type 2 diabetes. Metformin (Metf) is known to affect the cellular housekeeping of copper. Dysfunctional copper metabolism is implicated in the development of several diseases, particularly those involving protein misfolding, and in diabetes (Repiščák *et al.*, 2014). Indeed, Metf is considered to be a moderately strong base and combines with many transition metal ions, especially Cu^{II}, Ni^{II} and Pt^{II}, because of the presence of the two imine groups in the *cis* positions, which enables it to act as a chelating agent. Some metal complexes with Metf have shown to increase hypoglycemic activity significantly compared to the pure Metf·HCl drug (Adam *et al.*, 2015). On the other hand, acetylsalicylic acid, which is one of the most used general pain-relieving drugs, has been

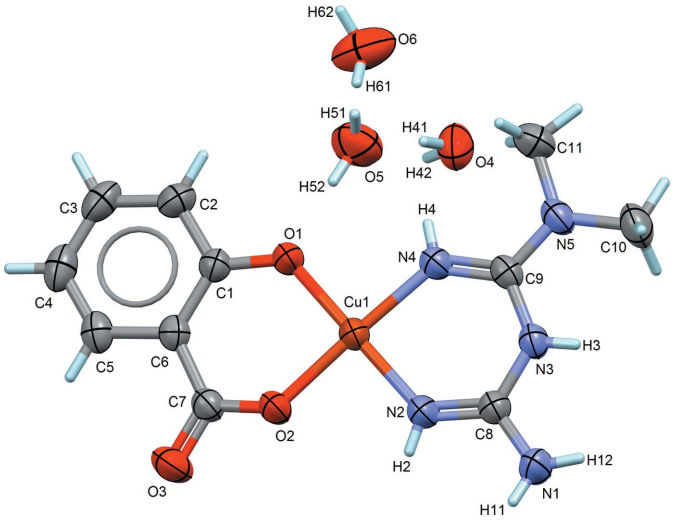


Figure 1
The structure of the molecular entities present in the title compound, with displacement ellipsoids for non-H atoms drawn at the 60% probability level. Labelled atoms are those for which coordinates were refined freely.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11···O3^{i}	0.80 (3)	2.22 (3)	2.9864 (18)	159 (3)
N1—H12···O4^{ii}	0.80 (3)	2.14 (3)	2.9023 (18)	160 (3)
N2—H2···O3^{i}	0.76 (2)	2.60 (3)	3.2948 (18)	152 (2)
N3—H3···O4^{ii}	0.79 (2)	2.24 (2)	2.9772 (17)	156 (2)
N4—H4···O5	0.75 (2)	2.56 (2)	3.208 (2)	145 (2)
O4—H41···O5	0.85 (2)	1.87 (2)	2.717 (2)	172 (3)
O4—H42···O3^{iii}	0.84 (2)	2.09 (2)	2.907 (2)	163 (3)
O5—H51···O6	0.91 (2)	1.83 (2)	2.726 (3)	171 (3)
O5—H52···O1	0.84 (2)	1.91 (2)	2.7336 (17)	169 (3)
O6—H61···O2^{iv}	0.88 (2)	1.99 (2)	2.847 (2)	165 (3)
O6—H62···O2^{v}	0.83 (2)	2.14 (2)	2.923 (2)	157 (4)
O6—H62···O3^{v}	0.83 (2)	2.42 (2)	3.112 (2)	142 (3)

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

associated with copper in the form of copper acetylsalicylate to treat rheumatoid arthritis and thromboembolic diseases (Liu *et al.*, 1998). Here, we present the synthesis and crystal structure of a new Cu^{II} complex that contains both active pharmaceutical ingredients chelating to the central metal cation, namely neutral metformin and the salicylate dianion.

