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Crystal structure and Hirshfeld surface analysis of 2,2′-{(1*E*,1′*E*)-[ethane-1,2-diylbis(azanylylidene)]-bis(methanylylidene)}bis[4-(trifluoromethoxy)-phenol]copper(II) hydroquinone hemisolvate

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In the title complex, $[Cu(C_{18}H_{12}F_6N_2O_4)]\cdot 0.5C_6H_6O_2$, the Cu^{II} ion has a square-planar coordination geometry, being ligated by two N and two O atoms of the tetradentate open-chain Schiff base ligand 6,6′-{(1*E*,1′*E*)-[ethane-1,2-diyl-bis(azanylylidene)]bis(methanylylidene)}bis[2-(trifluoromethoxy)phenol]. The crystal packing is stabilized by intramolecular O—H···O and intermolecular C—H···F, C—H···O and C—H···π hydrogen bonds. In addition, weak π–π interactions form a three-dimensional structure. Hirshfeld surface analysis and two-dimensional fingerprint plots were performed and created to analyze the intermolecular interactions present in the crystal, indicating that the most important contributions for the crystal packing are from F···H/H···F (25.7%), H···H (23.5%) and C···H/H···C (12.6%) interactions.

1. Chemical context

Metal complexes of Schiff bases have different applications because of their different heteroatoms (N, S, Cl *etc.*), functional groups, π-electron density, isomer structures and easy synthesis (El-Samanody *et al.*, 2017). Metal complexes with less oxophilic character exhibit attractive properties, such as targeting catalysts in many polymerization reactions (Ng *et al.*, 2016). On the other hand, in nature, metal complexes are encountered in many reactions, such as binding to DNA or enzymes (Li *et al.*, 2010). For this reason, metal complexes are of increasing interest in the fields of medicine and chemical synthesis with attractive functional properties and stable structures. Salen-type Schiff bases [salen is *N*,*N*′-bis(salicylidene)ethylenediamine] have been synthesized by many research groups from different diamines and derivatives of benzaldehyde (Prushan *et al.*, 2007). In addition, salen-type Schiff bases derived from 2-hydroxy-3-methoxybenzaldehyde (also called *o*-vanillin) are very effective ligands for many metal ions due to the two different binding sites, because of the presence of the methoxy group near the –OH group (Andruh, 2015). Each transition metal has different biological properties depending on the geometry of the complex and the structure of the ligand, so the biological activity of a drug may be controlled by changing the metal ion or the chemical structure of the ligand. Recently, it was reported that synthesized Schiff bases indicate antibacterial properties,

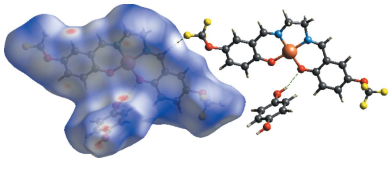


Table 1
Selected geometric parameters (Å, °).

Cu1—O2	1.883 (4)	N3—C10	1.455 (8)
Cu1—O3	1.906 (4)	N2—C8	1.275 (8)
Cu1—N2	1.927 (5)	O4—C18	1.269 (12)
Cu1—N3	1.929 (5)	O1—C1	1.267 (9)
O2—C5	1.309 (7)	F2—C1	1.271 (9)
O3—C17	1.317 (7)	F4—C18	1.265 (11)
O2—Cu1—O3	87.54 (17)	O2—Cu1—N3	177.82 (18)
O2—Cu1—N2	94.40 (18)	O3—Cu1—N3	93.9 (2)
O3—Cu1—N2	176.2 (2)	N2—Cu1—N3	84.3 (2)

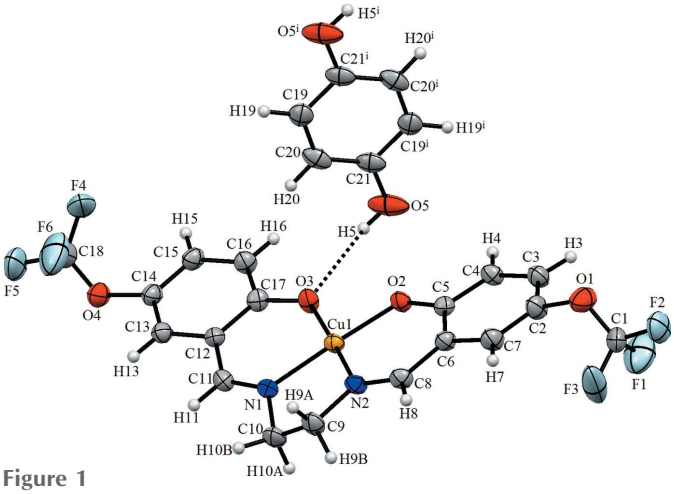


Figure 1
The molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level. The dashed line indicates a hydrogen bond. [Symmetry code: (i) $-x$, $-y$, $-z+1$.]

more pronounced in the case of metal complexes compared to the free Schiff bases (Wu *et al.*, 2011).

