

# catena-Poly[[tetrakis(1*H*-pyrazole- $\kappa$ N<sup>2</sup>)-copper(II)]- $\mu$ -hexafluoridosilicato- $\kappa^2$ F:F']

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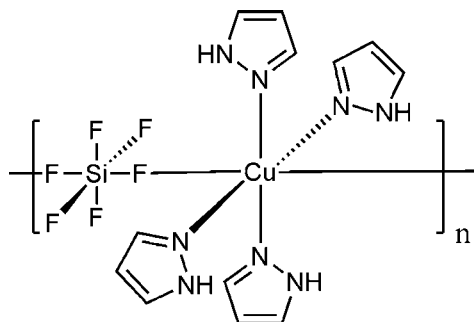
Received 22 February 2012; accepted 4 March 2012

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.007$  Å;  $R$  factor = 0.059;  $wR$  factor = 0.101; data-to-parameter ratio = 12.8.

In the title one-dimensional coordination polymer,  $[\text{Cu}(\text{SiF}_6)(\text{C}_3\text{H}_4\text{N}_2)_4]_n$ , the  $\text{Cu}^{\text{II}}$  atom is coordinated by two hexafluoridosilicate F atoms and four pyrazole N atoms in a distorted *trans*- $\text{CuF}_2\text{N}_4$  octahedral environment. The dihedral angle between the planes of the pyrazole rings in the asymmetric unit is  $74.4(3)^\circ$ . The hexafluoridosilicate dianion acts as a bridging ligand, connecting the  $\text{Cu}^{\text{II}}$  atoms into a  $[1\bar{1}0]$  chain. The Cu and Si atoms lie on special positions with  $2/m$  site symmetry. In the crystal, intrachain  $\text{N}-\text{H}\cdots\text{F}$  hydrogen bonds occur and weak  $\text{C}-\text{H}\cdots\text{F}$  interactions link the chains.

## Related literature

For background to coordination polymers with nitrogen-containing ligands, see: Li *et al.* (2011).



## Experimental

### Crystal data

$[\text{Cu}(\text{SiF}_6)(\text{C}_3\text{H}_4\text{N}_2)_4]$   
 $M_r = 477.96$

Monoclinic,  $C2/c$   
 $a = 10.617(2)$  Å

$b = 12.108(2)$  Å  
 $c = 14.652(3)$  Å  
 $\beta = 95.07(3)^\circ$   
 $V = 1876.2(6)$  Å<sup>3</sup>  
 $Z = 4$

Mo  $K\alpha$  radiation  
 $\mu = 1.30$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.25 \times 0.22 \times 0.20$  mm

### Data collection

Rigaku Mercury CCD diffractometer  
 Absorption correction: multi-scan (*CrystalClear*; Rigaku/MS, 2005)  
 $T_{\text{min}} = 0.730$ ,  $T_{\text{max}} = 0.771$

7864 measured reflections  
 1665 independent reflections  
 1283 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.079$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$   
 $wR(F^2) = 0.101$   
 $S = 1.16$   
 1665 reflections

130 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.44$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.31$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Cu1—N1	2.007 (4)	Si1—F1	1.679 (2)
Cu1—N3	2.008 (3)	Si1—F2	1.680 (3)
Cu1—F3	2.348 (2)	Si1—F3	1.695 (2)

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2A}\cdots\text{F2}^{\text{i}}$	0.86	1.99	2.849 (5)	174
$\text{N4}-\text{H4A}\cdots\text{F1}^{\text{i}}$	0.86	2.02	2.848 (4)	162
$\text{C1}-\text{H1}\cdots\text{F2}^{\text{ii}}$	0.93	2.46	3.317 (6)	153

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

Data collection: *CrystalClear* (Rigaku/MS, 2005); 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: *SHELXTL*.

We thank the young scientist fund of the NSFC of China (51101138) and the College Research Program of Yuncheng University (2008114) for funding.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6651).

