



IUCrData

ISSN 2414-3146

Received 10 June 2016

Accepted 24 June 2016

Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; copper(II); centrosymmetric dimer; dihydroxybipyridine.

CCDC reference: 1487651

Structural data: full structural data are available from iucrdata.iucr.org

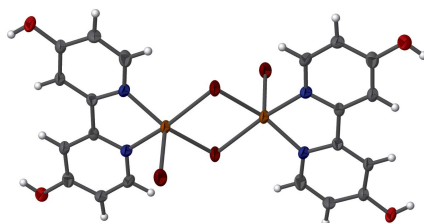
Di- μ -bromido-bis[bromido(4,4'-dihydroxy-2,2'-bipyridine- κ^2N,N')copper(II)]

Alan J Rodriguez-Santiago,* Carlos Acosta and Raphael G Raptis

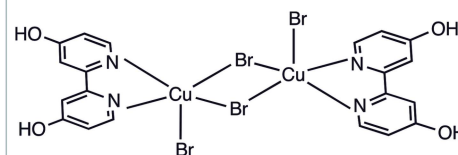
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The molecules of the title compound, $[\text{Cu}_2\text{Br}_4(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_2]$, are centrosymmetric dimers. The Cu^{II} atom exhibits a distorted square-pyramidal coordination geometry, with two bridging bromide ligands and the N atoms of the 4,4'-dihydroxy-2,2'-bipyridine chelate in the equatorial plane. π - π stacking and hydrogen-bonding interactions of the $\text{O}-\text{H}\cdots\text{Br}$, $\text{C}-\text{H}\cdots\text{Br}$ and $\text{C}-\text{H}\cdots\text{O}$ types consolidate the crystal packing.

3D view



Chemical scheme



Structure description

The synthesis of the title compound is a variation of the one reported by Yang *et al.* (2014), using the corresponding bipyridine derivative. The asymmetric unit contains one half-molecule which dimerizes and is related by an inversion center (Fig. 1). Each Cu^{II} atom is five-coordinated in a square-pyramidal coordination geometry, with the two N atoms of the 4,4'-dihydroxy-2,2'-bipyridine (DHBP) ligand and two bridging bromide ligands assuming equatorial positions and a terminal bromide ligand in the apical position. The $\text{Cu}-\text{Br}$ bond involving the apical bromide ligand is considerably longer [2.6462 (12) Å] than the $\text{Cu}-\text{Br}$ bonds to the bromide ligands in the equatorial positions [2.4458 (10) and 2.4647 (11) Å]. The crystal structure reveals π - π interactions between the pyridine rings of adjacent complex molecules, with a centroid-to-centroid distance of 3.57 Å, as well as hydrogen bonding between the hydroxy groups and the terminal bromide ligands. Additional $\text{C}-\text{H}\cdots\text{X}$ interactions ($\text{X} = \text{O}, \text{Br}$) are also found (Fig. 2 and Table 1).

Synthesis and crystallization

CuBr_2 (30 mg, 0.134 mmol) was dissolved in 10 ml of ethanol and the resulting solution added dropwise to a tetrahydrofuran solution (10 ml) containing 50 mg (0.266 mmol) of

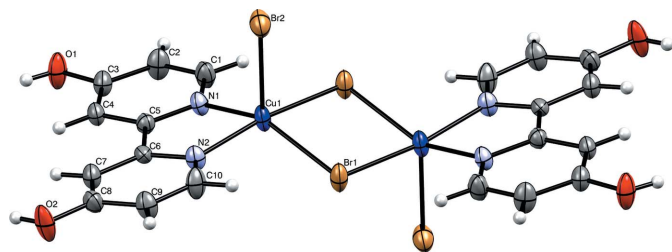


Figure 1

The structure of $[\text{Cu}_2(\mu\text{-Br})_2(\text{DHBP})_2(\text{Br})_2]$, showing displacement ellipsoids at the 50% probability level. All non-labeled atoms are generated by the symmetry code $(-x + 2, -y + 2, -z + 1)$.

