Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis(2,2′-bipyridine-κ^2N,N')(nitrato-κO)-copper(II) perchlorate

Yu Zhu, Yun-Long Wu, Chun-Xia Huang and Ji-Min Xie*

School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China
Correspondence e-mail: xiejm391@sohu.com

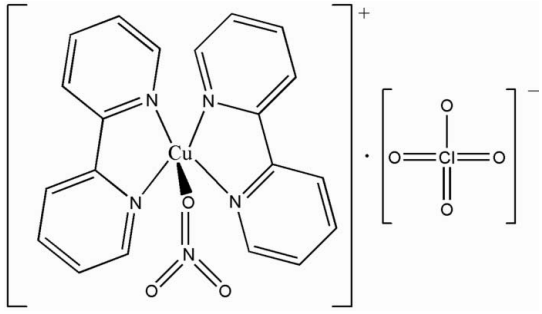
Received 10 January 2011; accepted 19 January 2011

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.034; wR factor = 0.088; data-to-parameter ratio = 11.5.

In the title compound, $[Cu(NO_3)(C_{10}H_8N_2)_2]ClO_4$, the five-coordinated Cu^{II} atom has a distorted square-pyramidal CuN_4O environment; the O atom is in the axial position whereas the N atoms from two bipyridine (bipy) ligands are in the equatorial plane. In the crystal, molecules are assembled by C—H···O hydrogen bonding and π–π interactions between bipy groups [centroid–centroid distances = 3.7686 (16) and 3.7002 (16) Å] into a three-dimensional network. The nitrite anion is equally disordered over two sets of sites.

Related literature

For the applications of complexes with bipyridine and its derivatives in catalysis and visible-light-driven water oxidation, see: Morrow & Trogler (1989) and Duan *et al.* (2010), respectively.



Experimental

Crystal data

$[Cu(NO_3)(C_{10}H_8N_2)_2]ClO_4$ M_r = 537.38
Triclinic, $P\overline{1}$
a = 7.5882 (15) Å
b = 10.473 (2) Å
c = 14.041 (3) Å
α = 76.15 (3)°
β = 81.46 (4)°
γ = 78.86 (3)°
V = 1056.9 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.22 mm^{-1}
T = 295 K
0.24 × 0.20 × 0.18 mm

Data collection

Rigaku Saturn 724 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2007)
T_{min} = 0.747, T_{max} = 0.803
10121 measured reflections
4037 independent reflections
3579 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.088
S = 1.05
4037 reflections
351 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—N1	1.986 (2)	Cu1—N3	2.0534 (18)
Cu1—N4	1.9890 (19)	Cu1—O3	2.38 (4)
Cu1—N2	2.0426 (19)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O5^{i}	0.93	2.58	3.276 (3)	132
C7—H7···O4^{ii}	0.93	2.53	3.322 (4)	144
C13—H13···O7^{iii}	0.93	2.43	3.249 (3)	147

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

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

We thank the Social Development Foundation of Jiangsu Province of China (BS2006038) and the Industry High Technology Foundation of Jiangsu (BG2007025).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2303).

References

Duan, L. L., Xu, Y. H., Zhang, P., Wang, M. & Sun, L. C. (2010). *Inorg. Chem.* **49**, 209–215.
Morrow, J. R. & Trogler, W. C. (1989). *Inorg. Chem.* **28**, 1330–2333.
Rigaku (2007). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2011). E**67**, m306 [doi:10.1107/S1600536811002571]

Bis(2,2′-bipyridine-κ^2N,N')(nitrato-κO)copper(II) perchlorate

Yu Zhu, Yun-Long Wu, Chun-Xia Huang and Ji-Min Xie

S1. Comment

Complexes with bipyridine and its derivatives have been extensively studied because of their potential applications in catalysis (Morrow & Trogler, 1989) and visible light driven water oxidation (Duan *et al.*, 2010). Herein we report the synthesis and structure of the title copper complex with 2, 2′-bipyridine.

The structure of the title complex (Fig. 1)consists of a discrete cation $[Cu(bipy)_2(NO_3)]^+$ and an uncoordinated ClO_4^- anion which is in disorder. The Cu(II) atom is five coordinated by four nitrogen atoms from two bipy ligands and one oxygen atom from one nitrate anion, exhibiting a distorted square pyramidal coordination with the oxygen atom in the axial position (Fig. 1 and Table 1). The uncoordinated perchlorate anion displays the expected tetrahedral geometry. There are weak intermolecular C—H···O hydrogen bonds in the crystal structure(C3—H3···O5^{i}, C7—H7···O4^{ii} and C13—H13···O7^{iii}; Table 2). Crystal packing is stabilised by the C—H···O hydrogen bonds and π-π interactions between two parallel bipy rings [centroid (N1, C1—C5)···centroid (N1, C1—C5)^{iv} = 3.77 Å; centroid (N2, C6—C10) ···centroid (N2, C6—C10)^{v}= 3.70 Å; centroid (N3, C16—C20)···centroid (N4, C11—C15)^{vi} = 3.75 Å; symmetry codes: (iv)-*x*, 1 - *y*, -*z*; (v) 1 - *x*, -*y*, -*z*; (vi) -*x*, -*y*, 1 - *z*)](Fig. 2).

