

Bis(di-2-pyridylmethanediol- κ^3N,O,N')-copper(II) bis(tetrafluoridoborate) dihydrate

Krystal L. Brown, Guy Crundwell and Barry L. Westcott*

Department of Chemistry and Biochemistry, Central Connecticut State University, New Britain, CT 06050, USA

Correspondence e-mail: westcottb@ccsu.edu

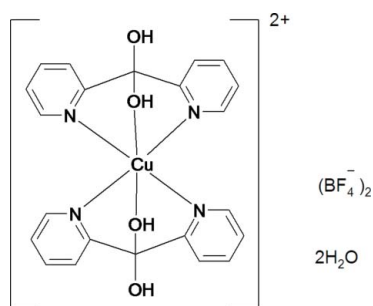
Received 7 April 2009; accepted 5 May 2009

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.004$ Å; disorder in solvent or counterion; R factor = 0.055; wR factor = 0.192; data-to-parameter ratio = 24.4.

The title complex, $[Cu(C_{11}H_{10}N_2O_2)_2](BF_4)_2 \cdot 2H_2O$, was isolated as a dihydrate from a 1:2 molar mixture of copper(II) tetrafluoridoborate hexahydrate with di-2-pyridyl ketone in aqueous solution. The centrosymmetric complex cation is structurally similar to that found in previously reported salts and exhibits Cu—O bonds deviating by 25 degrees from an octahedral geometry by the so-called 'off-axis angle' distortion. The BF_4^- anion exhibits a two site disorder of the fluorine atoms [ratio 0.210 (8):0.790 (8)].

Related literature

For related structures, see: Wang *et al.* (1986); Tangoulis *et al.* (1997); Yang *et al.* (1998); Tong *et al.* (1998); Serna *et al.* (1999); Reinoso *et al.* (2003); Li *et al.* (2005).



Experimental

Crystal data

$[Cu(C_{11}H_{10}N_2O_2)_2](BF_4)_2 \cdot 2H_2O$ $V = 1347.26$ (6) Å³
 $M_r = 677.61$ $Z = 2$
 Monoclinic, $P2_1/c$ Mo $K\alpha$ radiation
 $a = 7.8147$ (2) Å $\mu = 0.91$ mm⁻¹
 $b = 14.4225$ (4) Å $T = 293$ K
 $c = 12.1840$ (3) Å $0.8 \times 0.6 \times 0.6$ mm
 $\beta = 101.160$ (3)°

Data collection

Oxford Diffraction Sapphire CCD diffractometer 25175 measured reflections
 5349 independent reflections
 Absorption correction: multi-scan $SCALE3$ $ABSPACK$ in *CrysAlis RED* (Oxford Diffraction, 2006) 4145 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.036$
 $T_{min} = 0.474$, $T_{max} = 0.579$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$ H atoms treated by a mixture of independent and constrained refinement
 $wR(F^2) = 0.192$
 $S = 1.21$
 5349 reflections
 219 parameters
 10 restraints
 $\Delta\rho_{max} = 0.72$ e Å⁻³
 $\Delta\rho_{min} = -1.03$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—N1 ⁱ	2.0099 (19)	Cu1—N2 ⁱ	2.0147 (19)
Cu1—N1	2.0099 (19)	Cu1—O1	2.4312 (17)
Cu1—N2	2.0146 (19)	Cu1—O1 ⁱ	2.4312 (17)

Symmetry code: (i) $-x, -y, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O2-H2 \cdots O3$	0.82	1.87	2.686 (3)	172

Symmetry codes: .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

The diffractometer was purchased with funding from the National Science Foundation (NSF # 0420322). Additional funding is from a *CSUAAUP* research grant.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2210).