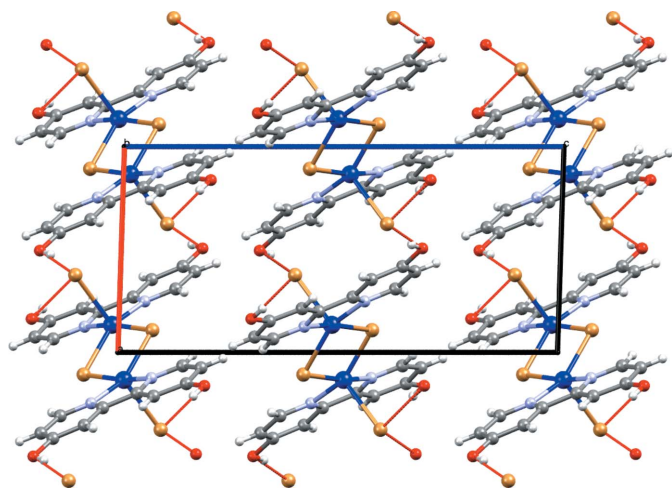


Figure 2

The crystal packing of $[\text{Cu}_2(\mu\text{-Br})_2(\text{DHBP})_2(\text{Br})_2]$, showing the $\text{O} \cdots \text{H} \cdots \text{Br}$ hydrogen bonding as red lines.

dihydroxybipyridine at room temperature. The mixture was stirred overnight to give a blue–green solution. Crystals were grown by layering the reaction solution over toluene.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

ARS was supported by NIH/NIGMS R25 GM061347. CA was supported by the Nuclear Regulatory Commission Scholarship grant NRC-HQ-13-G-38-0017 to FIU.

Table 1
Hydrogen-bond geometry ($\text{\AA}$, $^\circ$).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
$\text{C10}—\text{H10}\cdots\text{Br1}^{\text{i}}$	0.93	2.81	3.373 (7)	120
$\text{C2}—\text{H2A}\cdots\text{O1}^{\text{ii}}$	0.93	2.56	3.390 (9)	149
$\text{C4}—\text{H4}\cdots\text{Br1}^{\text{iii}}$	0.93	3.11	3.707 (7)	123
$\text{C1}—\text{H1A}\cdots\text{Br1}$	0.93	2.73	3.340 (7)	124
$\text{C7}—\text{H7}\cdots\text{Br2}^{\text{iii}}$	0.93	2.94	3.685 (7)	138
$\text{O1}—\text{H1}\cdots\text{Br2}^{\text{iv}}$	0.82	2.36	3.164 (5)	169
$\text{O2}—\text{H2}\cdots\text{Br2}^{\text{iii}}$	0.82	2.44	3.263 (5)	177

Symmetry codes: (i) $-x + 2, -y + 2, -z + 1$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, y - 1, z$; (iv) $-x + 1, -y + 1, -z + 1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{Cu}_2\text{Br}_4(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_2]$
M_r	823.09
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	300
a, b, c ($\text{\AA}$)	8.0636 (7), 8.4278 (7), 17.2516 (14)
β ($^\circ$)	91.820 (2)
V ($\text{\AA}^3$)	1171.80 (17)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	8.67
Crystal size (mm)	$0.25 \times 0.08 \times 0.03$
Data collection	
Diffractometer	Bruker D8 Quest CMOS
Absorption correction	Multi-scan (SADABS; Bruker, 2013)
$T_{\text{min}}, T_{\text{max}}$	0.53, 0.79
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	15036, 2414, 1936
R_{int}	0.047
$(\sin \theta/\lambda)_{\text{max}}$ ($\text{\AA}^{-1}$)	0.627
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.047, 0.106, 1.16
No. of reflections	2414
No. of parameters	156
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ($\text{e \AA}^{-3}$)	0.98, -0.76

Computer programs: APEX2 and SAINT (Bruker, 2013), SHELXT (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b), Mercury (Macrae *et al.*, 2008) and publCIF (Westrip, 2010).

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full crystallographic data

IUCrData (2016). **1**, x161029 [https://doi.org/10.1107/S2414314616010294]

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Crystal data

[Cu₂Br₄(C₁₀H₈N₂O₂)₂]

$M_r = 823.09$

Monoclinic, $P2_1/c$

$a = 8.0636$ (7) Å

$b = 8.4278$ (7) Å

$c = 17.2516$ (14) Å

$\beta = 91.820$ (2)°

$V = 1171.80$ (17) Å³

$Z = 2$

$F(000) = 788$

$D_x = 2.333$ Mg m⁻³

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

Cell parameters from 6190 reflections

$\theta = 3.4\text{--}26.3^\circ$

$\mu = 8.67$ mm⁻¹

$T = 300$ K

Plate, translucent light green-yellow

$0.25 \times 0.08 \times 0.03$ mm

Data collection

Bruker D8 Quest CMOS
diffractometer

Radiation source: fine-focus tube

Detector resolution: 10.4167 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2013)

