

catena-Poly[[μ -bromido-(μ -hydroxydi-2-pyridylmethanolato- κ^4 N,O:O,N')-dicopper(II)(Cu—Cu)]-di- μ -bromido]

Matthias Zeller,^a Barry L. Westcott,^{b*} Kristin M. Kopp-Vaughn^b and Allen D. Hunter^a

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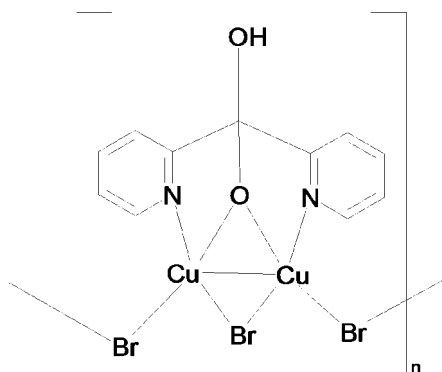
Received 19 June 2008; accepted 29 July 2008

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.023; wR factor = 0.061; data-to-parameter ratio = 19.4.

The title complex, $[\text{Cu}_2\text{Br}_3(\text{C}_{11}\text{H}_9\text{N}_2\text{O}_2)]_n$, was one of three isolated by slow evaporation of an acetonitrile reaction mixture of CuBr_2 with di-2-pyridyl ketone (1:1 molar ratio). The title complex contains a 2:1 metal-to-ligand ratio of copper(II) with the hydrated form of the ligand, di-2-pyridylmethanediol. The two copper centers are bridged by a bromide ion and the alkoxy O atom, and the Cu—Cu distance is 2.9801 (5) Å. The dimeric units are further linked by bromide ions, leading to a two-dimensional extended bridged structure. O—H...O hydrogen bonds are present in the crystal structure.

Related literature

Apart from the title complex, two others were isolated from the reaction mixture and structurally characterized. One was identical to that of Parker *et al.* (2000), the other is reported in the following paper by Westcott *et al.* (2008). For other related structures, see: Wang *et al.* (1986); Mariezcurrena *et al.* (1999).



Experimental

Crystal data

$[\text{Cu}_2\text{Br}_3(\text{C}_{11}\text{H}_9\text{N}_2\text{O}_2)]$
 $M_r = 568.01$
Triclinic, $P\bar{1}$
 $a = 8.7708$ (7) Å
 $b = 9.6018$ (8) Å
 $c = 10.1839$ (8) Å
 $\alpha = 73.7060$ (10)°
 $\beta = 70.8520$ (10)°

$\gamma = 63.9280$ (10)°
 $V = 718.28$ (10) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 11.30$ mm⁻¹
 $T = 100$ (2) K
 $0.39 \times 0.19 \times 0.08$ mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (SADABS in SAINT-Plus; Bruker, 2003)
 $T_{\min} = 0.122$, $T_{\max} = 0.424$

7397 measured reflections
3537 independent reflections
3305 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.061$
 $S = 1.09$
3537 reflections

182 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.02$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.60$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1...O2 ⁱ	0.84	2.33	3.014 (2)	139

Symmetry code: (i) $-x, -y + 2, -z + 1$.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT-Plus (Bruker, 2003); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL and ORTEP-3 (Farrugia, 1997); 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: FJ2131).

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Parker, O. J., Aubol, S. L. & Breneman, G. L. (2000). *Polyhedron*, **19**, 623–626.
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Wang, S.-L., Richardson, J. W. Jr, Briggs, S. J., Jacobson, R. A. & Jensen, W. P. (1986). *Inorg. Chim. Acta*, **111**, 67–72.
Westcott, B. L., Kopp-Vaughn, K. M., Daniels, L. & Zeller, M. (2008). *Acta Cryst.* **E64**, m1122–m1123.

supplementary materials

Acta Cryst. (2008). E64, m1121 [doi:10.1107/S1600536808024197]

***catena*-Poly[[μ -bromido-(μ -hydroxydi-2-pyridylmethanolato- $\kappa^4N,O:O,N'$)dicopper(II)(*Cu-Cu*)]-
di- μ -bromido]**

M. Zeller, B. L. Westcott, K. M. Kopp-Vaughn and A. D. Hunter

Comment

The structure of the title compound, is shown below. The complex was one of three Cu-dpkoh complexes isolated from the 1:1 molar mixture of copper(II)bromide and di-2-pyridyl ketone. The title complex was the second isolated from solution. One other complex had been reported previously by Parker, *et al.*, another unique complex is described elsewhere: Westcott, *et al.*(2008).

