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Crystal structure of [Cu(tmpen)]$(BF_4)_2$ {tmpen is *N*,*N*,*N*′,*N*′-tetrakis[(6-methylpyridin-2-yl)methyl]-ethane-1,2-diamine}

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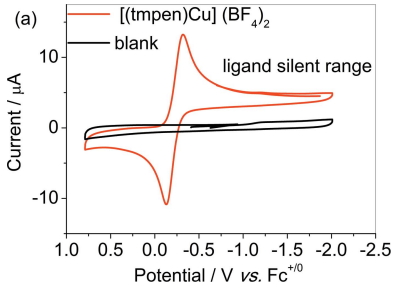
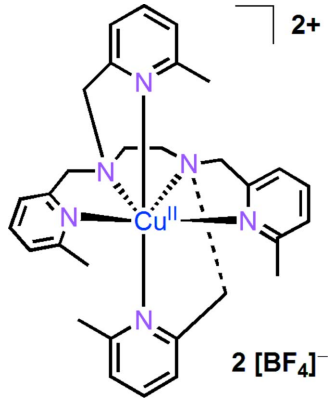
The mononuclear copper title complex {*N*,*N*,*N*′,*N*′-tetrakis[(6-methylpyridin-2-yl)methyl]ethane-1,2-diamine-κ^6N}copper(II) bis(tetrafluoridoborate), $[Cu(C_{30}H_{36}N_6)](BF_4)_2$, is conveniently prepared from the reaction of $Cu(BF_4)_2{\cdot}6H_2O$ with *N*,*N*,*N*′,*N*′-tetrakis[(6-methylpyridin-2-yl)methyl]ethane-1,2-diamine (tmpen) in acetonitrile at room temperature in air. The complex shows a distorted octahedral environment around the Cu^{II} cation (site symmetry 2) and adopts the centrosymmetric space group *C*2/*c*. The presence of the 6-methyl substituent hinders the approach of the pyridine group to the Cu^{II} core. The bond lengths about the Cu^{II} atom are significantly longer than those of analogues without the 6-methyl substituents.

1. Chemical context

Copper complexes with polypyridine ligands are of great interest in catalytic reactions. For example, the copper-based complex CuBr[*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine] (TPEN) is reported as a versatile and highly active catalyst for acrylic, methacrylic and styrenic monomers (Tang *et al.*, 2006). Copper(II) *N*-benzyl-*N*,*N*′,*N*′-tris(pyridin-2-ylmethyl)ethylenediamine (bztpen) displays high catalytic activity for electrochemical proton reduction in acidic aqueous solutions, with a calculated hydrogen-generation rate constant (k_{obs}) of over 10000 s^{-1} (Zhang *et al.*, 2014). $[Cu_2(m\text{-xpt})_2(NO_3)_2](PF_6)_2$ [m-xpt = *m*-xylylenebis(pyridyltriazole)] can selectively capture CO_2 from air and reduce it to oxalate, in the form of an oxalate-bridged complex (Pokharel *et al.*, 2014). Generally, the reduction of a metal complex is accompanied by ligand dissociation (reductive dissociation), which is able to give the appearance of an open site for catalytic reaction. Herein, we describe the structure of the title complex, **1**.





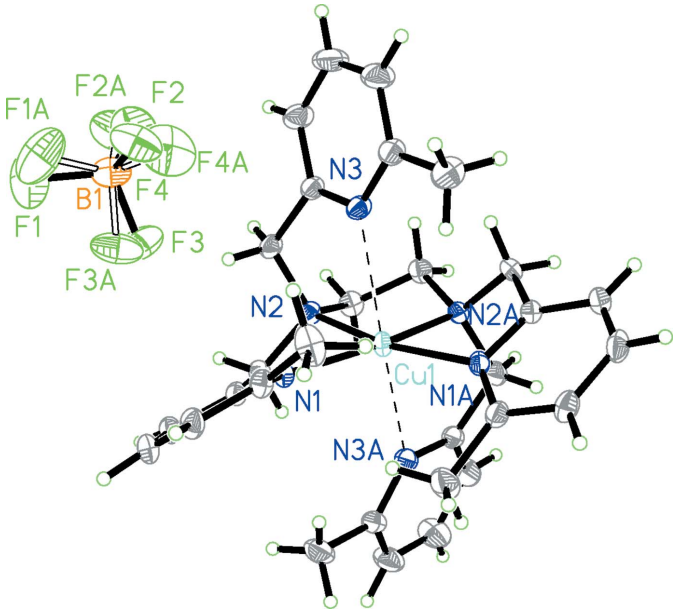


Figure 1
The molecular entities in the structure of complex **1**. Atoms N1*A*, N2*A* and N3*A* are generated by the symmetry operation $-x, y, \frac{1}{2} - z$.

