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Crystal structure of (2-amino-7-methyl-4-oxidopteridine-6-carboxylato-κ^3O^4,N^5,O^6)aqua(1,10-phenanthroline-κ^2N,N')copper(II) trihydrate

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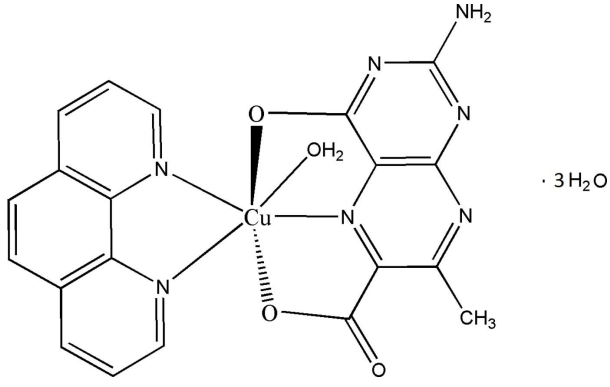
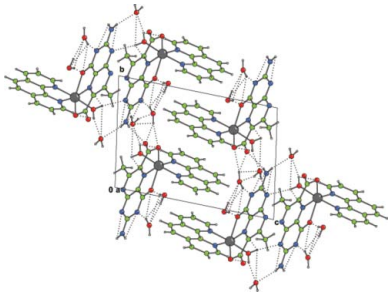
In the title compound, $[Cu(C_8H_5N_5O_3)(C_{12}H_8N_2)(H_2O)]\cdot 3H_2O$, the Cu^{II} cation is *O*,*N*,*O*′-chelated by the 2-amino-7-methyl-4-oxidopteridine-6-carboxylate anion and *N*,*N*′-chelated by the 1,10-phenanthroline (phen) ligand. A water molecule further coordinates to the Cu^{II} cation to complete the elongated distorted octahedral coordination geometry. In the molecule, the pteridine ring system is essentially planar [maximum deviation = 0.055 (4) Å], and its mean plane is nearly perpendicular to the phen ring system [dihedral angle = 85.97 (3)°]. In the crystal, N—H···O, O—H···N and O—H···O hydrogen bonds, as well as weak C—H···O hydrogen bonds and C—H···π interactions, link the complex molecules and lattice water molecules into a three-dimensional supramolecular architecture. Extensive π–π stacking between nearly parallel aromatic rings of adjacent molecules are also observed, the centroid-to-centroid distances being 3.352 (2), 3.546 (3), 3.706 (3) and 3.744 (3) Å.

1. Chemical context

The ubiquitous presence of pterins in nature including several classes of metalloenzymes, has catalysed developments of their coordination chemistry (Basu & Burgmayer, 2011; Burgmayer, 1998; Dix & Benkovic, 1988; Erlandsen *et al.*, 2000; Fitzpatrick, 2003). Literature survey reveals the paucity of structurally characterized Cu^{II} complexes involving tridentate pterin coordination (Kohzuma *et al.*, 1989). The present work is concerned with the title complex, possessing both a tridentate pterin ligand and a π-acidic ligand like phen.





2. Structural commentary

The hexacoordinated Cu^{II} atom is located in an axially elongated distorted octahedron (Fig. 1 and Table 1). The equatorial plane is formed by the two N atoms of phen, the pyrazine ring N atom of the pterin ligand and the aqua O atom. The axial positions are occupied by the two pterin O

Table 1
Selected bond lengths (Å).

Cu1—N1	2.002 (3)	Cu1—O1	2.384 (3)
Cu1—N2	2.037 (3)	Cu1—O2	2.304 (3)
Cu1—N6	1.999 (3)	Cu1—O4	2.019 (3)

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

Cg is the centroid of the N3/N4/C13–C16 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*C*···O5	0.82 (3)	1.92 (3)	2.722 (4)	169 (5)
O4—H4*D*···N4^{i}	0.81 (3)	2.26 (3)	3.038 (4)	161 (5)
O5—H5*C*···O6	0.82 (3)	1.96 (4)	2.748 (5)	162 (4)
O5—H5*D*···N4^{ii}	0.82 (5)	2.07 (5)	2.891 (5)	176 (3)
O6—H6*C*···O2	0.82 (3)	2.23 (3)	2.921 (4)	141 (5)
O6—H6*C*···O3	0.82 (3)	2.25 (4)	3.029 (4)	158 (5)
O7—H7*C*···O6	0.82 (2)	2.24 (3)	2.965 (6)	148 (5)
O7—H7*D*···O1^{iii}	0.81 (5)	2.16 (4)	2.943 (6)	162 (5)
N7—H7*E*···O5^{i}	0.85 (5)	2.17 (4)	2.998 (6)	162 (4)
N7—H7*F*···O3^{iv}	0.86 (4)	2.14 (5)	2.908 (5)	148 (4)
C1—H1···O3^{v}	0.93	2.47	3.175 (6)	133
C10—H10···O1^{vi}	0.93	2.54	3.406 (5)	155
C12—H12···O7^{vii}	0.93	2.57	3.343 (7)	140
C6—H6···*Cg*^{vi}	0.93	2.82	3.740 (5)	173

