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Bis(4-hydroxybenzoato-$\kappa^2 O,O'$)bis(pyridine-κN)copper(II)

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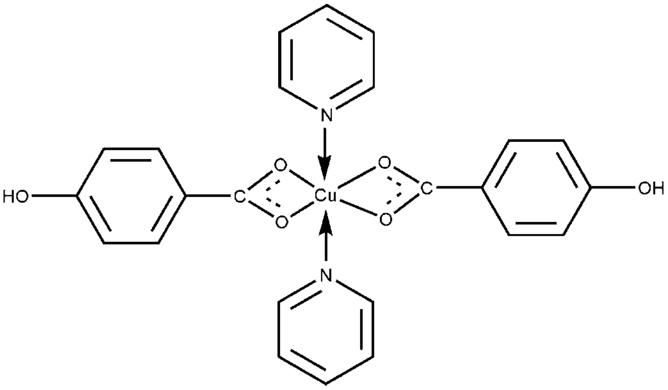
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.026; wR factor = 0.066; data-to-parameter ratio = 16.1.

In the title compound, $[Cu(C_7H_5O_3)_2(C_5H_5N)_2]$, the Cu atom is located on an inversion center and is coordinated by the N atoms of the two pyridine ligands, *trans* to each other, and to the carboxylate O atoms of two bidentate 4-hydroxybenzoate ligands [Cu—O = 1.9706 (10) and 2.5204 (11) Å]. Hydrogen bonding between hydroxy H and carboxylate O atoms results in a layer structure parallel to the *ab* plane.

Related literature

For the structure of bis(p-hydroxybenzoate)dipicoline–copper(II), see: Sharma *et al.* (2009).



Experimental

Crystal data

$[Cu(C_7H_5O_3)_2(C_5H_5N)_2]$
M_r = 495.96
Monoclinic, $P2_1/c$
a = 10.6715 (2) Å
b = 8.5385 (1) Å
c = 12.3988 (2) Å
β = 109.124 (1)°
V = 1067.41 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.07 mm^{-1}
T = 100 K
0.30 × 0.26 × 0.20 mm

Data collection

Bruker SMART APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.663, T_{max} = 0.746
9756 measured reflections
2448 independent reflections
2202 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.066
S = 1.06
2448 reflections
152 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$A\cdots$O2^i	0.84	1.87	2.7028 (16)	171

Symmetry code: (i) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2435).

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supplementary materials

Acta Cryst. (2011). E**67**, m952   [**doi:10.1107/S1600536811023038**]

Bis(4-hydroxybenzoato-κ^2*O*,*O*')bis(pyridine-κ*N*)copper(II)

L. N. Ozair, **N. Abdullah** and **K. M. Lo**

Comment

The copper atom in the title complex is located on an inversion center and adopts a distorted octahedral geometry, with the oxygen atoms of the carboxylic groups occupying the equatorial positions (Fig. 1). The axial Cu—N bond distance of 2.0076 (13) Å is comparable with that of bis(*p*-hydroxybenzoate)dipicoline-copper(II) which is 1.987 (2) Å (Sharma *et al.*, 2009). The 4-hydroxybenzoate group acts as a bidentate ligand with Cu—O bond distances of 1.9706 (10) and 2.5204 (11) Å. The dipicoline-copper(II) complex differs from the title complex in that the two picoline ligands are *cis* to each other (N—Cu—N 91.50 (10)^o) whereas the two pyridine ligands in the title complex are *trans* to each other. The distortion from ideal octahedral geometry for the title compound is mainly due to the small bite angle (57.60 (4)°) formed by the bidentate carboxylate moiety. In the crystal structure, intermolecular O—H···O hydrogen bonds link the molecules into layers parallel to the *ab* plane (Fig. 2). The π-π contacts between the pyridine rings, *Cg*1-*Cg*1' [symmetry code: 2 - *x*, 1 - *y*, 2 - *z*, where *Cg*1 is the centroid of the ring (N1, C8—C12)] may further stabilize the overall structure, with centroid-centroid distance of 3.7878 (10) Å.

Experimental

p-Hydroxybenzoic acid (0.35 g, 2.5 mmol) was dissolved in 100 ml of ethanol. While stirring and gently heating the solution, copper(II) acetate monohydrate (0.26 g, 1.3 mmol) was added portionwise. This was followed by 0.5 ml of pyridine and the mixture was heated for 30 minutes. The solution mixture was then filtered and upon cooling of the filtrate gave the title compound as a dark green crystalline solid.

