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Crystal structure of aqua(1*H*-pyrazole-κN^2)-(pyridine-2,6-dicarboxylato-$\kappa^3 O^2,N,O^6$)copper(II) dihydrate

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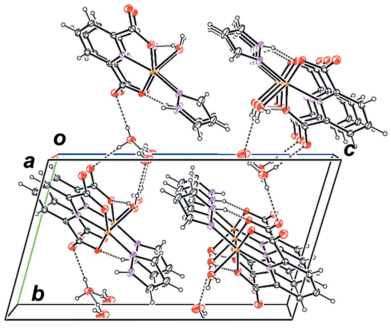
In the title compound, $[Cu(C_7H_3NO_4)(C_3H_4N_2)(H_2O)]\cdot 2H_2O$, the Cu^{II} atom is coordinated by three O atoms and two N atoms, provided by a tridentate pyridine-2,6-dicarboxylate (pdc), one pyrazole and one water ligand, forming a slightly distorted square-pyramidal geometry [range of O—Cu—O and O—Cu—N bond angles = 79.55 (8)–166.22 (10)°]. The water molecule is positioned at the apical position. In the crystal, the complex molecule and the two crystallographically independent non-coordinating water molecules are linked into a supramolecular layer structure parallel to the *ab* plane *via* O—H···O and N—H···O hydrogen bonds.

1. Chemical context

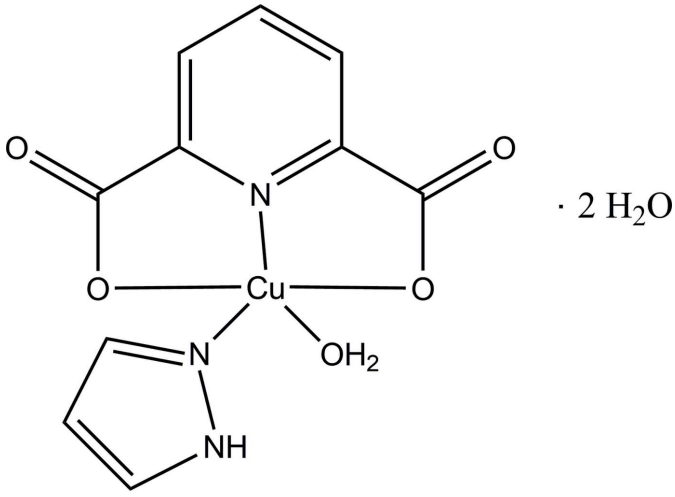
Metal complexes with the tridentate ligand 2,6-bis[(1*H*-pyrazol-1-yl)methyl]pyridine are known to be catalysts of polyethylene polymerization (Singh *et al.*, 2003; Watson *et al.*, 1987; Son *et al.*, 2014; Kim & Kang, 2015). 2,6-Bis[(1*H*-pyrazol-1-yl)methyl]pyridine was oxidized to pyridine-2,6-dicarboxylate (pdc) by metal nitrate (Unuigboje & Anyile, 2007). The pdc molecule has been recognized as a component of bacterial spores, and is also useful in a variety of processes as an enzyme inhibitor, plant preservative and food sanitizer (Cui *et al.*, 2011). The pdc molecule has been selected as a primary dibasic tridentate ligand and a metal complex with pdc was reported to be a new chemical sensor (Mistri *et al.*, 2013). Attention has been paid to the design of various *N*-donor ligands with special structural properties in order to investigate the specific stereochemical requirements of a particular metal-binding site (Mukherjee, 2000). Various substituted *N*-donor heterocyclic ligands such as imidazole and pyrazole have been selected as a second ligand, so that the structural and electronic effects on the biologically important Cu—N bond could be probed (Ang *et al.*, 1991; Chen *et al.*, 2011; Lin *et al.*, 2009; Liu *et al.*, 2005). As part of these continuing studies, the title complex has been synthesized and characterized by single crystal X-ray diffraction.