S2. Experimental

2, 2′-bipyridine (31.3 mg, 0.2 mmol), $Cu(NO_3)_2.3H_2O$(42 mg, 0.2 mmol), $NaClO_4$ (28 mg, 0.2 mmol), acetone (10 mL) and methanol (6 mL) were stirred for 8 h at 313 K. The solution was then filtered, evaporated in the air and prismatic blue crystals were formed after 2 days (yieled 78%).

S3. Refinement

All the H atoms were placed in calculated positions and refined using a riding model, with U_{iso} (H) =1.2U_{eq}(C, N) and C–H =0.93 and N–H=0.86 Å. The disorder of $[NO_3]^-$ with two locations of O1, O2, and O3 led in the refinement to 1:1 ratio in occupancy for each oxygen atom. However, a slight disorder of $[ClO_4]^-$ cannot be described geometrically.

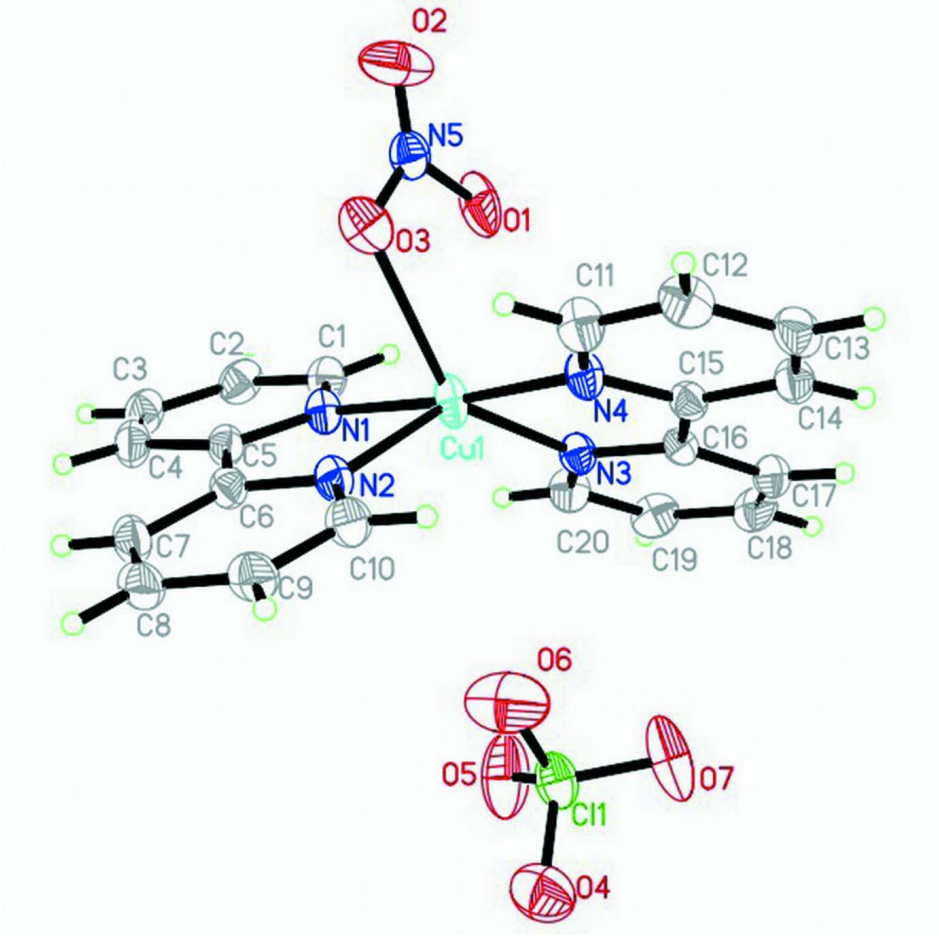


Figure 1

View of the title complex showing the labeling of the non-H atoms and 30% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii. Disorders of the coordinated $[NO_3]^-$ and uncoordinated $[ClO_4]^-$anions are not shown.