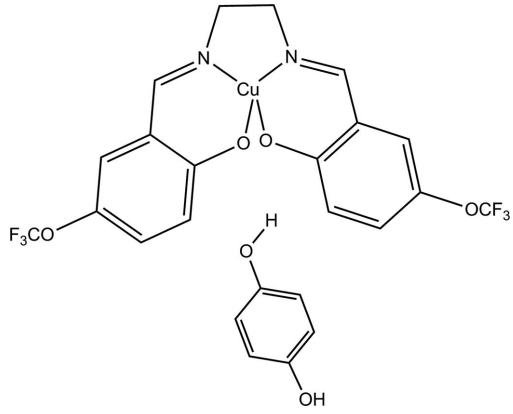
In this study, a salen-type Schiff base has been synthesized from 2-hydroxy-5-(trifluoromethoxy)benzaldehyde with ethylenediamine by a condensation reaction. The synthesized Schiff base was used as an *O*,*N*,*N*′,*O*′-type tetradentate ligand, and a copper(II) complex was obtained and the structure confirmed by single-crystal X-ray diffraction analysis. In this study, we describe the crystal structure and Hirshfeld surface analysis of the title compound, as determined by X-ray crystallographic analysis.

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

*Cg*1 is the centroid of the C19–C21/C19^{i}–C21^{i} ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···O3	0.82	2.20	2.993 (8)	165
C11—H11···F2^{i}	0.93	2.63	3.513 (8)	159
C10—H10*A*···O5^{ii}	0.97	2.53	3.469 (11)	162
C15—H15···O5^{iii}	0.93	2.55	3.345 (9)	144
C8—H8···*Cg*1^{iv}	0.93	2.82	3.740 (8)	173

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



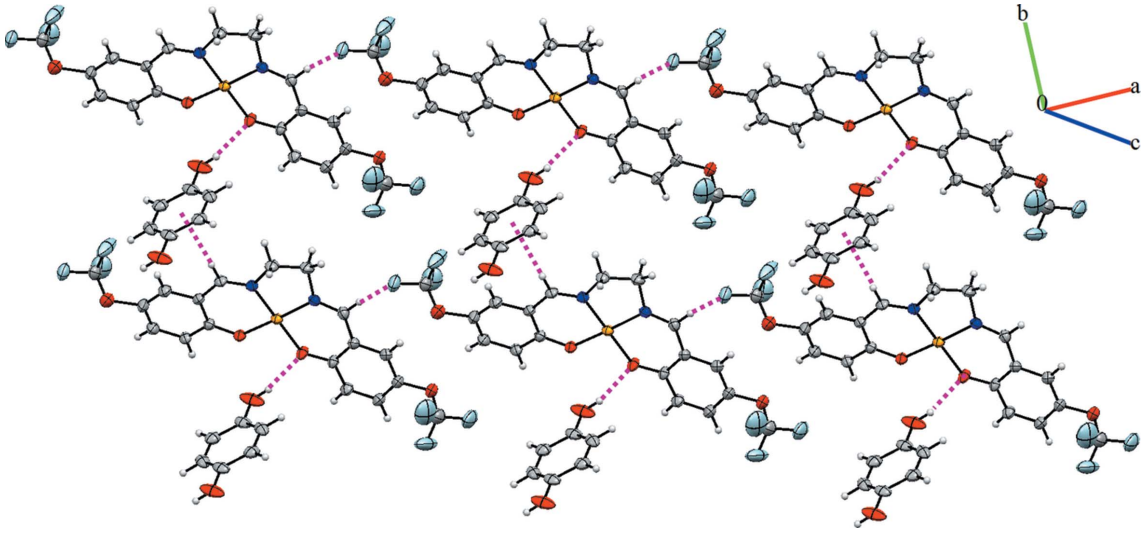


Figure 2
A view of the crystal packing of the title compound. Dashed lines denote intermolecular O—H···O, C—H···F and C—H···π hydrogen bonds.