2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. The Cu^{II} atom is coordinated by three O atoms and two N atoms from tridentate pyridine-2,6-dicarboxylate (pdc), pyrazole and water ligands. The coordination geometry around the Cu^{II} atom is a distorted square pyramid as indi-

cated by the τ value of 0.113 (Addison *et al.*, 1984). The Cu^{II} atom lies in the center of the basal plane defined by two nitrogen atoms (N2 from pdc and N14 from pyrazole) and two oxygen atoms (O9 and O12 from pdc). The plane including the Cu^{II} atom is almost planar, with an r.m.s. deviation of 0.0847 Å from the corresponding least-squares plane defined by the five constituent atoms. The pyrazole ring is twisted by 66.61 (10)° from the basal plane. The apical Cu1—O19 bond length of 2.217 (2) Å is much longer than those of the basal Cu—O lengths [Cu1—O9 = 2.026 (2) Å and Cu1—O12 = 2.058 (2) Å].



3. Supramolecular features

In the crystal, O—H···O hydrogen bonds (O19—H19*B*···O21, O20—H20*B*···O13 and O20—H20*A*···O10^{iii}; symmetry code as in Table 1) link the complex molecule to the non-coordinating water molecules (Fig. 1). Two crystallographically independent non-coordinating water molecules are also linked to each other by O—H···O hydrogen bonds (O21—H21*A*···O20^{iv} and O21—H21*B*···O20^{v}; Table 1). Adjacent complex molecules are connected by other O—H···O and N—H···O hydrogen bonds (N15—H15···O12^{i} and O19—H19*A*···O9^{ii}; Table 1). The above-mentioned intermolecular interactions stabilize and link the components into a two-dimensional network parallel to the *ab* plane (Fig. 2).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O19—H19*B*···O21	0.75 (4)	2.09 (5)	2.831 (5)	169 (4)
O20—H20*B*···O13	0.70 (5)	2.12 (5)	2.807 (4)	172 (6)
N15—H15···O12^{i}	0.93 (4)	1.93 (4)	2.832 (3)	164 (4)
O19—H19*A*···O9^{ii}	0.70 (5)	2.12 (5)	2.805 (3)	165 (5)
O20—H20*A*···O10^{iii}	0.78 (5)	2.01 (5)	2.784 (4)	171 (5)
O21—H21*A*···O20^{iv}	0.91 (6)	2.05 (6)	2.933 (5)	163 (5)
O21—H21*B*···O20^{v}	0.81 (6)	2.17 (6)	2.938 (5)	161 (6)

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

4. Database survey

A search of the Cambridge Structural Database (Version 5.37 with two updates, Groom *et al.*, 2016) returned 1448 entries for crystal structures related to the name pyridine-2,6-dicarboxylato. Most of them are crystal structures of metal complexes. However, there are only four entries with a secondary ligand of a pyrazolyl derivative bonded to a transition metal, *viz*. a Cu complex (Lin *et al.*, 2009; Wang *et al.*, 2014) and Zn and Co complexes (Zhang *et al.*, 2011).

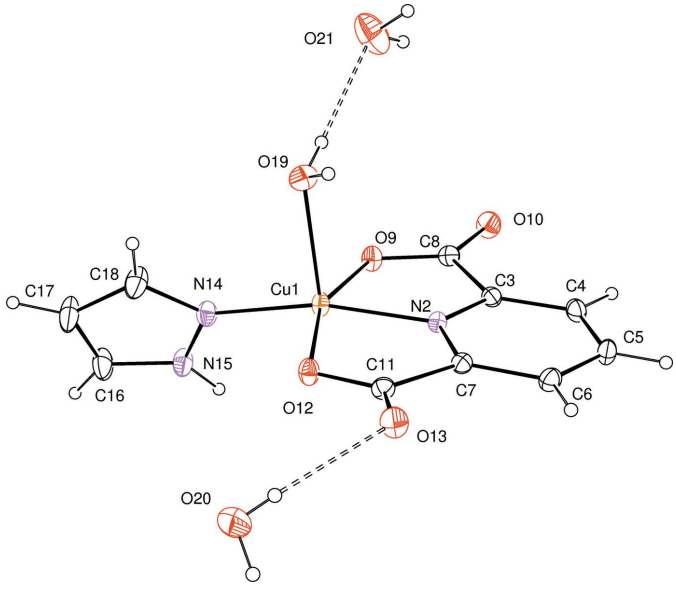


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme and 30% probability ellipsoids for non-H atoms. H atoms are drawn as small spheres of arbitrary radii. The O—H···O hydrogen bonds are indicated by dashed lines.

