

μ -1,6-Dioxo-1,6-diphenylhexane-3,4-diolato-bis[(2,2'-bipyridine)chloridocopper(II)] dihydrate

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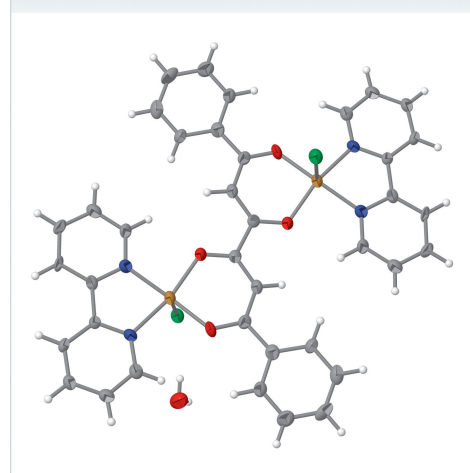
Keywords: Cu^{II}; hydrate; hydrogen-bonding; tetronediate; crystal structure.

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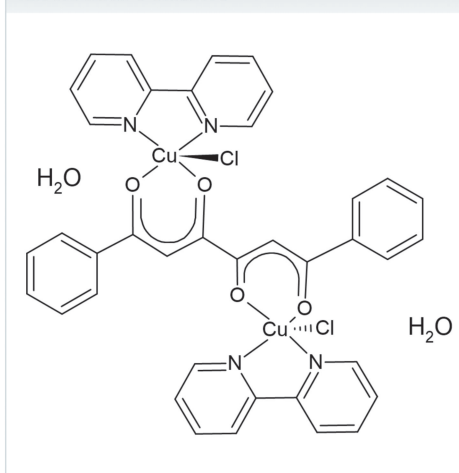
Structural data: full structural data are available from iucrdata.iucr.org

The reaction of CuCl₂ with 1,6-diphenyl-1,3,5,6-hexanetetronate and 2,2'-bipyridine (bipy) in ethanol gave crystals of the corresponding bimetallic complex, [Cu₂(C₁₈H₁₂O₄)Cl₂(C₁₀H₈N₂)₂]:2H₂O. The molecule is centrosymmetric with each Cu^{II} ion coordinated to two oxygen atoms from the tetronediate, two nitrogen atoms from a bipy ligand and one coordinated chloride ion. A water molecule of crystallization forms hydrogen bonds to the chloride ions, linking the molecules into a chain parallel to the *bc*-face diagonal.

3D view



Chemical scheme



Structure description

1,6-Diphenyl-1,3,4,6-hexanetetronate has been known for over 100 years (Widman & Virgin, 1909) and its structure has been reported (Kaitner *et al.*, 1992). Both its synthesis by oxidation (Balenović *et al.*, 1954) and its reactions with oxidizing agents have been studied (Balenović, 1948; Bird & Thorley, 1977; Poje *et al.*, 1978), as well as its use as a starting material for the preparation of a variety of aminated products (Lacan *et al.*, 1973; Unterhalt & Pindur, 1977; Kaitner *et al.*, 1992; Waring *et al.*, 2002; Kobelev *et al.*, 2019). The backbone core resembles a bis-acac structure and as such it has been used in the preparation of transition-metal complexes (Boucher & Bailar, 1964; Saalfrank *et al.*, 1998; Nawar, 1994). However, we were surprised to find that there are no reported structures of transition-metal complexes containing this ligand (Groom *et al.*, 2016). We investigated its coordination chemistry with Cu^{II} as part of our studies on potential magnetic ladders (Monroe *et al.*, 2022).

The molecule sits astride a crystallographic inversion center (Fig. 1). Each Cu^{II} ion is five-coordinate, including two oxygen atoms from the tetronediate ligand, two nitrogen atoms from a bipy molecule and one coordinated chloride ion. The CuN₂O₂ equatorial plane is nearly planar (mean deviation of the N₂O₂ donor set = 0.0219 Å) with the Cu^{II} ion displaced [0.2219 (15) Å] toward the chloride ion. The 1,3-dionato motif chelates a

