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(3-Carboxypyridine-2-carboxylato-κ^2N,O)(4′-phenyl-2,2′:6′,2″-terpyridine-κ^3N,N',N'')copper(II) tetrafluoridoborate

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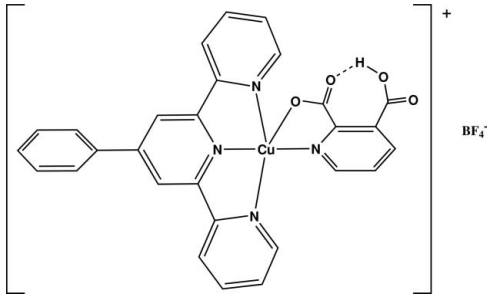
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; disorder in solvent or counterion; R factor = 0.043; wR factor = 0.084; data-to-parameter ratio = 10.0.

The title compound, $[Cu(C_7H_4NO_4)(C_{21}H_{15}N_3)]BF_4$, was obtained from an attempt to use 3-carboxypyridine-2-carboxylate as an *N*,*O*-bidentate ligand with the carboxyl group as an intermolecular hydrogen-bond site to organize the molecules in the crystal structure. Unfortunately, instead of an intermolecular hydrogen bond, an intramolecular O—H···O hydrogen bond was observed, and the molecules are organized by van der Waals and π–π stacking interactions [3.770 (2) Å]. The metal center has a square-pyramidal geometry, with the 4′-phenyl-2,2′:6′,2″-terpyridine coordinated in a tridentate manner in basal positions and the 3-carboxypyridine-2-carboxylate ligand coordinated as a bidentate ligand with the pyridine N atom basal and the O atom of the carboxylate group apical. The F atoms are disordered over three sites with occupancies of approximately 2:1:1.

Related literature

For related structures see: Turner *et al.* (2007); Xiang *et al.* (2006); Patrick *et al.* (2003); Sengupta *et al.* (2001); Okabe *et al.* (1996); Goher *et al.* (1993); Drew *et al.* (1971). For related literature, see: Constable *et al.* (1990).



Experimental

Crystal data

$[Cu(C_7H_4NO_4)(C_{21}H_{15}N_3)]BF_4$
M_r = 625.82
Monoclinic, $P2_1/n$
a = 9.7975 (5) Å
b = 25.102 (1) Å
c = 11.0414 (6) Å
β = 108.183 (1)°
V = 2579.9 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.92 mm^{-1}
T = 298 (2) K
0.24 × 0.16 × 0.06 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: analytical (Sheldrick, 2000)
T_{min} = 0.797, T_{max} = 0.946
21071 measured reflections
4561 independent reflections
3122 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.085
S = 0.88
4561 reflections
457 parameters
251 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2	0.897 (11)	1.539 (15)	2.412 (3)	163 (4)

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF* (Westrip, 2007) and *enCIFer* (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2202).

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supplementary materials

Acta Cryst. (2007). E**63**, m1975-m1976 [**doi:10.1107/S1600536807030073**]

(3-Carboxypyridine-2-carboxylato-κ^2N,O)(4'-phenyl-2,2':6',2''-terpyridine-κ^3N,N',N'')copper(II) tetrafluoridoborate

S. Martínez-Vargas, R. A. Toscano and J. Valdés-Martínez

Comment

Compounds with the 3-carboxylpyridine-2-carboxylato as ligand have been reported with the carboxyl group forming intermolecular (Turner *et al.*, 2007), (Patrick *et al.*, 2003), (Goher *et al.*, 1993) or intramolecular (Xiang *et al.*, 2006), (Sengupta *et al.*, 2001), (Okabe *et al.*, 1996), (Goher *et al.*, 1993), (Drew *et al.*, 1971), hydrogen bonds. In an attempt to use the carboxyl group in this ligand as an intermolecular H-bond site to organize the molecules in the crystal, the title compound, (I), was synthesized. Unfortunately, only an intramolecular O–H···O is observed.