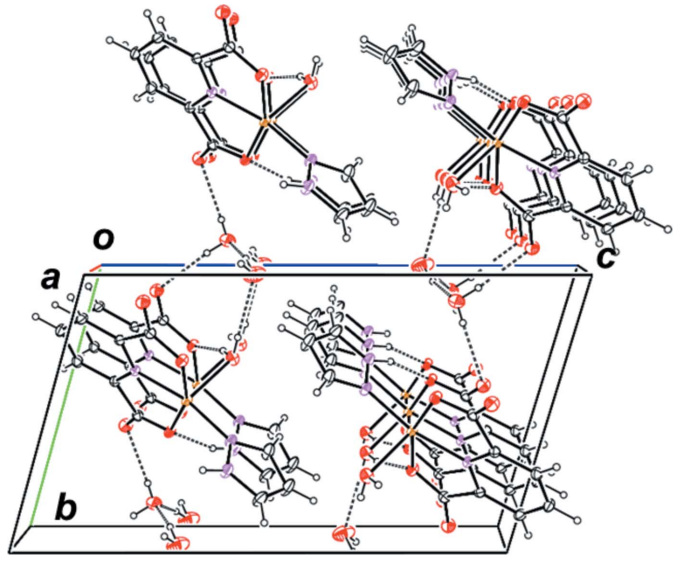


Figure 2
Part of the packing diagram of the title compound, showing molecules linked by intermolecular O—H···O and N—H···O hydrogen bonds (dashed lines).

5. Synthesis and crystallization

A solution of copper nitrate trihydrate (0.072 g, 0.3 mmol) in acetonitrile (5 ml) was added to a solution of 2,6-bis[(1*H*-pyrazol-1-yl)methyl]pyridine (0.072 g, 0.3 mmol) in acetonitrile (5 ml) in a high-pressure vessel. After sealing the high-pressure vessel, the resulting solution was stirred for three days at 403 K. The precipitate formed was removed by filtration, and the filtrate was washed with acetonitrile and dichloromethane to get a dark-green powder. Single crystals of the title compound were obtained from its aqueous solution by slow evaporation of the solvent at 333 K within five days.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms of the water molecules and the NH group were located in a difference-Fourier map and refined freely [refined distances; O—H = 0.70 (5)–0.91 (6) Å and N—H = 0.93 (4) Å]. Other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å, and with U_{iso}(H) = 1.2U_{eq}(C).

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_7H_3NO_4)(C_3H_4N_2)(H_2O)]\cdot 2H_2O$
M_r	350.77
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	5.2171 (9), 8.9249 (16), 15.309 (3)
α, β, γ (°)	105.289 (8), 94.523 (8), 93.295 (9)
V (Å^3)	683.2 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.64
Crystal size (mm)	0.25 × 0.23 × 0.12
Data collection	
Diffractometer	Bruker SMART CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.546, 0.726
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15587, 3312, 3110
R_{int}	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.088, 1.15
No. of reflections	3312
No. of parameters	214
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.68, −0.53

Computer programs: *SMART* and *SAINT* (Bruker, 2012), *SHELXS2013* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015) and *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012).

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Acta Cryst. (2017). E**73**, 1875-1877 [https://doi.org/10.1107/S2056989017016231]

Crystal structure of aqua(1*H*-pyrazole-κN^2)(pyridine-2,6-dicarboxylato-κ^3O^2,N,O^6)copper(II) dihydrate

Daeyoung Kim and Sung Kwon Kang

Computing details

Data collection: *SMART* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Aqua(1*H*-pyrazole-κN^2)(pyridine-2,6-dicarboxylato-κ^3O^2,N,O^6)copper(II) dihydrate