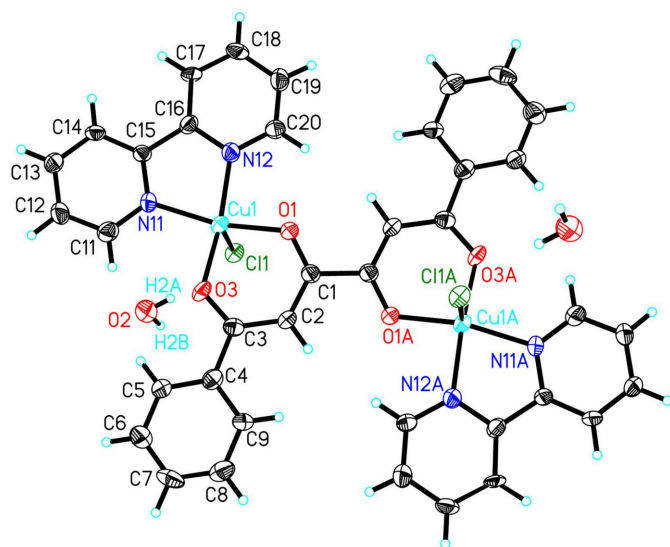


Figure 1
The molecular structure of the title compound. Only the asymmetric unit and Cu coordination spheres are labeled. Hydrogen atoms are shown as spheres of arbitrary size. Symmetry operation B: $-x, 1 - y, 2 - z$.

copper ion and generates a six-membered metallocyclic ring that is only slightly less planar (mean deviation of constituent atoms = 0.1207 Å). The two heterocyclic rings are co-planar as required by symmetry. The pyridyl rings are canted 0.67 (13)° from each other.

π -Stacking is observed between molecules. The Cu1-dionato ring sits above the N11-containing bpy ring with an interplanar distance of 3.33 (2) Å; the rings are canted 4.4 (2)° with respect to each other. The distance between the ring centroids is 3.73 (2) Å with a slip angle of 25.1 (3)°. This effectively blocks the vacant coordination site on Cu1, preventing the addition of a sixth ligand. π -Stacking is also observed between the phenyl rings of the tetrahydroxy-1,3,4,6-hexanetetronate ligand. Adjacent phenyl rings are parallel with an interplanar distance of 3.33 (2) Å with a slip angle of 22.8 (3)°. The bimetallic units are linked into chains *via* hydrogen bonds between the solvent water molecules and chloride ions (Table 1 and Fig. 2).

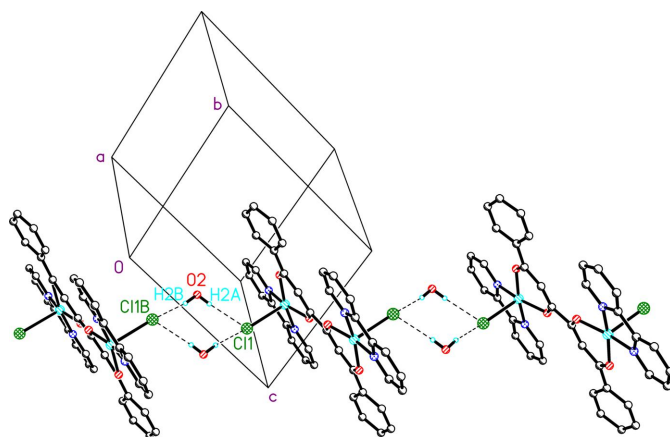


Figure 2
Chain formation *via* hydrogen bonding. Symmetry operation B: $-x, -y, 1 - z$.

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O2-H2A \cdots Cl1$	0.82 (5)	2.41 (5)	3.224 (3)	171 (5)
$O2-H2B \cdots Cl1^i$	0.98 (4)	2.33 (5)	3.307 (4)	172 (4)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu_2(C_{18}H_{12}O_4)Cl_2(C_{10}H_8N_2)_2] \cdot 2H_2O$
M_r	838.65
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	123
a, b, c (Å)	8.7211 (2), 10.4194 (2), 10.5243 (7)
α, β, γ (°)	106.426 (7), 109.090 (8), 90.373 (6)
V (Å ³)	861.67 (8)
Z	1
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	3.41
Crystal size (mm)	0.13 × 0.09 × 0.02
Data collection	
Diffractometer	Rigaku Spider
Absorption correction	Multi-scan (ABSCOR; Rigaku, 1995)
T_{min}, T_{max}	0.641, 0.929
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7470, 2552, 1901
R_{int}	0.046
θ_{max} (°)	61.1
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.568
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.047, 0.121, 1.13
No. of reflections	2552
No. of parameters	241
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.57, -0.49

Computer programs: *CrystalClear* (Rigaku, 2005), *PROCESS-AUTO* (Rigaku, 1998), *SHELXS97* (Sheldrick, 2008), and *SHELXL2018/3* (Sheldrick, 2015), *XP* (Sheldrick, 2008).