2. Structural commentary

In the title complex (Fig. 1), the coordination sphere of the copper(II) atom is distorted octahedral, presumably as a result of the introduction of the 6-methyl substituent. Two pyridine nitrogen atoms (N1, N1′) and two amino nitrogen atoms (N2, N2′) form the equatorial planar coordination, while the apical positions are occupied by the other two pyridine nitrogen atoms (N3, N3′). The Cu^{II} ion lies almost in the equatorial plane. The Cu—N bond lengths for the two axial pyridine-nitrogen atoms [Cu—N3 = 2.5742 (13) Å] are significantly longer than those for the other four nitrogen atoms [Cu—N1 = 2.0571 (13), Cu—N2 = 2.0311 (13) Å]. The long Cu—N3 distance indicates a weak connection between copper and pyridine, which is apt to dissociate under reductive conditions (Tang *et al.*, 2006). As a result of steric hindrance from the methyl group, the N3—Cu1—N3′ bond angle is not linear but rather 164.94 (5)°. The pyridine rings in the equatorial plane (N1/C2–C6 and N1′/C2′–C6′) subtend a dihedral angle of 35.03 (9)°.

The distortion about the Cu^{II} atom is in favour of the reductive dissociation of one pyridine group. On a cathodic scan under Ar, complex **1** features one reversible couple based on copper at 0.26 V (*vs* $Fc^{+/0}$), assigned to $Cu^{II/I}$ (Fig. 2). The free ligand tmpen is electrochemically silent in the potential range (Fig. 3). The good reversibility of the couple indicates negligible change in the configuation of **1** under reductive conditions.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···F2*A*^{i}	0.96	2.50	3.296 (17)	140
C4—H4*A*···F4*A*^{ii}	0.93	2.50	3.394 (15)	161
C5—H5*B*···F3^{iii}	0.93	2.45	3.355 (9)	164
C5—H5*B*···F3*A*^{iii}	0.93	2.33	3.194 (13)	155
C7—H7*A*···N3^{iv}	0.97	2.59	3.212 (2)	122
C8—H8*A*···F1*A*^{v}	0.97	2.48	3.298 (16)	142
C9—H9*A*···F3	0.97	2.55	3.436 (10)	152
C9—H9*B*···F4^{v}	0.97	2.34	3.303 (6)	173
C12—H12*A*···F4^{vi}	0.93	2.45	3.198 (7)	137

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

3. Supramolecular features

While there are no classical hydrogen bonds in the crystal structure, C—H···N and C—H···F interactions are observed (Fig. 4, Table 1).

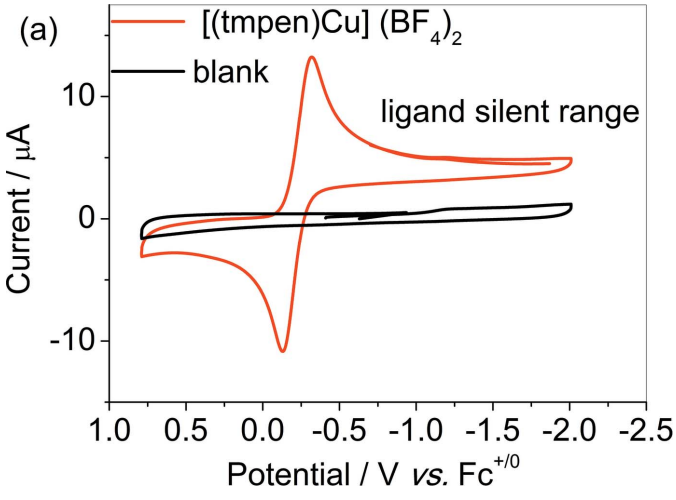


Figure 2
Cyclic voltammograms of complex **1** (1 m*M*) under Ar in CH_3CN with 0.1 *M* $^{n}Bu_4NBF_4$ as the supporting electrolyte.