Crystal data

$[Cu(C_7H_3NO_4)(C_3H_4N_2)(H_2O)]\cdot 2H_2O$
M_r = 350.77
Triclinic, $P\overline{1}$
a = 5.2171 (9) Å
b = 8.9249 (16) Å
c = 15.309 (3) Å
α = 105.289 (8)°
β = 94.523 (8)°
γ = 93.295 (9)°
V = 683.2 (2) Å^3
Z = 2
$F(000)$ = 358
D_x = 1.705 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9694 reflections
θ = 2.4–28.2°
μ = 1.64 mm^{-1}
T = 296 K
Block, green
0.25 × 0.23 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2012)
T_{min} = 0.546, T_{max} = 0.726
15587 measured reflections
3312 independent reflections
3110 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 28.3°, θ_{min} = 2.4°
h = −6→6
k = −11→11
l = −20→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.088
S = 1.15
3312 reflections
214 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0181P)^2 + 1.271P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.72303 (6)	0.46457 (4)	0.26827 (2)	0.02692 (10)
N2	0.6036 (4)	0.3633 (2)	0.14415 (14)	0.0245 (4)
C3	0.7285 (5)	0.2455 (3)	0.09966 (17)	0.0262 (5)
C4	0.6564 (6)	0.1715 (3)	0.00900 (19)	0.0332 (6)
H4	0.7444	0.0895	−0.0224	0.040*
C5	0.4473 (6)	0.2238 (3)	−0.03373 (19)	0.0363 (6)
H5	0.3942	0.1762	−0.0947	0.044*
C6	0.3182 (6)	0.3459 (3)	0.01379 (19)	0.0328 (6)
H6	0.1778	0.3807	−0.0143	0.039*
C7	0.4036 (5)	0.4151 (3)	0.10435 (17)	0.0253 (5)
C8	0.9466 (5)	0.2086 (3)	0.16040 (18)	0.0288 (5)
O9	0.9876 (4)	0.3056 (2)	0.23975 (13)	0.0327 (4)
O10	1.0648 (5)	0.0935 (3)	0.13212 (15)	0.0443 (5)
C11	0.2971 (5)	0.5503 (3)	0.16952 (18)	0.0282 (5)
O12	0.4307 (4)	0.6002 (2)	0.24738 (13)	0.0319 (4)
O13	0.0961 (4)	0.6013 (3)	0.14620 (15)	0.0417 (5)
N14	0.8880 (4)	0.6023 (3)	0.38160 (16)	0.0330 (5)
N15	1.1120 (5)	0.6903 (3)	0.39067 (18)	0.0409 (6)
H15	1.218 (8)	0.680 (5)	0.344 (3)	0.066 (12)*
C16	1.1553 (7)	0.7888 (4)	0.4734 (2)	0.0530 (9)
H16	1.2963	0.8616	0.4944	0.064*
C17	0.9590 (8)	0.7642 (5)	0.5214 (2)	0.0583 (10)
H17	0.9378	0.8150	0.5814	0.070*
C18	0.7951 (7)	0.6469 (4)	0.4620 (2)	0.0492 (8)
H18	0.6417	0.6053	0.4765	0.059*
O19	0.4765 (5)	0.3250 (3)	0.33442 (17)	0.0397 (5)
H19A	0.356 (9)	0.304 (5)	0.309 (3)	0.061 (15)*
H19B	0.521 (8)	0.246 (5)	0.333 (3)	0.057 (14)*
O20	0.0431 (7)	0.9056 (3)	0.2509 (2)	0.0657 (8)
H20A	0.061 (10)	0.952 (6)	0.215 (4)	0.079*
H20B	0.042 (10)	0.828 (6)	0.226 (4)	0.079*
O21	0.5720 (7)	0.0147 (4)	0.3314 (3)	0.0839 (11)
H21A	0.420 (11)	−0.039 (7)	0.303 (4)	0.101*
H21B	0.676 (12)	−0.028 (7)	0.299 (4)	0.101*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02439 (16)	0.03062 (17)	0.02206 (16)	0.00556 (12)	−0.00065 (11)	0.00077 (12)