The molecular complex is located on general positions, with three lattice water molecules completing the asymmetric unit (Fig. 1). The Cu^{II} ion is coordinated by the two ligands in an almost square configuration, with a slight deviation from planarity as evidenced by the dihedral angle between the two metallacyles of 4.31 (6)°. The salicylate ligand, which has a tendency to behave as a bridging ligand, here acts as a chelating ligand, as found in some other Cu^{II} complexes with square-planar coordination environments (*e.g.* Lemoine *et al.*, 2002). The neutral Metf ligand presents two imine C=N bonds with very similar bond lengths, C8=N2 and C9=N4, 1.2978 (17) and 1.3033 (17) Å. This feature could be a consequence of some delocalization including the central NH group in the metallacycle. This delocalization is consistent with the planar character of Metf, and was previously observed in the cationic complex $[Cu(Metf)_2]^{2+}$, which has been crystallized as the ClO_4^- (Olar *et al.*, 2010), HCO_3^- (Viossat *et al.*, 1995), and Cl^- (Lemoine *et al.*, 1996) salts. On the other hand, if the Metf ligand is deprotonated on the central N atom to form a neutral complex $[Cu(Metf^-)_2]$, the ligand remains almost planar but the central C···N···C angle is reduced to nearly 120° as a consequence of the increased π conjugation (Zhu *et al.*, 2002). In the title complex, the angle at the central N atom is 127.80 (11)°, and its H atom was clearly discernible in the structure refinement.

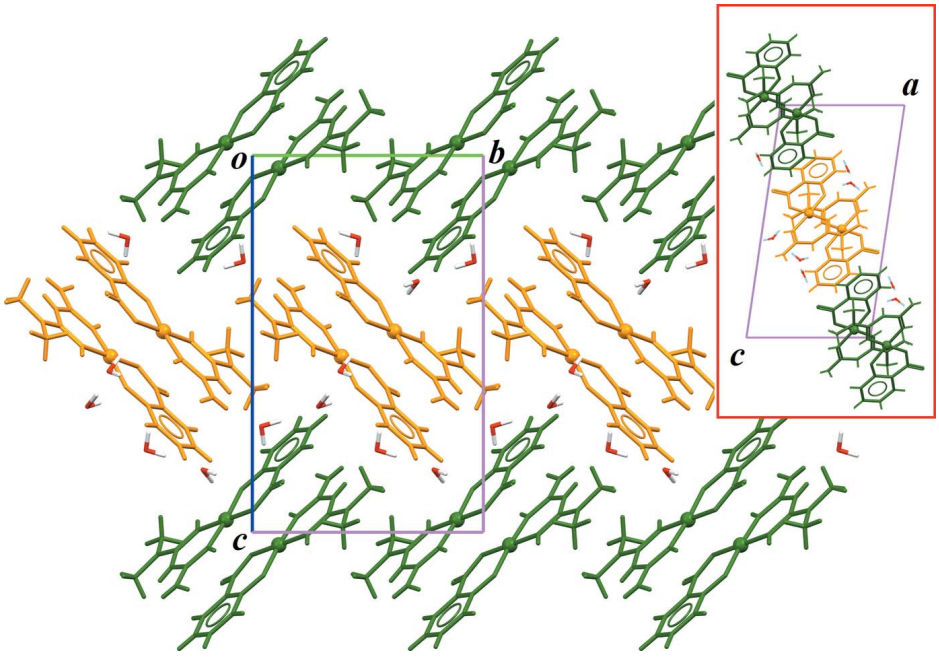


Figure 2
The crystal structure of the title compound, viewed down [100], with a colour scheme emphasizing the stacks formed along [010], and the distribution of water molecules. The inset is the same part of the crystal structure viewed along the stacking direction [010].

In the crystal structure, complexes are stacked to form centrosymmetric dimers, giving a short interaction between the central Cu^{II} cations, Cu1···Cu1^{i} = 3.5476 (3) Å [symmetry code: (i) $1-x, 1-y, 1-z$]. These dimers are arranged in a herringbone-like pattern (Fig. 2), with the stacking direction parallel to [010], and the water molecules filling the voids between the stacks. The majority of N—H bonds in Metf are donor groups for hydrogen bonding with water molecules (O4,O5) and the salicylate carbonyl