Synthesis and crystallization

CuCl₂ (0.403 g, 2.99 mmol) was dissolved in 50 ml of absolute ethanol to generate a green solution. 2,2'-Bipyridine (0.469 g, 3.01 mmol) was added to the solution with stirring to make a light-blue slurry. Addition of 1,6-diphenyl-1,3,4,6-hexanetetronate (0.438 g, 1.49 mmol) generated a lime green slurry, which was stirred for 1 h. The precipitate was recovered by vacuum filtration, washed with ethanol and dried in air to yield 0.973 g of lime green powder (77%). Crystals suitable for X-ray diffraction were grown by recrystallization from DMF.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Eight reflections were omitted from the final refinement owing to poor agreement; details are included in the CIF.

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full crystallographic data

IUCrData (2023). **8**, x230713 [https://doi.org/10.1107/S2414314623007137]

μ -1,6-Dioxo-1,6-diphenylhexane-3,4-diolato-bis[(2,2'-bipyridine)-chloridocopper(II)] dihydrate

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Crystal data

[Cu₂(C₁₈H₁₂O₄)Cl₂(C₁₀H₈N₂)₂] \cdot 2H₂O

$M_r = 838.65$

Triclinic, *P*1

$a = 8.7211$ (2) Å

$b = 10.4194$ (2) Å

$c = 10.5243$ (7) Å

$\alpha = 106.426$ (7)°

$\beta = 109.090$ (8)°

$\gamma = 90.373$ (6)°

$V = 861.67$ (8) Å³

$Z = 1$

$F(000) = 428$

$D_x = 1.616$ Mg m⁻³

Cu *K* α radiation, $\lambda = 1.54178$ Å

Cell parameters from 3450 reflections

$\theta = 6.6$ – 72.0 °

$\mu = 3.41$ mm⁻¹

$T = 123$ K

Plate, green

$0.13 \times 0.09 \times 0.02$ mm

Data collection

Rigaku Spider
diffractometer

Radiation source: rotating anode

Confocal optics monochromator

Detector resolution: 10 pixels mm⁻¹

ω -scans

Absorption correction: multi-scan
(ABSCOR; Rigaku, 1995)

$T_{\min} = 0.641$, $T_{\max} = 0.929$

7470 measured reflections

2552 independent reflections

1901 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.046$

$\theta_{\max} = 61.1$ °, $\theta_{\min} = 6.6$ °

$h = -9 \rightarrow 9$

$k = -8 \rightarrow 11$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.121$

$S = 1.13$

2552 reflections

241 parameters

0 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

$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.1469P]$

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

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

$\Delta\rho_{\max} = 0.57$ e Å⁻³

$\Delta\rho_{\min} = -0.49$ 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.

Refinement. Hydrogen atoms bonded to carbon atoms were placed geometrically and refined with fixed isotropic thermal parameters. Hydrogen atoms bonded to O2 were located in the difference map and their positions refined with fixed isotropic thermal parameters (O—H = 0.82 (5) & 0.98 (4) Å).