N2	0.0246 (10)	0.0259 (10)	0.0219 (10)	0.0018 (8)	0.0023 (8)	0.0047 (8)
C3	0.0272 (12)	0.0239 (11)	0.0268 (12)	0.0010 (9)	0.0047 (10)	0.0053 (9)
C4	0.0398 (15)	0.0276 (13)	0.0290 (13)	0.0014 (11)	0.0078 (11)	0.0011 (10)
C5	0.0445 (16)	0.0381 (15)	0.0217 (12)	−0.0033 (12)	−0.0001 (11)	0.0023 (11)
C6	0.0340 (14)	0.0364 (14)	0.0279 (13)	−0.0002 (11)	−0.0028 (11)	0.0107 (11)
C7	0.0239 (12)	0.0269 (12)	0.0253 (12)	0.0010 (9)	0.0025 (9)	0.0075 (9)
C8	0.0277 (13)	0.0292 (13)	0.0306 (13)	0.0043 (10)	0.0054 (10)	0.0089 (10)
O9	0.0276 (9)	0.0372 (10)	0.0306 (10)	0.0083 (8)	−0.0014 (7)	0.0042 (8)
O10	0.0511 (13)	0.0405 (12)	0.0425 (12)	0.0220 (10)	0.0085 (10)	0.0083 (9)
C11	0.0279 (13)	0.0290 (12)	0.0294 (13)	0.0057 (10)	0.0036 (10)	0.0097 (10)
O12	0.0311 (10)	0.0336 (10)	0.0277 (9)	0.0107 (8)	0.0012 (7)	0.0012 (8)
O13	0.0366 (11)	0.0424 (12)	0.0448 (12)	0.0166 (9)	−0.0044 (9)	0.0089 (9)
N14	0.0282 (11)	0.0387 (13)	0.0280 (11)	−0.0003 (9)	0.0003 (9)	0.0029 (10)
N15	0.0372 (14)	0.0487 (15)	0.0299 (13)	−0.0047 (11)	0.0072 (10)	−0.0011 (11)
C16	0.053 (2)	0.054 (2)	0.0371 (17)	−0.0137 (16)	0.0027 (15)	−0.0095 (15)
C17	0.059 (2)	0.072 (2)	0.0294 (16)	−0.0077 (19)	0.0098 (15)	−0.0112 (16)
C18	0.0427 (18)	0.068 (2)	0.0308 (15)	−0.0053 (16)	0.0080 (13)	0.0026 (15)
O19	0.0297 (12)	0.0496 (14)	0.0428 (13)	0.0017 (10)	0.0000 (10)	0.0188 (11)
O20	0.096 (2)	0.0400 (14)	0.0618 (19)	0.0135 (16)	0.0016 (16)	0.0158 (13)
O21	0.070 (2)	0.0589 (19)	0.106 (3)	0.0035 (16)	−0.021 (2)	0.0010 (18)

Geometric parameters (Å, º)

Cu1—N2	1.913 (2)	C11—O13	1.231 (3)
Cu1—N14	1.944 (2)	C11—O12	1.288 (3)
Cu1—O9	2.0255 (19)	N14—C18	1.329 (4)
Cu1—O12	2.0577 (19)	N14—N15	1.347 (3)
Cu1—O19	2.217 (2)	N15—C16	1.331 (4)
N2—C3	1.328 (3)	N15—H15	0.93 (4)
N2—C7	1.333 (3)	C16—C17	1.346 (5)
C3—C4	1.382 (4)	C16—H16	0.9300
C3—C8	1.519 (4)	C17—C18	1.388 (5)
C4—C5	1.394 (4)	C17—H17	0.9300
C4—H4	0.9300	C18—H18	0.9300
C5—C6	1.384 (4)	O19—H19A	0.70 (5)
C5—H5	0.9300	O19—H19B	0.75 (4)
C6—C7	1.386 (4)	O20—H20A	0.78 (5)
C6—H6	0.9300	O20—H20B	0.70 (5)
C7—C11	1.513 (4)	O21—H21A	0.91 (6)
C8—O10	1.226 (3)	O21—H21B	0.81 (6)
C8—O9	1.286 (3)		
N2—Cu1—N14	166.22 (10)	O10—C8—O9	125.9 (3)
N2—Cu1—O9	80.44 (8)	O10—C8—C3	119.8 (2)
N14—Cu1—O9	100.39 (9)	O9—C8—C3	114.3 (2)
N2—Cu1—O12	79.55 (8)	C8—O9—Cu1	114.62 (16)
N14—Cu1—O12	97.91 (9)	O13—C11—O12	125.8 (2)
O9—Cu1—O12	159.43 (8)	O13—C11—C7	119.7 (2)