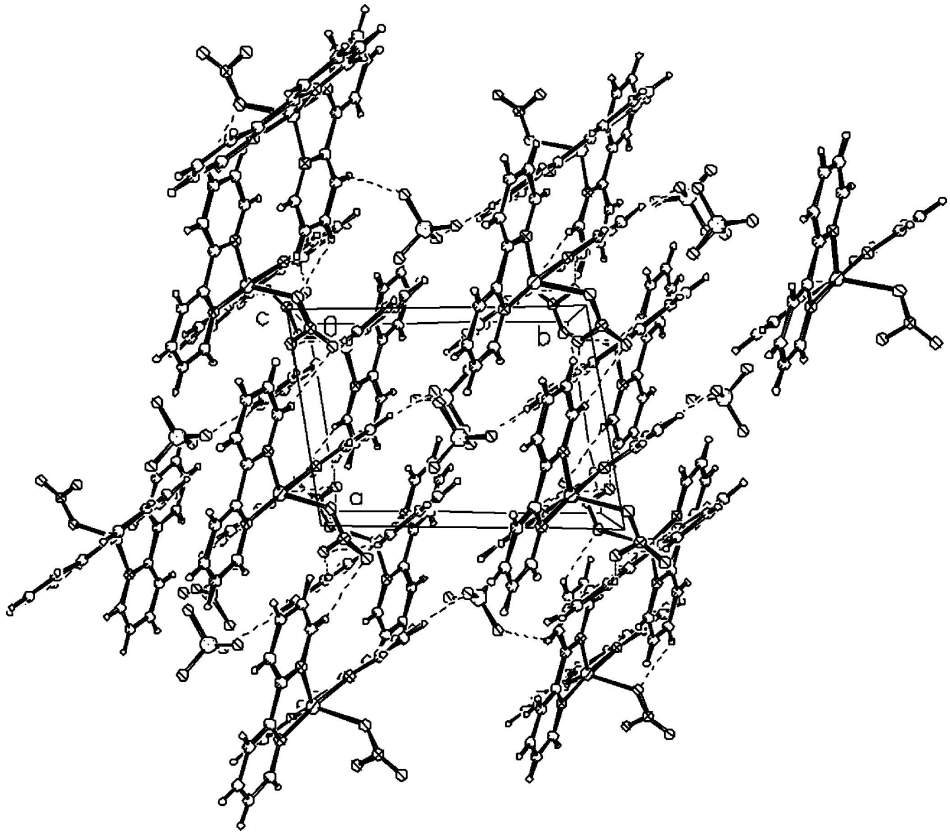


Figure 2

Three dimensional architecture constructed by intermolecular C—H···O hydrogen bonding (dashed lines) and π-π interactions.

Bis(2,2′-bipyridine-κ^2N,N')(nitrato-κO)copper(II) perchlorate

Crystal data

$[Cu(NO_3)(C_{10}H_8N_2)_2]ClO_4$
M_r = 537.38
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.5882 (15) Å
b = 10.473 (2) Å
c = 14.041 (3) Å
α = 76.15 (3)°
β = 81.46 (4)°
γ = 78.86 (3)°
V = 1056.9 (4) Å^3
Z = 2
$F(000)$ = 546
D_x = 1.689 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4693 reflections
θ = 3.1–29.0°
μ = 1.22 mm^{-1}
T = 295 K
Prism, blue
0.24 × 0.20 × 0.18 mm

Data collection

Rigaku Saturn 724 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2007)
T_{min} = 0.747, T_{max} = 0.803
10121 measured reflections
4037 independent reflections
3579 reflections with $I > 2\sigma(I)$

R_{int} = 0.019
θ_{max} = 26.0°, θ_{min} = 3.1°
h = −8→9
k = −12→12
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.088
S = 1.05
4037 reflections
351 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.3686P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.13510 (4)	0.14256 (3)	0.229930 (18)	0.04365 (11)	
N1	−0.0008 (3)	0.26435 (18)	0.12391 (13)	0.0413 (4)	
C1	−0.1751 (3)	0.3189 (2)	0.13465 (18)	0.0460 (5)	
H1	−0.2386	0.3047	0.1972	0.062 (8)*	
O1	−0.144 (6)	0.025 (3)	0.2791 (18)	0.072 (5)	0.42 (7)
O1′	−0.092 (3)	0.0253 (18)	0.2643 (12)	0.054 (3)	0.58 (7)
Cl1	0.40225 (9)	0.48718 (7)	0.29287 (4)	0.05741 (18)	
N2	0.3386 (2)	0.15087 (18)	0.11680 (13)	0.0405 (4)	
C2	−0.2638 (4)	0.3950 (2)	0.05677 (19)	0.0526 (6)	
H2	−0.3832	0.4358	0.0670	0.074 (9)*	
O2	−0.165 (6)	−0.127 (4)	0.212 (3)	0.093 (7)	0.42 (7)
O2′	−0.171 (4)	−0.151 (2)	0.2322 (14)	0.071 (3)	0.58 (7)
N3	0.0518 (2)	0.23533 (17)	0.34604 (13)	0.0377 (4)	
C3	−0.1733 (4)	0.4104 (3)	−0.03679 (19)	0.0561 (7)	
H3	−0.2314	0.4605	−0.0909	0.063 (8)*	
O3	0.070 (2)	−0.033 (3)	0.1678 (19)	0.063 (5)	0.42 (7)
O3′	0.047 (3)	−0.0583 (17)	0.1459 (15)	0.082 (3)	0.58 (7)
N4	0.2614 (2)	0.00723 (18)	0.33384 (13)	0.0412 (4)	
C4	0.0043 (4)	0.3504 (2)	−0.04923 (17)	0.0514 (6)	
H4	0.0664	0.3571	−0.1121	0.070 (9)*	
O4	0.5696 (3)	0.5366 (3)	0.26537 (19)	0.0918 (7)	
N5	−0.0741 (3)	−0.0584 (2)	0.21550 (15)	0.0465 (5)	