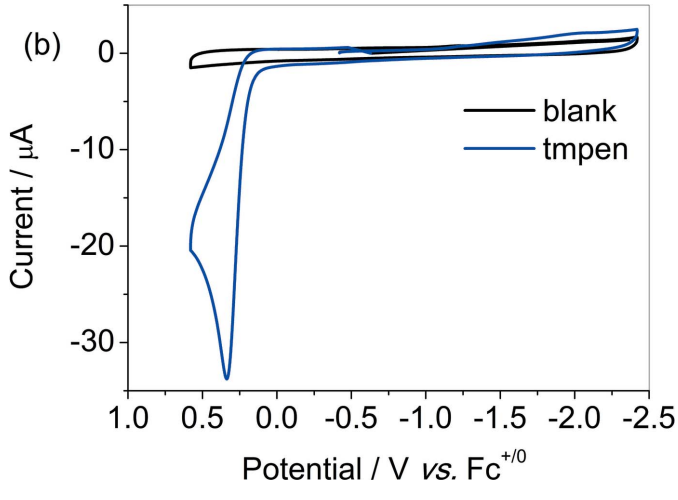


Figure 3
Cyclic voltammograms of the TMPEN ligand (1 m*M*) under Ar in CH_3CN with 0.1 *M* $^{n}Bu_4NBF_4$ as the supporting electrolyte.

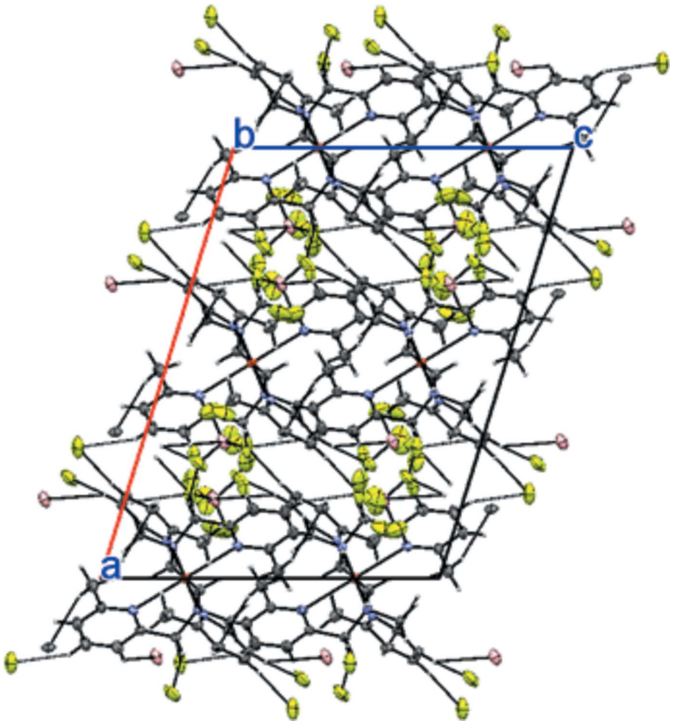


Figure 4
The crystal packing showing the C—H···F hydrogen bonds.

4. Database survey

There are four published reports of polypyridine copper complexes (Kaur *et al.*, 2015; Meyer *et al.*, 2015; Bania & Deka, 2012; Yoon *et al.*, 2005) , but to the best of our knowledge, the title compound has not been reported previously. Among the earliest reports, the copper complex with an *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) ligand is most similar to title complex in configuration. In the presence of ascorbic acid as a reducing agent, Cu^{2+}(TPEN) displays high activity in atom-transfer radical addition (ATRA) reactions (Kaur *et al.*, 2015). In contrast to Cu^{2+}(TPEN), the title complex exhibits greater steric hindrance, which results in an evident Jahn–Teller effect on the configuration. In the title complex, the axial Cu—N bonds to pyridyl nitrogen atoms [2.5742 (13) Å)] are significantly longer than in Cu^{2+}(TPEN) [2.377 (3) and 2.308 (2) Å] while the differences in the equatorial Cu—N distances are negligible (Yoon *et al.*, 2005). The other two reported polypyridine copper complexes show similar distorted octahedral coordination spheres around the Cu^{2+} cation, but the ligands are evidently different from the title complex.