In compound (I), the metal center has a square pyramidal geometry with the 4'-phenyl-2,2':6',2''-terpyridine coordinated as tridentate in equatorial position and the 3-carboxylpyridine-2-carboxylato coordinated as bidentate with the pyridine N atom in equatorial and the O atom of the carboxylate in axial position (Fig. 1). The 4-phenyl ring in the trpy (C26 - C31) forms an angle of 40.0 (2) Å with the central ring of the trpy (N14/C15—C19). The phenyl ring of the 3-carboxylpyridine-2-carboxylato is almost perpendicular to the trpy, the angle between the mean planes of N14/C15—C19 and N1/C2—C6 is 81.6 (2) Å.

The molecules intercalate with π - π stacking between N14/C15—C19 and N20/C21—C25 of a molecule generated by the symmetry code (1/2 + *x*,1/2 − *y*,1/2 + *z*), the rings are almost parallel (2.05 °) and have a centroid-centroid distance of 3.770 (2)Å an interplanar distance of 3.55 Å, and an offset angle of 19.7Â°.

Experimental

The 4'-Phenyl-2,2':6',2''-terpyridine was synthesized according to a published procedure (Constable *et al.*, 1990). The 4'-phenyl-2,2':6',2''-terpyridine (15.4 mg, 0.05 mmol) was dissolved on warm ethanol (10 ml), solid copper(II) tetrafluoroborate hydrate (11.9 mg, 0.05 mmol) was added and then a warm aqueous solution (5 ml) of 2,3-pyridinedicarboxylic acid (8.36 mg, 0.05 mmol) was added to form a blue solution. Blue crystals suitable for X-ray structure determination were obtained by slow evaporation after three days at room temperature.

Refinement

C-bound H atoms were placed in geometrically idealized positions and refined using a riding model with C–H = 0.93 Å, and U_{iso}(H) = 1.2U_{eq}(C). The O-bound H atom was located in a difference map and refined isotropically·The fluorine atoms of the tetrafluoroborate were refined with statistical disorder over three positions, with site occupancies of 0.54 (1) (for F1, F2 and F3), 0.25 (1) (for F1B, F2B and F3B) and 0.22 (1) (for F1C, F2C and F3C).

Figures

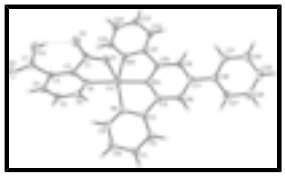


Fig. 1. The molecular structure of the complex cation in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

(3-Carboxypyridine-2-carboxylato-κ^2*N*,*O*)(4'-phenyl-2,2':6',2''-terpyridine- κ^3*N*,*N*',*N*'')copper(II) tetrafluoridoborate

Crystal data

$[Cu(C_7H_4NO_4)(C_{21}H_{15}N_3)]BF_4$	F_{000} = 1268.3
M_r = 625.82	D_x = 1.611 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 5948 reflections
a = 9.7975 (5) Å	θ = 2.3–30.9º
b = 25.1020 (10) Å	μ = 0.92 mm^{-1}
c = 11.0414 (6) Å	T = 298 (2) K
β = 108.1830 (10)º	Prism, blue
V = 2579.9 (2) Å^3	0.24 × 0.16 × 0.06 mm
Z = 4	

Data collection

Bruker SMART APEX CCD diffractometer	4561 independent reflections
Radiation source: fine-focus sealed tube	3122 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.058
Detector resolution: 0.661 pixels mm^{-1}	θ_{max} = 25.0º
T = 298(2) K	θ_{min} = 2.1º
ω scans	h = −11→11
Absorption correction: analytical (Sheldrick, 2000)	k = −29→29
T_{min} = 0.797, T_{max} = 0.946	l = −13→13
21071 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.043	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.085	$w = 1/[\sigma^2(F_o^2) + (0.036P)^2]$