The complex contains two copper centers that are 2.9801 (5) Å apart and are bridged by the hydrated form of the ligand di-2-pyridylketone. Each copper center is also coordinated to the ligand through one unique nitrogen atom and a by a μ -hydroxyl bridge. Additionally, each Cu center coordinates one bromide ion. The bromide ion then acts as a bridging ligand to the next di-copper unit, leading to a polymeric structure as shown in Figure 2.

Experimental

Di-2-pyridyl ketone (dpk) was purchased from Aldrich and used as received. Copper(II) bromide hexahydrate was dried in an oven at 110 C for 48 h before use. DPK (1 mmol) and copper(II) bromide (1 mmol) were combined in 40 ml of acetonitrile and stirred for 30 minutes. The resulting green crystals were isolated after 4 days 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 (C—H 0.95 Å; O—H 0.84 Å). All H atoms were refined with isotropic displacement parameter set equal to 1.5 times the isotropic equivalent value for the attached atom. All non-hydrogen atoms were refined anisotropically.

Figures

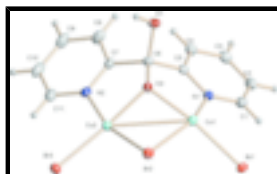


Fig. 1. *ORTEP-3* (Farrugia, 1997) representation of the asymmetric unit. Ellipsoids are drawn at the 30% probability level.

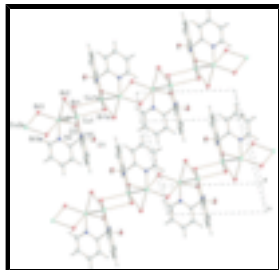


Fig. 2. Packing diagram showing the extended structure.

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Crystal data

[Cu₂Br₃(C₁₁H₉N₂O₂)]

$M_r = 568.01$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 8.7708$ (7) Å

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$\alpha = 73.7060$ (10)°

$\beta = 70.8520$ (10)°

$\gamma = 63.9280$ (10)°

$V = 718.28$ (10) Å³

$Z = 2$

$F_{000} = 536$

$D_x = 2.626$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 6753 reflections

$\theta = 2.4$ – 30.6 °

$\mu = 11.30$ mm⁻¹

$T = 100$ (2) K

Hexagon, green

$0.39 \times 0.19 \times 0.08$ mm

Data collection

Bruker SMART APEX CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100$ (2) K

ω scans

Absorption correction: multi-scan
(SADABS in SAINT-Plus; Bruker, 2003)

$T_{\min} = 0.122$, $T_{\max} = 0.424$

7397 measured reflections

3537 independent reflections

3305 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 28.3$ °

$\theta_{\min} = 2.1$ °

$h = -11 \rightarrow 11$

$k = -12 \rightarrow 12$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.061$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 0.561P]$