5. Synthesis and crystallization

The tetrapyridinediamine ligand *N*,*N*,*N*′,*N*′-tetrakis[(6-methylpyridin-2-yl)methyl]ethane-1,2-diamine (tmpen) was prepared according to literature procedures (Mikata *et al.*, 2005). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.44 (*d*, 4H), 7.31 (*m*, 4H), 6.94 (*d*, 4H), 3.74 (*s*, 8H), 2.75 (*s*, 4H), 2.48 (*s*, 12H). ESI–MS: calculated for $[M + H]^+$: *m*/*z* 481.65.19; found: 481.31.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_{30}H_{36}N_6)](BF_4)_2$
M_r	717.81
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	296
a, *b*, *c* (Å)	18.670 (2), 12.8309 (15), 14.0146 (16)
β (°)	107.193 (2)
V (Å^3)	3207.2 (6)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.76
Crystal size (mm)	0.30 × 0.20 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.833, 0.927
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10330, 3676, 3334
R_{int}	0.023
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.034, 0.097, 1.06
No. of reflections	3676
No. of parameters	254
No. of restraints	40
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.97, −0.25

Computer programs: *SMART* and *SAINT* (Bruker, 2013), *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

For the preparation of $[Cu(tmpen)](BF_4)_2$ (**1**), $Cu(BF_4)_2{\cdot}H_2O$ (0.16 g, 0.5 mmol) was added to an acetonitrile solution (5 ml) of tmpen (0.2 g, 0.5 mmol). The mixture was stirred at room temperature for 6 h. The blue solution was then transferred to tubes, which were placed in a flask containing ether. Block-shaped crystals were obtained in a yield of 85% (0.25 g). Analysis calculated for $C_{30}H_{36}B_2CuF_8N_6$ (%): C, 50.52; H, 5.09; N, 11.78; found: 50.51; H, 5.08; N, 11.75; MS (TOF–ES): *m*/*z* =272.6641 $\{[M - 2(BF_4)^-]/2\}^+$, 579.3025 $[M - 2(BF_4)^- + Cl^-]^+$.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All F atoms of the BF_4 group were split into two groups and their ccupancies determined *via* a free variable refinement. All hydrogen atoms were refined in riding mode with C—H= 0.93–0.97 and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C) for methyl H atoms.

Funding information

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Lin Chen, Yakun Guo, Gan Ren and Ge Sang

Computing details

Data collection: *SMART* (Bruker, 2013); cell refinement: *SMART* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

{*N*,*N*,*N*′,*N*′-Tetrakis[(6-methylpyridin-2-yl)methyl]ethane-1,2-diamine-κ^6N}copper(II) bis(tetrafluoridoborate)

Crystal data

[Cu(C$_{30}$H$_{36}$N$_6$)](BF$_4$)$_2$
M_r = 717.81
Monoclinic, *C*2/*c*
a = 18.670 (2) Å
b = 12.8309 (15) Å
c = 14.0146 (16) Å
β = 107.193 (2)°
V = 3207.2 (6) Å^3
Z = 4
F(000) = 1476
D_x = 1.487 Mg m^{-3}
D_m = 1.485 Mg m^{-3}
D_m measured by none
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 5092 reflections
θ = 2.3–27.5°
μ = 0.76 mm^{-1}
T = 296 K
Block, purple
0.30 × 0.20 × 0.10 mm