	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.88$	$(\Delta/\sigma)_{max} = 0.001$
4561 reflections	$\Delta\rho_{max} = 0.63$ e Å^{-3}
457 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
251 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.93735 (4)	0.164025 (14)	0.23849 (4)	0.03900 (14)	
O1	0.8720 (2)	0.14954 (8)	0.4057 (2)	0.0472 (6)	
O2	0.7696 (3)	0.08826 (9)	0.4917 (2)	0.0698 (8)	
O3	0.7734 (3)	−0.00739 (10)	0.5131 (3)	0.0752 (8)	
H3	0.754 (4)	0.0275 (5)	0.501 (3)	0.090*	
O4	0.8507 (3)	−0.07591 (9)	0.4332 (2)	0.0640 (7)	
C1	0.8353 (3)	0.10311 (13)	0.4160 (3)	0.0433 (8)	
N1	0.8989 (3)	0.08547 (9)	0.2279 (2)	0.0369 (6)	
C2	0.8651 (3)	0.06176 (11)	0.3245 (3)	0.0345 (8)	
C3	0.8586 (3)	0.00616 (12)	0.3314 (3)	0.0371 (8)	
C4	0.8873 (3)	−0.02276 (12)	0.2352 (3)	0.0469 (9)	
H4	0.8897	−0.0598	0.2397	0.056*	
C5	0.9120 (4)	0.00184 (13)	0.1340 (4)	0.0549 (10)	
H5	0.9243	−0.0179	0.0669	0.066*	
C6	0.9182 (4)	0.05619 (13)	0.1337 (3)	0.0507 (9)	
H6	0.9365	0.0733	0.0657	0.061*	
C7	0.8259 (4)	−0.02882 (14)	0.4319 (3)	0.0480 (9)	
N8	1.1567 (3)	0.16328 (10)	0.3086 (2)	0.0370 (6)	
C9	1.2439 (4)	0.12160 (13)	0.3443 (3)	0.0454 (9)	
H9	1.2034	0.0878	0.3380	0.055*	
C10	1.3912 (4)	0.12612 (14)	0.3902 (3)	0.0518 (9)	
H10	1.4483	0.0960	0.4160	0.062*	
C11	1.4525 (4)	0.17548 (14)	0.3974 (3)	0.0537 (10)	
H11	1.5518	0.1794	0.4259	0.064*	
C12	1.3637 (3)	0.21937 (13)	0.3616 (3)	0.0478 (9)	