Refinement

Hydrogen atoms were placed at calculated positions (C–H 0.95 Å) and were treated as riding on their parent carbon atoms, with *U*(H) set to 1.2–1.5 times *U*\~eq\~(C). The hydroxy-H was refined with a restraint of 0.84 ± 0.01 Å.

Figures

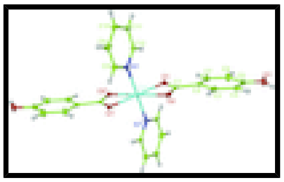

Fig. 1. The molecular structure of bis(4-hydroxybenzoato-*O*, *O*')dipyridylcopper(II), showing 50% probability displacement ellipsoids and the atom numbering. Hydrogen atoms are drawn as spheres of arbitrary radius. (Symmetry code (i): -*x* + 2, -*y*, -*z* + 2).

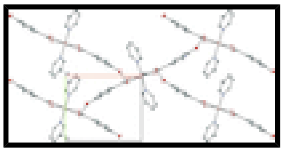

Fig. 2. A view down the *c*-axis of the crystal packing of the title compound. Hydrogen atoms have been omitted for clarity and the O—H···O hydrogen bonds are shown as red dotted lines.

Bis(4-hydroxybenzoato-κ^2*O*,*O*')bis(pyridine-κ*N*)copper(II)

Crystal data

$[Cu(C_7H_5O_3)_2(C_5H_5N)_2]$

$M_r = 495.96$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 10.6715$ (2) Å

$b = 8.5385$ (1) Å

$c = 12.3988$ (2) Å

$\beta = 109.124$ (1)°

$V = 1067.41$ (3) Å^3

$Z = 2$

$F(000) = 510$

$D_x = 1.543$ Mg m^{-3}

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

Cell parameters from 4633 reflections

$\theta = 3.0$–28.2°

$\mu = 1.07$ mm^{-1}

$T = 100$ K

Block, dark green

0.30 × 0.26 × 0.20 mm

Data collection

Bruker SMART APEXII diffractometer

Radiation source: fine-focus sealed tube

graphite

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)

$T_{min} = 0.663$, $T_{max} = 0.746$

9756 measured reflections

2448 independent reflections

2202 reflections with $I > 2\sigma(I)$

$R_{int} = 0.023$

$\theta_{max} = 27.5°$, $\theta_{min} = 2.0°$

$h = -13 \rightarrow 13$

$k = -11 \rightarrow 11$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.066$

$S = 1.06$

2448 reflections

152 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 0.7197P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.38$ e Å^{-3}

$\Delta\rho_{min} = -0.32$ e Å^{-3}

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}
Cu1	1.0000	0.0000	1.0000	0.01147 (8)
O1	0.82299 (10)	0.04277 (13)	1.01071 (9)	0.0143 (2)
O2	0.81152 (11)	0.10333 (13)	0.83387 (9)	0.0162 (2)
O3	0.28650 (12)	0.42997 (16)	0.85782 (10)	0.0258 (3)
H3A	0.2618	0.4788	0.7956	0.039*
N1	1.05579 (12)	0.21481 (15)	1.06344 (11)	0.0139 (3)
C1	0.76211 (15)	0.10384 (17)	0.91341 (13)	0.0138 (3)
C2	0.63226 (15)	0.18074 (17)	0.89663 (13)	0.0152 (3)
C3	0.56256 (16)	0.24646 (19)	0.79114 (14)	0.0181 (3)
H3	0.5956	0.2350	0.7291	0.022*
C4	0.44571 (16)	0.32832 (19)	0.77537 (14)	0.0191 (3)
H4	0.3985	0.3717	0.7028	0.023*
C5	0.39815 (16)	0.3465 (2)	0.86627 (14)	0.0193 (3)
C6	0.46532 (18)	0.2783 (2)	0.97123 (15)	0.0270 (4)
H6	0.4314	0.2881	1.0328	0.032*
C7	0.58159 (17)	0.1960 (2)	0.98591 (14)	0.0232 (4)
H7	0.6271	0.1496	1.0577	0.028*
C8	1.01481 (17)	0.27077 (19)	1.14781 (14)	0.0188 (3)
H8	0.9540	0.2105	1.1719	0.023*
C9	1.05787 (19)	0.4126 (2)	1.20074 (15)	0.0242 (4)
H9	1.0285	0.4478	1.2611	0.029*
C10	1.14449 (18)	0.50256 (19)	1.16446 (15)	0.0226 (3)
H10	1.1758	0.6003	1.1996	0.027*
C11	1.18455 (16)	0.4474 (2)	1.07611 (15)	0.0205 (3)
H11	1.2425	0.5076	1.0485	0.025*
C12	1.13899 (15)	0.30311 (18)	1.02847 (14)	0.0170 (3)
H12	1.1678	0.2651	0.9685	0.020*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01118 (13)	0.00913 (13)	0.01483 (14)	−0.00004 (9)	0.00523 (9)	−0.00102 (10)
O1	0.0129 (5)	0.0132 (5)	0.0172 (5)	0.0019 (4)	0.0054 (4)	0.0005 (4)
O2	0.0161 (5)	0.0159 (5)	0.0175 (5)	−0.0010 (4)	0.0066 (4)	−0.0009 (4)
O3	0.0220 (6)	0.0344 (7)	0.0245 (6)	0.0126 (5)	0.0124 (5)	0.0100 (5)
N1	0.0142 (6)	0.0115 (6)	0.0158 (6)	0.0012 (5)	0.0045 (5)	0.0001 (5)
C1	0.0132 (7)	0.0085 (6)	0.0193 (7)	−0.0027 (5)	0.0047 (6)	−0.0019 (6)