$T_{\min} = 0.53$, $T_{\max} = 0.79$

15036 measured reflections

2414 independent reflections

1936 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

$\theta_{\max} = 26.5^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -10 \rightarrow 10$

$k = -10 \rightarrow 10$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.106$

$S = 1.16$

2414 reflections

156 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 10.5467P]$

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

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.98$ e Å⁻³

$\Delta\rho_{\min} = -0.76$ 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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.89203 (9)	1.04991 (8)	0.57654 (4)	0.0314 (2)
Br2	0.62406 (10)	0.95551 (9)	0.39730 (5)	0.0355 (2)
Cu1	0.86595 (11)	0.82989 (9)	0.48451 (5)	0.0256 (2)
O2	0.8375 (8)	0.2138 (6)	0.3009 (3)	0.0404 (14)
H2	0.7877	0.1466	0.3255	0.061*
O1	0.4946 (7)	0.3622 (6)	0.6850 (3)	0.0400 (14)
H1	0.4760	0.2804	0.6605	0.060*
N2	0.8753 (7)	0.6318 (6)	0.4220 (3)	0.0242 (12)
N1	0.7524 (7)	0.6839 (6)	0.5573 (3)	0.0235 (12)
C6	0.8010 (8)	0.5057 (7)	0.4538 (4)	0.0199 (13)
C5	0.7311 (8)	0.5351 (8)	0.5306 (4)	0.0216 (14)
C7	0.7873 (9)	0.3626 (8)	0.4157 (4)	0.0261 (15)
H7	0.7376	0.2764	0.4394	0.031*
C3	0.5822 (9)	0.4625 (8)	0.6417 (4)	0.0259 (15)
C9	0.9252 (9)	0.4769 (8)	0.3099 (4)	0.0300 (16)
H9	0.9697	0.4705	0.2609	0.036*
C1	0.6915 (9)	0.7206 (9)	0.6267 (4)	0.0329 (17)
H1A	0.7076	0.8225	0.6461	0.040*
C8	0.8481 (9)	0.3480 (8)	0.3422 (4)	0.0280 (16)
C4	0.6459 (8)	0.4215 (8)	0.5713 (4)	0.0235 (14)
H4	0.6319	0.3196	0.5515	0.028*
C2	0.6074 (10)	0.6141 (9)	0.6694 (4)	0.0334 (17)
H2A	0.5668	0.6434	0.7172	0.040*
C10	0.9346 (10)	0.6144 (9)	0.3518 (4)	0.0332 (17)
H10	0.9860	0.7013	0.3296	0.040*

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

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0407 (4)	0.0218 (3)	0.0324 (4)	−0.0124 (3)	0.0112 (3)	−0.0071 (3)
Br2	0.0416 (4)	0.0233 (4)	0.0411 (5)	−0.0050 (3)	−0.0056 (3)	0.0008 (3)
Cu1	0.0368 (5)	0.0152 (4)	0.0250 (4)	−0.0078 (4)	0.0065 (3)	−0.0020 (3)
O2	0.074 (4)	0.023 (3)	0.025 (3)	−0.011 (3)	0.018 (3)	−0.013 (2)
O1	0.060 (4)	0.031 (3)	0.030 (3)	−0.023 (3)	0.017 (3)	−0.003 (2)
N2	0.033 (3)	0.021 (3)	0.020 (3)	−0.004 (2)	0.007 (2)	−0.002 (2)
N1	0.031 (3)	0.017 (3)	0.023 (3)	−0.003 (2)	0.004 (2)	0.001 (2)
C6	0.018 (3)	0.015 (3)	0.026 (4)	0.001 (2)	0.000 (3)	−0.001 (3)
C5	0.023 (3)	0.019 (3)	0.023 (3)	−0.002 (3)	0.003 (3)	−0.003 (3)
C7	0.032 (4)	0.019 (3)	0.027 (4)	−0.006 (3)	0.003 (3)	−0.001 (3)
C3	0.031 (4)	0.021 (3)	0.026 (4)	−0.007 (3)	0.002 (3)	−0.001 (3)
C9	0.044 (4)	0.025 (4)	0.021 (4)	−0.005 (3)	0.007 (3)	−0.003 (3)
C1	0.038 (4)	0.024 (4)	0.037 (4)	−0.006 (3)	0.012 (3)	−0.010 (3)
C8	0.030 (4)	0.020 (3)	0.035 (4)	0.000 (3)	0.006 (3)	−0.006 (3)
C4	0.029 (4)	0.016 (3)	0.026 (4)	−0.004 (3)	0.002 (3)	−0.002 (3)
C2	0.046 (5)	0.033 (4)	0.021 (4)	−0.012 (3)	0.012 (3)	−0.006 (3)