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

atoms, with the former one forming the longest axial bond [2.384 (3) Å]. Apart from the characteristic Jahn–Teller effect, another reason for distortion from a regular octahedral geometry is that the pterin ligand forms two five-membered chelate rings with small bite angles [76.47 (10) and 74.66 (11)°]. Consideration of the charge balance of this complex indicates that this pterin ligand acts as a binegative tridentate *O*,*N*,*O*′-donor. A near orthogonal disposition of the phen ligand and pterin chelate ring helps to minimize the steric repulsion. Of the three axes, the least deviation from

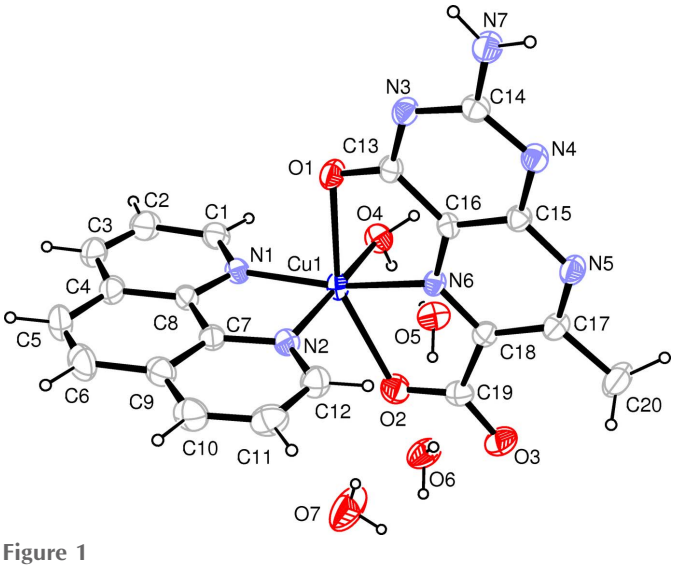


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

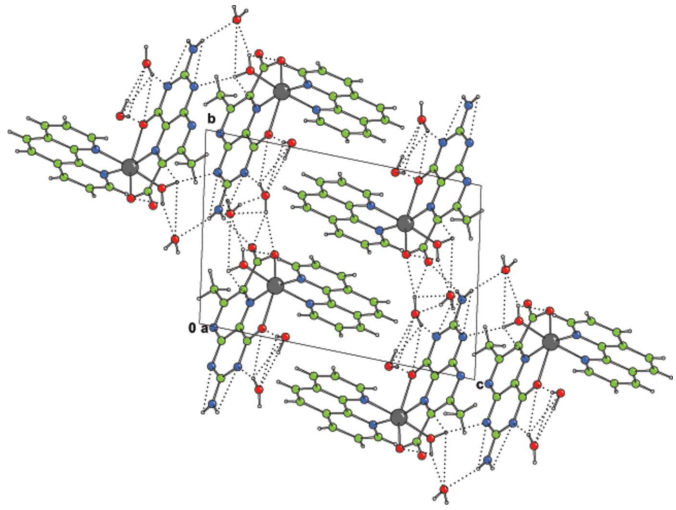


Figure 2
The crystal packing diagram of the title compound, viewed along the *a* axis. Hydrogen bonds (dotted lines) assist the formation of a layer structure parallel to (001).

linearity is observed in the O4—Cu1—N2 direction [174.45 (13)°]. Location of the pyrazine ring N atom (N6) in the equatorial plane is in agreement with earlier observations on related copper and cobalt complexes (Baisya *et al.*, 2013; Odani *et al.*, 1992); the Cu1—N6 bond length [1.999 (3) Å] is the shortest one in this case.

The multiple bond character of the O1—C13 bond [1.237 (4) Å] may be elucidated in the light of Joule's hypothesis (Beddoes *et al.*, 1993; Russell *et al.*, 1992), suggesting electron-density withdrawal from the pyrazine ring N5 by the pyrimidine ring C13 carbonyl group through mesomeric interaction. Formation of the O1—Cu1 bond assists this electron flow towards atom O1, with possible participation of the electron-rich N7—C14 [1.327 (5) Å] bond in this process.