Data collection

Bruker APEXII CCD area detector diffractometer
Radiation source: sealed tube
phi and *ω* scans
Absorption correction: multi-scan (SADABS; Bruker, 2013)
T_{min} = 0.833, T_{max} = 0.927
10330 measured reflections
3676 independent reflections
3334 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.5°, θ_{min} = 2.0°
h = −12→24
k = −16→16
l = −18→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.097
S = 1.06
3676 reflections
254 parameters
40 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 2.078P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.97 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 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}	Occ. (<1)
Cu1	0.0000	0.23649 (2)	0.2500	0.02731 (10)	
N1	0.08743 (7)	0.15031 (11)	0.33863 (10)	0.0289 (3)	
N2	0.07204 (7)	0.35197 (10)	0.31608 (10)	0.0286 (3)	
N3	0.07474 (8)	0.26278 (11)	0.12413 (11)	0.0333 (3)	
C1	0.08575 (13)	0.00170 (16)	0.22917 (16)	0.0537 (6)	
H1A	0.0358	0.0242	0.1945	0.081*	
H1B	0.0863	−0.0726	0.2372	0.081*	
H1C	0.1190	0.0209	0.1914	0.081*	
C2	0.11081 (9)	0.05237 (13)	0.32937 (13)	0.0336 (4)	
C3	0.16060 (10)	0.00215 (15)	0.40983 (15)	0.0401 (4)	
H3A	0.1747	−0.0665	0.4036	0.048*	
C4	0.18899 (10)	0.05447 (16)	0.49875 (14)	0.0429 (4)	
H4A	0.2195	0.0201	0.5544	0.052*	
C5	0.17170 (10)	0.15836 (16)	0.50451 (13)	0.0387 (4)	
H5B	0.1938	0.1967	0.5620	0.046*	
C6	0.12094 (9)	0.20416 (14)	0.42312 (12)	0.0302 (3)	
C7	0.09995 (10)	0.31833 (13)	0.42177 (12)	0.0325 (3)	
H7A	0.0613	0.3280	0.4545	0.039*	
H7B	0.1434	0.3593	0.4569	0.039*	
C8	0.02775 (10)	0.45062 (13)	0.30188 (13)	0.0359 (4)	
H8A	0.0611	0.5101	0.3096	0.043*	
H8B	0.0012	0.4556	0.3517	0.043*	
C9	0.13719 (9)	0.36030 (14)	0.27541 (13)	0.0351 (4)	
H9A	0.1751	0.3108	0.3107	0.042*	
H9B	0.1585	0.4295	0.2903	0.042*	
C10	0.12107 (9)	0.34140 (14)	0.16498 (13)	0.0328 (4)	
C11	0.15943 (12)	0.39957 (17)	0.11282 (16)	0.0485 (5)	
H11A	0.1896	0.4552	0.1429	0.058*	
C12	0.15162 (15)	0.3728 (2)	0.01508 (17)	0.0619 (6)	
H12A	0.1770	0.4098	−0.0220	0.074*	
C13	0.10602 (14)	0.2910 (2)	−0.02692 (16)	0.0550 (6)	
H13A	0.1008	0.2714	−0.0925	0.066*	
C14	0.06769 (11)	0.23748 (15)	0.02882 (15)	0.0394 (4)	
C15	0.01701 (13)	0.14901 (19)	−0.01745 (17)	0.0551 (6)	
H15A	0.0011	0.1136	0.0331	0.083*	
H15B	0.0435	0.1012	−0.0475	0.083*	
H15C	−0.0260	0.1755	−0.0676	0.083*	
B1	0.31688 (17)	0.1726 (2)	0.2629 (2)	0.0555 (6)	
F1	0.3874 (4)	0.1486 (8)	0.3288 (7)	0.124 (2)	0.639 (19)