where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.09$ $(\Delta/\sigma)_{\max} = 0.002$
 3537 reflections $\Delta\rho_{\max} = 1.02 \text{ e } \text{\AA}^{-3}$
 182 parameters $\Delta\rho_{\min} = -0.60 \text{ e } \text{\AA}^{-3}$
 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. 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	$U_{\text{iso}}^*/U_{\text{eq}}$
Br2	0.12154 (3)	1.22298 (3)	0.70734 (3)	0.01693 (7)
Br3	-0.23030 (3)	1.19011 (3)	1.00202 (3)	0.01823 (7)
Br1	0.57965 (3)	0.99477 (3)	0.65263 (3)	0.01507 (7)
Cu1	0.32811 (4)	0.96542 (3)	0.64120 (3)	0.01335 (8)
Cu2	-0.03366 (4)	1.04405 (4)	0.82256 (3)	0.01406 (8)
O2	0.1101 (2)	0.9459 (2)	0.65750 (18)	0.0130 (3)
O1	0.1005 (2)	0.7855 (2)	0.53023 (19)	0.0181 (4)
H1	0.0027	0.8513	0.5168	0.027*
N1	0.4203 (3)	0.7340 (2)	0.6562 (2)	0.0142 (4)
C6	0.1192 (3)	0.7966 (3)	0.6588 (3)	0.0136 (5)
N2	-0.1178 (3)	0.8719 (3)	0.8672 (2)	0.0148 (4)
C7	-0.0283 (3)	0.7649 (3)	0.7798 (3)	0.0146 (5)
C5	0.3027 (3)	0.6743 (3)	0.6683 (2)	0.0132 (5)
C4	0.3512 (3)	0.5141 (3)	0.6783 (3)	0.0165 (5)
H4	0.2670	0.4726	0.6880	0.020*
C3	0.5248 (3)	0.4151 (3)	0.6739 (3)	0.0181 (5)
H3	0.5603	0.3051	0.6801	0.022*
C11	-0.2540 (3)	0.8573 (3)	0.9709 (3)	0.0194 (5)
H11	-0.3182	0.9345	1.0310	0.023*
C1	0.5880 (3)	0.6375 (3)	0.6519 (3)	0.0181 (5)
H1A	0.6702	0.6812	0.6426	0.022*
C10	-0.3034 (4)	0.7321 (4)	0.9924 (3)	0.0231 (6)
H10	-0.3998	0.7232	1.0667	0.028*
C9	-0.2103 (4)	0.6209 (3)	0.9042 (3)	0.0250 (6)
H9	-0.2400	0.5328	0.9187	0.030*
C2	0.6449 (3)	0.4767 (3)	0.6606 (3)	0.0185 (5)
H2	0.7641	0.4106	0.6575	0.022*

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C8	-0.0737 (4)	0.6390 (3)	0.7948 (3)	0.0213 (5)
H8	-0.0116	0.5661	0.7305	0.026*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br2	0.01628 (12)	0.01244 (12)	0.02349 (13)	-0.00619 (10)	-0.00358 (10)	-0.00520 (10)
Br3	0.01571 (12)	0.01965 (14)	0.01898 (13)	-0.00469 (10)	-0.00213 (9)	-0.00841 (10)
Br1	0.01576 (12)	0.01633 (13)	0.01651 (12)	-0.00878 (10)	-0.00493 (9)	-0.00191 (9)
Cu1	0.01234 (14)	0.01089 (15)	0.01833 (16)	-0.00526 (12)	-0.00342 (11)	-0.00347 (12)
Cu2	0.01375 (15)	0.01408 (15)	0.01601 (15)	-0.00656 (12)	-0.00140 (11)	-0.00535 (12)
O2	0.0129 (8)	0.0090 (8)	0.0178 (8)	-0.0051 (6)	-0.0021 (6)	-0.0038 (6)
O1	0.0200 (9)	0.0172 (9)	0.0191 (9)	-0.0040 (7)	-0.0094 (7)	-0.0055 (7)
N1	0.0152 (10)	0.0135 (10)	0.0149 (10)	-0.0050 (8)	-0.0044 (8)	-0.0034 (8)
C6	0.0159 (11)	0.0111 (11)	0.0162 (11)	-0.0057 (9)	-0.0054 (9)	-0.0028 (9)
N2	0.0146 (10)	0.0163 (10)	0.0153 (10)	-0.0068 (8)	-0.0055 (8)	-0.0014 (8)
C7	0.0130 (11)	0.0138 (12)	0.0191 (12)	-0.0063 (9)	-0.0062 (9)	-0.0010 (9)
C5	0.0155 (11)	0.0130 (12)	0.0110 (10)	-0.0056 (9)	-0.0027 (9)	-0.0023 (9)
C4	0.0181 (12)	0.0144 (12)	0.0177 (12)	-0.0074 (10)	-0.0028 (9)	-0.0033 (9)
C3	0.0222 (13)	0.0105 (11)	0.0174 (12)	-0.0041 (10)	-0.0036 (10)	-0.0010 (9)
C11	0.0174 (12)	0.0253 (14)	0.0162 (12)	-0.0098 (11)	-0.0051 (10)	-0.0005 (10)
C1	0.0168 (12)	0.0207 (13)	0.0186 (12)	-0.0064 (10)	-0.0045 (9)	-0.0065 (10)
C10	0.0208 (13)	0.0283 (15)	0.0228 (13)	-0.0165 (12)	-0.0082 (10)	0.0074 (11)
C9	0.0230 (14)	0.0217 (14)	0.0346 (16)	-0.0151 (12)	-0.0106 (12)	0.0044 (12)
C2	0.0170 (12)	0.0158 (12)	0.0205 (13)	-0.0021 (10)	-0.0057 (10)	-0.0051 (10)
C8	0.0191 (12)	0.0146 (12)	0.0329 (15)	-0.0085 (10)	-0.0083 (11)	-0.0021 (11)