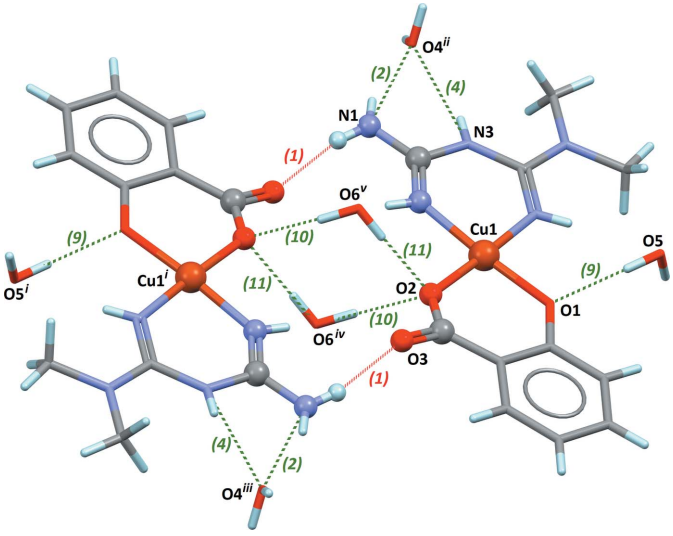


Figure 3
Ring motif $R_2^2(16)$ formed between stacks in the crystal and water molecules connected to the ring. Hydrogen bonds are depicted with dashed lines and a bracketed index corresponding to entries in Table 1. The red bond (1) is that forming the ring motif. [Symmetry codes: (i) $2-x$, $1-y$, $1-z$; (ii) $1-x$, $-y$, $1-z$; (iii) $1+x$, $1+y$, z; (iv) $1-x$, $1-y$, $1-z$; (v) $1+x$, y, z.]

O atom (O3) as acceptors. The crystal is further stabilized by O—H···O hydrogen bonds involving the two water molecules and the three O atoms from the salicylate ligand as acceptors (Table 1). As a consequence, stacks are connected to form $R_2^2(16)$ ring motifs in the crystal, including two complexes related by inversion (Fig. 3).

Synthesis and crystallization

Ligands were obtained from pharmaceutical drugs purchased over-the-counter, taking advantage of the fact that they were very pure and inexpensive. A mixture containing a half tablet of metformin hydrochloride (0.425 g of Metf·HCl, 2.56 mmol, Alpharma laboratories), one tablet of aspirin (0.5 g of acetylsalicylic acid, 2.76 mmol, Bayer Co.) and one tablet of Pepto-Bismol (0.262 mg of bismuth subsalicylate, 0.72 mmol, Procter & Gamble Co.) were ground in 80 ml of ethanol (pharmaceutical grade, 70% *v*/*v*). After filtering the mixture to separate the excipients off, the solution was transferred to a single-compartment electrochemical cell provided with a graphite pencil lead as cathode and a copper wire as sacrificial anode. The electrodes were connected to a battery eliminator universal AC–DC adapter, and electrolysis was carried out at 3.0 V and room temperature, for 12 h. Over the course of the reaction, the colour of the solution turned purple, and the copper wire electrode was replaced if passivated. Moreover, an unpleasant odour was noted, indicating the presence of free Metf. Once the electrolysis had stopped, the solution was evaporated, and a pink solid, presumably $[Cu(Metf)_2]Cl_2$ (Lemoine *et al.*, 1996), and other impurities were filtered off. After fractional crystallization, the solvent was removed, affording small purple crystals of the title compound.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_7H_4O_3)(C_4H_{11}N_5)]\cdot 3H_2O$
M_r	382.87
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	295
a, b, c (Å)	9.0515 (4), 10.3922 (3), 17.1327 (7)
β (°)	98.351 (3)
V (Å^3)	1594.50 (11)
Z	4
Radiation type	Ag $K\alpha$, λ = 0.56083 Å
μ (mm^{-1})	0.75
Crystal size (mm)	0.60 × 0.40 × 0.15
Data collection	
Diffractometer	Stoe Stadivari
Absorption correction	Integration (*X-RED32*; Stoe & Cie, 2015)
T_{min}, T_{max}	0.744, 0.899
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	87163, 9511, 5144
R_{int}	0.072
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.899
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.102, 0.93
No. of reflections	9511
No. of parameters	243
No. of restraints	9
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.54, −0.27

Computer programs: *X-AREA* (Stoe & Cie, 2015), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2017* (Sheldrick, 2015*b*) and *Mercury* (Macrae *et al.*, 2008).

