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## Structure Reports

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# catena-Poly[[[tetraaquacopper(II)]- $\mu$ -4,4'-bipyridyl- $\kappa^2$ N:N'] tetrafluorido-succinate tetrahydrate]

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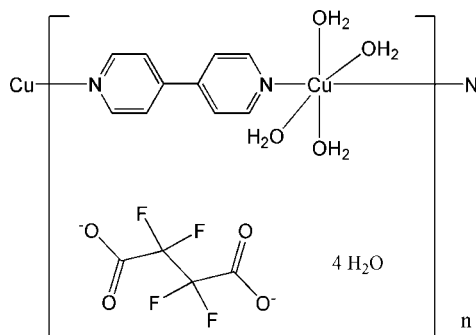
Received 22 March 2012; accepted 5 April 2012

Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.027;  $wR$  factor = 0.085; data-to-parameter ratio = 16.6.

In the title compound,  $\{[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4](\text{C}_4\text{F}_4\text{O}_4) \cdot 4\text{H}_2\text{O}\}_n$ , the  $\text{Cu}^{\text{II}}$  atom adopts an elongated octahedral geometry because of the Jahn–Teller effect. Both cation and anion have crystallographic twofold rotation symmetry with the twofold axes passing through the Cu and N atoms and through the midpoint of the central C–C bond. The 4,4'-bipyridyl ligand links the  $\text{Cu}^{\text{II}}$  atoms into a linear chain along the  $b$  axis. O–H...O hydrogen-bonding interactions between the cationic chains and the tetrafluoridosuccinate anions and the free water molecules generate a three-dimensional supra-molecular network.

## Related literature

For background to metal-organic framework structures, see: Allendorf *et al.* (2009). For the construction of hybrid frameworks with perfluorinated ligands, see: Yang *et al.* (2007); Hulvey *et al.* (2009).



## Experimental

## Crystal data

 $[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4](\text{C}_4\text{F}_4\text{O}_4) \cdot 4\text{H}_2\text{O}$  $M_r = 551.89$ Monoclinic,  $C2/c$  $a = 17.112$  (3) Å $b = 11.135$  (2) Å $c = 12.126$  (2) Å $\beta = 104.85$  (3) $^\circ$  $V = 2233.3$  (7) Å $^3$  $Z = 4$ Mo  $K\alpha$  radiation $\mu = 1.07$  mm $^{-1}$  $T = 298$  K $0.44 \times 0.22 \times 0.10$  mm

## Data collection

Bruker SMART APEX diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2005)

 $T_{\text{min}} = 0.650$ ,  $T_{\text{max}} = 0.900$ 

10662 measured reflections

2546 independent reflections

2115 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.026$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.027$  $wR(F^2) = 0.085$  $S = 1.28$ 

2546 reflections

153 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.70$  e Å $^{-3}$  $\Delta\rho_{\text{min}} = -0.78$  e Å $^{-3}$ 

Table 1

Hydrogen-bond geometry (Å,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6–H11...O4 <sup>i</sup>	0.82	2.01	2.826 (3)	172
O6–H12...O3 <sup>ii</sup>	0.82	2.07	2.879 (3)	168
O5–H10...O6	0.82	2.02	2.830 (3)	168
O5–H9...O6 <sup>i</sup>	0.82	2.11	2.871 (3)	155
O4–H8...O3 <sup>i</sup>	0.82	1.90	2.725 (3)	176
O4–H7...O2 <sup>iii</sup>	0.82	2.01	2.824 (3)	170
O1–H4...O2 <sup>i</sup>	0.82	1.81	2.630 (2)	172
O1–H3...O5	0.82	1.88	2.697 (3)	174

Symmetry codes: (i)  $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$ ; (ii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ .

Data collection: SMART (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; 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: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MW2062).