C5	0.0898 (3)	0.2800 (2)	0.03288 (15)	0.0406 (5)
O5	0.2613 (4)	0.5915 (3)	0.25784 (17)	0.1054 (9)
C6	0.2824 (3)	0.2197 (2)	0.02926 (15)	0.0398 (5)
O6	0.4111 (4)	0.3772 (3)	0.2508 (2)	0.1198 (11)
C7	0.4017 (4)	0.2356 (2)	−0.05599 (17)	0.0496 (6)
H7	0.3614	0.2841	−0.1156	0.055 (7)*
O7	0.3702 (4)	0.4516 (2)	0.39655 (15)	0.0995 (9)
C8	0.5801 (4)	0.1788 (3)	−0.05135 (19)	0.0534 (6)
H8	0.6618	0.1882	−0.1079	0.054 (7)*
C9	0.6372 (3)	0.1078 (3)	0.03760 (19)	0.0516 (6)
H9	0.7572	0.0679	0.0420	0.075 (9)*
C10	0.5128 (3)	0.0971 (2)	0.11998 (18)	0.0476 (5)
H10	0.5518	0.0505	0.1804	0.053 (7)*
C11	0.3604 (3)	−0.1094 (2)	0.32214 (18)	0.0510 (6)
H11	0.3782	−0.1292	0.2599	0.062 (8)*
C12	0.4372 (3)	−0.2012 (2)	0.3986 (2)	0.0541 (6)
H12	0.5064	−0.2812	0.3883	0.065 (8)*
C13	0.4095 (3)	−0.1719 (2)	0.4905 (2)	0.0532 (6)
H13	0.4616	−0.2316	0.5432	0.059 (8)*
C14	0.3040 (3)	−0.0538 (2)	0.50390 (17)	0.0451 (5)
H14	0.2812	−0.0342	0.5662	0.052 (7)*
C15	0.2321 (3)	0.0353 (2)	0.42427 (15)	0.0363 (5)
C16	0.1165 (3)	0.1643 (2)	0.43096 (15)	0.0356 (4)
C17	0.0741 (3)	0.2098 (2)	0.51762 (16)	0.0452 (5)
H17	0.1225	0.1607	0.5750	0.055 (7)*
C18	−0.0408 (4)	0.3290 (3)	0.51792 (19)	0.0541 (6)
H18	−0.0735	0.3599	0.5759	0.061 (8)*
C19	−0.1059 (3)	0.4013 (3)	0.4320 (2)	0.0541 (6)
H19	−0.1838	0.4819	0.4308	0.062 (8)*
C20	−0.0546 (3)	0.3528 (2)	0.34734 (18)	0.0478 (6)
H20	−0.0957	0.4039	0.2886	0.051 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.04732 (18)	0.04701 (18)	0.02684 (15)	0.00769 (13)	0.00054 (11)	−0.00424 (11)
N1	0.0475 (10)	0.0413 (10)	0.0313 (9)	−0.0004 (8)	−0.0030 (8)	−0.0065 (8)
C1	0.0471 (13)	0.0464 (13)	0.0430 (13)	−0.0012 (11)	−0.0041 (10)	−0.0124 (10)
O1	0.103 (12)	0.060 (5)	0.036 (5)	0.009 (7)	0.021 (7)	−0.012 (4)
O1′	0.068 (5)	0.060 (3)	0.031 (4)	−0.014 (4)	0.014 (3)	−0.012 (3)
Cl1	0.0584 (4)	0.0596 (4)	0.0441 (3)	0.0051 (3)	0.0029 (3)	−0.0088 (3)
N2	0.0449 (10)	0.0414 (10)	0.0325 (9)	−0.0048 (8)	0.0011 (8)	−0.0076 (8)
C2	0.0539 (15)	0.0484 (14)	0.0573 (15)	0.0009 (12)	−0.0205 (12)	−0.0135 (12)
O2	0.088 (11)	0.054 (8)	0.136 (17)	−0.029 (5)	−0.030 (12)	0.004 (9)
O2′	0.079 (5)	0.065 (8)	0.074 (5)	−0.037 (6)	−0.002 (4)	−0.008 (5)
N3	0.0402 (9)	0.0369 (9)	0.0334 (9)	−0.0021 (8)	−0.0014 (7)	−0.0076 (7)
C3	0.0705 (17)	0.0509 (15)	0.0477 (14)	−0.0035 (13)	−0.0271 (13)	−0.0050 (11)
O3	0.047 (4)	0.065 (7)	0.064 (7)	−0.001 (4)	0.004 (4)	−0.006 (4)