References

- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Li, C.-J., Li, W., Tong, M.-L. & Ng, S. W. (2005). *Acta Cryst.* **E61**, m232–m234.
 Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction, Abingdon, England.
 Reinoso, S., Vitoria, P., San Felices, L., Lezama, L. & Gutierrez-Zorrilla, J. M. (2003). *Acta Cryst.* **E59**, m548.
 Serna, Z., Barandika, M. G., Cortés, R., Urtiaga, M. K. & Arriortua, M. I. (1999). *Polyhedron*, **18**, 249–255.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Tangoulis, V., Raptopoulou, C. P., Terzis, A., Paschalidou, S., Perlepes, S. P. & Bakalbassis, E. G. (1997). *Inorg. Chem.* **36**, 3996–4006.
 Tong, M.-L., Yang, G., Chen, X.-M. & Ng, S. W. (1998). *Acta Cryst.* **C54**, 217–219.
 Wang, S. L., Richardson, J. W., Briggs, S. J. & Jacobson, R. A. (1986). *Inorg. Chim. Acta*, **111**, 67–68.
 Yang, G., Tong, M.-L., Chen, X.-M. & Ng, S. W. (1998). *Acta Cryst.* **C54**, 732–734.

supplementary materials

Acta Cryst. (2009). E65, m642 [doi:10.1107/S1600536809016973]

Bis(di-2-pyridylmethanediol- κ^3N,O,N')copper(II) bis(tetrafluoridoborate) dihydrate

K. L. Brown, G. Crundwell and B. L. Westcott

Experimental

All chemicals and reagents were purchased from Aldrich and used as received. di-2-pyridyl ketone (2 mmol) and copper(II) tetrafluoroborate hexahydrate (1 mmol) were combined in 40 ml of water and stirred for 30 minutes. The resulting violet crystals were isolated after 48 h by slow evaporation of the solution.

Refinement

For structure solution, direct methods were used to locate the initial structural model that consisted of all non-hydrogen atoms. All ligand-based H atoms were added during the refinement stage at idealized positions. Water-based H atoms were found during subsequent cycles from difference maps and their bond lengths to oxygen were free to refine. All H atoms were refined isotropically and all non-hydrogen atoms were refined anisotropically.

Figures

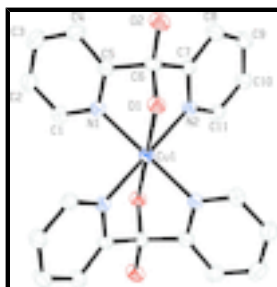


Fig. 1. ORTEP representation of the title complex. Thermal ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

Bis(di-2-pyridylmethanediol- κ^3N,O,N')copper(II) bis(tetrafluoridoborate) dihydrate

Crystal data

[Cu(C₁₁H₁₀N₂O₂)₂](BF₄)₂·2H₂O

M_r = 677.61

Monoclinic, *P*2₁/*c*

Hall symbol: -*P* 2ybc

a = 7.8147 (2) Å

b = 14.4225 (4) Å

c = 12.1840 (3) Å

β = 101.160 (3)°

V = 1347.26 (6) Å³

Z = 2

*F*₀₀₀ = 686

D_x = 1.670 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 5349 reflections

θ = 3.8–32.0°

μ = 0.91 mm⁻¹

T = 293 K

Parallelepiped, violet

0.8 × 0.6 × 0.6 mm

Data collection

Oxford Diffraction Sapphire CCD diffractometer	5349 independent reflections
Radiation source: fine-focus sealed tube	4145 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.036$
$T = 293$ K	$\theta_{\text{max}} = 34.7^\circ$
ω scans	$\theta_{\text{min}} = 3.9^\circ$
Absorption correction: multi-scan SCALE3 ABSPACK in CrysAlis RED (Oxford Diffraction, 2006)	$h = -12 \rightarrow 11$
$T_{\text{min}} = 0.474$, $T_{\text{max}} = 0.579$	$k = -22 \rightarrow 22$
25175 measured reflections	$l = -18 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.055$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.192$	$w = 1/[\sigma^2(F_o^2) + (0.0959P)^2 + 1.P]$
$S = 1.21$	where $P = (F_o^2 + 2F_c^2)/3$
5349 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
219 parameters	$\Delta\rho_{\text{max}} = 0.72 \text{ e } \text{\AA}^{-3}$
10 restraints	$\Delta\rho_{\text{min}} = -1.03 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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. Hydrogen atoms were included in calculated positions for the ring carbons on the dpk ligand (0.93\AA for sp^2 carbons) and were included in the refinement in riding motion approximation with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the carrier atom for sp^2 carbons. Oxygen hydrogens were found in difference maps.