Recrystallization from a hot methanol solution afforded single crystals suitable for physical measurements.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Single crystals proved to be highly diffracting samples, and diffraction data were collected at high resolution [(sin θ)/λ = 0.9 Å^{-1}; d = 0.56 Å], with the hope of determining accurate positions for all H atoms in the structure. This was indeed the case; however, C-bound H atoms were placed in idealized positions (C—H = 0.93 and 0.96 Å for aromatic and methyl groups, respectively). In the Metf ligand, N-bonded H atoms were refined freely [N—H bond lengths in the range 0.75 (2)–0.80 (3) Å]. Finally, H atoms for water molecules were refined with free coordinates, although the molecular shape was restrained to a sensible target, with O—H = 0.85 (2) and H···H = 1.34 (2) Å (Sheldrick, 2015*b*). Isotropic displacement parameters for H atoms were calculated from the equivalent displacement parameters of their carrier atoms.

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full crystallographic data

IUCrData (2018). **3**, x180180 [https://doi.org/10.1107/S2414314618001803]

(Metformin-κ^2N,N')(salicylato-κ^2O,O')copper(II) trihydrate

Sandra Julieta Gutiérrez Ojeda, Ulises Salazar Kuri, Sylvain Bernès and Aarón Pérez-Benítez

(1,1-Dimethylbiguanide-κ^2N^2,N^4)(2-oxidobenzoato-κ^2O,O')copper(II) trihydrate

Crystal data

$[Cu(C_7H_4O_3)(C_4H_{11}N_5)]\cdot 3H_2O$
M_r = 382.87
Monoclinic, $P2_1/n$
a = 9.0515 (4) Å
b = 10.3922 (3) Å
c = 17.1327 (7) Å
β = 98.351 (3)°
V = 1594.50 (11) Å^3
Z = 4
$F(000)$ = 796
D_x = 1.595 Mg m^{-3}
Melting point: 482 K
Ag $K\alpha$ radiation, λ = 0.56083 Å
Cell parameters from 29242 reflections
θ = 2.4–33.9°
μ = 0.75 mm^{-1}
T = 295 K
Prism, purple
0.60 × 0.40 × 0.15 mm

Data collection

Stoe Stadivari diffractometer
Radiation source: Sealed X-ray tube, Axo Astix-f Microfocus source
Graded multilayer mirror monochromator
Detector resolution: 5.81 pixels mm^{-1}
ω scans
Absorption correction: integration (X-RED32; Stoe & Cie, 2015)
T_{min} = 0.744, T_{max} = 0.899
87163 measured reflections
9511 independent reflections
5144 reflections with $I > 2\sigma(I)$
R_{int} = 0.072
θ_{max} = 30.3°, θ_{min} = 2.4°
h = −16→16
k = −18→12
l = −30→30

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.102
S = 0.93
9511 reflections
243 parameters
9 restraints
0 constraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.64053 (2)	0.38569 (2)	0.53349 (2)	0.03056 (5)
O1	0.53829 (12)	0.45265 (10)	0.61413 (7)	0.0429 (2)