3. Supramolecular features

In the crystal, intermolecular N—H···O, O—H···N and O—H···O hydrogen bonds (Table 2) link the complex molecules and lattice water molecules into a layer parallel to (001) (Fig. 2). Intermolecular weak C—H···O hydrogen bonds and C—H···π interactions are also observed in the crystal. In addition, π–π stacking between nearly parallel pterin ring systems of adjacent molecules occurs in the crystal structure, the centroid–centroid distance being 3.352 (2) Å (Fig. 3). Again, the nearly parallel phen rings of adjacent molecules also display π–π stacking interactions with centroids distances of 3.546 (3), 3.706 (3) and 3.744 (3) Å. These intermolecular interactions link the molecules into a three-dimensional supramolecular architecture.

4. Database survey

The crystal structures of copper(II) complexes chelated by the pterin-6-carboxylate anion have been reported by Kohzuma *et*

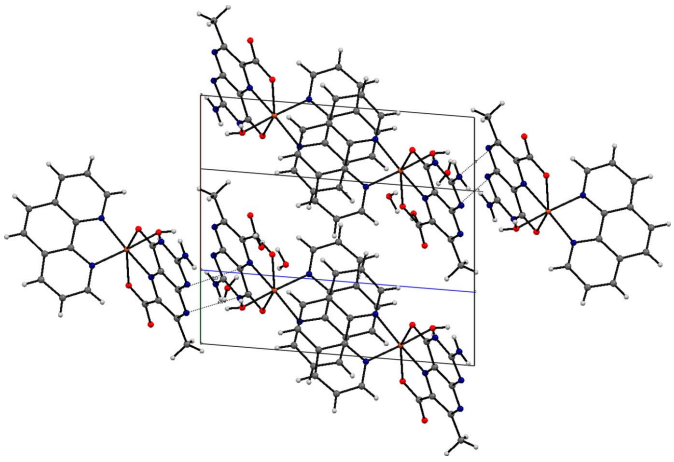


Figure 3
A molecular packing diagram highlighting π–π stacking interactions between neighbouring phen–phen and pterin–pterin rings.

al. (1989) and Funahashi *et al.* (1999). In both complexes, the Cu^{II} atom has the elongated distorted octahedral coordination geometry.

5. Synthesis and crystallization

2-Amino-4-hydroxy-7-methylpteridine-6-carboxylic acid sesquihydrate ($C_8H_7N_5O_3{\cdot}1.5H_2O$) was obtained by a published procedure (Wittle *et al.*, 1947). The title complex could be obtained by two different methods; the crystals obtained by method B have been used for the present structural study. The X-ray structural data of the crystals synthesized by method A, are available from the Cambridge Crystallographic Data Center (CCDC deposition No. 985054).

Method A. The title complex was synthesized by bubbling oxygen into an aqueous reaction mixture (50 ml) containing $Cu(NO_3)_2{\cdot}3H_2O$ (30 mg, 0.125 mmol), 1,10-phenanthroline monohydrate (25 mg, 0.125 mmol) and pterin (31 mg, 0.125 mmol) dissolved in NaOH (11 mg, 0.275 mmol) for 60 h at 310–312 K under subdued light; additional NaOH solution was added for adjusting the initial pH at 10.5. Within a short while the initial bright-green solution turned hazy blue due to the presence of a fine white precipitate which gradually disappeared substantially. The final blue solution was slightly hazy. Upon storage under aerobic conditions for one week the clear blue solution yielded green crystals, suitable for X-ray structure determination. Analysis calculated for $C_{20}H_{21}CuN_7O_7$: C 44.90, H 3.93, N 18.33%; found: C 44.38, H 4.06, N 17.65%. ESIMS data: the molecular ion peak $[M + 2H]^+$ appeared at 536.4 (relative abundance = 41.2%); the $[M - 4H_2O - 3H]^+$ peak was observed at 459.2 (relative abundance = 100%), indicating stability of the desolvated ternary species arising from the title complex.

Method B. Using $NaBH_4$ reduction in equimolar proportion of the original complex (obtained by **Method A**) and subsequent aerial reoxidation of the reduced complex to the present crystals merits attention due to the involvement of intricate redox chemistry. The $NaBH_4$ treatment (Beddoes *et al.*, 1993; Russell *et al.*, 1992) leads to the formation of a dark-brown compound in solution, which could be isolated in the solid state and characterized (microanalysis, ESIMS, 2DNMR, *etc.*,) to be $Na_2[Cu_2^I(L')_2(phen)(H_2O)_4]{\cdot}2H_2O$, where L' is the 7,8-dihydro form of the present pterin ligand anion ($C_8H_5N_5O_3$) (Burgmayer, 1998); it is able to convert bromobenzene into 4-bromophenol in the presence of oxygen (Baisya & Roy, unpublished results). However, in the absence of any substrate (*e.g.* bromobenzene; Dix & Benkovic, 1988), aerial oxidation reconverts the reduced compound to the title complex (**Method B**).