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.0000	0.0000	0.5000	0.02185 (12)	
C1	0.2975 (3)	0.04790 (18)	0.3891 (2)	0.0289 (5)	
H1	0.2514	0.0035	0.3363	0.035*	
C2	0.4472 (4)	0.0936 (2)	0.3777 (2)	0.0335 (5)	
H2A	0.5001	0.0810	0.3172	0.040*	
C3	0.5190 (4)	0.1586 (2)	0.4571 (2)	0.0348 (5)	
H3	0.6217	0.1894	0.4517	0.042*	
C4	0.4334 (3)	0.17694 (18)	0.5455 (2)	0.0310 (5)	
H4	0.4780	0.2203	0.6001	0.037*	
C5	0.2824 (3)	0.12975 (15)	0.55022 (18)	0.0243 (4)	
C6	0.1798 (3)	0.14291 (15)	0.64412 (18)	0.0240 (4)	
C7	0.1983 (3)	0.05478 (15)	0.71483 (18)	0.0228 (4)	
C8	0.2869 (4)	0.05111 (17)	0.8236 (2)	0.0294 (5)	
H8	0.3411	0.1036	0.8587	0.035*	
C9	0.2936 (4)	-0.03360 (19)	0.8802 (2)	0.0322 (5)	
H9	0.3511	-0.0383	0.9543	0.039*	
C10	0.2138 (4)	-0.11005 (17)	0.8244 (2)	0.0289 (4)	
H10	0.2176	-0.1671	0.8604	0.035*	
C11	0.1283 (3)	-0.10113 (16)	0.71447 (19)	0.0250 (4)	
H11	0.0746	-0.1529	0.6772	0.030*	
N1	0.2158 (3)	0.06543 (13)	0.47416 (15)	0.0230 (3)	
N2	0.1204 (3)	-0.02000 (13)	0.65999 (15)	0.0214 (3)	
O1	0.0028 (2)	0.15157 (12)	0.58765 (14)	0.0252 (3)	
O2	0.2355 (3)	0.21705 (12)	0.71285 (15)	0.0310 (4)	
H2	0.2214	0.2651	0.6763	0.047*	
H50	-0.064 (5)	0.153 (3)	0.633 (3)	0.034 (9)*	
H51	0.181 (7)	0.416 (4)	0.599 (4)	0.058 (13)*	
H52	0.133 (6)	0.354 (3)	0.529 (4)	0.044 (11)*	
O3	0.2110 (4)	0.36785 (16)	0.5814 (2)	0.0419 (5)	
B1	0.8127 (4)	0.13674 (19)	0.8480 (2)	0.0302 (5)	0.790 (8)
F1	0.7868 (2)	0.16783 (13)	0.73741 (13)	0.0381 (4)	0.790 (8)
F2	0.8638 (9)	0.0451 (3)	0.8536 (8)	0.0471 (13)	0.790 (8)
F3	0.9557 (7)	0.1892 (2)	0.9056 (3)	0.0674 (14)	0.790 (8)
F4	0.6729 (5)	0.1531 (3)	0.8951 (3)	0.0661 (12)	0.790 (8)
B1B	0.8127 (4)	0.13674 (19)	0.8480 (2)	0.0302 (5)	0.210 (8)
F1B	0.7868 (2)	0.16783 (13)	0.73741 (13)	0.0381 (4)	0.210 (8)
F2B	0.894 (4)	0.0519 (14)	0.854 (3)	0.0471 (13)	0.210 (8)
F3B	0.866 (3)	0.1927 (9)	0.9307 (11)	0.0674 (14)	0.210 (8)
F4B	0.6394 (16)	0.1147 (11)	0.8558 (12)	0.0661 (12)	0.210 (8)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0261 (2)	0.02088 (19)	0.01787 (18)	-0.00313 (13)	0.00248 (13)	-0.00088 (12)