O2	0.80378 (12)	0.50442 (10)	0.56014 (7)	0.0420 (2)
O3	0.96126 (14)	0.62921 (13)	0.63268 (8)	0.0545 (3)
N1	0.80015 (17)	0.17062 (14)	0.35829 (9)	0.0460 (3)
H11	0.864 (3)	0.219 (2)	0.3488 (16)	0.069*
H12	0.766 (3)	0.114 (2)	0.3292 (16)	0.069*
N2	0.75107 (15)	0.30699 (13)	0.45872 (9)	0.0419 (3)
H2	0.826 (3)	0.334 (2)	0.4524 (15)	0.063*
N3	0.57934 (13)	0.14914 (11)	0.40745 (7)	0.0332 (2)
H3	0.564 (2)	0.1002 (19)	0.3721 (14)	0.050*
N4	0.48227 (14)	0.26258 (11)	0.50551 (8)	0.0356 (2)
H4	0.418 (2)	0.263 (2)	0.5286 (13)	0.053*
N5	0.35066 (14)	0.09055 (12)	0.44111 (8)	0.0385 (2)
C1	0.58179 (15)	0.54802 (11)	0.66440 (8)	0.0322 (2)
C2	0.48295 (18)	0.58554 (14)	0.71644 (10)	0.0413 (3)
H2A	0.392262	0.542826	0.714786	0.050*
C3	0.5172 (2)	0.68377 (15)	0.76965 (10)	0.0448 (3)
H3A	0.449736	0.706703	0.803326	0.054*
C4	0.6523 (2)	0.74922 (14)	0.77347 (9)	0.0446 (3)
H4A	0.674690	0.816811	0.808790	0.054*
C5	0.75166 (17)	0.71283 (13)	0.72462 (8)	0.0369 (3)
H5A	0.842790	0.755336	0.728034	0.044*
C6	0.71971 (15)	0.61260 (11)	0.66919 (7)	0.0298 (2)
C7	0.83387 (15)	0.58195 (12)	0.61897 (8)	0.0324 (2)
C8	0.71272 (15)	0.21386 (12)	0.40946 (8)	0.0325 (2)
C9	0.46896 (14)	0.17067 (11)	0.45320 (8)	0.0297 (2)
C10	0.3321 (2)	−0.00931 (15)	0.38073 (11)	0.0489 (4)
H10A	0.310542	0.029825	0.329586	0.073*
H10B	0.251188	−0.064873	0.389145	0.073*
H10C	0.422435	−0.058642	0.383693	0.073*
C11	0.22570 (19)	0.10863 (16)	0.48457 (12)	0.0495 (4)
H11A	0.260271	0.102452	0.540125	0.074*
H11B	0.151946	0.043413	0.469492	0.074*
H11C	0.182361	0.191961	0.472777	0.074*
O4	0.37716 (16)	0.03873 (13)	0.71842 (9)	0.0581 (3)
H41	0.358 (3)	0.1162 (18)	0.7044 (17)	0.087*
H42	0.426 (3)	0.049 (3)	0.7637 (12)	0.087*
O5	0.34109 (18)	0.28522 (14)	0.66621 (11)	0.0651 (4)
H51	0.263 (3)	0.324 (3)	0.6362 (17)	0.098*
H52	0.408 (3)	0.336 (2)	0.6562 (19)	0.098*
O6	0.0949 (2)	0.37829 (17)	0.57260 (12)	0.0753 (5)
H61	0.140 (3)	0.420 (3)	0.5379 (17)	0.113*
H62	0.023 (3)	0.422 (3)	0.582 (2)	0.113*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02925 (8)	0.02880 (7)	0.03419 (8)	−0.00506 (6)	0.00652 (5)	−0.00626 (6)
O1	0.0374 (5)	0.0411 (5)	0.0543 (6)	−0.0133 (4)	0.0203 (5)	−0.0200 (4)

O2	0.0370 (5)	0.0451 (5)	0.0470 (6)	−0.0167 (4)	0.0165 (4)	−0.0175 (4)
O3	0.0391 (6)	0.0722 (8)	0.0541 (7)	−0.0238 (6)	0.0130 (5)	−0.0192 (6)
N1	0.0451 (7)	0.0471 (7)	0.0498 (8)	−0.0120 (6)	0.0204 (6)	−0.0199 (6)
N2	0.0318 (6)	0.0444 (6)	0.0516 (7)	−0.0112 (5)	0.0129 (5)	−0.0193 (5)
N3	0.0348 (5)	0.0312 (4)	0.0337 (5)	−0.0072 (4)	0.0056 (4)	−0.0077 (4)
N4	0.0316 (5)	0.0376 (5)	0.0391 (6)	−0.0086 (4)	0.0097 (4)	−0.0085 (4)
N5	0.0348 (6)	0.0374 (5)	0.0431 (6)	−0.0118 (4)	0.0044 (5)	−0.0053 (5)
C1	0.0339 (6)	0.0297 (5)	0.0340 (6)	−0.0013 (4)	0.0083 (5)	−0.0046 (4)
C2	0.0387 (7)	0.0428 (7)	0.0454 (8)	0.0013 (6)	0.0161 (6)	−0.0065 (6)
C3	0.0508 (9)	0.0460 (7)	0.0393 (7)	0.0133 (6)	0.0127 (6)	−0.0072 (6)
C4	0.0587 (9)	0.0368 (6)	0.0364 (7)	0.0073 (6)	0.0003 (7)	−0.0093 (5)
C5	0.0431 (7)	0.0318 (5)	0.0340 (6)	−0.0023 (5)	−0.0009 (5)	−0.0033 (5)
C6	0.0330 (6)	0.0269 (4)	0.0291 (5)	0.0001 (4)	0.0032 (4)	−0.0006 (4)
C7	0.0317 (6)	0.0321 (5)	0.0335 (6)	−0.0056 (4)	0.0050 (5)	−0.0018 (4)
C8	0.0315 (6)	0.0322 (5)	0.0344 (6)	−0.0037 (4)	0.0065 (5)	−0.0044 (5)
C9	0.0303 (6)	0.0271 (5)	0.0308 (5)	−0.0042 (4)	0.0018 (4)	0.0014 (4)
C10	0.0514 (9)	0.0401 (7)	0.0536 (9)	−0.0152 (6)	0.0020 (7)	−0.0113 (6)
C11	0.0375 (7)	0.0488 (8)	0.0646 (11)	−0.0109 (6)	0.0150 (7)	−0.0035 (7)
O4	0.0550 (8)	0.0509 (6)	0.0664 (9)	−0.0024 (6)	0.0017 (6)	−0.0232 (6)
O5	0.0600 (9)	0.0587 (8)	0.0808 (11)	−0.0132 (7)	0.0242 (8)	0.0103 (7)
O6	0.0668 (10)	0.0820 (10)	0.0851 (12)	0.0254 (8)	0.0381 (9)	0.0290 (9)