## References

- Li, Z. X., Chu, X., Cui, G. H., Liu, Y., Li, L. & Xue, G. L. (2011). *CrystEngComm*, **13**, 1984–1989.  
 Rigaku/MS (2005). *CrystalClear*. Rigaku/MS Inc., The Woodlands, Texas, USA.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

## supporting information

*Acta Cryst.* (2012). E68, m405 [https://doi.org/10.1107/S1600536812009531]

**catena-Poly[[tetrakis(1*H*-pyrazole- $\kappa$ N<sup>2</sup>)copper(II)]- $\mu$ -hexafluorosilicato- $\kappa^2$ F:F']****Hui Li, Qiuping Han, Xiaochuan Chai, Jian Wang and Chenzhong Yao****S1. Comment**

In recent years, nitrogen-containing ligands have been extensively studied (Li *et al.*, 2011). Pyrazole have been well used as a kind of N-containing ligands.

Single-crystal X-ray diffraction analysis reveals that the title compound (I) crystallizes in the monoclinic space group *C2/c*. For the title compound, the geometry of the Cu(II) ion is bound by four pyrazole ligands and two hexafluorosilicate dianions, which illustrates a distorted octahedral coordination environment (Fig 1). The dihedral angle between the pyrazole rings is 105.6°.

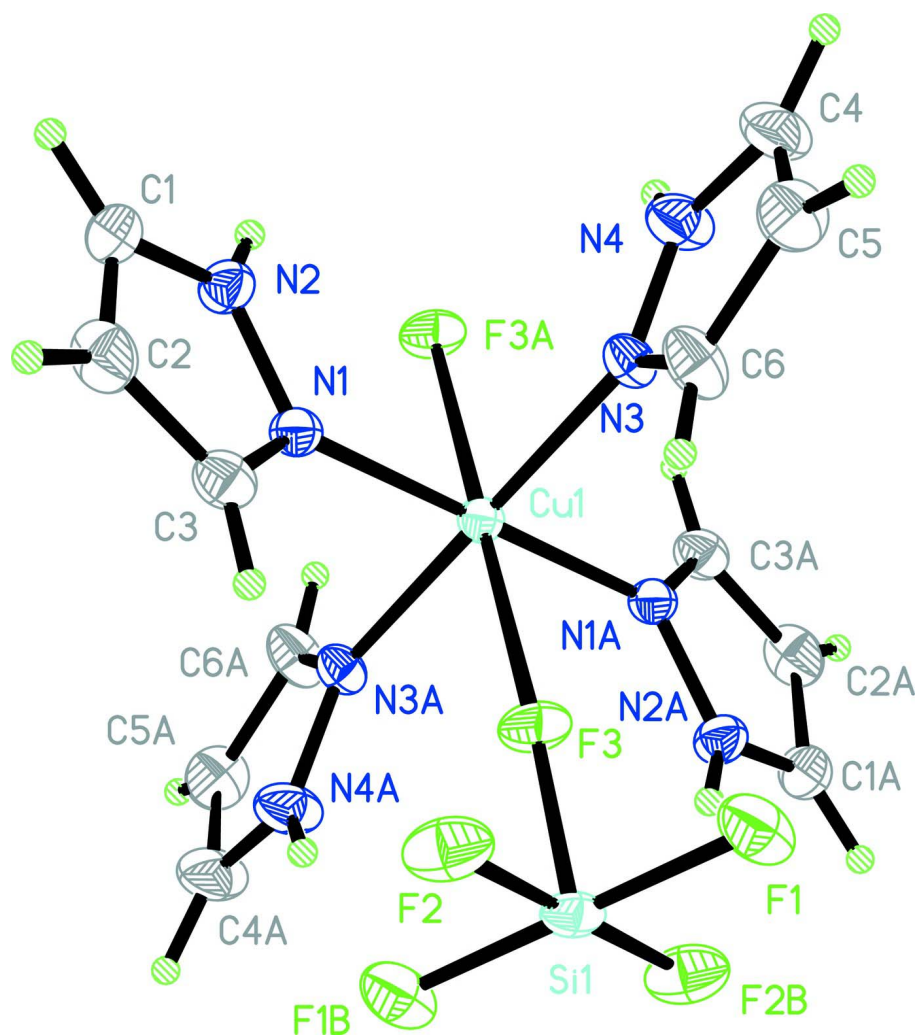
**S2. Experimental**

A buffer layer of a solution (8 ml) of methanol and chloroform (1:1) was carefully layered over the chloroform solution of pyrazole (0.06 mmol, 6 ml). Then a methanol solution of CuSiF<sub>6</sub> (0.02 mmol, 6 ml) was layered over the buffer layer. The resultant reaction was left to stand at room temperature. After *ca* three weeks, colorless blocks appeared at the boundary. Yield: ~20% (based on pyrazole).