## References

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## supplementary materials

*Acta Cryst.* (2012). E68, m598 [doi:10.1107/S1600536812014948]

**catena-Poly[[[tetraaquacopper(II)]- $\mu$ -4,4'-bipyridyl- $\kappa^2$ N:N']  
tetrafluoridosuccinate tetrahydrate]**

**Guo-Jun Yu, Lan-Ping Xu, Lan Qin and Lei Han**

### Comment

Metal-organic frameworks have been widely studied over the past few decades owing to their important applications in gas storage, catalysis, sensing, nonlinear optics, magnetism, luminescence and ferroelectricity (Allendorf *et al.*, 2009). Recently, the construction of hybrid framework materials using perfluorinated ligands has attracted much attention based on reports of interesting gas storage properties for such materials containing porous surfaces with exposed fluorine atoms (Yang *et al.*, 2007). Tetrafluorosuccinic acid, as a perfluorinated dicarboxylate ligand, is an excellent candidate for the construction of hybrid frameworks with diverse structures (Hulvey *et al.*, 2009) and with which the title compound,  $\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4 \cdot \text{C}_4\text{F}_4\text{O}_4 \cdot 4\text{H}_2\text{O}$ , was hydrothermally prepared from  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 4,4'-bipyridyl as coligand.

Both cation and anion have crystallographic 2-fold rotation symmetry with the 2-fold axes passing through Cu1, N1 and N2 and through the midpoint of the central C—C bond. The metal adopts a tetragonally elongated octahedral geometry because of the Jahn-Teller effect. The O4 atom occupies the elongated vertex with a Cu1—O4 distance of 2.462 (2) Å. The O1, N1 and N2 atoms occupy the equatorial plane with a Cu1—O1 distance of 1.976 (2) Å and Cu1—N1 and Cu1—N2 distances of 2.019 (3) and 2.027 (3) Å respectively (Figure 1). Adjacent Cu<sup>II</sup> centers are bridged by 4,4'-bipy ligands to generate a one-dimensional linear chain structure parallel to the *b* axis. As shown in Figure 2 and Table 1, O—H $\cdots$ O hydrogen-bonding interactions between the cationic one-dimensional chains and the tetrafluorosuccinate anions and the free water molecules generate a three-dimensional supramolecular network.

### Experimental

A mixture of tetrafluorosuccinic acid (18.7 mg), 4,4'-bipyridyl (24.7 mg) and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (15.2 mg) was dissolved in water (8 ml) and stirred for 0.5 h at room temperature. It was then sealed in a 25 ml Teflon-lined stainless steel reactor and heated at 393 K for 48 h. Blue crystals suitable for X-ray analysis were obtained after cooling the solution to room temperature. The yield is *ca* 70% based on  $\text{Cu}^{2+}$ .

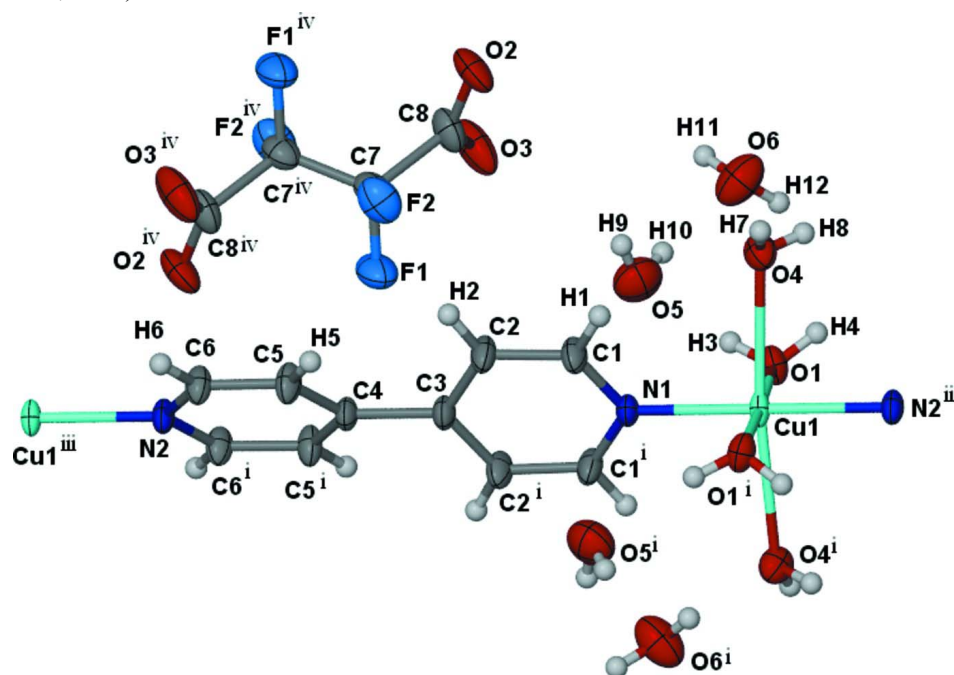
### Refinement

H atoms on O were located in difference maps and the O—H distances adjusted to 0.82 Å while H atoms on C were positioned geometrically with C—H = 0.93 Å. All were allowed to ride on their respective parent atoms with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C or O})$ .