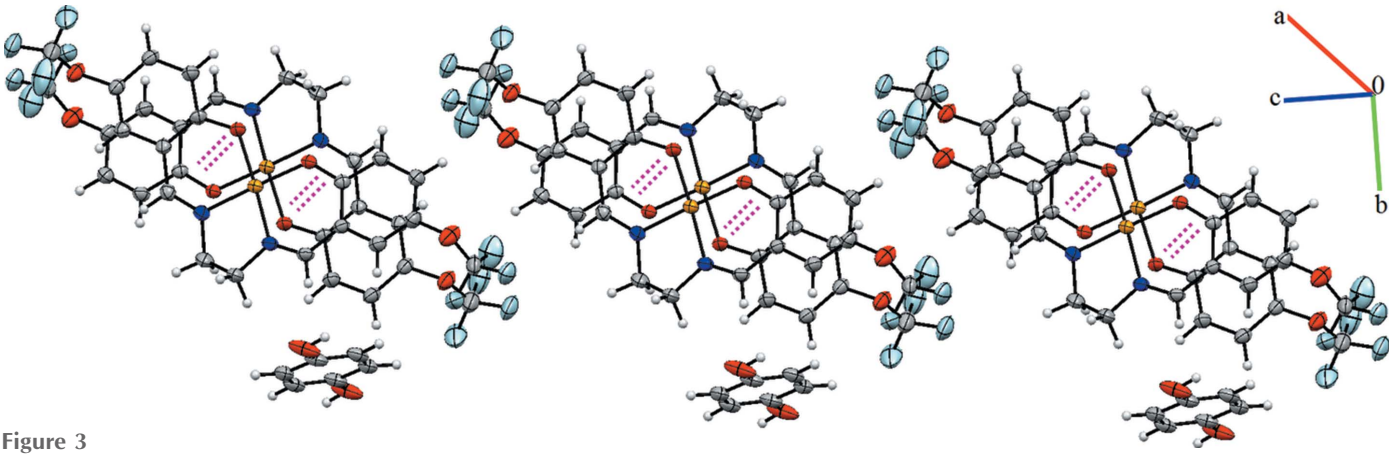


Figure 3
A view of the crystal packing of the title compound. The π–π interactions are shown as pink dashed lines. **[The direction of the unitcell parameters is missing. It might be better to show the unitcell outline]**

2. Structural commentary

Fig. 1 illustrates the title metal complex formed by a Cu^{II} ion chelated by a doubly deprotonated tetradentate Schiff base ligand and a hydrogen-bonded molecule of hydroquinone. The Cu1 ion is coordinated by two imine N atoms (N6 and N7) and two phenoxo O atoms (O2 and O3) of the tetradentate Schiff base ligand 6,6′-{(1*E*,1′*E*)-[ethane-1,2-diylbis(azanylylidene)]-bis(methanylylidene)}bis[2-(trifluoromethoxy)phenol] (**L1**). The hydroquinone molecule is located on an inversion centre and is linked to neighbouring complex cations *via* O—H···O hydrogen bonds. The bond lengths Cu1—O2 and Cu1—O3 [1.883 (4) and 1.906 (4) Å, respectively] and Cu1—N1 and Cu1—N2 [1.929 (5) and 1.927 (5) Å, respectively] are close to the values observed for related copper(II) complexes reported in the literature (Şen *et al.*, 2017; Fritsky *et al.*, 2004; Strotmeyer *et al.*, 2003). Selected geometric parameters of the title compound are listed in Table 1.

3. Supramolecular features

The crystal packing of the title compound is stabilized by intermolecular C—H···O, C—H···F and C—H···*Cg*1 (*Cg*1 is the centroid of the C19–C21/C19^{i}–C21^{i} ring) hydrogen bonds (Table 2 and Fig. 2). In addition, weak π–π interactions connect the molecules into a three-dimensional supramolecular architecture (Fig. 3). The *Cg*2···*Cg*3 distance is 3.507 (2) Å, where *Cg*2 and *Cg*3 are the centroids of the Cu1/O2/C5/C6/C8/N2 and Cu1/O3/C17/C12/C11/N1 rings, respectively.

4. Hirshfeld surface analysis

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots were performed and created with *CrystalExplorer17* (Turner *et al.*, 2017). The Hirshfeld surface was mapped with d_{norm} (Fig. 4). The view of surface were obtained in the range −0.4385 to 1.6105 a.u. (d_{norm}). The blue, white and red colour conventions used for the d_{norm}-mapped Hirshfeld surfaces recognize the interatomic contacts as longer, at van der Waals separations and short interatomic contacts, respectively.

A fingerprint plot delineated into specific interatomic contacts contains information related to specific intermolecular interactions. The blue colour refers to the frequency

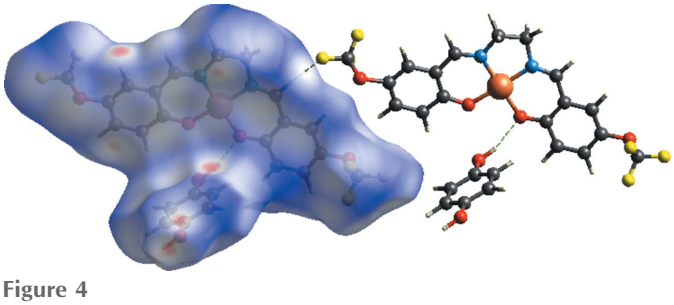


Figure 4
The d_{norm}-mapped Hirshfeld surface for visualizing the intermolecular contacts of the title compound.

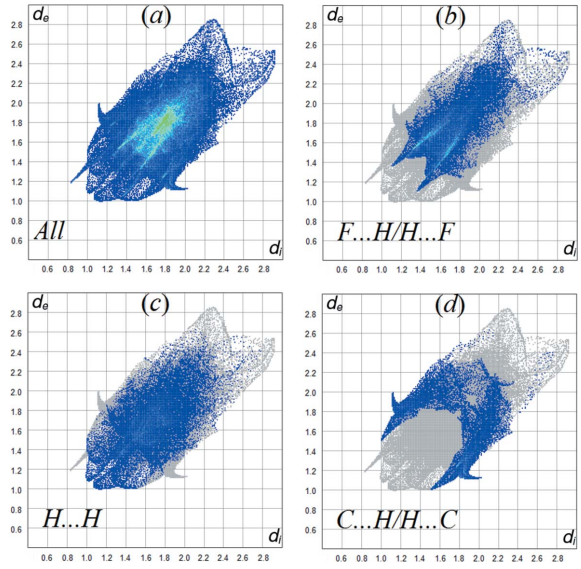


Figure 5
Two-dimensional fingerprint plots of the title compound.