O3′	0.065 (4)	0.099 (5)	0.084 (5)	−0.022 (4)	0.030 (4)	−0.042 (5)
N4	0.0443 (10)	0.0405 (10)	0.0328 (9)	0.0020 (8)	−0.0006 (8)	−0.0059 (8)
C4	0.0746 (17)	0.0465 (13)	0.0325 (12)	−0.0088 (12)	−0.0098 (12)	−0.0059 (10)
O4	0.0823 (16)	0.0942 (17)	0.0956 (17)	−0.0216 (13)	0.0108 (13)	−0.0207 (14)
N5	0.0438 (12)	0.0518 (13)	0.0397 (11)	−0.0028 (11)	−0.0084 (9)	−0.0034 (10)
C5	0.0555 (13)	0.0339 (11)	0.0321 (11)	−0.0064 (10)	−0.0045 (10)	−0.0076 (9)
O5	0.1019 (18)	0.125 (2)	0.0643 (14)	0.0473 (16)	−0.0261 (13)	−0.0138 (14)
C6	0.0537 (13)	0.0335 (11)	0.0323 (11)	−0.0077 (10)	0.0013 (10)	−0.0106 (9)
O6	0.1064 (19)	0.111 (2)	0.157 (3)	−0.0352 (17)	0.0496 (19)	−0.084 (2)
C7	0.0662 (16)	0.0484 (13)	0.0329 (12)	−0.0125 (12)	0.0050 (11)	−0.0104 (10)
O7	0.1140 (19)	0.0939 (16)	0.0472 (11)	0.0367 (14)	0.0124 (12)	0.0126 (11)
C8	0.0591 (15)	0.0578 (15)	0.0456 (14)	−0.0197 (13)	0.0178 (12)	−0.0221 (12)
C9	0.0467 (14)	0.0554 (15)	0.0536 (15)	−0.0114 (12)	0.0077 (11)	−0.0192 (12)
C10	0.0461 (13)	0.0499 (13)	0.0447 (13)	−0.0046 (11)	−0.0009 (11)	−0.0112 (11)
C11	0.0565 (14)	0.0455 (13)	0.0459 (14)	0.0046 (11)	−0.0013 (11)	−0.0128 (11)
C12	0.0505 (14)	0.0396 (13)	0.0657 (17)	0.0041 (11)	−0.0075 (12)	−0.0071 (11)
C13	0.0502 (14)	0.0467 (14)	0.0559 (15)	−0.0061 (11)	−0.0171 (12)	0.0076 (11)
C14	0.0453 (13)	0.0498 (13)	0.0380 (12)	−0.0101 (11)	−0.0084 (10)	−0.0013 (10)
C15	0.0344 (10)	0.0401 (11)	0.0330 (11)	−0.0086 (9)	−0.0013 (9)	−0.0047 (9)
C16	0.0357 (11)	0.0393 (11)	0.0310 (10)	−0.0102 (9)	0.0017 (8)	−0.0060 (8)
C17	0.0505 (13)	0.0527 (13)	0.0337 (12)	−0.0123 (11)	0.0009 (10)	−0.0121 (10)
C18	0.0565 (15)	0.0630 (16)	0.0495 (14)	−0.0128 (13)	0.0057 (12)	−0.0298 (13)
C19	0.0524 (14)	0.0462 (14)	0.0661 (17)	0.0012 (12)	−0.0043 (12)	−0.0254 (12)
C20	0.0515 (13)	0.0412 (12)	0.0484 (13)	0.0005 (11)	−0.0066 (11)	−0.0106 (10)

Geometric parameters (Å, º)

Cu1—N1	1.986 (2)	N4—C11	1.338 (3)
Cu1—N4	1.9890 (19)	N4—C15	1.348 (3)
Cu1—N2	2.0426 (19)	C4—C5	1.387 (3)
Cu1—N3	2.0534 (18)	C4—H4	0.9301
Cu1—O1′	2.233 (15)	C5—C6	1.474 (3)
Cu1—O3	2.38 (4)	C6—C7	1.386 (3)
Cu1—O1	2.57 (5)	C7—C8	1.374 (4)
Cu1—O3′	2.87 (3)	C7—H7	0.9301
N1—C1	1.338 (3)	C8—C9	1.375 (4)
N1—C5	1.347 (3)	C8—H8	0.9300
C1—C2	1.370 (3)	C9—C10	1.377 (3)
C1—H1	0.9299	C9—H9	0.9300
O1—N5	1.38 (2)	C10—H10	0.9299
O1′—N5	1.213 (19)	C11—C12	1.375 (3)
Cl1—O6	1.402 (3)	C11—H11	0.9300
Cl1—O7	1.410 (2)	C12—C13	1.374 (4)
Cl1—O5	1.424 (2)	C12—H12	0.9300
Cl1—O4	1.429 (2)	C13—C14	1.375 (4)
N2—C10	1.336 (3)	C13—H13	0.9300
N2—C6	1.351 (3)	C14—C15	1.380 (3)
C2—C3	1.377 (4)	C14—H14	0.9300