### Computing details

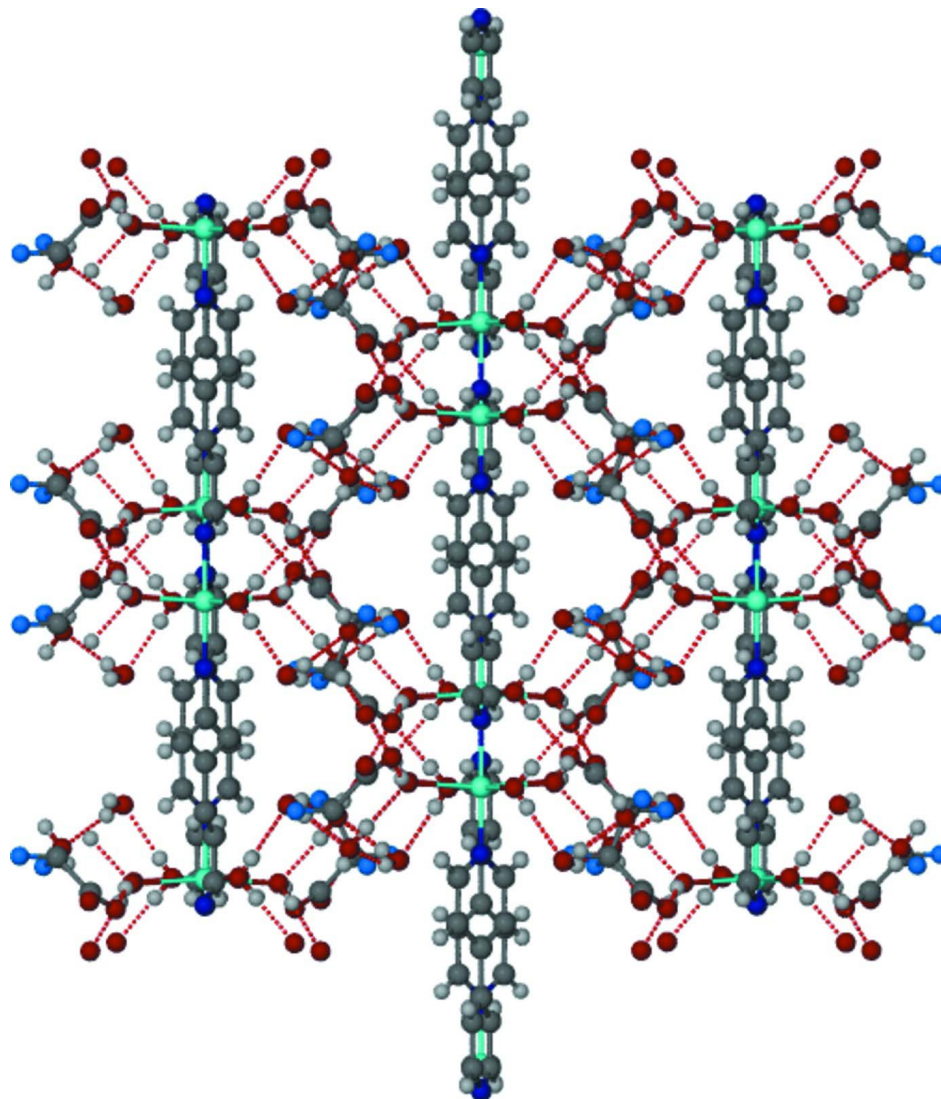
Data collection: *SMART* (Bruker, 2005); cell refinement: *SAINTE* (Bruker, 2005); data reduction: *SAINTE* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication:

SHELXTL (Sheldrick, 2008).