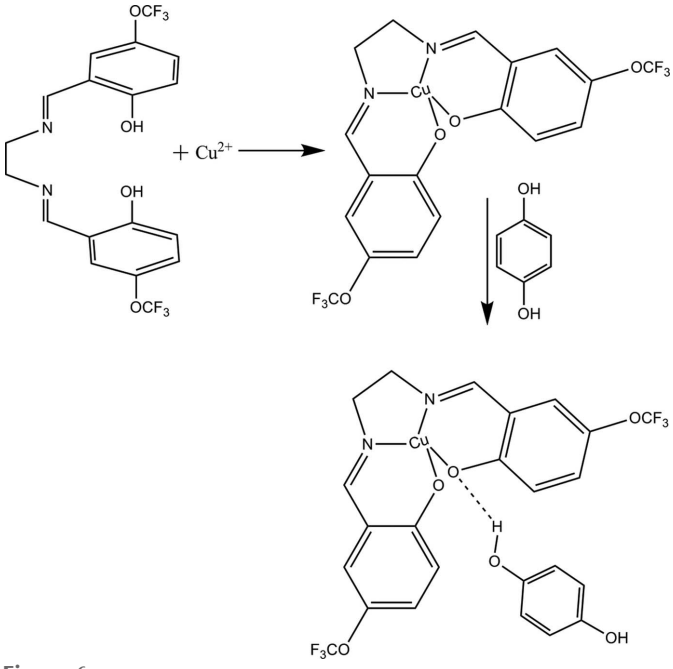


Figure 6
The synthesis of the title compound.

of occurrence of the (d_i, d_e) pair with the full fingerprint plot outlined in gray. Fig. 5(*a*) shows the two-dimensional fingerprint plot of the sum of the contacts contributing to the Hirshfeld surface represented in normal mode. The most significant contribution to the Hirshfeld surface is from F···H/H···F contacts (25.7%) (Fig. 5*b*). Here, H···H interactions are only the second most significant contribution to the total Hirshfeld surface (23.5%). In addition, C···H/H···C and O···H/H···O contacts contribute 12.6 and 11.2% to the Hirshfeld surface, respectively.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_{18}H_{12}F_6N_2O_4)]\cdot0.5C_6H_6O_2$
M_r	552.89
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	9.3167 (10), 10.0363 (10), 11.8052 (13)
α, β, γ (°)	92.633 (9), 97.310 (9), 98.670 (9)
V (Å^3)	1080.0 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.10
Crystal size (mm)	0.57 × 0.25 × 0.06
Data collection	
Diffractometer	Stoe *IPDS* 2
Absorption correction	Integration (*X-RED32*; Stoe & Cie, 2002)
T_{min}, T_{max}	0.695, 0.944
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9277, 4105, 2818
R_{int}	0.105
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.067, 0.217, 1.08
No. of reflections	4105
No. of parameters	317
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.88, −0.43

Computer programs: *X-AREA* (Stoe & Cie, 2002), *X-RED* (Stoe & Cie, 2002), *SHELXT2017* (Sheldrick, 2015*a*), *SHELXL2017* (Sheldrick, 2015*b*), *PLATON* (Spek, 2009) and *WinGX* (Farrugia, 2012).

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40, update of February 2019; Groom *et al.*, 2016) related to the title complex revealed six hits. These structures are Cu(5-hexyloxySalen)·$CHCl_3$ (FAGLOP; Paschke *et al.*, 2002), $C_{30}H_{54}Cu_2F_{12}N_{10}O_2P_2$ (ICUHEU; Margraf *et al.*, 2006), $C_{38}H_{44}Cu_2N_4O_{10}$ (PIFKOE01; Liu, 2016), $C_{36}H_{36}Cu_2N_4O_8\cdot2CH_4O$ (PIFKOE02; Zhang, 2016), $C_{18}H_{18}CuN_2O_4\cdot1.5H_2O$ (QARPAB; Yao *et al.*, 2005) and $C_{18}H_{18}CuN_2O_4$ (XOZZUH; Atria *et al.*, 2002). All of these structures have square-planar environments, as in the title copper(II) complex. The Cu—O and Cu—N bond lengths range from *ca* 1.898 to 1.915 Å and from *ca* 1.936 to 2.271 Å, respectively. In the title complex, the Cu—N bond lengths [1.927 (5) and 1.929 (5) Å] fall within these limits. While the Cu1—O3 and C1—O2 bond length [1.906 (4) and 1.883 (4) Å, respectively] are within and close to these limits, respectively, the Cu1—O2 bond length is outside these limits, with a shorter value of 1.883 (4) Å.