Although the title compound could be obtained by two alternative methods, the present structural data obtained using the crystals from **Method B**, represent better accuracy [R = 0.057 and $wR(F^2)$= 0.135] as compared to the other one [R = 0.113 and $wR(F^2)$ = 0.279].

Cyclic voltammetry data of this complex indicate an $E^{\circ\prime}$ value of −0.68 V; now using an $E^{\circ\prime}$ value of −0.80 V for $NaBH_4$ in neutral medium (Chatenet *et al.*, 2006; Celikkan *et al.*, 2007), an E_{cell} value ($E_{cell} = E_1 - E_2$; Segel, 1976) of 0.12 V is obtained for the $Cu^{II} \rightarrow Cu^{I}$ reduction in the title complex; it is within the range of E_{cell} value (0.033 V) for the Fe^{III}–tetrahydrobiopterin reduction in phenylalanine hydroxylase (Hagedoorn *et al.*, 2001; Gorren *et al.*, 2001). The dark-brown reduced complex (as above) shows an $E^{\circ\prime}$ value of −0.67 V (cyclic voltammetry); using an $E^{\circ\prime}$ value of 0.70 V for the

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_8H_5N_5O_3)(C_{12}H_8N_2)(H_2O)]{\cdot}3H_2O$
M_r	534.98
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	273
a, b, c (Å)	8.5399 (17), 10.038 (2), 13.601 (3)
α, β, γ (°)	97.292 (3), 94.587 (3), 110.999 (3)
V (Å^3)	1069.8 (4)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.08
Crystal size (mm)	0.20 × 0.05 × 0.03
Data collection	
Diffractometer	Bruker Kappa APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2001)
T_{min}, T_{max}	0.813, 0.968
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8227, 4134, 3590
R_{int}	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.136, 1.15
No. of reflections	4134
No. of parameters	349
No. of restraints	10
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.66, −0.31

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008), *CRYSTALS* (Betteridge *et al.*, 2003) and *CAMERON* (Watkin *et al.*, 1996).

O_2/H_2O_2 couple, an E_{cell} value of 1.37 V is obtained, indicating facile aerial oxidation. Now using an $E^{\circ\prime}$ value of 0.19 V for the chelated pterin ligand (oxidized/aromatic; Eberlein *et al.*, 1984), synchronization of its reduction or oxidation with the above redox process may be rationalized. Actually, for pterin-containing metalloenzymes the redox processes at the metal centres could be linked to the changes in the pterin ring oxidation level (Burgmayer, 1998; Erlandsen *et al.*, 2000).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms attached to N and O atoms were located in a difference Fourier map and refined with distance constraints of N—H = 0.86 (1) Å and O—H = 0.82 (1) Å. H atoms attached to C atoms were positioned geometrically, with C—H = 0.93–0.96 Å, and refined in riding mode. For all atoms, U_{iso}(H) = 1.2–1.5U_{eq}(C,N,O).

Acknowledgements

The authors express their gratitude to UGC, New Delhi, for financial assistance (SAP–DRS program). Thanks are due to CSMCRI, Bhavnagar, India, for the X-ray structural and microanalytical data. ESIMS data have been obtained from the SAIF, CDRI, Lucknow. Infrastructural support of University of North Bengal is duly acknowledged. Cyclic voltammetric data have been recorded by Professor J. P. Naskar, Jadavpur University, Kolkata, India.

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supporting information

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Crystal structure of (2-amino-7-methyl-4-oxidopteridine-6-carboxylato-κ^3O^4,N^5,O^6)aqua(1,10-phenanthroline-κ^2N,N')copper(II) trihydrate

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Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS* (Betteridge *et al.*, 2003).