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	0.33000 (7)	0.32164 (6)	0.96525 (6)	0.0307 (2)
Cl1	0.11639 (12)	0.13154 (10)	0.77171 (10)	0.0345 (3)
O1	0.1754 (3)	0.4177 (3)	1.0408 (3)	0.0324 (7)
C1	0.0704 (5)	0.4796 (4)	0.9723 (4)	0.0254 (10)
C2	0.0728 (5)	0.5143 (4)	0.8569 (4)	0.0294 (10)
H2	−0.017613	0.555390	0.812000	0.035*
O3	0.3211 (3)	0.4301 (3)	0.8421 (3)	0.0330 (7)
C3	0.2001 (5)	0.4937 (4)	0.7987 (4)	0.0271 (10)
C4	0.1975 (5)	0.5506 (4)	0.6837 (4)	0.0303 (10)
C5	0.2992 (5)	0.5074 (4)	0.6059 (4)	0.0329 (11)
H5	0.372026	0.443341	0.628745	0.039*
C6	0.2963 (5)	0.5555 (5)	0.4963 (5)	0.0411 (12)
H6	0.365425	0.523306	0.443454	0.049*
C7	0.1939 (6)	0.6503 (5)	0.4627 (5)	0.0422 (12)
H7	0.193055	0.683511	0.387222	0.051*
C8	0.0922 (5)	0.6969 (4)	0.5389 (5)	0.0393 (12)
H8	0.022438	0.763064	0.516788	0.047*
C9	0.0926 (5)	0.6469 (4)	0.6470 (4)	0.0310 (10)
H9	0.020939	0.677797	0.697730	0.037*
N11	0.5341 (4)	0.2451 (3)	0.9445 (3)	0.0282 (8)
C11	0.6014 (5)	0.2564 (4)	0.8501 (4)	0.0339 (11)
H11	0.549680	0.303493	0.785150	0.041*
C12	0.7425 (5)	0.2020 (4)	0.8441 (4)	0.0343 (11)
H12	0.788780	0.212980	0.777127	0.041*
C13	0.8170 (5)	0.1309 (4)	0.9368 (4)	0.0302 (10)
H13	0.914522	0.092053	0.933922	0.036*
C14	0.7475 (5)	0.1177 (4)	1.0326 (4)	0.0277 (10)
H14	0.796296	0.069566	1.097313	0.033*
C15	0.6054 (5)	0.1754 (4)	1.0339 (4)	0.0237 (9)
C16	0.5227 (5)	0.1699 (4)	1.1351 (4)	0.0275 (10)
C17	0.5733 (5)	0.1040 (4)	1.2364 (4)	0.0273 (10)
H17	0.667767	0.057482	1.244906	0.033*
C18	0.4850 (5)	0.1061 (4)	1.3261 (4)	0.0318 (11)
H18	0.519826	0.063659	1.398103	0.038*
C19	0.3447 (5)	0.1721 (4)	1.3075 (4)	0.0362 (11)
H19	0.280783	0.173765	1.365635	0.043*

C20	0.2994 (5)	0.2349 (4)	1.2041 (4)	0.0316 (11)
H20	0.203908	0.280215	1.193139	0.038*
N12	0.3846 (4)	0.2349 (3)	1.1175 (3)	0.0282 (8)
O2	0.2128 (4)	0.0355 (4)	0.4911 (4)	0.0538 (10)
H2A	0.178 (6)	0.059 (5)	0.557 (5)	0.065*
H2B	0.110 (6)	-0.013 (4)	0.420 (5)	0.065*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0320 (4)	0.0347 (4)	0.0347 (4)	0.0178 (3)	0.0164 (3)	0.0183 (3)
Cl1	0.0317 (6)	0.0400 (7)	0.0367 (6)	0.0129 (5)	0.0136 (5)	0.0164 (5)
O1	0.0366 (17)	0.0391 (18)	0.0347 (17)	0.0202 (14)	0.0200 (14)	0.0217 (14)
C1	0.030 (2)	0.022 (2)	0.027 (2)	0.0052 (19)	0.012 (2)	0.0094 (19)
C2	0.027 (2)	0.034 (3)	0.032 (2)	0.0130 (19)	0.011 (2)	0.016 (2)
O3	0.0297 (16)	0.0351 (17)	0.0388 (17)	0.0198 (14)	0.0135 (13)	0.0156 (14)
C3	0.031 (3)	0.024 (2)	0.026 (2)	0.0026 (19)	0.009 (2)	0.0098 (19)
C4	0.025 (2)	0.032 (3)	0.030 (2)	0.0030 (19)	0.0050 (19)	0.009 (2)
C5	0.029 (2)	0.039 (3)	0.038 (3)	0.011 (2)	0.014 (2)	0.021 (2)
C6	0.039 (3)	0.050 (3)	0.042 (3)	0.004 (2)	0.018 (2)	0.021 (2)
C7	0.052 (3)	0.046 (3)	0.036 (3)	-0.005 (2)	0.013 (2)	0.025 (2)
C8	0.036 (3)	0.035 (3)	0.048 (3)	0.008 (2)	0.008 (2)	0.020 (2)
C9	0.031 (2)	0.038 (3)	0.030 (2)	0.008 (2)	0.010 (2)	0.020 (2)
N11	0.027 (2)	0.032 (2)	0.031 (2)	0.0111 (16)	0.0163 (17)	0.0114 (17)
C11	0.038 (3)	0.032 (3)	0.034 (3)	0.013 (2)	0.014 (2)	0.012 (2)
C12	0.038 (3)	0.037 (3)	0.037 (3)	0.012 (2)	0.022 (2)	0.013 (2)
C13	0.032 (2)	0.028 (2)	0.036 (3)	0.0114 (19)	0.015 (2)	0.013 (2)
C14	0.034 (2)	0.028 (2)	0.027 (2)	0.0105 (19)	0.011 (2)	0.017 (2)
C15	0.028 (2)	0.021 (2)	0.025 (2)	0.0064 (18)	0.0106 (19)	0.0097 (19)
C16	0.024 (2)	0.027 (2)	0.034 (2)	0.0078 (18)	0.0102 (19)	0.013 (2)
C17	0.034 (2)	0.024 (2)	0.034 (3)	0.0095 (19)	0.011 (2)	0.023 (2)
C18	0.043 (3)	0.030 (3)	0.029 (2)	0.006 (2)	0.013 (2)	0.019 (2)
C19	0.038 (3)	0.037 (3)	0.041 (3)	0.013 (2)	0.022 (2)	0.013 (2)
C20	0.038 (3)	0.029 (3)	0.039 (3)	0.013 (2)	0.019 (2)	0.021 (2)
N12	0.031 (2)	0.027 (2)	0.032 (2)	0.0085 (16)	0.0155 (17)	0.0119 (17)
O2	0.044 (2)	0.079 (3)	0.046 (2)	0.0153 (18)	0.0187 (17)	0.028 (2)