6. Synthesis and crystallization

2,2′-{(1*E*,1′*E*)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)}bis[4-(trifluoromethoxy)phenol] (H_2**L1**) was synthesized by condensation of 2-hydroxy-5-(trifluoromethoxy)-benzaldehyde (0.0095 mmol) and 1,2-ethanediamine (0.0095 mmol) in ethanol under reflux for about 18 h. The yellow product was washed with ether and dried at room temperature. 0.0080 mmol H_2**L1** was dissolved in 20 ml ethanol and 0.0080 mmol $Cu(CH_3COO)_2\cdot H_2O$ was dissolved in 20 ml ethanol. The metal solution was added dropwise to the Schiff base solution and the resulting solution refluxed for about 6 h. The product (Cu**L1**) was washed with toluene and crystallized from ethanol at room temperature. 2,2′-{(1*E*,1′*E*)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)}bis-[4-(trifluoromethoxy)phenol]copper(II) hydroquinone hemisolvate was obtained even after 0.0040 mmol hydroquinone was added to 0.0040 mmol Cu**L1** in 20 ml ethanol and refluxed for about 6 h. A purple crystal suitable for X-ray diffraction analysis was obtained from the reaction (m.p. 568 K; yield 80%) (Fig. 6).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were fixed geometrically and treated as riding, with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C) for methylene, C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic, C—H = 0.93 Å and U_{iso}(H) =

1.2U_{eq}(C) for methine, and O—H = 0.82 Å and U_{iso}(H) = 1.5U_{eq}(O) for hydroxy H atoms.

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supporting information

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: SHELXT2017 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015b); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

2,2′-{(1*E*,1′*E*)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)}bis[4-(trifluoromethoxy)phenol]copper(II) hydroquinone hemisolvate

Crystal data

$[Cu(C_{18}H_{12}F_6N_2O_4)]\cdot 0.5C_6H_6O_2$
$M_r = 552.89$
Triclinic, $P\overline{1}$
$a = 9.3167$ (10) Å
$b = 10.0363$ (10) Å
$c = 11.8052$ (13) Å
$\alpha = 92.633$ (9)°
$\beta = 97.310$ (9)°
$\gamma = 98.670$ (9)°
$V = 1080.0$ (2) Å^3
$Z = 2$
$F(000) = 556$
$D_x = 1.700$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9488 reflections
$\theta = 2.1$–$31.6°$
$\mu = 1.10$ mm^{-1}
$T = 296$ K
Stick, orange
0.57 × 0.25 × 0.06 mm

Data collection

Stoe IPDS 2 diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration (X-RED32; Stoe & Cie, 2002)
$T_{min} = 0.695$, $T_{max} = 0.944$
9277 measured reflections
4105 independent reflections
2818 reflections with $I > 2\sigma(I)$
$R_{int} = 0.105$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.1°$
$h = -11\rightarrow11$
$k = -11\rightarrow12$
$l = -14\rightarrow14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.217$
$S = 1.08$
4105 reflections
317 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1271P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ 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}
Cu1	0.34081 (8)	0.48948 (6)	0.55458 (5)	0.0543 (3)
O2	0.2235 (5)	0.4083 (4)	0.4202 (3)	0.0623 (10)
O3	0.4268 (5)	0.3290 (4)	0.5642 (3)	0.0725 (12)
N3	0.4629 (6)	0.5787 (5)	0.6891 (4)	0.0615 (12)
N2	0.2498 (5)	0.6496 (4)	0.5547 (4)	0.0599 (11)
O4	0.8058 (6)	0.1792 (5)	0.9159 (5)	0.0941 (16)
O1	−0.2353 (6)	0.5831 (6)	0.1519 (6)	0.1072 (19)
F2	−0.3405 (7)	0.6958 (6)	0.0275 (5)	0.1250 (19)
C5	0.1234 (6)	0.4598 (5)	0.3559 (5)	0.0562 (12)
C17	0.5157 (6)	0.2963 (6)	0.6508 (5)	0.0594 (13)
C12	0.5756 (7)	0.3861 (6)	0.7474 (5)	0.0607 (14)
C13	0.6693 (7)	0.3408 (6)	0.8348 (5)	0.0656 (14)
H13	0.708436	0.398326	0.898891	0.079*
C11	0.5502 (7)	0.5230 (6)	0.7574 (5)	0.0652 (15)
H11	0.602434	0.576870	0.819803	0.078*
C4	0.0563 (7)	0.3889 (6)	0.2529 (5)	0.0640 (14)
H4	0.086152	0.308254	0.231398	0.077*
O5	0.2281 (8)	0.1271 (6)	0.3981 (7)	0.133 (3)
H5	0.291517	0.170047	0.446142	0.199*
C6	0.0774 (7)	0.5844 (5)	0.3848 (5)	0.0600 (13)
C8	0.1441 (7)	0.6725 (6)	0.4822 (5)	0.0637 (14)
H8	0.107514	0.752591	0.493445	0.076*
C14	0.7035 (7)	0.2153 (6)	0.8275 (6)	0.0701 (16)
C20	0.1237 (8)	0.0623 (7)	0.5681 (7)	0.083 (2)
H20	0.206608	0.107143	0.614594	0.099*
F5	0.8619 (9)	0.0840 (7)	1.0705 (6)	0.165 (3)
C2	−0.1012 (8)	0.5510 (7)	0.2184 (6)	0.0809 (19)
C16	0.5574 (8)	0.1686 (6)	0.6466 (6)	0.0716 (16)
H16	0.521840	0.109651	0.582720	0.086*
C1	−0.2238 (10)	0.6854 (8)	0.0927 (6)	0.089 (2)
F4	0.6940 (12)	−0.0204 (7)	0.9451 (6)	0.213 (5)
C9	0.3081 (9)	0.7467 (6)	0.6522 (6)	0.0793 (19)
H9A	0.243130	0.737135	0.710360	0.095*
H9B	0.313865	0.838005	0.627497	0.095*