Geometric parameters (\AA , $^\circ$)

Br2—Cu1	2.4592 (4)	N2—C11	1.341 (3)
Br2—Cu2	2.4613 (4)	N2—C7	1.346 (3)
Br3—Cu2	2.3507 (4)	C7—C8	1.386 (4)
Br1—Cu1	2.3862 (4)	C5—C4	1.387 (3)
Br1—Cu1 ⁱ	2.7923 (4)	C4—C3	1.389 (4)
Cu1—O2	1.9513 (17)	C4—H4	0.9500
Cu1—N1	1.981 (2)	C3—C2	1.374 (4)
Cu1—Br1 ⁱ	2.7923 (4)	C3—H3	0.9500
Cu1—Cu2	2.9801 (5)	C11—C10	1.389 (4)
Cu2—O2	1.9386 (17)	C11—H11	0.9500
Cu2—N2	1.979 (2)	C1—C2	1.384 (4)
O2—C6	1.396 (3)	C1—H1A	0.9500
O1—C6	1.410 (3)	C10—C9	1.380 (4)
O1—H1	0.8400	C10—H10	0.9500
N1—C1	1.344 (3)	C9—C8	1.381 (4)
N1—C5	1.344 (3)	C9—H9	0.9500
C6—C5	1.535 (3)	C2—H2	0.9500
C6—C7	1.542 (3)	C8—H8	0.9500
Cu1—Br2—Cu2	74.551 (13)	O2—C6—C7	108.55 (19)