(2-Amino-7-methyl-4-oxidopteridine-6-carboxylato-κ^3O^4,N^5,O^6)aqua(1,10-phenanthroline-κ^2N,N')copper(II) trihydrate

Crystal data

$[Cu(C_8H_5N_5O_3)(C_{12}H_8N_2)(H_2O)]\cdot 3H_2O$
$M_r = 534.98$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 8.5399$ (17) Å
$b = 10.038$ (2) Å
$c = 13.601$ (3) Å
$\alpha = 97.292$ (3)°
$\beta = 94.587$ (3)°
$\gamma = 110.999$ (3)°
$V = 1069.8$ (4) Å^3
$Z = 2$
$F(000) = 550$
$D_x = 1.661$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4804 reflections
$\theta = 3.0$–$29.0°$
$\mu = 1.08$ mm^{-1}
$T = 273$ K
Needle, green
0.20 × 0.05 × 0.03 mm

Data collection

Bruker Kappa APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ & ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.813$, $T_{max} = 0.968$
8227 measured reflections
4134 independent reflections
3590 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 26.0°$, $\theta_{min} = 1.5°$
$h = -10\rightarrow10$
$k = -12\rightarrow12$
$l = -16\rightarrow16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.136$
$S = 1.15$
4134 reflections
349 parameters
10 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 1.8801P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems open-flow nitrogen cryostat (Cosier & Glazer, 1986) with a nominal stability of 0.1 K.
Cosier, J. & Glazer, A. M., 1986. J. Appl. Cryst. 105–107.

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. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.96752 (6)	0.72720 (5)	0.73038 (3)	0.02733 (16)
O1	1.1883 (3)	0.9602 (3)	0.7732 (2)	0.0353 (7)
O2	0.6970 (4)	0.5696 (3)	0.7379 (2)	0.0402 (7)
O3	0.4778 (4)	0.5558 (3)	0.8185 (3)	0.0463 (8)
O4	1.0500 (4)	0.6534 (3)	0.8475 (2)	0.0356 (7)
O5	0.8413 (4)	0.4056 (3)	0.9019 (3)	0.0425 (7)
O6	0.5380 (4)	0.2754 (3)	0.7786 (3)	0.0496 (8)
O7	0.5000 (6)	−0.0210 (5)	0.6878 (5)	0.0974 (17)
N1	1.1082 (4)	0.6636 (3)	0.6383 (2)	0.0288 (7)
N2	0.8823 (4)	0.7835 (4)	0.6039 (2)	0.0296 (7)
N3	1.2193 (4)	1.1811 (3)	0.8566 (2)	0.0309 (7)
N4	0.9983 (4)	1.2067 (3)	0.9516 (2)	0.0303 (7)
N5	0.7502 (4)	1.0056 (4)	0.9482 (3)	0.0330 (8)
N6	0.8684 (4)	0.8399 (3)	0.8203 (2)	0.0247 (7)
N7	1.2417 (5)	1.3974 (4)	0.9441 (3)	0.0410 (9)
C1	1.2221 (5)	0.6068 (5)	0.6587 (3)	0.0360 (9)
H1	1.2374	0.5846	0.7223	0.043*
C2	1.3205 (6)	0.5790 (5)	0.5872 (4)	0.0454 (11)
H2	1.4011	0.5403	0.6039	0.054*
C3	1.2988 (6)	0.6084 (5)	0.4932 (4)	0.0450 (11)
H3	1.3617	0.5871	0.4452	0.054*
C4	1.1804 (5)	0.6712 (5)	0.4691 (3)	0.0374 (10)
C5	1.1463 (6)	0.7074 (6)	0.3733 (3)	0.0502 (12)
H5	1.2072	0.6912	0.3224	0.060*
C6	1.0283 (7)	0.7643 (5)	0.3551 (3)	0.0485 (12)
H6	1.0084	0.7855	0.2918	0.058*
C7	0.9651 (5)	0.7606 (4)	0.5263 (3)	0.0291 (8)
C8	1.0885 (5)	0.6975 (4)	0.5453 (3)	0.0295 (8)