C3	−0.0517 (8)	0.4351 (7)	0.1834 (6)	0.0784 (19)
H3	−0.091257	0.389063	0.113585	0.094*
F3	−0.1763 (13)	0.7969 (6)	0.1498 (6)	0.220 (5)
C19	0.0109 (9)	−0.0032 (6)	0.6171 (6)	0.084 (2)
H19	0.019589	−0.007714	0.696149	0.101*
C7	−0.0395 (8)	0.6257 (7)	0.3149 (6)	0.0793 (19)
H7	−0.074097	0.704473	0.335183	0.095*
C10	0.4551 (9)	0.7224 (6)	0.7003 (6)	0.086 (2)
H10A	0.528371	0.772004	0.660172	0.104*
H10B	0.475229	0.754184	0.780449	0.104*
F1	−0.1335 (8)	0.6744 (10)	0.0196 (7)	0.179 (3)
C21	0.1175 (9)	0.0633 (6)	0.4511 (7)	0.085 (2)
C15	0.6497 (7)	0.1268 (7)	0.7341 (6)	0.0730 (16)
H15	0.675021	0.040716	0.729992	0.088*
F6	0.6605 (12)	0.1453 (14)	1.0406 (8)	0.215 (5)
C18	0.7608 (15)	0.0945 (11)	0.9851 (10)	0.122 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0612 (5)	0.0452 (4)	0.0562 (4)	0.0114 (3)	0.0058 (3)	−0.0023 (2)
O2	0.073 (3)	0.0482 (19)	0.064 (2)	0.0178 (17)	−0.0043 (18)	−0.0075 (16)
O3	0.094 (3)	0.059 (2)	0.064 (2)	0.037 (2)	−0.012 (2)	−0.0105 (18)
N3	0.068 (3)	0.052 (2)	0.060 (3)	0.002 (2)	0.003 (2)	−0.0008 (19)
N2	0.062 (3)	0.046 (2)	0.071 (3)	0.012 (2)	0.004 (2)	−0.006 (2)
O4	0.088 (3)	0.082 (3)	0.106 (4)	0.015 (3)	−0.022 (3)	0.029 (3)
O1	0.091 (4)	0.096 (4)	0.132 (5)	0.013 (3)	−0.005 (3)	0.038 (4)
F2	0.130 (4)	0.118 (4)	0.120 (4)	0.043 (3)	−0.042 (3)	0.018 (3)
C5	0.054 (3)	0.054 (3)	0.062 (3)	0.011 (2)	0.009 (2)	0.004 (2)
C17	0.054 (3)	0.062 (3)	0.068 (3)	0.026 (3)	0.010 (3)	0.003 (3)
C12	0.065 (4)	0.054 (3)	0.060 (3)	0.003 (3)	0.002 (3)	0.007 (2)
C13	0.065 (4)	0.059 (3)	0.071 (3)	0.008 (3)	0.003 (3)	0.006 (3)
C11	0.061 (3)	0.068 (4)	0.062 (3)	0.006 (3)	0.000 (3)	−0.003 (3)
C4	0.061 (3)	0.056 (3)	0.074 (3)	0.018 (3)	0.002 (3)	−0.008 (3)
O5	0.146 (6)	0.068 (3)	0.188 (7)	−0.016 (3)	0.094 (6)	−0.049 (4)
C6	0.062 (3)	0.049 (3)	0.070 (3)	0.016 (2)	0.002 (3)	0.005 (2)
C8	0.069 (4)	0.048 (3)	0.076 (4)	0.021 (3)	0.008 (3)	−0.004 (2)
C14	0.067 (4)	0.063 (3)	0.078 (4)	0.012 (3)	−0.004 (3)	0.018 (3)
C20	0.070 (4)	0.057 (4)	0.119 (6)	0.017 (3)	0.004 (4)	−0.029 (4)
F5	0.219 (7)	0.133 (5)	0.126 (4)	0.032 (5)	−0.067 (5)	0.044 (4)
C2	0.081 (5)	0.068 (4)	0.090 (4)	0.025 (3)	−0.018 (4)	0.007 (3)
C16	0.078 (4)	0.061 (3)	0.077 (4)	0.025 (3)	0.000 (3)	−0.003 (3)
C1	0.105 (6)	0.093 (5)	0.060 (4)	0.004 (4)	−0.007 (4)	0.014 (4)
F4	0.351 (12)	0.082 (4)	0.151 (6)	−0.054 (5)	−0.078 (7)	0.038 (4)
C9	0.102 (5)	0.054 (3)	0.077 (4)	0.020 (3)	−0.008 (4)	−0.013 (3)
C3	0.090 (5)	0.063 (4)	0.075 (4)	0.011 (3)	−0.010 (3)	−0.005 (3)
F3	0.390 (13)	0.087 (4)	0.149 (5)	0.083 (6)	−0.138 (7)	−0.026 (4)
C19	0.117 (6)	0.055 (3)	0.081 (4)	0.022 (4)	0.009 (4)	−0.008 (3)