H12	1.4027	0.2534	0.3668	0.057*	
C13	1.2169 (3)	0.21217 (12)	0.3179 (3)	0.0363 (8)	
N14	0.9758 (2)	0.23913 (9)	0.2358 (2)	0.0340 (6)	
C15	1.1114 (3)	0.25650 (11)	0.2800 (3)	0.0352 (8)	
C16	1.1407 (3)	0.31016 (11)	0.2911 (3)	0.0388 (8)	
H16	1.2352	0.3220	0.3212	0.047*	
C17	1.0275 (3)	0.34679 (11)	0.2569 (3)	0.0365 (8)	
C18	0.8878 (3)	0.32764 (11)	0.2081 (3)	0.0379 (8)	
H18	0.8107	0.3511	0.1827	0.045*	
C19	0.8651 (3)	0.27295 (11)	0.1976 (3)	0.0343 (7)	
N20	0.7350 (3)	0.19182 (10)	0.1475 (2)	0.0381 (6)	
C21	0.7243 (3)	0.24570 (12)	0.1464 (3)	0.0348 (7)	
C22	0.5939 (3)	0.27147 (13)	0.1016 (3)	0.0432 (8)	
H22	0.5892	0.3085	0.1008	0.052*	
C23	0.4704 (3)	0.24127 (14)	0.0578 (3)	0.0514 (9)	
H23	0.3813	0.2578	0.0269	0.062*	
C24	0.4804 (4)	0.18665 (14)	0.0600 (3)	0.0524 (10)	
H24	0.3983	0.1657	0.0316	0.063*	
C25	0.6140 (3)	0.16369 (13)	0.1053 (3)	0.0490 (9)	
H25	0.6204	0.1267	0.1065	0.059*	
C26	1.0554 (3)	0.40427 (12)	0.2780 (3)	0.0384 (8)	
C27	1.1720 (4)	0.42823 (13)	0.2552 (3)	0.0536 (10)	
H27	1.2338	0.4080	0.2246	0.064*	
C28	1.1973 (4)	0.48222 (14)	0.2775 (4)	0.0648 (11)	
H28	1.2756	0.4979	0.2611	0.078*	
C29	1.1096 (4)	0.51244 (14)	0.3230 (3)	0.0614 (11)	
H29	1.1283	0.5485	0.3385	0.074*	
C30	0.9930 (4)	0.48949 (13)	0.3459 (3)	0.0565 (10)	
H30	0.9318	0.5101	0.3762	0.068*	
C31	0.9662 (4)	0.43578 (12)	0.3240 (3)	0.0483 (9)	
H31	0.8873	0.4205	0.3403	0.058*	
B1	1.0843 (4)	0.15628 (14)	−0.0468 (4)	0.0564 (12)	
F1	0.9637 (6)	0.1576 (3)	−0.0024 (8)	0.048 (2)	0.537 (14)
F2	1.1713 (14)	0.1141 (4)	0.0048 (14)	0.087 (4)	0.537 (14)
F3	1.1512 (9)	0.2052 (2)	−0.0138 (14)	0.071 (4)	0.537 (14)
F4	1.0292 (13)	0.1520 (4)	−0.1777 (5)	0.097 (3)	0.537 (14)
F1B	0.9442 (8)	0.1429 (7)	−0.0690 (19)	0.092 (5)	0.250 (8)
F2B	1.159 (3)	0.1154 (10)	0.031 (3)	0.068 (5)	0.250 (8)
F3B	1.127 (2)	0.2018 (6)	0.0264 (18)	0.067 (5)	0.250 (8)
F4B	1.1384 (18)	0.1567 (6)	−0.1481 (11)	0.093 (4)	0.250 (8)
F1C	1.007 (2)	0.1714 (9)	0.0328 (17)	0.070 (5)	0.215 (12)
F2C	1.186 (3)	0.1190 (12)	0.013 (4)	0.080 (7)	0.215 (12)
F3C	1.1472 (17)	0.1973 (7)	−0.093 (2)	0.080 (4)	0.215 (12)
F4C	0.9825 (19)	0.1355 (9)	−0.1543 (17)	0.084 (5)	0.215 (12)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