C2—H2	0.9301	C15—C16	1.477 (3)
O2—N5	1.10 (4)	C16—C17	1.383 (3)
O2′—N5	1.28 (2)	C17—C18	1.378 (4)
N3—C20	1.337 (3)	C17—H17	0.9300
N3—C16	1.350 (3)	C18—C19	1.367 (4)
C3—C4	1.378 (4)	C18—H18	0.9300
C3—H3	0.9299	C19—C20	1.378 (3)
O3—N5	1.231 (16)	C19—H19	0.9300
O3′—N5	1.238 (13)	C20—H20	0.9300

N1—Cu1—N4	174.76 (8)	C5—C4—H4	120.3
N1—Cu1—N2	81.03 (8)	O2—N5—O1′	130.3 (17)
N4—Cu1—N2	99.78 (8)	O2—N5—O3	133.1 (18)
N1—Cu1—N3	101.94 (8)	O1′—N5—O3	96.5 (13)
N4—Cu1—N3	81.12 (7)	O2—N5—O3′	109.6 (16)
N2—Cu1—N3	135.94 (7)	O1′—N5—O3′	119.0 (9)
N1—Cu1—O1′	87.4 (4)	O1′—N5—O2′	124.5 (11)
N4—Cu1—O1′	88.2 (4)	O3—N5—O2′	138 (2)
N2—Cu1—O1′	130.0 (5)	O3′—N5—O2′	116.5 (15)
N3—Cu1—O1′	94.0 (5)	O2—N5—O1	113 (2)
N1—Cu1—O3	85.8 (4)	O3—N5—O1	113.3 (9)
N4—Cu1—O3	89.1 (4)	O3′—N5—O1	135.0 (10)
N2—Cu1—O3	84.1 (4)	O2′—N5—O1	108 (2)
N3—Cu1—O3	139.8 (4)	N1—C5—C4	120.9 (2)
O1′—Cu1—O3	46.5 (6)	N1—C5—C6	114.93 (19)
N1—Cu1—O1	86.4 (5)	C4—C5—C6	124.1 (2)
N4—Cu1—O1	89.5 (5)	N2—C6—C7	121.3 (2)
N2—Cu1—O1	135.3 (5)	N2—C6—C5	115.16 (18)
N3—Cu1—O1	88.6 (5)	C7—C6—C5	123.5 (2)
O1′—Cu1—O1	5.8 (7)	C8—C7—C6	119.2 (2)
O3—Cu1—O1	52.1 (6)	C8—C7—H7	120.4
N1—Cu1—O3′	82.6 (3)	C6—C7—H7	120.4
N4—Cu1—O3′	92.3 (3)	C7—C8—C9	119.5 (2)
N2—Cu1—O3′	83.3 (2)	C7—C8—H8	120.3
N3—Cu1—O3′	140.7 (3)	C9—C8—H8	120.2
O1′—Cu1—O3′	46.9 (6)	C8—C9—C10	118.6 (2)
O3—Cu1—O3′	3.3 (5)	C8—C9—H9	120.7
O1—Cu1—O3′	52.5 (6)	C10—C9—H9	120.7
C1—N1—C5	119.1 (2)	N2—C10—C9	122.8 (2)
C1—N1—Cu1	125.44 (16)	N2—C10—H10	118.6
C5—N1—Cu1	115.08 (15)	C9—C10—H10	118.6
N1—C1—C2	122.4 (2)	N4—C11—C12	122.5 (2)
N1—C1—H1	118.9	N4—C11—H11	118.8
C2—C1—H1	118.8	C12—C11—H11	118.8
N5—O1—Cu1	90 (2)	C13—C12—C11	118.5 (2)
N5—O1′—Cu1	113.1 (13)	C13—C12—H12	120.8
O6—Cl1—O7	111.08 (19)	C11—C12—H12	120.7
O6—Cl1—O5	111.0 (2)	C12—C13—C14	119.5 (2)