C9	0.9327 (6)	0.7929 (5)	0.4312 (3)	0.0384 (10)
C10	0.8072 (6)	0.8508 (5)	0.4183 (3)	0.0449 (11)
H10	0.7811	0.8741	0.3566	0.054*
C11	0.7228 (6)	0.8730 (5)	0.4962 (4)	0.0459 (11)
H11	0.6386	0.9106	0.4877	0.055*
C12	0.7642 (5)	0.8386 (5)	0.5887 (3)	0.0376 (10)
H12	0.7070	0.8550	0.6415	0.045*
C13	1.1328 (5)	1.0386 (4)	0.8256 (3)	0.0275 (8)
C14	1.1494 (5)	1.2573 (4)	0.9168 (3)	0.0298 (8)
C15	0.9039 (5)	1.0639 (4)	0.9189 (3)	0.0276 (8)
C16	0.9640 (5)	0.9774 (4)	0.8548 (3)	0.0245 (8)
C17	0.6568 (5)	0.8674 (4)	0.9142 (3)	0.0330 (9)
C18	0.7141 (5)	0.7807 (4)	0.8461 (3)	0.0274 (8)
C19	0.6205 (5)	0.6222 (4)	0.7984 (3)	0.0316 (9)
C20	0.4884 (6)	0.8090 (5)	0.9510 (4)	0.0537 (13)
H20A	0.4874	0.8722	1.0100	0.081*
H20B	0.4695	0.7143	0.9666	0.081*
H20C	0.4006	0.8032	0.9000	0.081*
H4C	0.984 (5)	0.575 (3)	0.856 (4)	0.050*
H4D	1.062 (6)	0.702 (5)	0.9021 (19)	0.050*
H5C	0.750 (3)	0.351 (4)	0.871 (3)	0.046 (15)*
H5D	0.882 (6)	0.346 (4)	0.915 (4)	0.054 (16)*
H6C	0.540 (6)	0.358 (2)	0.778 (4)	0.050*
H6D	0.448 (3)	0.215 (4)	0.750 (3)	0.050*
H7C	0.548 (6)	0.0668 (15)	0.705 (4)	0.050*
H7D	0.415 (4)	−0.043 (6)	0.715 (4)	0.050*
H7E	1.204 (6)	1.455 (4)	0.977 (3)	0.050*
H7F	1.338 (3)	1.442 (5)	0.926 (4)	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0323 (3)	0.0302 (3)	0.0238 (3)	0.0159 (2)	0.00750 (18)	0.00499 (18)
O1	0.0324 (15)	0.0302 (15)	0.0431 (17)	0.0104 (12)	0.0163 (13)	0.0017 (12)
O2	0.0420 (17)	0.0321 (16)	0.0416 (17)	0.0097 (13)	0.0077 (14)	0.0001 (13)
O3	0.0329 (16)	0.0410 (18)	0.055 (2)	0.0011 (14)	0.0115 (14)	0.0083 (15)
O4	0.0413 (17)	0.0350 (17)	0.0323 (16)	0.0151 (14)	0.0047 (13)	0.0092 (13)
O5	0.0405 (19)	0.0339 (18)	0.053 (2)	0.0139 (15)	0.0021 (16)	0.0098 (15)
O6	0.0364 (17)	0.0333 (17)	0.076 (3)	0.0082 (14)	0.0124 (17)	0.0077 (17)
O7	0.073 (3)	0.065 (3)	0.155 (5)	0.025 (3)	0.057 (3)	−0.004 (3)
N1	0.0300 (17)	0.0279 (17)	0.0277 (17)	0.0113 (14)	0.0037 (13)	0.0000 (13)
N2	0.0300 (17)	0.0322 (18)	0.0267 (17)	0.0114 (14)	0.0043 (13)	0.0058 (13)
N3	0.0299 (17)	0.0273 (17)	0.0348 (18)	0.0083 (14)	0.0109 (14)	0.0058 (14)
N4	0.0328 (18)	0.0244 (16)	0.0339 (18)	0.0108 (14)	0.0080 (14)	0.0029 (13)
N5	0.0303 (18)	0.0308 (18)	0.040 (2)	0.0128 (15)	0.0123 (15)	0.0034 (15)
N6	0.0257 (16)	0.0248 (16)	0.0249 (16)	0.0090 (13)	0.0077 (13)	0.0069 (12)
N7	0.039 (2)	0.0264 (19)	0.050 (2)	0.0044 (16)	0.0169 (18)	−0.0010 (16)
C1	0.035 (2)	0.036 (2)	0.037 (2)	0.0165 (19)	0.0012 (18)	−0.0006 (18)