Cu1	0.0377 (2)	0.0258 (2)	0.0521 (3)	−0.00247 (19)	0.01201 (19)	0.0014 (2)
O1	0.0622 (16)	0.0309 (13)	0.0509 (15)	−0.0032 (11)	0.0214 (12)	−0.0050 (11)
O2	0.105 (2)	0.0463 (15)	0.083 (2)	−0.0069 (14)	0.0654 (18)	−0.0038 (14)
O3	0.119 (2)	0.0430 (16)	0.080 (2)	−0.0027 (17)	0.0537 (19)	0.0127 (15)
O4	0.087 (2)	0.0342 (14)	0.0670 (18)	−0.0035 (13)	0.0185 (15)	0.0097 (13)
C1	0.046 (2)	0.039 (2)	0.044 (2)	−0.0005 (17)	0.0123 (18)	−0.0020 (17)
N1	0.0406 (16)	0.0258 (14)	0.0457 (17)	−0.0039 (12)	0.0156 (14)	−0.0030 (13)
C2	0.0277 (17)	0.0314 (18)	0.042 (2)	−0.0031 (14)	0.0075 (15)	0.0001 (15)
C3	0.0304 (18)	0.0299 (18)	0.047 (2)	−0.0034 (14)	0.0062 (16)	0.0011 (16)
C4	0.046 (2)	0.0252 (18)	0.070 (3)	−0.0041 (16)	0.0203 (19)	−0.0049 (18)
C5	0.071 (3)	0.034 (2)	0.072 (3)	−0.0080 (18)	0.041 (2)	−0.0120 (19)
C6	0.064 (2)	0.038 (2)	0.059 (3)	−0.0078 (18)	0.033 (2)	−0.0015 (18)
C7	0.051 (2)	0.041 (2)	0.049 (2)	−0.0081 (18)	0.0099 (19)	0.0021 (19)
N8	0.0393 (15)	0.0281 (14)	0.0433 (16)	0.0033 (13)	0.0123 (13)	0.0023 (13)
C9	0.049 (2)	0.036 (2)	0.052 (2)	0.0038 (18)	0.0171 (18)	0.0042 (17)
C10	0.048 (2)	0.044 (2)	0.062 (3)	0.0175 (19)	0.0144 (19)	0.0061 (18)
C11	0.037 (2)	0.055 (2)	0.065 (3)	0.0059 (19)	0.0096 (18)	−0.005 (2)
C12	0.037 (2)	0.037 (2)	0.066 (3)	−0.0050 (17)	0.0115 (18)	−0.0077 (17)
C13	0.0365 (19)	0.0322 (19)	0.040 (2)	−0.0007 (15)	0.0117 (16)	−0.0020 (15)
N14	0.0296 (15)	0.0266 (14)	0.0431 (16)	−0.0004 (12)	0.0074 (13)	0.0011 (12)
C15	0.0361 (19)	0.0285 (18)	0.041 (2)	−0.0026 (15)	0.0128 (16)	0.0004 (15)
C16	0.0324 (18)	0.0340 (18)	0.047 (2)	−0.0033 (15)	0.0081 (16)	−0.0012 (15)
C17	0.038 (2)	0.0319 (18)	0.0393 (19)	−0.0027 (15)	0.0122 (16)	−0.0002 (15)
C18	0.0367 (18)	0.0282 (18)	0.046 (2)	0.0024 (15)	0.0084 (15)	0.0032 (15)
C19	0.0338 (18)	0.0306 (17)	0.038 (2)	0.0002 (15)	0.0101 (15)	0.0013 (15)
N20	0.0351 (16)	0.0297 (15)	0.0472 (17)	−0.0035 (12)	0.0095 (13)	−0.0002 (12)
C21	0.0331 (18)	0.0354 (19)	0.0360 (19)	−0.0003 (15)	0.0108 (15)	0.0009 (15)
C22	0.040 (2)	0.0361 (19)	0.051 (2)	0.0006 (16)	0.0101 (17)	0.0036 (17)
C23	0.033 (2)	0.055 (2)	0.061 (3)	0.0025 (18)	0.0076 (18)	0.0060 (19)
C24	0.032 (2)	0.052 (2)	0.067 (3)	−0.0107 (18)	0.0065 (18)	0.0030 (19)
C25	0.043 (2)	0.038 (2)	0.063 (2)	−0.0076 (18)	0.0122 (18)	−0.0006 (18)
C26	0.0376 (19)	0.0323 (18)	0.042 (2)	−0.0031 (16)	0.0080 (16)	0.0003 (16)
C27	0.061 (2)	0.039 (2)	0.065 (3)	−0.0039 (19)	0.027 (2)	0.0024 (19)
C28	0.069 (3)	0.042 (2)	0.085 (3)	−0.020 (2)	0.027 (2)	0.003 (2)
C29	0.077 (3)	0.031 (2)	0.067 (3)	−0.010 (2)	0.008 (2)	−0.0044 (19)
C30	0.056 (2)	0.039 (2)	0.068 (3)	0.0030 (19)	0.010 (2)	−0.0080 (19)
C31	0.045 (2)	0.034 (2)	0.061 (2)	−0.0051 (17)	0.0107 (18)	−0.0014 (17)
B1	0.047 (3)	0.046 (3)	0.075 (4)	−0.006 (2)	0.016 (3)	0.008 (3)
F1	0.034 (3)	0.053 (4)	0.044 (5)	−0.013 (3)	−0.008 (3)	−0.005 (3)
F2	0.057 (7)	0.043 (5)	0.146 (8)	0.011 (5)	0.012 (6)	0.000 (5)
F3	0.040 (3)	0.042 (3)	0.137 (10)	−0.006 (2)	0.036 (5)	0.004 (4)
F4	0.121 (7)	0.118 (6)	0.064 (4)	0.007 (5)	0.045 (4)	0.012 (3)
F1B	0.049 (6)	0.096 (8)	0.092 (10)	−0.024 (6)	−0.032 (7)	0.024 (8)
F2B	0.059 (9)	0.058 (9)	0.100 (9)	0.019 (8)	0.041 (7)	0.035 (7)
F3B	0.059 (9)	0.068 (7)	0.083 (8)	−0.005 (6)	0.035 (6)	−0.019 (6)
F4B	0.111 (9)	0.109 (8)	0.067 (7)	−0.029 (8)	0.036 (7)	−0.006 (6)
F1C	0.078 (10)	0.072 (10)	0.052 (8)	0.011 (8)	0.009 (8)	−0.020 (6)
F2C	0.046 (10)	0.063 (11)	0.132 (13)	0.005 (9)	0.028 (11)	0.028 (11)
F3C	0.078 (7)	0.084 (8)	0.085 (9)	0.001 (7)	0.035 (7)	0.027 (7)