Cu1—Br1—Cu1 ⁱ	87.045 (12)	O1—C6—C7	109.37 (19)
O2—Cu1—N1	82.07 (8)	C5—C6—C7	113.9 (2)
O2—Cu1—Br1	172.49 (5)	C11—N2—C7	119.6 (2)
N1—Cu1—Br1	99.71 (6)	C11—N2—Cu2	126.15 (19)
O2—Cu1—Br2	81.11 (5)	C7—N2—Cu2	114.21 (17)
N1—Cu1—Br2	155.54 (6)	N2—C7—C8	121.3 (2)
Br1—Cu1—Br2	94.848 (14)	N2—C7—C6	115.8 (2)
O2—Cu1—Br1 ⁱ	94.28 (5)	C8—C7—C6	122.8 (2)
N1—Cu1—Br1 ⁱ	91.84 (6)	N1—C5—C4	121.0 (2)
Br1—Cu1—Br1 ⁱ	92.955 (12)	N1—C5—C6	115.0 (2)
Br2—Cu1—Br1 ⁱ	107.004 (14)	C4—C5—C6	123.9 (2)
O2—Cu1—Cu2	39.84 (5)	C5—C4—C3	119.0 (2)
N1—Cu1—Cu2	103.54 (6)	C5—C4—H4	120.5
Br1—Cu1—Cu2	132.975 (15)	C3—C4—H4	120.5
Br2—Cu1—Cu2	52.757 (10)	C2—C3—C4	119.8 (2)
Br1 ⁱ —Cu1—Cu2	126.084 (13)	C2—C3—H3	120.1
O2—Cu2—N2	82.40 (8)	C4—C3—H3	120.1
O2—Cu2—Br3	172.22 (6)	N2—C11—C10	121.6 (3)
N2—Cu2—Br3	99.71 (6)	N2—C11—H11	119.2
O2—Cu2—Br2	81.30 (5)	C10—C11—H11	119.2
N2—Cu2—Br2	163.70 (6)	N1—C1—C2	122.2 (2)
Br3—Cu2—Br2	96.420 (15)	N1—C1—H1A	118.9
O2—Cu2—Cu1	40.15 (5)	C2—C1—H1A	118.9
N2—Cu2—Cu1	113.10 (6)	C9—C10—C11	119.0 (3)
Br3—Cu2—Cu1	142.336 (15)	C9—C10—H10	120.5
Br2—Cu2—Cu1	52.692 (10)	C11—C10—H10	120.5
C6—O2—Cu2	117.17 (15)	C10—C9—C8	119.3 (3)
C6—O2—Cu1	117.19 (14)	C10—C9—H9	120.3
Cu2—O2—Cu1	100.01 (8)	C8—C9—H9	120.3
C6—O1—H1	109.5	C3—C2—C1	118.3 (2)
C1—N1—C5	119.6 (2)	C3—C2—H2	120.8
C1—N1—Cu1	124.95 (18)	C1—C2—H2	120.8
C5—N1—Cu1	115.39 (17)	C9—C8—C7	119.2 (3)
O2—C6—O1	111.3 (2)	C9—C8—H8	120.4
O2—C6—C5	109.75 (19)	C7—C8—H8	120.4
O1—C6—C5	104.04 (19)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 ⁱⁱ —O2 ⁱⁱ	0.84	2.33	3.014 (2)	139

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Fig. 1

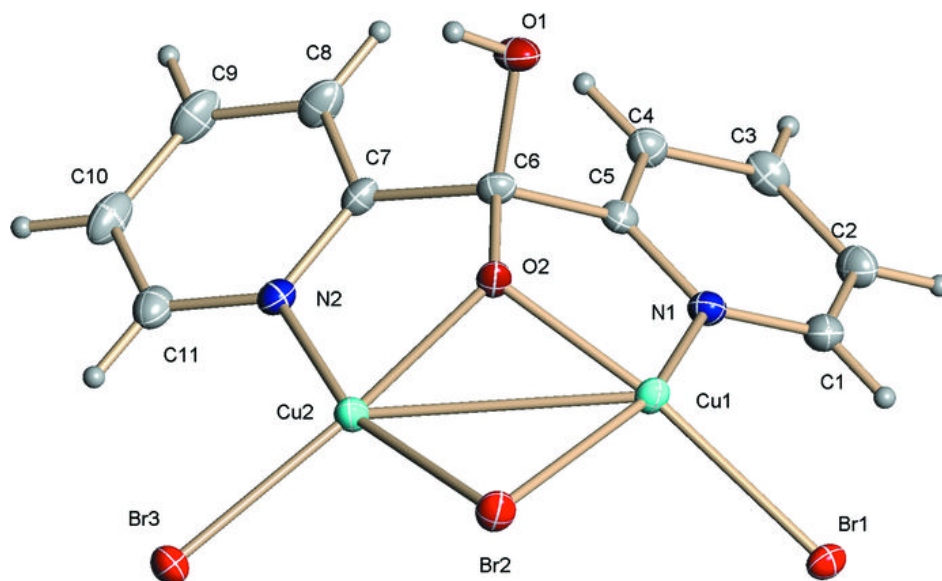


Fig. 2

