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Di-μ-bromido-bis[bromido(4,4′-dihydroxy-2,2′-bipyridine-κ2N,N′)copper(II)]

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IUCrData

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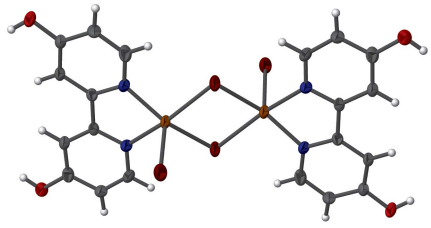
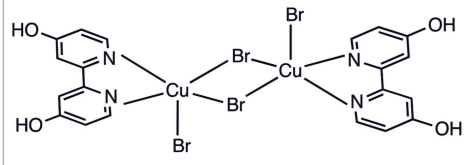
Structural data: full structural data are available from iucrdata.iucr.org

The molecules of the title compound, $[Cu_2Br_4(C_{10}H_8N_2O_2)_2]$, 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 O—H···Br, C—H···Br and C—H···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 Cu—Br bond involving the apical bromide ligand is considerably longer [2.6462 (12) Å] than the Cu—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 C—H···X interactions (X = O, 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

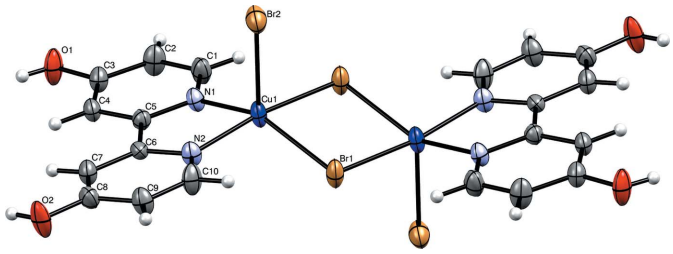


Figure 1
The structure of $[Cu_2(\mu\text{-}Br)_2(DHBP)_2(Br)_2]$, showing displacement ellipsoids at the 50% probability level. All non-labeled atoms are generated by the symmetry code $(-x+2, -y+2, -z+1)$.

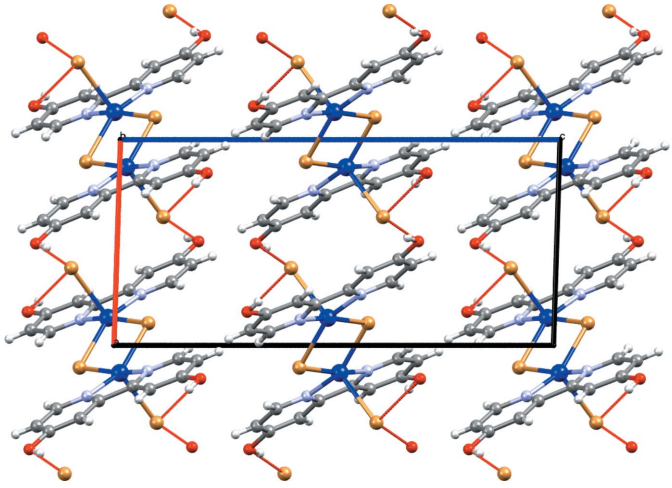


Figure 2
The crystal packing of $[Cu_2(\mu\text{-}Br)_2(DHBP)_2(Br)_2]$, showing the O—H···Br hydrogen bonding as red lines.

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

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

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10···Br1^{i}	0.93	2.81	3.373 (7)	120
C2—H2A···O1^{ii}	0.93	2.56	3.390 (9)	149
C4—H4···Br1^{iii}	0.93	3.11	3.707 (7)	123
C1—H1A···Br1	0.93	2.73	3.340 (7)	124
C7—H7···Br2^{iii}	0.93	2.94	3.685 (7)	138
O1—H1···Br2^{iv}	0.82	2.36	3.164 (5)	169
O2—H2···Br2^{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	$[Cu_2Br_4(C_{10}H_8N_2O_2)_2]$
M_r	823.09
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	300
a, b, c (Å)	8.0636 (7), 8.4278 (7), 17.2516 (14)
β (°)	91.820 (2)
V (Å^3)	1171.80 (17)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	8.67
Crystal size (mm)	0.25 × 0.08 × 0.03
Data collection	
Diffractometer	Bruker D8 Quest CMOS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.53, 0.79
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	15036, 2414, 1936
R_{int}	0.047
$(\sin\theta/\lambda)_{max}$ (Å^{-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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.98, −0.76

Computer programs: *APEX2* and*SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *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

$[Cu_2Br_4(C_{10}H_8N_2O_2)_2]$
M_r = 823.09
Monoclinic, $P2_1/c$
a = 8.0636 (7) Å
b = 8.4278 (7) Å
c = 17.2516 (14) Å
β = 91.820 (2)°
V = 1171.80 (17) Å^3
Z = 2
$F(000)$ = 788
D_x = 2.333 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6190 reflections
θ = 3.4–26.3°
μ = 8.67 mm^{-1}
T = 300 K
Plate, translucent light green-yellow
0.25 × 0.08 × 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_{int} = 0.047
θ_{max} = 26.5°, θ_{min} = 3.4°
h = −10→10
k = −10→10
l = −21→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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{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 (Å²)

	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)

Geometric parameters (Å, º)

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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···Br1^{i}	0.93	2.81	3.373 (7)	120
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