O7—Cl1—O5	108.19 (14)	C12—C13—H13	120.2
O6—Cl1—O4	108.65 (16)	C14—C13—H13	120.3
O7—Cl1—O4	109.62 (17)	C13—C14—C15	119.5 (2)
O5—Cl1—O4	108.20 (18)	C13—C14—H14	120.2
C10—N2—C6	118.6 (2)	C15—C14—H14	120.2
C10—N2—Cu1	128.24 (16)	N4—C15—C14	120.9 (2)
C6—N2—Cu1	113.12 (15)	N4—C15—C16	115.32 (18)
C1—C2—C3	119.0 (2)	C14—C15—C16	123.7 (2)
C1—C2—H2	120.5	N3—C16—C17	121.7 (2)
C3—C2—H2	120.5	N3—C16—C15	115.19 (18)
C20—N3—C16	118.09 (19)	C17—C16—C15	123.1 (2)
C20—N3—Cu1	128.80 (16)	C18—C17—C16	119.2 (2)
C16—N3—Cu1	113.10 (14)	C18—C17—H17	120.3
C2—C3—C4	119.1 (2)	C16—C17—H17	120.5
C2—C3—H3	120.5	C19—C18—C17	119.3 (2)
C4—C3—H3	120.4	C19—C18—H18	120.4
N5—O3—Cu1	104 (2)	C17—C18—H18	120.4
N5—O3′—Cu1	80.4 (14)	C18—C19—C20	118.9 (2)
C11—N4—C15	119.03 (19)	C18—C19—H19	120.5
C11—N4—Cu1	125.60 (16)	C20—C19—H19	120.6
C15—N4—Cu1	115.23 (14)	N3—C20—C19	122.8 (2)
C3—C4—C5	119.4 (2)	N3—C20—H20	118.6
C3—C4—H4	120.3	C19—C20—H20	118.6

N2—Cu1—N1—C1	−179.4 (2)	O1—Cu1—N4—C11	88.5 (5)
N3—Cu1—N1—C1	−44.1 (2)	O3′—Cu1—N4—C11	36.1 (3)
O1′—Cu1—N1—C1	49.5 (6)	N2—Cu1—N4—C15	136.89 (16)
O3—Cu1—N1—C1	96.0 (4)	N3—Cu1—N4—C15	1.56 (15)
O1—Cu1—N1—C1	43.7 (5)	O1′—Cu1—N4—C15	−92.8 (6)
O3′—Cu1—N1—C1	96.3 (3)	O3—Cu1—N4—C15	−139.3 (4)
N2—Cu1—N1—C5	7.62 (15)	O1—Cu1—N4—C15	−87.1 (5)
N3—Cu1—N1—C5	142.88 (15)	O3′—Cu1—N4—C15	−139.5 (3)
O1′—Cu1—N1—C5	−123.6 (6)	C2—C3—C4—C5	−2.3 (4)
O3—Cu1—N1—C5	−77.0 (4)	Cu1—O1′—N5—O2	−176 (3)
O1—Cu1—N1—C5	−129.3 (5)	Cu1—O1′—N5—O3	−0.6 (10)
O3′—Cu1—N1—C5	−76.7 (3)	Cu1—O1′—N5—O3′	−9.5 (14)
C5—N1—C1—C2	−2.7 (3)	Cu1—O1′—N5—O2′	168.7 (15)
Cu1—N1—C1—C2	−175.45 (18)	Cu1—O1′—N5—O1	−172 (6)
N1—Cu1—O1—N5	89.4 (10)	Cu1—O3—N5—O2	176 (3)
N4—Cu1—O1—N5	−87.4 (10)	Cu1—O3—N5—O1′	0.6 (9)
N2—Cu1—O1—N5	16.0 (15)	Cu1—O3—N5—O3′	161 (3)
N3—Cu1—O1—N5	−168.6 (10)	Cu1—O3—N5—O2′	−166.3 (16)
O1′—Cu1—O1—N5	−10 (8)	Cu1—O3—N5—O1	3.4 (13)
O3—Cu1—O1—N5	1.8 (7)	Cu1—O3′—N5—O2	176 (2)
O3′—Cu1—O1—N5	5.9 (7)	Cu1—O3′—N5—O1′	6.9 (10)
N1—Cu1—O1′—N5	87.2 (10)	Cu1—O3′—N5—O3	−15 (3)
N4—Cu1—O1′—N5	−90.1 (10)	Cu1—O3′—N5—O2′	−171.4 (13)
N2—Cu1—O1′—N5	11.2 (14)	Cu1—O3′—N5—O1	14.1 (15)