**S3. Refinement**

C-bound H atoms were positioned geometrically and refined in the riding-model approximation, with C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

The N-bound H atoms were located in a difference map and their positions were freely refined with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ .



**Figure 1**

The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

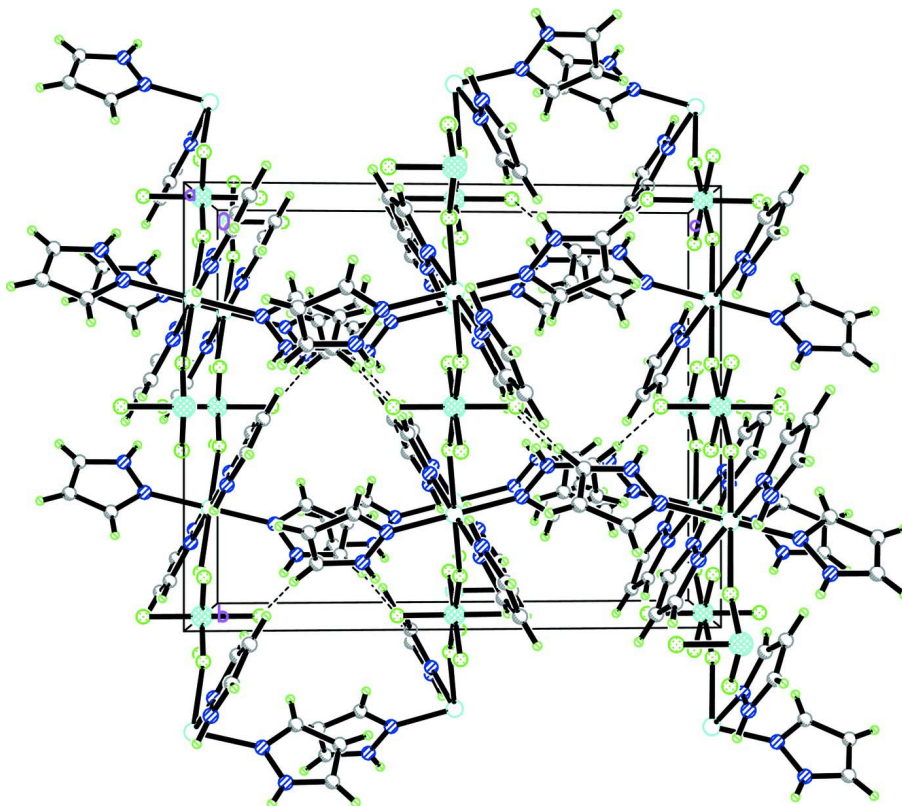


Figure 2

The crystal packing for (I).

*catena*-Poly[[tetrakis(1*H*-pyrazole- $\kappa$ N<sup>2</sup>)copper(II)]- $\mu$ -hexafluorosilicato- $\kappa^2$ F:F']

*Crystal data*

[Cu(SiF<sub>6</sub>)(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)<sub>4</sub>]

$M_r = 477.96$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 10.617$  (2) Å

$b = 12.108$  (2) Å

$c = 14.652$  (3) Å

$\beta = 95.07$  (3)°

$V = 1876.2$  (6) Å<sup>3</sup>

$Z = 4$

$F(000) = 964$

$D_x = 1.692$  Mg m<sup>-3</sup>

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

Cell parameters from 7871 reflections

$\theta = 3.0$ – $27.5$ °

$\mu = 1.30$  mm<sup>-1</sup>

$T = 293$  K

Block, colorless

$0.25 \times 0.22 \times 0.20$  mm

*Data collection*

Rigaku Mercury CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 9 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(*CrystalClear*; Rigaku/MSC, 2005)