C7	0.088 (5)	0.059 (3)	0.090 (4)	0.023 (3)	−0.006 (4)	0.001 (3)
C10	0.112 (6)	0.051 (3)	0.085 (4)	0.002 (3)	−0.012 (4)	−0.008 (3)
F1	0.151 (6)	0.259 (10)	0.144 (6)	0.038 (6)	0.057 (5)	0.058 (6)
C21	0.093 (5)	0.047 (3)	0.114 (6)	0.007 (3)	0.026 (4)	−0.021 (3)
C15	0.076 (4)	0.061 (3)	0.085 (4)	0.021 (3)	0.003 (3)	0.016 (3)
F6	0.202 (9)	0.316 (14)	0.137 (6)	0.034 (9)	0.043 (6)	0.097 (7)
C18	0.149 (10)	0.098 (7)	0.101 (6)	−0.003 (6)	−0.028 (7)	0.026 (5)

Geometric parameters (Å, º)

Cu1—O2	1.883 (4)	O5—H5	0.8200
Cu1—O3	1.906 (4)	C6—C7	1.407 (9)
Cu1—N2	1.927 (5)	C6—C8	1.431 (8)
Cu1—N3	1.929 (5)	C8—H8	0.9300
O2—C5	1.309 (7)	C14—C15	1.375 (9)
O3—C17	1.317 (7)	C20—C19	1.361 (11)
N3—C11	1.279 (8)	C20—C21	1.375 (11)
N3—C10	1.455 (8)	C20—H20	0.9300
N2—C8	1.275 (8)	F5—C18	1.309 (11)
N2—C9	1.465 (7)	C2—C7	1.348 (10)
O4—C18	1.269 (12)	C2—C3	1.379 (10)
O4—C14	1.419 (7)	C16—C15	1.381 (9)
O1—C1	1.267 (9)	C16—H16	0.9300
O1—C2	1.475 (8)	C1—F3	1.268 (9)
F2—C1	1.271 (9)	C1—F1	1.292 (10)
C5—C4	1.403 (8)	F4—C18	1.265 (11)
C5—C6	1.423 (8)	C9—C10	1.474 (11)
C17—C16	1.395 (8)	C9—H9A	0.9700
C17—C12	1.420 (8)	C9—H9B	0.9700
C12—C13	1.403 (8)	C3—H3	0.9300
C12—C11	1.431 (9)	C19—C21^{i}	1.392 (11)
C13—C14	1.346 (9)	C19—H19	0.9300
C13—H13	0.9300	C7—H7	0.9300
C11—H11	0.9300	C10—H10A	0.9700
C4—C3	1.366 (9)	C10—H10B	0.9700
C4—H4	0.9300	C15—H15	0.9300
O5—C21	1.366 (9)	F6—C18	1.353 (15)
O2—Cu1—O3	87.54 (17)	C21—C20—H20	119.4
O2—Cu1—N2	94.40 (18)	C7—C2—C3	122.2 (6)
O3—Cu1—N2	176.2 (2)	C7—C2—O1	120.4 (7)
O2—Cu1—N3	177.82 (18)	C3—C2—O1	117.0 (6)
O3—Cu1—N3	93.9 (2)	C15—C16—C17	122.2 (6)
N2—Cu1—N3	84.3 (2)	C15—C16—H16	118.9
C5—O2—Cu1	127.1 (3)	C17—C16—H16	118.9
C17—O3—Cu1	127.0 (4)	F3—C1—O1	114.8 (7)
C11—N3—C10	122.4 (5)	F3—C1—F2	109.4 (8)
C11—N3—Cu1	125.0 (4)	O1—C1—F2	113.7 (7)