F2	0.3115 (7)	0.2722 (5)	0.2310 (10)	0.101 (3)	0.639 (19)
F3	0.2668 (5)	0.1626 (7)	0.3154 (7)	0.091 (2)	0.639 (19)
F4	0.3036 (5)	0.1037 (4)	0.1872 (4)	0.0811 (16)	0.639 (19)
F1A	0.3844 (7)	0.1315 (12)	0.2879 (15)	0.122 (3)	0.361 (19)
F4A	0.2738 (11)	0.1220 (13)	0.1767 (8)	0.119 (4)	0.361 (19)
F3A	0.2862 (10)	0.1559 (10)	0.3370 (10)	0.083 (3)	0.361 (19)
F2A	0.3273 (13)	0.2753 (11)	0.2471 (18)	0.107 (4)	0.361 (19)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02415 (15)	0.02360 (15)	0.02934 (16)	0.000	0.00043 (11)	0.000
N1	0.0245 (6)	0.0307 (7)	0.0284 (6)	0.0006 (5)	0.0030 (5)	−0.0015 (5)
N2	0.0284 (6)	0.0289 (7)	0.0272 (6)	−0.0029 (5)	0.0063 (5)	−0.0041 (5)
N3	0.0315 (7)	0.0364 (8)	0.0341 (7)	−0.0066 (6)	0.0127 (6)	−0.0055 (6)
C1	0.0595 (13)	0.0401 (11)	0.0500 (12)	0.0127 (9)	−0.0017 (10)	−0.0144 (9)
C2	0.0275 (8)	0.0323 (8)	0.0385 (9)	0.0028 (6)	0.0058 (7)	−0.0014 (7)
C3	0.0311 (8)	0.0348 (9)	0.0503 (11)	0.0071 (7)	0.0061 (8)	0.0059 (8)
C4	0.0303 (9)	0.0528 (11)	0.0395 (9)	0.0074 (8)	0.0008 (7)	0.0110 (8)
C5	0.0310 (8)	0.0518 (11)	0.0294 (8)	0.0013 (8)	0.0031 (7)	−0.0006 (7)
C6	0.0251 (7)	0.0361 (8)	0.0280 (8)	−0.0007 (6)	0.0056 (6)	−0.0023 (6)
C7	0.0340 (8)	0.0359 (9)	0.0255 (8)	−0.0018 (7)	0.0054 (6)	−0.0055 (6)
C8	0.0412 (9)	0.0254 (8)	0.0396 (9)	−0.0019 (7)	0.0095 (8)	−0.0048 (7)
C9	0.0292 (8)	0.0410 (9)	0.0343 (8)	−0.0108 (7)	0.0083 (7)	−0.0063 (7)
C10	0.0295 (8)	0.0365 (9)	0.0332 (8)	−0.0044 (6)	0.0108 (7)	−0.0036 (7)
C11	0.0513 (11)	0.0490 (11)	0.0486 (11)	−0.0181 (9)	0.0199 (9)	−0.0020 (9)
C12	0.0711 (15)	0.0762 (16)	0.0472 (12)	−0.0258 (13)	0.0311 (11)	0.0008 (11)
C13	0.0630 (14)	0.0714 (15)	0.0368 (10)	−0.0142 (12)	0.0243 (10)	−0.0099 (10)
C14	0.0370 (9)	0.0468 (10)	0.0359 (9)	−0.0035 (7)	0.0134 (8)	−0.0100 (7)
C15	0.0571 (13)	0.0637 (14)	0.0487 (12)	−0.0175 (11)	0.0222 (10)	−0.0265 (10)
B1	0.0770 (18)	0.0415 (12)	0.0585 (15)	−0.0006 (12)	0.0363 (14)	−0.0085 (11)
F1	0.090 (3)	0.132 (5)	0.130 (5)	0.017 (3)	−0.001 (3)	−0.019 (3)
F2	0.130 (5)	0.043 (2)	0.123 (6)	−0.001 (3)	0.026 (4)	0.012 (3)
F3	0.086 (3)	0.109 (4)	0.105 (5)	−0.009 (2)	0.067 (3)	−0.023 (3)
F4	0.143 (4)	0.0526 (17)	0.0577 (18)	0.016 (2)	0.045 (2)	−0.0101 (15)
F1A	0.089 (5)	0.102 (5)	0.193 (10)	0.023 (4)	0.068 (6)	−0.033 (7)
F4A	0.169 (9)	0.102 (6)	0.085 (5)	−0.024 (6)	0.036 (5)	−0.057 (4)
F3A	0.146 (9)	0.059 (4)	0.061 (4)	−0.017 (5)	0.056 (5)	−0.011 (3)
F2A	0.166 (9)	0.057 (5)	0.097 (6)	−0.053 (5)	0.034 (7)	0.000 (4)

Geometric parameters (Å, º)

Cu1—N2^{i}	2.0311 (13)	C7—H7B	0.9700
Cu1—N2	2.0312 (13)	C8—C8^{i}	1.516 (3)
Cu1—N1	2.0571 (13)	C8—H8A	0.9700
Cu1—N1^{i}	2.0571 (13)	C8—H8B	0.9700
Cu1—N3	2.5742 (13)	C9—C10	1.506 (2)
Cu1—N3^{i}	2.5742 (13)	C9—H9A	0.9700