Geometric parameters (Å, º)

Cu1—O1	1.9029 (10)	C2—C3	1.374 (2)
Cu1—N2	1.9192 (13)	C2—H2A	0.9300
Cu1—O2	1.9283 (10)	C3—C4	1.393 (3)
Cu1—N4	1.9285 (11)	C3—H3A	0.9300
O1—C1	1.3343 (16)	C4—C5	1.368 (2)
O2—C7	1.2881 (17)	C4—H4A	0.9300
O3—C7	1.2439 (18)	C5—C6	1.4110 (18)
N1—C8	1.3410 (19)	C5—H5A	0.9300
N1—H11	0.80 (3)	C6—C7	1.4723 (19)
N1—H12	0.80 (3)	C10—H10A	0.9600
N2—C8	1.2978 (17)	C10—H10B	0.9600
N2—H2	0.76 (2)	C10—H10C	0.9600
N3—C9	1.3748 (18)	C11—H11A	0.9600
N3—C8	1.3781 (17)	C11—H11B	0.9600
N3—H3	0.79 (2)	C11—H11C	0.9600
N4—C9	1.3033 (17)	O4—H41	0.850 (16)
N4—H4	0.75 (2)	O4—H42	0.841 (17)
N5—C9	1.3485 (16)	O5—H51	0.906 (17)
N5—C11	1.454 (2)	O5—H52	0.838 (17)
N5—C10	1.458 (2)	O6—H61	0.884 (17)
C1—C2	1.4068 (19)	O6—H62	0.826 (17)
C1—C6	1.4092 (18)		
O1—Cu1—N2	174.97 (6)	C5—C4—H4A	120.4

O1—Cu1—O2	91.77 (4)	C3—C4—H4A	120.4
N2—Cu1—O2	88.56 (5)	C4—C5—C6	121.82 (14)
O1—Cu1—N4	90.06 (5)	C4—C5—H5A	119.1
N2—Cu1—N4	89.53 (5)	C6—C5—H5A	119.1
O2—Cu1—N4	177.92 (5)	C1—C6—C5	118.95 (13)
C1—O1—Cu1	127.68 (9)	C1—C6—C7	123.64 (11)
C7—O2—Cu1	130.78 (9)	C5—C6—C7	117.42 (12)
C8—N1—H11	115.9 (18)	O3—C7—O2	118.66 (13)
C8—N1—H12	116 (2)	O3—C7—C6	120.95 (12)
H11—N1—H12	124 (3)	O2—C7—C6	120.39 (12)
C8—N2—Cu1	129.47 (11)	N2—C8—N1	123.20 (13)
C8—N2—H2	110.3 (19)	N2—C8—N3	122.06 (13)
Cu1—N2—H2	120.0 (19)	N1—C8—N3	114.72 (12)
C9—N3—C8	127.80 (11)	N4—C9—N5	123.38 (13)
C9—N3—H3	118.6 (16)	N4—C9—N3	120.60 (11)
C8—N3—H3	113.2 (16)	N5—C9—N3	116.01 (11)
C9—N4—Cu1	130.41 (10)	N5—C10—H10A	109.5
C9—N4—H4	111.3 (17)	N5—C10—H10B	109.5
Cu1—N4—H4	118.3 (16)	H10A—C10—H10B	109.5
C9—N5—C11	120.07 (13)	N5—C10—H10C	109.5
C9—N5—C10	123.75 (14)	H10A—C10—H10C	109.5
C11—N5—C10	115.95 (13)	H10B—C10—H10C	109.5
O1—C1—C2	117.37 (12)	N5—C11—H11A	109.5
O1—C1—C6	124.55 (12)	N5—C11—H11B	109.5
C2—C1—C6	118.08 (12)	H11A—C11—H11B	109.5
C3—C2—C1	121.57 (15)	N5—C11—H11C	109.5
C3—C2—H2A	119.2	H11A—C11—H11C	109.5
C1—C2—H2A	119.2	H11B—C11—H11C	109.5
C2—C3—C4	120.41 (15)	H41—O4—H42	102 (2)
C2—C3—H3A	119.8	H51—O5—H52	97 (2)
C4—C3—H3A	119.8	H61—O6—H62	108 (3)
C5—C4—C3	119.15 (13)		