F4C	0.070 (9)	0.112 (10)	0.072 (9)	−0.006 (7)	0.023 (8)	−0.020 (8)

Geometric parameters (Å, °)

Cu1—N14	1.925 (2)	C17—C18	1.390 (4)
Cu1—N1	2.004 (2)	C17—C26	1.474 (4)
Cu1—N8	2.045 (2)	C18—C19	1.390 (4)
Cu1—N20	2.045 (2)	C18—H18	0.9300
Cu1—O1	2.165 (2)	C19—C21	1.485 (4)
Cu1—F1	2.756 (7)	N20—C25	1.333 (4)
O1—C1	1.236 (3)	N20—C21	1.356 (3)
O2—C1	1.260 (4)	C21—C22	1.378 (4)
O3—C7	1.283 (4)	C22—C23	1.381 (4)
O3—H3	0.897 (11)	C22—H22	0.9300
O4—C7	1.206 (4)	C23—C24	1.374 (4)
C1—C2	1.539 (4)	C23—H23	0.9300
N1—C6	1.334 (4)	C24—C25	1.374 (4)
N1—C2	1.350 (3)	C24—H24	0.9300
C2—C3	1.400 (4)	C25—H25	0.9300
C3—C4	1.386 (4)	C26—C27	1.382 (4)
C3—C7	1.526 (4)	C26—C31	1.387 (4)
C4—C5	1.362 (4)	C27—C28	1.386 (4)
C4—H4	0.9300	C27—H27	0.9300
C5—C6	1.366 (4)	C28—C29	1.354 (5)
C5—H5	0.9300	C28—H28	0.9300
C6—H6	0.9300	C29—C30	1.372 (5)
N8—C9	1.330 (4)	C29—H29	0.9300
N8—C13	1.351 (3)	C30—C31	1.380 (4)
C9—C10	1.377 (4)	C30—H30	0.9300
C9—H9	0.9300	C31—H31	0.9300
C10—C11	1.368 (4)	B1—F1B	1.360 (6)
C10—H10	0.9300	B1—F2	1.366 (6)
C11—C12	1.383 (4)	B1—F3C	1.376 (7)
C11—H11	0.9300	B1—F2C	1.379 (7)
C12—C13	1.379 (4)	B1—F4B	1.379 (6)
C12—H12	0.9300	B1—F4	1.380 (5)
C13—C15	1.487 (4)	B1—F1C	1.382 (7)
N14—C15	1.337 (3)	B1—F3	1.385 (5)
N14—C19	1.338 (3)	B1—F3B	1.385 (7)
C15—C16	1.375 (4)	B1—F2B	1.390 (7)
C16—C17	1.399 (4)	B1—F4C	1.392 (7)
C16—H16	0.9300	B1—F1	1.414 (5)
N14—Cu1—N1	175.58 (10)	C15—C16—H16	120.2
N14—Cu1—N8	80.04 (10)	C17—C16—H16	120.2
N1—Cu1—N8	99.75 (10)	C18—C17—C16	118.6 (3)
N14—Cu1—N20	79.78 (10)	C18—C17—C26	120.8 (3)
N1—Cu1—N20	99.86 (10)	C16—C17—C26	120.5 (3)
N8—Cu1—N20	158.79 (10)	C19—C18—C17	119.1 (3)
N14—Cu1—O1	106.81 (9)	C19—C18—H18	120.4