$T_{\min} = 0.730$ ,  $T_{\max} = 0.771$

7864 measured reflections

1665 independent reflections

1283 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.079$

$\theta_{\max} = 25.0$ °,  $\theta_{\min} = 3.0$ °

$h = -12 \rightarrow 12$

$k = -14 \rightarrow 14$

$l = -17 \rightarrow 17$

Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.059$   
 $wR(F^2) = 0.101$   
 $S = 1.16$   
 1665 reflections  
 130 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0309P)^2 + 3.0774P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$

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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.2500	0.2500	0.5000	0.0262 (2)
F1	0.3887 (2)	-0.0988 (2)	0.4884 (2)	0.0540 (8)
F2	0.5087 (3)	0.0006 (2)	0.38606 (17)	0.0533 (8)
F3	0.3866 (2)	0.09883 (19)	0.48968 (18)	0.0429 (7)
Si1	0.5000	0.0000	0.5000	0.0313 (4)
N1	0.2744 (3)	0.2900 (3)	0.3698 (2)	0.0304 (9)
N2	0.2000 (3)	0.3633 (3)	0.3217 (3)	0.0362 (9)
H2A	0.1452	0.4044	0.3451	0.043*
N3	0.1011 (3)	0.1589 (3)	0.4510 (2)	0.0309 (9)
N4	-0.0206 (4)	0.1865 (3)	0.4494 (3)	0.0490 (11)
H4A	-0.0480	0.2459	0.4730	0.059*
C1	0.2212 (5)	0.3646 (4)	0.2340 (3)	0.0476 (13)
H1	0.1801	0.4084	0.1885	0.057*
C2	0.3147 (5)	0.2895 (4)	0.2227 (3)	0.0487 (14)
H2	0.3503	0.2723	0.1687	0.058*
C3	0.3449 (4)	0.2448 (4)	0.3085 (3)	0.0389 (11)
H3	0.4059	0.1907	0.3219	0.047*
C4	-0.0944 (5)	0.1099 (4)	0.4063 (4)	0.0611 (17)
H4	-0.1822	0.1118	0.3971	0.073*
C5	-0.0190 (5)	0.0291 (4)	0.3785 (3)	0.0522 (15)
H5	-0.0430	-0.0351	0.3467	0.063*
C6	0.1020 (4)	0.0633 (4)	0.4078 (3)	0.0446 (13)
H6	0.1749	0.0238	0.3984	0.054*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0254 (4)	0.0244 (4)	0.0285 (4)	0.0000 (4)	0.0012 (3)	-0.0008 (4)
F1	0.0361 (15)	0.0378 (16)	0.088 (2)	-0.0014 (13)	0.0064 (15)	-0.0160 (15)
F2	0.0553 (17)	0.0645 (19)	0.0392 (17)	0.0229 (16)	-0.0006 (14)	-0.0063 (15)
F3	0.0389 (15)	0.0348 (15)	0.0540 (18)	0.0193 (12)	-0.0006 (13)	-0.0025 (13)
Si1	0.0268 (9)	0.0263 (9)	0.0397 (11)	0.0087 (8)	-0.0032 (8)	-0.0072 (8)
N1	0.028 (2)	0.028 (2)	0.035 (2)	0.0005 (16)	-0.0005 (18)	0.0004 (17)
N2	0.035 (2)	0.038 (2)	0.036 (2)	0.0079 (18)	0.0058 (19)	0.0050 (19)
N3	0.026 (2)	0.028 (2)	0.039 (2)	-0.0013 (16)	0.0062 (17)	-0.0066 (17)
N4	0.034 (2)	0.031 (2)	0.080 (3)	0.0045 (19)	-0.005 (2)	-0.005 (2)
C1	0.042 (3)	0.064 (4)	0.036 (3)	-0.005 (3)	0.001 (2)	0.015 (3)
C2	0.047 (3)	0.069 (4)	0.032 (3)	-0.006 (3)	0.012 (2)	-0.007 (3)
C3	0.032 (2)	0.040 (3)	0.045 (3)	0.003 (2)	0.006 (2)	-0.004 (3)
C4	0.039 (3)	0.042 (3)	0.097 (5)	-0.009 (3)	-0.021 (3)	0.002 (3)
C5	0.062 (4)	0.041 (3)	0.052 (3)	-0.012 (3)	-0.009 (3)	-0.011 (3)
C6	0.038 (3)	0.041 (3)	0.057 (3)	-0.009 (2)	0.013 (3)	-0.018 (3)