C10—N3—Cu1	112.3 (4)	F3—C1—F1	105.7 (9)
C8—N2—C9	120.3 (5)	O1—C1—F1	110.6 (9)
C8—N2—Cu1	125.9 (4)	F2—C1—F1	101.6 (7)
C9—N2—Cu1	113.8 (4)	N2—C9—C10	109.6 (6)
C18—O4—C14	118.9 (7)	N2—C9—H9A	109.7
C1—O1—C2	118.1 (6)	C10—C9—H9A	109.7
O2—C5—C4	118.9 (5)	N2—C9—H9B	109.7
O2—C5—C6	123.6 (5)	C10—C9—H9B	109.7
C4—C5—C6	117.5 (5)	H9A—C9—H9B	108.2
O3—C17—C16	118.8 (5)	C4—C3—C2	119.0 (6)
O3—C17—C12	123.4 (5)	C4—C3—H3	120.5
C16—C17—C12	117.8 (5)	C2—C3—H3	120.5
C13—C12—C17	118.7 (6)	C20—C19—C21^{i}	119.9 (7)
C13—C12—C11	118.3 (5)	C20—C19—H19	120.0
C17—C12—C11	123.0 (5)	C21^{i}—C19—H19	120.0
C14—C13—C12	121.1 (6)	C2—C7—C6	119.8 (6)
C14—C13—H13	119.5	C2—C7—H7	120.1
C12—C13—H13	119.5	C6—C7—H7	120.1
N3—C11—C12	126.5 (5)	N3—C10—C9	109.9 (5)
N3—C11—H11	116.7	N3—C10—H10A	109.7
C12—C11—H11	116.7	C9—C10—H10A	109.7
C3—C4—C5	121.9 (6)	N3—C10—H10B	109.7
C3—C4—H4	119.1	C9—C10—H10B	109.7
C5—C4—H4	119.1	H10A—C10—H10B	108.2
C21—O5—H5	109.5	O5—C21—C20	123.4 (7)
C7—C6—C5	119.3 (5)	O5—C21—C19^{i}	117.9 (8)
C7—C6—C8	117.1 (5)	C20—C21—C19^{i}	118.7 (7)
C5—C6—C8	123.6 (5)	C14—C15—C16	118.5 (6)
N2—C8—C6	125.1 (5)	C14—C15—H15	120.7
N2—C8—H8	117.5	C16—C15—H15	120.7
C6—C8—H8	117.5	F4—C18—O4	118.6 (10)
C13—C14—C15	121.7 (6)	F4—C18—F5	111.2 (9)
C13—C14—O4	117.9 (6)	O4—C18—F5	112.4 (10)
C15—C14—O4	120.2 (6)	F4—C18—F6	103.2 (13)
C19—C20—C21	121.3 (7)	O4—C18—F6	108.5 (10)
C19—C20—H20	119.4	F5—C18—F6	101.1 (11)

O3—Cu1—O2—C5	179.3 (5)	C18—O4—C14—C15	−74.5 (11)
N2—Cu1—O2—C5	2.6 (5)	C1—O1—C2—C7	74.4 (11)
Cu1—O2—C5—C4	174.2 (4)	C1—O1—C2—C3	−111.7 (9)
Cu1—O2—C5—C6	−6.2 (8)	O3—C17—C16—C15	−179.8 (6)
Cu1—O3—C17—C16	174.3 (5)	C12—C17—C16—C15	2.2 (10)
Cu1—O3—C17—C12	−7.8 (9)	C2—O1—C1—F3	−61.3 (13)
O3—C17—C12—C13	−180.0 (6)	C2—O1—C1—F2	171.7 (7)
C16—C17—C12—C13	−2.0 (9)	C2—O1—C1—F1	58.2 (10)
O3—C17—C12—C11	−2.9 (10)	C8—N2—C9—C10	−161.6 (6)
C16—C17—C12—C11	175.0 (6)	Cu1—N2—C9—C10	21.2 (7)
C17—C12—C13—C14	0.6 (10)	C5—C4—C3—C2	−3.4 (11)

C11—C12—C13—C14	−176.5 (6)	C7—C2—C3—C4	4.9 (12)
C10—N3—C11—C12	−173.9 (7)	O1—C2—C3—C4	−168.9 (6)
Cu1—N3—C11—C12	0.6 (10)	C21—C20—C19—C21^{i}	−4.1 (12)
C13—C12—C11—N3	−176.2 (6)	C3—C2—C7—C6	−1.4 (12)
C17—C12—C11—N3	6.8 (10)	O1—C2—C7—C6	172.2 (6)
O2—C5—C4—C3	178.2 (6)	C5—C6—C7—C2	−3.6 (10)
C6—C5—C4—C3	−1.5 (9)	C8—C6—C7—C2	176.2 (7)
O2—C5—C6—C7	−174.7 (6)	C11—N3—C10—C9	−153.1 (6)
C4—C5—C6—C7	4.9 (9)	Cu1—N3—C10—C9	31.8 (8)
O2—C5—C6—C8	5.5 (9)	N2—C9—C10—N3	−33.6 (9)
C4—C5—C6—C8	−174.8 (6)	C19—C20—C21—O5	−179.7 (7)
C9—N2—C8—C6	−179.2 (6)	C19—C20—C21—C19^{i}	4.1 (12)
Cu1—N2—C8—C6	−2.3 (9)	C13—C14—C15—C16	−0.6 (11)
C7—C6—C8—N2	179.2 (6)	O4—C14—C15—C16	−176.1 (6)
C5—C6—C8—N2	−1.0 (10)	C17—C16—C15—C14	−0.9 (11)
C12—C13—C14—C15	0.7 (11)	C14—O4—C18—F4	56.4 (17)
C12—C13—C14—O4	176.3 (6)	C14—O4—C18—F5	−171.6 (9)
C18—O4—C14—C13	109.8 (10)	C14—O4—C18—F6	−60.7 (11)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···O3	0.82	2.20	2.993 (8)	165
C11—H11···F2^{ii}	0.93	2.63	3.513 (8)	159
C10—H10*A*···O5^{iii}	0.97	2.53	3.469 (11)	162
C15—H15···O5^{iv}	0.93	2.55	3.345 (9)	144
C8—H8···*Cg*1^{v}	0.93	2.82	3.740 (8)	173

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