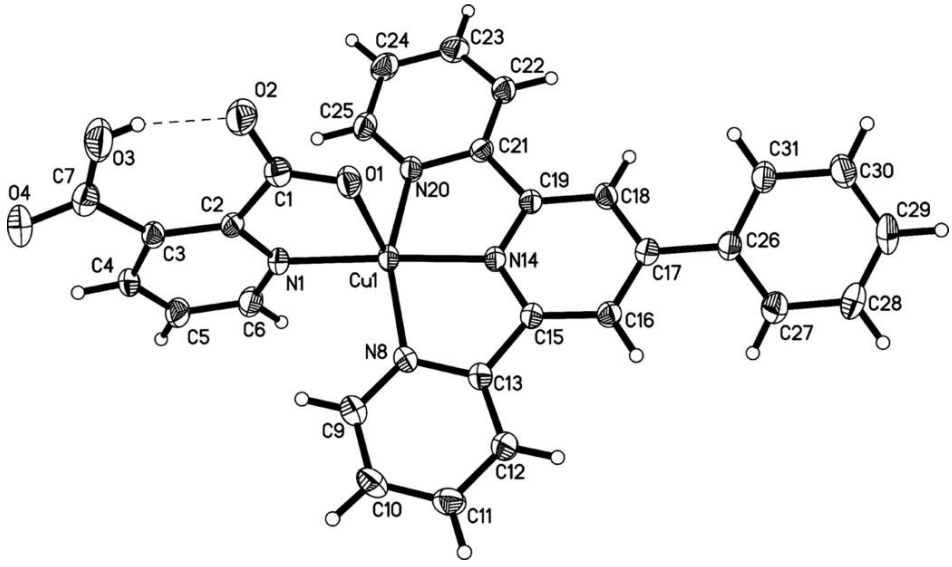
N1—Cu1—O1	77.56 (9)	C17—C18—H18	120.4
N8—Cu1—O1	103.36 (9)	N14—C19—C18	120.5 (3)
N20—Cu1—O1	88.70 (9)	N14—C19—C21	113.2 (3)
N14—Cu1—F1	87.96 (17)	C18—C19—C21	126.3 (3)
N1—Cu1—F1	87.62 (17)	C25—N20—C21	117.8 (3)
N8—Cu1—F1	87.76 (15)	C25—N20—Cu1	127.7 (2)
N20—Cu1—F1	85.07 (14)	C21—N20—Cu1	113.92 (19)
O1—Cu1—F1	162.70 (17)	N20—C21—C22	122.1 (3)
C1—O1—Cu1	114.2 (2)	N20—C21—C19	113.3 (3)
C7—O3—H3	114 (2)	C22—C21—C19	124.6 (3)
O1—C1—O2	124.3 (3)	C21—C22—C23	118.7 (3)
O1—C1—C2	117.1 (3)	C21—C22—H22	120.6
O2—C1—C2	118.5 (3)	C23—C22—H22	120.6
C6—N1—C2	120.2 (3)	C24—C23—C22	119.5 (3)
C6—N1—Cu1	121.2 (2)	C24—C23—H23	120.3
C2—N1—Cu1	118.4 (2)	C22—C23—H23	120.3
N1—C2—C3	120.6 (3)	C25—C24—C23	118.6 (3)
N1—C2—C1	111.4 (3)	C25—C24—H24	120.7
C3—C2—C1	128.0 (3)	C23—C24—H24	120.7
C4—C3—C2	117.2 (3)	N20—C25—C24	123.2 (3)
C4—C3—C7	113.3 (3)	N20—C25—H25	118.4
C2—C3—C7	129.5 (3)	C24—C25—H25	118.4
C5—C4—C3	121.4 (3)	C27—C26—C31	118.0 (3)
C5—C4—H4	119.3	C27—C26—C17	121.4 (3)
C3—C4—H4	119.3	C31—C26—C17	120.6 (3)
C4—C5—C6	118.3 (3)	C26—C27—C28	120.3 (3)
C4—C5—H5	120.8	C26—C27—H27	119.8
C6—C5—H5	120.8	C28—C27—H27	119.8
N1—C6—C5	122.1 (3)	C29—C28—C27	121.0 (3)
N1—C6—H6	119.0	C29—C28—H28	119.5
C5—C6—H6	119.0	C27—C28—H28	119.5
O4—C7—O3	121.7 (3)	C28—C29—C30	119.6 (3)