C2	0.038 (2)	0.046 (3)	0.053 (3)	0.022 (2)	0.004 (2)	−0.005 (2)
C3	0.038 (2)	0.046 (3)	0.046 (3)	0.013 (2)	0.013 (2)	−0.006 (2)
C4	0.036 (2)	0.034 (2)	0.037 (2)	0.0077 (18)	0.0114 (18)	−0.0016 (17)
C5	0.054 (3)	0.060 (3)	0.033 (2)	0.016 (3)	0.018 (2)	0.002 (2)
C6	0.062 (3)	0.053 (3)	0.029 (2)	0.016 (2)	0.011 (2)	0.013 (2)
C7	0.029 (2)	0.0248 (19)	0.029 (2)	0.0055 (16)	0.0053 (16)	0.0025 (15)
C8	0.030 (2)	0.027 (2)	0.026 (2)	0.0059 (16)	0.0054 (16)	−0.0001 (15)
C9	0.041 (2)	0.036 (2)	0.032 (2)	0.0060 (19)	0.0026 (18)	0.0075 (18)
C10	0.048 (3)	0.050 (3)	0.035 (2)	0.014 (2)	0.000 (2)	0.018 (2)
C11	0.038 (2)	0.050 (3)	0.052 (3)	0.017 (2)	0.000 (2)	0.017 (2)
C12	0.038 (2)	0.040 (2)	0.039 (2)	0.019 (2)	0.0067 (19)	0.0082 (19)
C13	0.029 (2)	0.030 (2)	0.0250 (19)	0.0112 (16)	0.0066 (15)	0.0077 (15)
C14	0.032 (2)	0.0254 (19)	0.031 (2)	0.0090 (16)	0.0032 (16)	0.0052 (16)
C15	0.027 (2)	0.0265 (19)	0.029 (2)	0.0104 (16)	0.0052 (15)	0.0047 (15)
C16	0.0288 (19)	0.0242 (19)	0.0216 (18)	0.0105 (16)	0.0056 (15)	0.0044 (14)
C17	0.027 (2)	0.034 (2)	0.039 (2)	0.0114 (17)	0.0088 (17)	0.0074 (17)
C18	0.0260 (19)	0.029 (2)	0.028 (2)	0.0110 (16)	0.0049 (15)	0.0076 (15)
C19	0.031 (2)	0.031 (2)	0.031 (2)	0.0085 (17)	0.0003 (17)	0.0091 (16)
C20	0.036 (3)	0.045 (3)	0.076 (4)	0.009 (2)	0.026 (2)	−0.001 (2)

Geometric parameters (Å, º)

Cu1—N1	2.002 (3)	N7—H7E	0.856 (10)
Cu1—N2	2.037 (3)	N7—H7F	0.854 (11)
Cu1—N6	1.999 (3)	C1—C2	1.400 (6)
Cu1—O1	2.384 (3)	C1—H1	0.9300
Cu1—O2	2.304 (3)	C2—C3	1.361 (7)
Cu1—O4	2.019 (3)	C2—H2	0.9300
O1—C13	1.237 (5)	C3—C4	1.408 (7)
O2—C19	1.267 (5)	C3—H3	0.9300
O3—C19	1.234 (5)	C4—C8	1.404 (6)
O4—H4C	0.819 (10)	C4—C5	1.432 (7)
O4—H4D	0.812 (10)	C5—C6	1.346 (7)
O5—H5C	0.819 (10)	C5—H5	0.9300
O5—H5D	0.820 (10)	C6—C9	1.430 (7)
O6—H6C	0.823 (10)	C6—H6	0.9300
O6—H6D	0.817 (10)	C7—C9	1.403 (6)
O7—H7C	0.819 (10)	C7—C8	1.433 (6)
O7—H7D	0.815 (10)	C9—C10	1.400 (6)
N1—C1	1.321 (5)	C10—C11	1.367 (7)
N1—C8	1.363 (5)	C10—H10	0.9300
N2—C12	1.328 (5)	C11—C12	1.398 (6)
N2—C7	1.357 (5)	C11—H11	0.9300
N3—C13	1.345 (5)	C12—H12	0.9300
N3—C14	1.364 (5)	C13—C16	1.460 (5)
N4—C14	1.355 (5)	C15—C16	1.405 (5)
N4—C15	1.363 (5)	C17—C18	1.425 (6)
N5—C17	1.326 (5)	C17—C20	1.499 (6)