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

Cu1—N1 <sup>i</sup>	2.007 (4)	N2—H2A	0.8600
Cu1—N1	2.007 (4)	N3—C6	1.320 (5)
Cu1—N3 <sup>i</sup>	2.008 (3)	N3—N4	1.332 (5)
Cu1—N3	2.008 (3)	N4—C4	1.337 (6)
Cu1—F3 <sup>i</sup>	2.348 (2)	N4—H4A	0.8600
Cu1—F3	2.348 (2)	C1—C2	1.366 (6)
Si1—F1	1.679 (2)	C1—H1	0.9300
Si1—F2	1.680 (3)	C2—C3	1.381 (6)
Si1—F3	1.695 (2)	C2—H2	0.9300
Si1—F1 <sup>ii</sup>	1.679 (2)	C3—H3	0.9300
Si1—F2 <sup>ii</sup>	1.680 (3)	C4—C5	1.350 (7)
Si1—F3 <sup>ii</sup>	1.695 (2)	C4—H4	0.9300
N1—C3	1.336 (5)	C5—C6	1.381 (6)
N1—N2	1.345 (5)	C5—H5	0.9300
N2—C1	1.324 (6)	C6—H6	0.9300
N1 <sup>i</sup> —Cu1—N1	180.0	C3—N1—N2	104.9 (4)
N1 <sup>i</sup> —Cu1—N3 <sup>i</sup>	87.50 (14)	C3—N1—Cu1	131.8 (3)
N1—Cu1—N3 <sup>i</sup>	92.50 (14)	N2—N1—Cu1	122.6 (3)
N1 <sup>i</sup> —Cu1—N3	92.50 (14)	C1—N2—N1	111.9 (4)
N1—Cu1—N3	87.50 (14)	C1—N2—H2A	124.0
N3 <sup>i</sup> —Cu1—N3	180.00 (16)	N1—N2—H2A	124.0
N1 <sup>i</sup> —Cu1—F3 <sup>i</sup>	89.70 (12)	C6—N3—N4	105.1 (4)
N1—Cu1—F3 <sup>i</sup>	90.30 (12)	C6—N3—Cu1	127.9 (3)
N3 <sup>i</sup> —Cu1—F3 <sup>i</sup>	91.15 (11)	N4—N3—Cu1	126.9 (3)
N3—Cu1—F3 <sup>i</sup>	88.85 (11)	N3—N4—C4	111.2 (4)
N1 <sup>i</sup> —Cu1—F3	90.30 (12)	N3—N4—H4A	124.4