**Figure 1**

ORTEP drawing showing the coordination sphere of the  $\text{Cu}^{2+}$  center in the title compound with 50% probability displacement ellipsoids. Symmetry codes i:  $1-x, y, 1.5-z$ ; ii:  $x, 1+y, z$ ; iii:  $x, 1-y, z$ ; iv:  $0.5-z, 0.5-y, 1-z$ .

**Figure 2**

View down the *c* axis of the three-dimensional hydrogen bonding supramolecular network of the title compound.

***catena*-Poly[[[tetraaquacopper(II)]- $\mu$ -4,4'-bipyridyl- $\kappa^2$ N:N'] tetrafluoridosuccinate tetrahydrate]**

*Crystal data*

[Cu(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)<sub>4</sub>](C<sub>4</sub>F<sub>4</sub>O<sub>4</sub>)·4H<sub>2</sub>O

*M<sub>r</sub>* = 551.89

Monoclinic, *C2/c*

Hall symbol: -C 2yc

*a* = 17.112 (3) Å

*b* = 11.135 (2) Å

*c* = 12.126 (2) Å

$\beta$  = 104.85 (3)°

*V* = 2233.3 (7) Å<sup>3</sup>

*Z* = 4

*F*(000) = 1132

*D<sub>x</sub>* = 1.641 Mg m<sup>-3</sup>

Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 8384 reflections

$\theta$  = 3.0–27.4°

$\mu$  = 1.07 mm<sup>-1</sup>

*T* = 298 K

Block, blue

0.44 × 0.22 × 0.10 mm

*Data collection*

Bruker SMART APEX diffractometer	10662 measured reflections 2546 independent reflections
Radiation source: fine-focus sealed tube	2115 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.026$
Detector resolution: 28 pixels $\text{mm}^{-1}$	$\theta_{\text{max}} = 27.4^\circ$ , $\theta_{\text{min}} = 3.0^\circ$
$\omega$ scans	$h = -22 \rightarrow 21$
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 2005)	$k = -14 \rightarrow 14$
$T_{\text{min}} = 0.650$ , $T_{\text{max}} = 0.900$	$l = -15 \rightarrow 15$

*Refinement*

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.027$	$w = 1/[\sigma^2(F_o^2) + (0.0175P)^2 + 4.9756P]$
$wR(F^2) = 0.085$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.28$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2546 reflections	$\Delta\rho_{\text{max}} = 0.70 \text{ e } \text{\AA}^{-3}$
153 parameters	$\Delta\rho_{\text{min}} = -0.78 \text{ e } \text{\AA}^{-3}$
0 restraints	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0077 (3)
Secondary atom site location: difference Fourier map	

*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.** 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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.87438 (3)	0.7500	0.02173 (14)
F1	0.33513 (10)	0.31057 (16)	0.46607 (16)	0.0488 (5)
F2	0.29291 (11)	0.33959 (16)	0.61875 (14)	0.0457 (4)
O1	0.43960 (11)	0.87146 (15)	0.58758 (13)	0.0277 (4)
H3	0.4154	0.8089	0.5664	0.033*
H4	0.4087	0.9285	0.5680	0.033*
O2	0.16201 (13)	0.45430 (18)	0.49626 (16)	0.0426 (5)
O3	0.20898 (16)	0.4317 (2)	0.34192 (18)	0.0559 (7)
O4	0.36711 (11)	0.88591 (16)	0.79355 (15)	0.0307 (4)
H7	0.3579	0.8968	0.8561	0.037*
H8	0.3448	0.9399	0.7503	0.037*
O5	0.35115 (14)	0.6752 (2)	0.5062 (2)	0.0533 (6)
H9	0.3262	0.6610	0.5542	0.064*
H10	0.3197	0.7005	0.4479	0.064*
O6	0.23890 (14)	0.7923 (2)	0.32616 (18)	0.0540 (6)