N5—C15	1.348 (5)	C18—C19	1.528 (5)
N6—C16	1.326 (5)	C20—H20A	0.9600
N6—C18	1.333 (5)	C20—H20B	0.9600
N7—C14	1.327 (5)	C20—H20C	0.9600
N6—Cu1—N1	165.66 (13)	C6—C5—H5	119.2
N6—Cu1—O4	91.01 (12)	C4—C5—H5	119.2
N1—Cu1—O4	93.79 (13)	C5—C6—C9	121.4 (4)
N6—Cu1—N2	93.79 (13)	C5—C6—H6	119.3
N1—Cu1—N2	82.20 (13)	C9—C6—H6	119.3
O4—Cu1—N2	174.45 (13)	N2—C7—C9	123.3 (4)
N6—Cu1—O2	74.74 (11)	N2—C7—C8	116.3 (3)
N1—Cu1—O2	118.84 (12)	C9—C7—C8	120.4 (4)
O4—Cu1—O2	88.62 (12)	N1—C8—C4	123.1 (4)
N2—Cu1—O2	89.98 (12)	N1—C8—C7	117.1 (3)
N6—Cu1—O1	76.45 (11)	C4—C8—C7	119.8 (4)
N1—Cu1—O1	89.79 (11)	C10—C9—C7	116.7 (4)
O4—Cu1—O1	93.07 (12)	C10—C9—C6	125.0 (4)
N2—Cu1—O1	90.74 (12)	C7—C9—C6	118.3 (4)
O2—Cu1—O1	151.17 (10)	C11—C10—C9	120.1 (4)
C13—O1—Cu1	107.2 (2)	C11—C10—H10	120.0
C19—O2—Cu1	113.0 (3)	C9—C10—H10	120.0
Cu1—O4—H4C	114 (4)	C10—C11—C12	119.4 (4)
Cu1—O4—H4D	116 (4)	C10—C11—H11	120.3
H4C—O4—H4D	101 (5)	C12—C11—H11	120.3
H5C—O5—H5D	100 (5)	N2—C12—C11	122.4 (4)
H6C—O6—H6D	111 (5)	N2—C12—H12	118.8
H7C—O7—H7D	106 (5)	C11—C12—H12	118.8
C1—N1—C8	118.7 (3)	O1—C13—N3	123.3 (3)
C1—N1—Cu1	128.8 (3)	O1—C13—C16	119.8 (3)
C8—N1—Cu1	112.3 (3)	N3—C13—C16	116.9 (3)
C12—N2—C7	118.2 (3)	N7—C14—N4	116.9 (4)
C12—N2—Cu1	129.9 (3)	N7—C14—N3	115.4 (4)
C7—N2—Cu1	111.9 (3)	N4—C14—N3	127.6 (3)
C13—N3—C14	118.8 (3)	N5—C15—N4	119.1 (3)
C14—N4—C15	115.3 (3)	N5—C15—C16	119.8 (3)
C17—N5—C15	119.0 (3)	N4—C15—C16	121.0 (3)
C16—N6—C18	120.8 (3)	N6—C16—C15	120.5 (3)
C16—N6—Cu1	117.0 (2)	N6—C16—C13	119.4 (3)
C18—N6—Cu1	122.2 (3)	C15—C16—C13	120.1 (3)
C14—N7—H7E	122 (4)	N5—C17—C18	121.4 (3)
C14—N7—H7F	125 (3)	N5—C17—C20	116.2 (4)
H7E—N7—H7F	112 (5)	C18—C17—C20	122.4 (4)
N1—C1—C2	121.7 (4)	N6—C18—C17	118.3 (3)
N1—C1—H1	119.2	N6—C18—C19	114.0 (3)
C2—C1—H1	119.2	C17—C18—C19	127.7 (3)
C3—C2—C1	120.3 (4)	O3—C19—O2	124.7 (4)
C3—C2—H2	119.9	O3—C19—C18	119.5 (4)

C1—C2—H2	119.9	O2—C19—C18	115.8 (3)
C2—C3—C4	119.6 (4)	C17—C20—H20A	109.5
C2—C3—H3	120.2	C17—C20—H20B	109.5
C4—C3—H3	120.2	H20A—C20—H20B	109.5
C8—C4—C3	116.6 (4)	C17—C20—H20C	109.5
C8—C4—C5	118.5 (4)	H20A—C20—H20C	109.5
C3—C4—C5	124.9 (4)	H20B—C20—H20C	109.5
C6—C5—C4	121.6 (4)		

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the N3/N4/C13–C16 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*C*···O5	0.82 (3)	1.92 (3)	2.722 (4)	169 (5)
O4—H4*D*···N4^{i}	0.81 (3)	2.26 (3)	3.038 (4)	161 (5)
O5—H5*C*···O6	0.82 (3)	1.96 (4)	2.748 (5)	162 (4)
O5—H5*D*···N4^{ii}	0.82 (5)	2.07 (5)	2.891 (5)	176 (3)
O6—H6*C*···O2	0.82 (3)	2.23 (3)	2.921 (4)	141 (5)
O6—H6*C*···O3	0.82 (3)	2.25 (4)	3.029 (4)	158 (5)
O7—H7*C*···O6	0.82 (2)	2.24 (3)	2.965 (6)	148 (5)
O7—H7*D*···O1^{iii}	0.81 (5)	2.16 (4)	2.943 (6)	162 (5)
N7—H7*E*···O5^{i}	0.85 (5)	2.17 (4)	2.998 (6)	162 (4)
N7—H7*F*···O3^{iv}	0.86 (4)	2.14 (5)	2.908 (5)	148 (4)
C1—H1···O3^{v}	0.93	2.47	3.175 (6)	133
C10—H10···O1^{vi}	0.93	2.54	3.406 (5)	155
C12—H12···O7^{vii}	0.93	2.57	3.343 (7)	140
C6—H6···*Cg*^{vi}	0.93	2.82	3.740 (5)	173

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