N1—C2	1.349 (2)	C9—H9B	0.9700
N1—C6	1.354 (2)	C10—C11	1.384 (3)
N2—C7	1.482 (2)	C11—C12	1.378 (3)
N2—C9	1.492 (2)	C11—H11A	0.9300
N2—C8	1.493 (2)	C12—C13	1.370 (3)
N3—C10	1.342 (2)	C12—H12A	0.9300
N3—C14	1.343 (2)	C13—C14	1.387 (3)
C1—C2	1.492 (3)	C13—H13A	0.9300
C1—H1A	0.9600	C14—C15	1.497 (3)
C1—H1B	0.9600	C15—H15A	0.9600
C1—H1C	0.9600	C15—H15B	0.9600
C2—C3	1.390 (2)	C15—H15C	0.9600
C3—C4	1.376 (3)	B1—F1A	1.315 (11)
C3—H3A	0.9300	B1—F3A	1.343 (10)
C4—C5	1.379 (3)	B1—F4	1.347 (6)
C4—H4A	0.9300	B1—F2	1.347 (7)
C5—C6	1.380 (2)	B1—F3	1.356 (6)
C5—H5B	0.9300	B1—F2A	1.360 (12)
C6—C7	1.515 (2)	B1—F4A	1.398 (10)
C7—H7A	0.9700	B1—F1	1.401 (6)

$N2^{i}$—Cu1—N2	86.31 (8)	H7A—C7—H7B	108.4
$N2^{i}$—Cu1—N1	165.41 (5)	N2—C8—$C8^{i}$	108.82 (11)
N2—Cu1—N1	79.43 (6)	N2—C8—H8A	109.9
$N2^{i}$—Cu1—$N1^{i}$	79.43 (6)	$C8^{i}$—C8—H8A	109.9
N2—Cu1—$N1^{i}$	165.41 (5)	N2—C8—H8B	109.9
N1—Cu1—$N1^{i}$	114.97 (8)	$C8^{i}$—C8—H8B	109.9
N1—Cu1—N3	89.43 (5)	H8A—C8—H8B	108.3
N1—Cu1—$N3^{i}$	98.67 (5)	N2—C9—C10	116.30 (13)
N2—Cu1—N3	78.28 (5)	N2—C9—H9A	108.2
N2—Cu1—$N3^{i}$	90.69 (5)	C10—C9—H9A	108.2
N3—Cu1—$N3^{i}$	164.94 (5)	N2—C9—H9B	108.2
C2—N1—C6	118.72 (14)	C10—C9—H9B	108.2
C2—N1—Cu1	131.62 (11)	H9A—C9—H9B	107.4
C6—N1—Cu1	109.44 (11)	N3—C10—C11	123.31 (16)
C7—N2—C9	108.49 (13)	N3—C10—C9	117.86 (15)
C7—N2—C8	113.42 (13)	C11—C10—C9	118.59 (16)
C9—N2—C8	111.74 (13)	C12—C11—C10	118.13 (19)
C7—N2—Cu1	103.48 (10)	C12—C11—H11A	120.9
C9—N2—Cu1	112.51 (10)	C10—C11—H11A	120.9
C8—N2—Cu1	106.97 (10)	C13—C12—C11	119.23 (19)
C10—N3—C14	117.87 (15)	C13—C12—H12A	120.4
C2—C1—H1A	109.5	C11—C12—H12A	120.4
C2—C1—H1B	109.5	C12—C13—C14	119.71 (19)
H1A—C1—H1B	109.5	C12—C13—H13A	120.1
C2—C1—H1C	109.5	C14—C13—H13A	120.1
H1A—C1—H1C	109.5	N3—C14—C13	121.70 (18)
H1B—C1—H1C	109.5	N3—C14—C15	118.54 (17)