H12	0.2530	0.8407	0.2843	0.065*
H11	0.2113	0.7397	0.2874	0.065*
N1	0.5000	0.6931 (2)	0.7500	0.0212 (6)
N2	0.5000	0.0563 (2)	0.7500	0.0231 (6)
C1	0.45882 (16)	0.6311 (2)	0.8111 (2)	0.0296 (5)
H1	0.4301	0.6731	0.8541	0.035*
C2	0.45722 (17)	0.5067 (2)	0.8129 (2)	0.0315 (6)
H2	0.4276	0.4668	0.8561	0.038*
C3	0.5000	0.4417 (3)	0.7500	0.0244 (7)
C4	0.5000	0.3076 (3)	0.7500	0.0246 (7)
C5	0.48432 (17)	0.2427 (2)	0.8399 (2)	0.0298 (6)
H5	0.4737	0.2827	0.9019	0.036*
C6	0.48451 (16)	0.1187 (2)	0.8369 (2)	0.0277 (5)
H6	0.4735	0.0766	0.8975	0.033*
C7	0.26765 (16)	0.3133 (2)	0.5056 (2)	0.0339 (6)
C8	0.20728 (18)	0.4103 (2)	0.4409 (2)	0.0363 (6)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0336 (3)	0.01019 (19)	0.0216 (2)	0.000	0.00738 (16)	0.000
F1	0.0408 (10)	0.0482 (10)	0.0676 (12)	0.0108 (8)	0.0323 (9)	0.0130 (9)
F2	0.0502 (10)	0.0491 (10)	0.0327 (8)	0.0104 (8)	0.0014 (7)	0.0004 (7)
O1	0.0379 (10)	0.0199 (8)	0.0241 (8)	0.0054 (7)	0.0058 (7)	0.0010 (7)
O2	0.0532 (13)	0.0414 (11)	0.0369 (10)	0.0262 (10)	0.0185 (9)	0.0090 (9)
O3	0.0837 (17)	0.0539 (14)	0.0366 (11)	0.0379 (13)	0.0276 (11)	0.0198 (10)
O4	0.0366 (10)	0.0288 (9)	0.0296 (9)	0.0033 (8)	0.0135 (7)	0.0058 (7)
O5	0.0492 (13)	0.0590 (14)	0.0498 (13)	-0.0107 (11)	0.0090 (10)	-0.0077 (11)
O6	0.0659 (15)	0.0598 (14)	0.0361 (11)	-0.0240 (12)	0.0125 (10)	-0.0009 (10)
N1	0.0260 (14)	0.0129 (12)	0.0245 (13)	0.000	0.0063 (11)	0.000
N2	0.0333 (16)	0.0125 (12)	0.0273 (14)	0.000	0.0145 (12)	0.000
C1	0.0395 (14)	0.0167 (11)	0.0392 (13)	0.0029 (10)	0.0224 (11)	-0.0002 (10)
C2	0.0433 (16)	0.0166 (11)	0.0427 (14)	-0.0001 (10)	0.0260 (12)	0.0033 (10)
C3	0.0317 (18)	0.0126 (14)	0.0307 (17)	0.000	0.0115 (14)	0.000
C4	0.0319 (18)	0.0121 (14)	0.0325 (17)	0.000	0.0130 (14)	0.000
C5	0.0484 (16)	0.0163 (11)	0.0303 (13)	-0.0009 (10)	0.0206 (11)	-0.0027 (9)
C6	0.0429 (15)	0.0178 (11)	0.0282 (12)	0.0002 (10)	0.0194 (11)	0.0016 (9)
C7	0.0338 (14)	0.0386 (15)	0.0323 (13)	0.0102 (12)	0.0140 (11)	0.0063 (11)
C8	0.0484 (17)	0.0291 (13)	0.0312 (13)	0.0147 (12)	0.0101 (12)	0.0082 (11)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Cu1—O1 <sup>i</sup>	1.9760 (17)	N1—C1	1.338 (3)
Cu1—O1	1.9761 (17)	N2—C6	1.344 (3)
Cu1—N1	2.018 (3)	N2—C6 <sup>i</sup>	1.344 (3)
Cu1—N2 <sup>ii</sup>	2.025 (3)	N2—Cu1 <sup>iii</sup>	2.025 (3)
F1—C7	1.360 (3)	C1—C2	1.386 (3)
F2—C7	1.360 (3)	C1—H1	0.9300
O1—H3	0.8180	C2—C3	1.388 (3)
O1—H4	0.8212	C2—H2	0.9300