Geometric parameters (Å, °)

Cu1—O1	1.929 (3)	N11—C11	1.338 (5)
Cu1—O3	1.930 (3)	N11—C15	1.345 (5)
Cu1—N12	1.984 (3)	C11—C12	1.371 (5)
Cu1—N11	2.006 (3)	C11—H11	0.9500
Cu1—Cl1	2.5944 (12)	C12—C13	1.387 (5)
O1—C1	1.270 (4)	C12—H12	0.9500
C1—C2	1.369 (5)	C13—C14	1.372 (5)
C1—C1 ⁱ	1.537 (7)	C13—H13	0.9500
C2—C3	1.424 (5)	C14—C15	1.383 (5)

C2—H2	0.9500	C14—H14	0.9500
O3—C3	1.275 (4)	C15—C16	1.481 (5)
C3—C4	1.485 (5)	C16—N12	1.371 (5)
C4—C5	1.390 (5)	C16—C17	1.384 (5)
C4—C9	1.412 (5)	C17—C18	1.396 (5)
C5—C6	1.374 (6)	C17—H17	0.9500
C5—H5	0.9500	C18—C19	1.393 (5)
C6—C7	1.378 (6)	C18—H18	0.9500
C6—H6	0.9500	C19—C20	1.375 (5)
C7—C8	1.385 (6)	C19—H19	0.9500
C7—H7	0.9500	C20—N12	1.352 (5)
C8—C9	1.378 (5)	C20—H20	0.9500
C8—H8	0.9500	O2—H2A	0.82 (5)
C9—H9	0.9500	O2—H2B	0.98 (4)
O1—Cu1—O3	93.44 (11)	C4—C9—H9	119.4
O1—Cu1—N12	89.27 (12)	C11—N11—C15	118.8 (3)
O3—Cu1—N12	167.52 (12)	C11—N11—Cu1	125.9 (3)
O1—Cu1—N11	163.37 (13)	C15—N11—Cu1	115.3 (3)
O3—Cu1—N11	93.59 (12)	N11—C11—C12	122.1 (4)
N12—Cu1—N11	80.78 (13)	N11—C11—H11	118.9
O1—Cu1—Cl1	95.59 (9)	C12—C11—H11	118.9
O3—Cu1—Cl1	94.10 (9)	C11—C12—C13	119.3 (4)
N12—Cu1—Cl1	97.76 (10)	C11—C12—H12	120.4
N11—Cu1—Cl1	98.92 (9)	C13—C12—H12	120.4
C1—O1—Cu1	122.0 (2)	C14—C13—C12	118.9 (4)
O1—C1—C2	126.3 (4)	C14—C13—H13	120.6
O1—C1—C1 ⁱ	115.8 (4)	C12—C13—H13	120.6
C2—C1—C1 ⁱ	117.8 (5)	C13—C14—C15	119.1 (4)
C1—C2—C3	125.1 (4)	C13—C14—H14	120.4
C1—C2—H2	117.4	C15—C14—H14	120.4
C3—C2—H2	117.4	N11—C15—C14	121.9 (4)
C3—O3—Cu1	123.6 (3)	N11—C15—C16	114.7 (3)
O3—C3—C2	123.4 (4)	C14—C15—C16	123.5 (4)
O3—C3—C4	116.9 (4)	N12—C16—C17	121.7 (4)
C2—C3—C4	119.7 (4)	N12—C16—C15	113.3 (3)
C5—C4—C9	117.5 (4)	C17—C16—C15	125.0 (3)
C5—C4—C3	119.9 (4)	C16—C17—C18	119.7 (4)
C9—C4—C3	122.6 (4)	C16—C17—H17	120.2
C6—C5—C4	121.2 (4)	C18—C17—H17	120.2
C6—C5—H5	119.4	C19—C18—C17	118.3 (4)
C4—C5—H5	119.4	C19—C18—H18	120.8
C5—C6—C7	120.5 (4)	C17—C18—H18	120.8
C5—C6—H6	119.7	C20—C19—C18	119.4 (4)
C7—C6—H6	119.7	C20—C19—H19	120.3
C6—C7—C8	119.9 (4)	C18—C19—H19	120.3
C6—C7—H7	120.0	N12—C20—C19	122.9 (4)
C8—C7—H7	120.0	N12—C20—H20	118.5