C10	0.048 (5)	0.027 (4)	0.025 (4)	-0.013 (3)	0.008 (3)	0.003 (3)
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Geometric parameters (Å, °)

Br1—Cu1	2.4458 (10)	C6—C5	1.477 (9)
Br1—Cu1 ⁱ	2.4647 (11)	C5—C4	1.382 (9)
Br2—Cu1	2.6462 (12)	C7—C8	1.381 (10)
Cu1—N2	1.990 (5)	C7—H7	0.9300
Cu1—N1	2.001 (5)	C3—C2	1.376 (10)
Cu1—Br1 ⁱ	2.4647 (11)	C3—C4	1.379 (9)
O2—C8	1.338 (8)	C9—C10	1.367 (10)
O2—H2	0.8200	C9—C8	1.378 (10)
O1—C3	1.343 (8)	C9—H9	0.9300
O1—H1	0.8200	C1—C2	1.356 (10)
N2—C10	1.324 (9)	C1—H1A	0.9300
N2—C6	1.346 (8)	C4—H4	0.9300
N1—C1	1.344 (9)	C2—H2A	0.9300
N1—C5	1.345 (8)	C10—H10	0.9300
C6—C7	1.376 (9)		
Cu1—Br1—Cu1 ⁱ	95.00 (4)	C6—C7—C8	119.4 (6)
N2—Cu1—N1	81.4 (2)	C6—C7—H7	120.3
N2—Cu1—Br1	169.65 (17)	C8—C7—H7	120.3
N1—Cu1—Br1	95.19 (16)	O1—C3—C2	117.8 (6)
N2—Cu1—Br1 ⁱ	93.97 (16)	O1—C3—C4	123.3 (6)
N1—Cu1—Br1 ⁱ	154.89 (17)	C2—C3—C4	118.9 (6)
Br1—Cu1—Br1 ⁱ	85.00 (4)	C10—C9—C8	118.2 (6)
N2—Cu1—Br2	93.88 (17)	C10—C9—H9	120.9
N1—Cu1—Br2	105.01 (17)	C8—C9—H9	120.9
Br1—Cu1—Br2	96.45 (4)	N1—C1—C2	122.3 (7)
Br1 ⁱ —Cu1—Br2	99.90 (4)	N1—C1—H1A	118.8
C8—O2—H2	109.5	C2—C1—H1A	118.8
C3—O1—H1	109.5	O2—C8—C9	118.3 (6)
C10—N2—C6	117.6 (6)	O2—C8—C7	123.1 (6)
C10—N2—Cu1	127.5 (5)	C9—C8—C7	118.6 (6)
C6—N2—Cu1	114.7 (4)	C3—C4—C5	118.6 (6)
C1—N1—C5	118.2 (6)	C3—C4—H4	120.7
C1—N1—Cu1	127.2 (5)	C5—C4—H4	120.7
C5—N1—Cu1	114.5 (4)	C1—C2—C3	119.8 (7)
N2—C6—C7	121.9 (6)	C1—C2—H2A	120.1
N2—C6—C5	114.8 (5)	C3—C2—H2A	120.1
C7—C6—C5	123.3 (6)	N2—C10—C9	124.2 (7)
N1—C5—C4	122.1 (6)	N2—C10—H10	117.9
N1—C5—C6	114.6 (6)	C9—C10—H10	117.9
C4—C5—C6	123.3 (6)		

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

Hydrogen-bond geometry (Å, °)

<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>
C10—H10 $\cdots$ Br1 ⁱ	0.93	2.81	3.373 (7)	120
C2—H2A $\cdots$ O1 ⁱⁱ	0.93	2.56	3.390 (9)	149
C4—H4 $\cdots$ Br1 ⁱⁱⁱ	0.93	3.11	3.707 (7)	123
C1—H1A $\cdots$ Br1	0.93	2.73	3.340 (7)	124
C7—H7 $\cdots$ Br2 ⁱⁱⁱ	0.93	2.94	3.685 (7)	138
O1—H1 $\cdots$ Br2 ^{iv}	0.82	2.36	3.164 (5)	169
O2—H2 $\cdots$ Br2 ⁱⁱⁱ	0.82	2.44	3.263 (5)	177

Symmetry codes: (i) $-x+2, -y+2, -z+1$; (ii) $-x+1, y+1/2, -z+3/2$; (iii) $x, y-1, z$; (iv) $-x+1, -y+1, -z+1$.