O2—C8	1.248 (3)	C3—C2 <sup>i</sup>	1.388 (3)
O3—C8	1.232 (3)	C3—C4	1.494 (4)
O4—H7	0.8224	C4—C5	1.390 (3)
O4—H8	0.8241	C4—C5 <sup>i</sup>	1.390 (3)
O5—H9	0.8196	C5—C6	1.382 (3)
O5—H10	0.8200	C5—H5	0.9300
O6—H12	0.8182	C6—H6	0.9300
O6—H11	0.8207	C7—C7 <sup>iv</sup>	1.525 (6)
N1—C1 <sup>i</sup>	1.338 (3)	C7—C8	1.560 (4)
O1 <sup>i</sup> —Cu1—O1	178.11 (10)	C3—C2—H2	120.1
O1 <sup>i</sup> —Cu1—N1	89.06 (5)	C2—C3—C2 <sup>i</sup>	117.2 (3)
O1—Cu1—N1	89.06 (5)	C2—C3—C4	121.38 (15)
O1 <sup>i</sup> —Cu1—N2 <sup>ii</sup>	90.94 (5)	C2 <sup>i</sup> —C3—C4	121.38 (15)
O1—Cu1—N2 <sup>ii</sup>	90.94 (5)	C5—C4—C5 <sup>i</sup>	117.4 (3)
N1—Cu1—N2 <sup>ii</sup>	180.000 (1)	C5—C4—C3	121.31 (15)
Cu1—O1—H3	114.9	C5 <sup>i</sup> —C4—C3	121.30 (15)
Cu1—O1—H4	114.1	C6—C5—C4	119.8 (2)
H3—O1—H4	109.3	C6—C5—H5	120.1
H7—O4—H8	108.2	C4—C5—H5	120.1
H9—O5—H10	109.4	N2—C6—C5	122.6 (2)
H12—O6—H11	109.5	N2—C6—H6	118.7
C1 <sup>i</sup> —N1—C1	117.8 (3)	C5—C6—H6	118.7
C1 <sup>i</sup> —N1—Cu1	121.09 (14)	F1—C7—F2	106.3 (2)
C1—N1—Cu1	121.09 (14)	F1—C7—C7 <sup>iv</sup>	107.5 (3)
C6—N2—C6 <sup>i</sup>	117.8 (3)	F2—C7—C7 <sup>iv</sup>	107.8 (3)
C6—N2—Cu1 <sup>iii</sup>	121.12 (14)	F1—C7—C8	110.5 (2)
C6 <sup>i</sup> —N2—Cu1 <sup>iii</sup>	121.12 (14)	F2—C7—C8	110.9 (2)
N1—C1—C2	122.7 (2)	C7 <sup>iv</sup> —C7—C8	113.5 (3)
N1—C1—H1	118.7	O3—C8—O2	128.4 (3)
C2—C1—H1	118.7	O3—C8—C7	116.5 (2)
C1—C2—C3	119.8 (2)	O2—C8—C7	115.1 (2)
C1—C2—H2	120.1		

Symmetry codes: (i)  $-x+1, y, -z+3/2$ ; (ii)  $x, y+1, z$ ; (iii)  $x, y-1, z$ ; (iv)  $-x+1/2, -y+1/2, -z+1$ .

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H11 $\cdots$ O4 <sup>v</sup>	0.82	2.01	2.826 (3)	172
O6—H12 $\cdots$ O3 <sup>vi</sup>	0.82	2.07	2.879 (3)	168
O5—H10 $\cdots$ O6	0.82	2.02	2.830 (3)	168
O5—H9 $\cdots$ O6 <sup>v</sup>	0.82	2.11	2.871 (3)	155
O4—H8 $\cdots$ O3 <sup>v</sup>	0.82	1.90	2.725 (3)	176
O4—H7 $\cdots$ O2 <sup>vii</sup>	0.82	2.01	2.824 (3)	170
O1—H4 $\cdots$ O2 <sup>v</sup>	0.82	1.81	2.630 (2)	172
O1—H3 $\cdots$ O5	0.82	1.88	2.697 (3)	174

Symmetry codes: (v)  $-x+1/2, -y+3/2, -z+1$ ; (vi)  $-x+1/2, y+1/2, -z+1/2$ ; (vii)  $-x+1/2, y+1/2, -z+3/2$ .