C9—C8—C7	119.7 (4)	C19—C20—H20	118.5
C9—C8—H8	120.2	C20—N12—C16	118.0 (4)
C7—C8—H8	120.2	C20—N12—Cu1	126.2 (3)
C8—C9—C4	121.2 (4)	C16—N12—Cu1	115.9 (3)
C8—C9—H9	119.4	H2A—O2—H2B	96 (4)
Cu1—O1—C1—C2	-16.0 (6)	C11—C12—C13—C14	-0.4 (6)
Cu1—O1—C1—C1 ⁱ	165.1 (3)	C12—C13—C14—C15	0.1 (6)
O1—C1—C2—C3	-4.0 (7)	C11—N11—C15—C14	1.3 (6)
C1 ⁱ —C1—C2—C3	174.9 (4)	Cu1—N11—C15—C14	-179.5 (3)
Cu1—O3—C3—C2	12.9 (5)	C11—N11—C15—C16	179.4 (3)
Cu1—O3—C3—C4	-168.5 (2)	Cu1—N11—C15—C16	-1.4 (4)
C1—C2—C3—O3	5.8 (6)	C13—C14—C15—N11	-0.6 (6)
C1—C2—C3—C4	-172.7 (4)	C13—C14—C15—C16	-178.5 (4)
O3—C3—C4—C5	15.4 (6)	N11—C15—C16—N12	1.4 (5)
C2—C3—C4—C5	-166.0 (4)	C14—C15—C16—N12	179.5 (3)
O3—C3—C4—C9	-165.8 (4)	N11—C15—C16—C17	179.8 (4)
C2—C3—C4—C9	12.9 (6)	C14—C15—C16—C17	-2.1 (6)
C9—C4—C5—C6	-0.7 (6)	N12—C16—C17—C18	-1.8 (6)
C3—C4—C5—C6	178.2 (4)	C15—C16—C17—C18	179.9 (4)
C4—C5—C6—C7	1.2 (7)	C16—C17—C18—C19	1.8 (6)
C5—C6—C7—C8	-0.4 (7)	C17—C18—C19—C20	-1.3 (6)
C6—C7—C8—C9	-0.8 (6)	C18—C19—C20—N12	0.6 (6)
C7—C8—C9—C4	1.3 (6)	C19—C20—N12—C16	-0.4 (6)
C5—C4—C9—C8	-0.6 (6)	C19—C20—N12—Cu1	179.9 (3)
C3—C4—C9—C8	-179.4 (4)	C17—C16—N12—C20	1.0 (6)
C15—N11—C11—C12	-1.7 (6)	C15—C16—N12—C20	179.5 (3)
Cu1—N11—C11—C12	179.3 (3)	C17—C16—N12—Cu1	-179.2 (3)
N11—C11—C12—C13	1.2 (6)	C15—C16—N12—Cu1	-0.7 (4)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2A \cdots C11	0.82 (5)	2.41 (5)	3.224 (3)	171 (5)
O2—H2B \cdots C11 ⁱⁱ	0.98 (4)	2.33 (5)	3.307 (4)	172 (4)

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