N1—Cu1—F3	89.70 (12)	C4—N4—H4A	124.4
N3 <sup>i</sup> —Cu1—F3	88.85 (11)	N2—C1—C2	107.3 (4)
N3—Cu1—F3	91.15 (11)	N2—C1—H1	126.3
F3 <sup>i</sup> —Cu1—F3	180.0	C2—C1—H1	126.3
Si1—F3—Cu1	169.24 (15)	C1—C2—C3	105.2 (4)
F1 <sup>ii</sup> —Si1—F1	180.00 (17)	C1—C2—H2	127.4
F1 <sup>ii</sup> —Si1—F2 <sup>ii</sup>	90.16 (15)	C3—C2—H2	127.4
F1—Si1—F2 <sup>ii</sup>	89.84 (15)	N1—C3—C2	110.6 (4)
F1 <sup>ii</sup> —Si1—F2	89.84 (15)	N1—C3—H3	124.7
F1—Si1—F2	90.16 (15)	C2—C3—H3	124.7
F2 <sup>ii</sup> —Si1—F2	180.000 (1)	N4—C4—C5	107.8 (5)
F1 <sup>ii</sup> —Si1—F3	89.69 (12)	N4—C4—H4	126.1
F1—Si1—F3	90.31 (12)	C5—C4—H4	126.1
F2 <sup>ii</sup> —Si1—F3	89.49 (13)	C4—C5—C6	104.5 (4)
F2—Si1—F3	90.51 (13)	C4—C5—H5	127.8
F1 <sup>ii</sup> —Si1—F3 <sup>ii</sup>	90.31 (12)	C6—C5—H5	127.8
F1—Si1—F3 <sup>ii</sup>	89.69 (12)	N3—C6—C5	111.4 (4)
F2 <sup>ii</sup> —Si1—F3 <sup>ii</sup>	90.51 (13)	N3—C6—H6	124.3
F2—Si1—F3 <sup>ii</sup>	89.49 (13)	C5—C6—H6	124.3
F3—Si1—F3 <sup>ii</sup>	180.0		
N1 <sup>i</sup> —Cu1—F3—Si1	-53.9 (8)	N1—Cu1—N3—C6	73.5 (4)
N1—Cu1—F3—Si1	126.1 (8)	F3 <sup>i</sup> —Cu1—N3—C6	163.9 (4)
N3 <sup>i</sup> —Cu1—F3—Si1	33.6 (8)	F3—Cu1—N3—C6	-16.1 (4)
N3—Cu1—F3—Si1	-146.4 (8)	N1 <sup>i</sup> —Cu1—N3—N4	78.8 (4)
Cu1—F3—Si1—F1 <sup>ii</sup>	-48.7 (8)	N1—Cu1—N3—N4	-101.2 (4)
Cu1—F3—Si1—F1	131.3 (8)	F3 <sup>i</sup> —Cu1—N3—N4	-10.9 (4)
Cu1—F3—Si1—F2 <sup>ii</sup>	41.4 (8)	F3—Cu1—N3—N4	169.1 (4)
Cu1—F3—Si1—F2	-138.6 (8)	C6—N3—N4—C4	0.0 (5)
N3 <sup>i</sup> —Cu1—N1—C3	87.4 (4)	Cu1—N3—N4—C4	175.7 (3)
N3—Cu1—N1—C3	-92.6 (4)	N1—N2—C1—C2	-0.5 (5)
F3 <sup>i</sup> —Cu1—N1—C3	178.5 (4)	N2—C1—C2—C3	0.5 (6)
F3—Cu1—N1—C3	-1.5 (4)	N2—N1—C3—C2	0.0 (5)
N3 <sup>i</sup> —Cu1—N1—N2	-104.4 (3)	Cu1—N1—C3—C2	169.7 (3)
N3—Cu1—N1—N2	75.6 (3)	C1—C2—C3—N1	-0.3 (6)
F3 <sup>i</sup> —Cu1—N1—N2	-13.2 (3)	N3—N4—C4—C5	0.0 (6)
F3—Cu1—N1—N2	166.8 (3)	N4—C4—C5—C6	0.0 (6)
C3—N1—N2—C1	0.3 (5)	N4—N3—C6—C5	0.0 (5)
Cu1—N1—N2—C1	-170.6 (3)	Cu1—N3—C6—C5	-175.7 (3)
N1 <sup>i</sup> —Cu1—N3—C6	-106.5 (4)	C4—C5—C6—N3	0.0 (6)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A $\cdots$ F2 <sup>iii</sup>	0.86	1.99	2.849 (5)	174

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N4—H4A···F1 <sup>iii</sup>	0.86	2.02	2.848 (4)	162
C1—H1···F2 <sup>iv</sup>	0.93	2.46	3.317 (6)	153

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