N2—Cu1—O19	98.60 (9)	O12—C11—C7	114.5 (2)
N14—Cu1—O19	95.05 (10)	C11—O12—Cu1	114.43 (16)
O9—Cu1—O19	94.79 (9)	C18—N14—N15	105.1 (2)
O12—Cu1—O19	92.87 (9)	C18—N14—Cu1	129.0 (2)
C3—N2—C7	122.1 (2)	N15—N14—Cu1	125.41 (19)
C3—N2—Cu1	118.43 (17)	C16—N15—N14	111.1 (3)
C7—N2—Cu1	119.42 (17)	C16—N15—H15	126 (3)
N2—C3—C4	121.0 (2)	N14—N15—H15	122 (3)
N2—C3—C8	111.8 (2)	N15—C16—C17	108.0 (3)
C4—C3—C8	127.3 (2)	N15—C16—H16	126.0
C3—C4—C5	117.7 (3)	C17—C16—H16	126.0
C3—C4—H4	121.1	C16—C17—C18	105.3 (3)
C5—C4—H4	121.1	C16—C17—H17	127.4
C6—C5—C4	120.6 (3)	C18—C17—H17	127.4
C6—C5—H5	119.7	N14—C18—C17	110.5 (3)
C4—C5—H5	119.7	N14—C18—H18	124.7
C5—C6—C7	118.3 (3)	C17—C18—H18	124.7
C5—C6—H6	120.9	Cu1—O19—H19A	110 (4)
C7—C6—H6	120.9	Cu1—O19—H19B	115 (3)
N2—C7—C6	120.3 (2)	H19A—O19—H19B	101 (5)
N2—C7—C11	111.7 (2)	H20A—O20—H20B	103 (6)
C6—C7—C11	128.0 (2)	H21A—O21—H21B	102 (5)

C7—N2—C3—C4	0.4 (4)	C4—C3—C8—O9	173.6 (3)
Cu1—N2—C3—C4	−177.8 (2)	O10—C8—O9—Cu1	−172.0 (2)
C7—N2—C3—C8	−179.6 (2)	C3—C8—O9—Cu1	7.5 (3)
Cu1—N2—C3—C8	2.3 (3)	N2—C7—C11—O13	−172.6 (2)
N2—C3—C4—C5	−0.5 (4)	C6—C7—C11—O13	7.5 (4)
C8—C3—C4—C5	179.4 (3)	N2—C7—C11—O12	6.4 (3)
C3—C4—C5—C6	0.1 (4)	C6—C7—C11—O12	−173.5 (3)
C4—C5—C6—C7	0.5 (4)	O13—C11—O12—Cu1	171.0 (2)
C3—N2—C7—C6	0.2 (4)	C7—C11—O12—Cu1	−7.9 (3)
Cu1—N2—C7—C6	178.3 (2)	C18—N14—N15—C16	−1.2 (4)
C3—N2—C7—C11	−179.7 (2)	Cu1—N14—N15—C16	170.8 (3)
Cu1—N2—C7—C11	−1.6 (3)	N14—N15—C16—C17	1.2 (5)
C5—C6—C7—N2	−0.6 (4)	N15—C16—C17—C18	−0.7 (5)
C5—C6—C7—C11	179.2 (3)	N15—N14—C18—C17	0.7 (4)
N2—C3—C8—O10	173.0 (3)	Cu1—N14—C18—C17	−170.9 (3)
C4—C3—C8—O10	−6.9 (4)	C16—C17—C18—N14	0.0 (5)
N2—C3—C8—O9	−6.5 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O19—H19*B*···O21	0.75 (4)	2.09 (5)	2.831 (5)	169 (4)
O20—H20*B*···O13	0.70 (5)	2.12 (5)	2.807 (4)	172 (6)
N15—H15···O12^{i}	0.93 (4)	1.93 (4)	2.832 (3)	164 (4)
O19—H19*A*···O9^{ii}	0.70 (5)	2.12 (5)	2.805 (3)	165 (5)

O20—H20*A*···O10^{iii}	0.78 (5)	2.01 (5)	2.784 (4)	171 (5)
O21—H21*A*···O20^{iv}	0.91 (6)	2.05 (6)	2.933 (5)	163 (5)
O21—H21*B*···O20^{v}	0.81 (6)	2.17 (6)	2.938 (5)	161 (6)

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