supplementary materials

C1	0.0302 (11)	0.0331 (12)	0.0238 (10)	-0.0027 (9)	0.0066 (8)	0.0000 (8)
C2	0.0302 (12)	0.0398 (14)	0.0323 (12)	-0.0002 (10)	0.0109 (9)	0.0049 (10)
C3	0.0271 (12)	0.0358 (13)	0.0423 (14)	-0.0049 (9)	0.0088 (10)	0.0050 (11)
C4	0.0308 (12)	0.0257 (10)	0.0350 (12)	-0.0068 (9)	0.0024 (9)	0.0008 (9)
C5	0.0271 (10)	0.0209 (9)	0.0234 (9)	-0.0013 (7)	0.0016 (7)	0.0019 (7)
C6	0.0313 (11)	0.0184 (8)	0.0210 (9)	-0.0036 (7)	0.0016 (7)	-0.0010 (7)
C7	0.0248 (10)	0.0206 (9)	0.0223 (9)	-0.0026 (7)	0.0030 (7)	-0.0012 (7)
C8	0.0352 (12)	0.0263 (10)	0.0246 (10)	-0.0040 (9)	0.0006 (8)	-0.0005 (8)
C9	0.0397 (13)	0.0323 (12)	0.0222 (10)	-0.0016 (10)	0.0004 (9)	0.0025 (9)
C10	0.0351 (12)	0.0249 (10)	0.0259 (10)	-0.0006 (9)	0.0037 (9)	0.0046 (8)
C11	0.0259 (10)	0.0206 (9)	0.0285 (10)	-0.0024 (7)	0.0053 (8)	0.0008 (7)
N1	0.0239 (8)	0.0236 (8)	0.0213 (8)	-0.0030 (6)	0.0036 (6)	0.0005 (6)
N2	0.0241 (8)	0.0198 (7)	0.0201 (7)	-0.0016 (6)	0.0035 (6)	-0.0003 (6)
O1	0.0270 (8)	0.0252 (7)	0.0227 (7)	0.0009 (6)	0.0026 (6)	0.0011 (6)
O2	0.0455 (11)	0.0198 (7)	0.0257 (8)	-0.0050 (7)	0.0019 (7)	-0.0033 (6)
O3	0.0584 (14)	0.0259 (9)	0.0390 (11)	0.0041 (9)	0.0035 (10)	0.0029 (8)
B1	0.0412 (15)	0.0245 (11)	0.0250 (11)	0.0042 (10)	0.0064 (10)	0.0002 (9)
F1	0.0457 (10)	0.0417 (9)	0.0268 (7)	0.0064 (7)	0.0072 (6)	0.0068 (6)
F2	0.069 (3)	0.0238 (11)	0.0477 (10)	0.0088 (16)	0.010 (2)	0.0005 (10)
F3	0.094 (3)	0.0412 (13)	0.0503 (17)	-0.0201 (19)	-0.0284 (19)	0.0030 (12)
F4	0.084 (2)	0.072 (3)	0.054 (2)	0.0369 (19)	0.0436 (18)	0.0173 (17)
B1B	0.0412 (15)	0.0245 (11)	0.0250 (11)	0.0042 (10)	0.0064 (10)	0.0002 (9)
F1B	0.0457 (10)	0.0417 (9)	0.0268 (7)	0.0064 (7)	0.0072 (6)	0.0068 (6)
F2B	0.069 (3)	0.0238 (11)	0.0477 (10)	0.0088 (16)	0.010 (2)	0.0005 (10)
F3B	0.094 (3)	0.0412 (13)	0.0503 (17)	-0.0201 (19)	-0.0284 (19)	0.0030 (12)
F4B	0.084 (2)	0.072 (3)	0.054 (2)	0.0369 (19)	0.0436 (18)	0.0173 (17)

Geometric parameters (Å, °)