O4—C7—C3	119.0 (3)	C28—C29—H29	120.2
O3—C7—C3	119.2 (3)	C30—C29—H29	120.2
C9—N8—C13	117.9 (3)	C29—C30—C31	120.1 (3)
C9—N8—Cu1	128.4 (2)	C29—C30—H30	119.9
C13—N8—Cu1	113.7 (2)	C31—C30—H30	119.9
N8—C9—C10	123.1 (3)	C30—C31—C26	120.9 (3)
N8—C9—H9	118.4	C30—C31—H31	119.5
C10—C9—H9	118.4	C26—C31—H31	119.5
C11—C10—C9	119.1 (3)	F3C—B1—F2C	110.2 (15)
C11—C10—H10	120.4	F1B—B1—F4B	118.5 (9)
C9—C10—H10	120.4	F2—B1—F4	111.5 (7)
C10—C11—C12	118.7 (3)	F3C—B1—F1C	115.4 (11)
C10—C11—H11	120.7	F2C—B1—F1C	109.8 (16)
C12—C11—H11	120.7	F2—B1—F3	113.2 (7)
C13—C12—C11	119.3 (3)	F4—B1—F3	110.0 (5)
C13—C12—H12	120.3	F1B—B1—F3B	114.3 (11)
C11—C12—H12	120.3	F4B—B1—F3B	110.3 (9)

N8—C13—C12	121.9 (3)	F1B—B1—F2B	103.6 (14)
N8—C13—C15	114.2 (3)	F4B—B1—F2B	104.3 (13)
C12—C13—C15	123.9 (3)	F3B—B1—F2B	104.0 (15)
C15—N14—C19	121.6 (2)	F3C—B1—F4C	104.4 (10)
C15—N14—Cu1	119.39 (19)	F2C—B1—F4C	112.1 (17)
C19—N14—Cu1	118.89 (19)	F1C—B1—F4C	104.8 (10)
N14—C15—C16	120.5 (3)	F2—B1—F1	110.7 (7)
N14—C15—C13	112.5 (2)	F4—B1—F1	105.6 (5)
C16—C15—C13	126.9 (3)	F3—B1—F1	105.4 (5)
C15—C16—C17	119.6 (3)	B1—F1—Cu1	132.5 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2	0.897 (11)	1.539 (15)	2.412 (3)	163 (4)

Fig. 1


C24
C23
C22
O2
C25
C21
C31
O3
C7
O1
N20
C19
C30
O4
C2
C1
C18
C29
C3
C26
C4
N1
Cu1
N14
C17
C28
C5
C6
C15
C16
C27
N8
C13
C9
C12
C10
C11