N3—Cu1—O1′—N5	−171.0 (10)	Cu1—O1—N5—O2	−177 (2)
O3—Cu1—O1′—N5	0.4 (7)	Cu1—O1—N5—O1′	7 (5)
O1—Cu1—O1′—N5	167 (10)	Cu1—O1—N5—O3	−3.1 (12)
O3′—Cu1—O1′—N5	4.9 (7)	Cu1—O1—N5—O3′	−15.6 (17)
N1—Cu1—N2—C10	175.1 (2)	Cu1—O1—N5—O2′	169.7 (13)
N4—Cu1—N2—C10	−10.2 (2)	C1—N1—C5—C4	−0.6 (3)
N3—Cu1—N2—C10	77.1 (2)	Cu1—N1—C5—C4	172.88 (17)
O1′—Cu1—N2—C10	−106.0 (6)	C1—N1—C5—C6	178.16 (19)
O3—Cu1—N2—C10	−98.2 (4)	Cu1—N1—C5—C6	−8.3 (2)
O1—Cu1—N2—C10	−109.4 (8)	C3—C4—C5—N1	3.1 (3)
O3′—Cu1—N2—C10	−101.4 (4)	C3—C4—C5—C6	−175.6 (2)
N1—Cu1—N2—C6	−5.48 (15)	C10—N2—C6—C7	−0.3 (3)
N4—Cu1—N2—C6	169.28 (14)	Cu1—N2—C6—C7	−179.83 (17)
N3—Cu1—N2—C6	−103.42 (16)	C10—N2—C6—C5	−177.82 (19)
O1′—Cu1—N2—C6	73.4 (6)	Cu1—N2—C6—C5	2.7 (2)
O3—Cu1—N2—C6	81.2 (4)	N1—C5—C6—N2	3.6 (3)
O1—Cu1—N2—C6	70.1 (8)	C4—C5—C6—N2	−177.6 (2)
O3′—Cu1—N2—C6	78.1 (4)	N1—C5—C6—C7	−173.8 (2)
N1—C1—C2—C3	3.4 (4)	C4—C5—C6—C7	4.9 (3)
N1—Cu1—N3—C20	−4.9 (2)	N2—C6—C7—C8	0.7 (3)
N4—Cu1—N3—C20	179.4 (2)	C5—C6—C7—C8	178.0 (2)
N2—Cu1—N3—C20	84.5 (2)	C6—C7—C8—C9	−0.2 (4)
O1′—Cu1—N3—C20	−93.1 (5)	C7—C8—C9—C10	−0.6 (4)
O3—Cu1—N3—C20	−102.7 (6)	C6—N2—C10—C9	−0.6 (3)
O1—Cu1—N3—C20	−90.9 (6)	Cu1—N2—C10—C9	178.80 (17)
O3′—Cu1—N3—C20	−97.8 (6)	C8—C9—C10—N2	1.1 (4)
N1—Cu1—N3—C16	175.01 (14)	C15—N4—C11—C12	−1.4 (4)
N4—Cu1—N3—C16	−0.67 (14)	Cu1—N4—C11—C12	−176.91 (19)
N2—Cu1—N3—C16	−95.60 (16)	N4—C11—C12—C13	0.6 (4)
O1′—Cu1—N3—C16	86.8 (5)	C11—C12—C13—C14	1.1 (4)
O3—Cu1—N3—C16	77.2 (5)	C12—C13—C14—C15	−2.0 (4)
O1—Cu1—N3—C16	89.0 (6)	C11—N4—C15—C14	0.5 (3)
O3′—Cu1—N3—C16	82.1 (6)	Cu1—N4—C15—C14	176.48 (16)
C1—C2—C3—C4	−0.8 (4)	C11—N4—C15—C16	−178.1 (2)
N1—Cu1—O3—N5	−90.8 (8)	Cu1—N4—C15—C16	−2.1 (2)
N4—Cu1—O3—N5	87.9 (8)	C13—C14—C15—N4	1.1 (3)
N2—Cu1—O3—N5	−172.2 (8)	C13—C14—C15—C16	179.6 (2)
N3—Cu1—O3—N5	12.8 (12)	C20—N3—C16—C17	0.5 (3)
O1′—Cu1—O3—N5	−0.4 (7)	Cu1—N3—C16—C17	−179.47 (16)
O1—Cu1—O3—N5	−2.1 (8)	C20—N3—C16—C15	179.68 (19)
O3′—Cu1—O3—N5	−96 (11)	Cu1—N3—C16—C15	−0.3 (2)
N1—Cu1—O3′—N5	−97.8 (7)	N4—C15—C16—N3	1.6 (3)
N4—Cu1—O3′—N5	80.8 (7)	C14—C15—C16—N3	−177.00 (19)
N2—Cu1—O3′—N5	−179.6 (8)	N4—C15—C16—C17	−179.2 (2)
N3—Cu1—O3′—N5	2.0 (11)	C14—C15—C16—C17	2.2 (3)
O1′—Cu1—O3′—N5	−4.5 (7)	N3—C16—C17—C18	1.7 (3)
O3—Cu1—O3′—N5	77 (11)	C15—C16—C17—C18	−177.4 (2)
O1—Cu1—O3′—N5	−6.7 (8)	C16—C17—C18—C19	−1.9 (4)

N2—Cu1—N4—C11	−47.5 (2)	C17—C18—C19—C20	−0.1 (4)
N3—Cu1—N4—C11	177.2 (2)	C16—N3—C20—C19	−2.6 (3)
O1′—Cu1—N4—C11	82.8 (6)	Cu1—N3—C20—C19	177.36 (18)
O3—Cu1—N4—C11	36.4 (4)	C18—C19—C20—N3	2.4 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O5^{i}	0.93	2.58	3.276 (3)	132
C7—H7···O4^{ii}	0.93	2.53	3.322 (4)	144
C13—H13···O7^{iii}	0.93	2.43	3.249 (3)	147

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