N1—C2—C3	120.78 (16)	C13—C14—C15	119.76 (18)
N1—C2—C1	118.43 (15)	C14—C15—H15A	109.5
C3—C2—C1	120.68 (17)	C14—C15—H15B	109.5
C4—C3—C2	119.65 (17)	H15A—C15—H15B	109.5
C4—C3—H3A	120.2	C14—C15—H15C	109.5
C2—C3—H3A	120.2	H15A—C15—H15C	109.5
C3—C4—C5	119.35 (17)	H15B—C15—H15C	109.5
C3—C4—H4A	120.3	F1A—B1—F3A	108.9 (10)
C5—C4—H4A	120.3	F4—B1—F2	112.5 (7)
C4—C5—C6	118.58 (17)	F4—B1—F3	111.6 (5)
C4—C5—H5B	120.7	F2—B1—F3	105.9 (6)
C6—C5—H5B	120.7	F1A—B1—F2A	105.1 (10)
N1—C6—C5	122.16 (16)	F3A—B1—F2A	113.3 (10)
N1—C6—C7	115.57 (13)	F1A—B1—F4A	107.8 (6)
C5—C6—C7	122.26 (15)	F3A—B1—F4A	109.0 (8)
N2—C7—C6	107.90 (12)	F2A—B1—F4A	112.5 (12)
N2—C7—H7A	110.1	F4—B1—F1	107.0 (4)
C6—C7—H7A	110.1	F2—B1—F1	113.0 (7)
N2—C7—H7B	110.1	F3—B1—F1	106.6 (5)
C6—C7—H7B	110.1		

C6—N1—C2—C3	9.0 (2)	C7—N2—C8—C8^{i}	−152.37 (17)
Cu1—N1—C2—C3	−165.01 (13)	C9—N2—C8—C8^{i}	84.61 (19)
C6—N1—C2—C1	−167.28 (18)	Cu1—N2—C8—C8^{i}	−38.93 (19)
Cu1—N1—C2—C1	18.7 (3)	C7—N2—C9—C10	151.06 (15)
N1—C2—C3—C4	−2.9 (3)	C8—N2—C9—C10	−83.17 (18)
C1—C2—C3—C4	173.28 (19)	Cu1—N2—C9—C10	37.18 (18)
C2—C3—C4—C5	−4.6 (3)	C14—N3—C10—C11	2.4 (3)
C3—C4—C5—C6	5.7 (3)	C14—N3—C10—C9	−171.80 (17)
C2—N1—C6—C5	−7.8 (2)	N2—C9—C10—N3	−41.5 (2)
Cu1—N1—C6—C5	167.40 (14)	N2—C9—C10—C11	143.95 (18)
C2—N1—C6—C7	171.25 (15)	N3—C10—C11—C12	−2.4 (3)
Cu1—N1—C6—C7	−13.52 (17)	C9—C10—C11—C12	171.8 (2)
C4—C5—C6—N1	0.5 (3)	C10—C11—C12—C13	0.6 (4)
C4—C5—C6—C7	−178.54 (16)	C11—C12—C13—C14	0.9 (4)
C9—N2—C7—C6	−73.22 (16)	C10—N3—C14—C13	−0.7 (3)
C8—N2—C7—C6	162.00 (13)	C10—N3—C14—C15	179.19 (19)
Cu1—N2—C7—C6	46.47 (14)	C12—C13—C14—N3	−0.9 (4)
N1—C6—C7—N2	−22.45 (19)	C12—C13—C14—C15	179.2 (2)
C5—C6—C7—N2	156.64 (16)		

Symmetry code: (i) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···F2*A*^{ii}	0.96	2.50	3.296 (17)	140
C4—H4*A*···F4*A*^{iii}	0.93	2.50	3.394 (15)	161

C5—H5*B*···F3^{iv}	0.93	2.45	3.355 (9)	164
C5—H5*B*···F3*A*^{iv}	0.93	2.33	3.194 (13)	155
C7—H7*A*···N3^{i}	0.97	2.59	3.212 (2)	122
C8—H8*A*···F1*A*^{v}	0.97	2.48	3.298 (16)	142
C9—H9*A*···F3	0.97	2.55	3.436 (10)	152
C9—H9*B*···F4^{v}	0.97	2.34	3.303 (6)	173
C12—H12*A*···F4^{vi}	0.93	2.45	3.198 (7)	137

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