Cu1—O1—C1—C2	176.62 (11)	C5—C6—C7—O3	10.3 (2)
Cu1—O1—C1—C6	−3.9 (2)	C1—C6—C7—O2	9.4 (2)
O1—C1—C2—C3	−179.22 (15)	C5—C6—C7—O2	−170.32 (13)
C6—C1—C2—C3	1.2 (2)	Cu1—N2—C8—N1	177.81 (13)
C1—C2—C3—C4	−0.1 (3)	Cu1—N2—C8—N3	−4.1 (2)
C2—C3—C4—C5	−1.2 (2)	C9—N3—C8—N2	0.9 (2)
C3—C4—C5—C6	1.4 (2)	C9—N3—C8—N1	179.20 (14)
O1—C1—C6—C5	179.45 (13)	Cu1—N4—C9—N5	179.17 (11)
C2—C1—C6—C5	−1.04 (19)	Cu1—N4—C9—N3	0.3 (2)
O1—C1—C6—C7	−0.2 (2)	C11—N5—C9—N4	3.4 (2)
C2—C1—C6—C7	179.26 (13)	C10—N5—C9—N4	177.57 (14)
C4—C5—C6—C1	−0.3 (2)	C11—N5—C9—N3	−177.72 (14)
C4—C5—C6—C7	179.44 (13)	C10—N5—C9—N3	−3.5 (2)
Cu1—O2—C7—O3	164.92 (12)	C8—N3—C9—N4	1.0 (2)
Cu1—O2—C7—C6	−14.5 (2)	C8—N3—C9—N5	−177.97 (13)

C1—C6—C7—O3	−170.02 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O3^{i}	0.80 (3)	2.22 (3)	2.9864 (18)	159 (3)
N1—H12···O4^{ii}	0.80 (3)	2.14 (3)	2.9023 (18)	160 (3)
N2—H2···O3^{i}	0.76 (2)	2.60 (3)	3.2948 (18)	152 (2)
N3—H3···O4^{ii}	0.79 (2)	2.24 (2)	2.9772 (17)	156 (2)
N4—H4···O5	0.75 (2)	2.56 (2)	3.208 (2)	145 (2)
O4—H41···O5	0.85 (2)	1.87 (2)	2.717 (2)	172 (3)
O4—H42···O3^{iii}	0.84 (2)	2.09 (2)	2.907 (2)	163 (3)
O5—H51···O6	0.91 (2)	1.83 (2)	2.726 (3)	171 (3)
O5—H52···O1	0.84 (2)	1.91 (2)	2.7336 (17)	169 (3)
O6—H61···O2^{iv}	0.88 (2)	1.99 (2)	2.847 (2)	165 (3)
O6—H62···O2^{v}	0.83 (2)	2.14 (2)	2.923 (2)	157 (4)
O6—H62···O3^{v}	0.83 (2)	2.42 (2)	3.112 (2)	142 (3)

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*+3/2, *y*−1/2, −*z*+3/2; (iv) −*x*+1, −*y*+1, −*z*+1; (v) *x*−1, *y*, *z*.