Cu1—N1 ⁱ	2.0099 (19)	C6—C7	1.527 (3)
Cu1—N1	2.0099 (19)	C7—N2	1.350 (3)
Cu1—N2	2.0146 (19)	C7—C8	1.372 (3)
Cu1—N2 ⁱ	2.0147 (19)	C8—C9	1.399 (4)
Cu1—O1	2.4312 (17)	C8—H8	0.9300
Cu1—O1 ⁱ	2.4312 (17)	C9—C10	1.379 (4)
C1—N1	1.343 (3)	C9—H9	0.9300
C1—C2	1.373 (4)	C10—C11	1.382 (3)
C1—H1	0.9300	C10—H10	0.9300
C2—C3	1.385 (4)	C11—N2	1.341 (3)
C2—H2A	0.9300	C11—H11	0.9300
C3—C4	1.399 (4)	O1—H50	0.83 (4)
C3—H3	0.9300	O2—H2	0.8200
C4—C5	1.373 (3)	O3—H51	0.78 (5)
C4—H4	0.9300	O3—H52	0.82 (5)
C5—N1	1.343 (3)	B1—F4	1.350 (4)
C5—C6	1.531 (3)	B1—F2	1.378 (5)
C6—O2	1.376 (3)	B1—F1	1.397 (3)
C6—O1	1.427 (3)	B1—F3	1.417 (5)

N1 ⁱ —Cu1—N1	179.999 (1)	O1—C6—C5	104.48 (17)
N1 ⁱ —Cu1—N2	91.74 (8)	C7—C6—C5	108.21 (18)
N1—Cu1—N2	88.27 (8)	N2—C7—C8	122.8 (2)
N1 ⁱ —Cu1—N2 ⁱ	88.26 (8)	N2—C7—C6	113.67 (19)
N1—Cu1—N2 ⁱ	91.73 (8)	C8—C7—C6	123.5 (2)
N2—Cu1—N2 ⁱ	180.0	C7—C8—C9	118.3 (2)
N1 ⁱ —Cu1—O1	106.84 (7)	C7—C8—H8	120.9
N1—Cu1—O1	73.16 (7)	C9—C8—H8	120.9
N2—Cu1—O1	74.99 (7)	C10—C9—C8	119.0 (2)
N2 ⁱ —Cu1—O1	105.01 (7)	C10—C9—H9	120.5
N1 ⁱ —Cu1—O1 ⁱ	73.16 (7)	C8—C9—H9	120.5
N1—Cu1—O1 ⁱ	106.84 (7)	C11—C10—C9	119.4 (2)
N2—Cu1—O1 ⁱ	105.01 (7)	C11—C10—H10	120.3
N2 ⁱ —Cu1—O1 ⁱ	74.99 (7)	C9—C10—H10	120.3
O1—Cu1—O1 ⁱ	180.00 (8)	N2—C11—C10	121.9 (2)
N1—C1—C2	122.0 (2)	N2—C11—H11	119.1
N1—C1—H1	119.0	C10—C11—H11	119.1
C2—C1—H1	119.0	C5—N1—C1	118.9 (2)
C1—C2—C3	119.5 (2)	C5—N1—Cu1	116.18 (15)
C1—C2—H2A	120.2	C1—N1—Cu1	124.86 (16)
C3—C2—H2A	120.2	C11—N2—C7	118.63 (19)
C2—C3—C4	118.4 (2)	C11—N2—Cu1	124.89 (15)
C2—C3—H3	120.8	C7—N2—Cu1	116.48 (15)
C4—C3—H3	120.8	C6—O1—Cu1	93.35 (12)
C5—C4—C3	118.8 (2)	C6—O1—H50	111 (3)
C5—C4—H4	120.6	Cu1—O1—H50	111 (3)
C3—C4—H4	120.6	C6—O2—H2	109.5
N1—C5—C4	122.3 (2)	H51—O3—H52	103 (5)
N1—C5—C6	114.34 (19)	F4—B1—F2	113.4 (4)
C4—C5—C6	123.3 (2)	F4—B1—F1	112.1 (3)
O2—C6—O1	112.86 (19)	F2—B1—F1	110.0 (4)
O2—C6—C7	108.62 (18)	F4—B1—F3	108.8 (3)
O1—C6—C7	108.78 (18)	F2—B1—F3	107.1 (4)
O2—C6—C5	113.67 (19)	F1—B1—F3	105.0 (3)

Symmetry codes: (i) $-x, -y, -z+1$.

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2 \cdots O3	0.82	1.87	2.686 (3)	172