C2	0.0128 (7)	0.0117 (7)	0.0200 (8)	−0.0013 (6)	0.0039 (6)	−0.0020 (6)
C3	0.0199 (8)	0.0170 (7)	0.0186 (8)	0.0011 (6)	0.0080 (6)	−0.0001 (6)
C4	0.0204 (8)	0.0188 (8)	0.0173 (7)	0.0026 (6)	0.0050 (6)	0.0027 (6)
C5	0.0140 (7)	0.0208 (8)	0.0237 (8)	0.0024 (6)	0.0070 (6)	0.0037 (7)
C6	0.0255 (9)	0.0378 (11)	0.0227 (9)	0.0111 (8)	0.0148 (7)	0.0085 (8)
C7	0.0207 (8)	0.0299 (9)	0.0197 (8)	0.0066 (7)	0.0076 (6)	0.0075 (7)
C8	0.0265 (8)	0.0140 (7)	0.0199 (8)	−0.0026 (6)	0.0130 (7)	−0.0004 (6)
C9	0.0374 (10)	0.0175 (8)	0.0222 (8)	−0.0034 (7)	0.0160 (7)	−0.0052 (7)
C10	0.0292 (9)	0.0139 (7)	0.0251 (8)	−0.0052 (7)	0.0094 (7)	−0.0049 (7)
C11	0.0202 (8)	0.0151 (7)	0.0281 (9)	−0.0039 (6)	0.0107 (7)	−0.0009 (7)
C12	0.0169 (7)	0.0151 (7)	0.0210 (8)	−0.0003 (6)	0.0089 (6)	−0.0016 (6)

Geometric parameters (Å, °)

Cu1—O1	1.9706 (10)	C4—H4	0.9500
Cu1—N1	2.0076 (13)	C5—C6	1.391 (2)
Cu1—O2	2.5204 (11)	C6—C7	1.385 (2)
O1—C1	1.2790 (19)	C6—H6	0.9500
O2—C1	1.2614 (18)	C7—H7	0.9500
O3—C5	1.3624 (19)	C8—C9	1.382 (2)
O3—H3A	0.8400	C8—H8	0.9500
N1—C12	1.340 (2)	C9—C10	1.386 (2)
N1—C8	1.347 (2)	C9—H9	0.9500
C1—C2	1.485 (2)	C10—C11	1.383 (2)
C2—C7	1.388 (2)	C10—H10	0.9500
C2—C3	1.393 (2)	C11—C12	1.384 (2)
C3—C4	1.386 (2)	C11—H11	0.9500
C3—H3	0.9500	C12—H12	0.9500
C4—C5	1.388 (2)		
O1—Cu1—O1^{i}	180.0	C5—C4—H4	120.2
O1—Cu1—N1^{i}	91.60 (5)	O3—C5—C4	122.64 (15)
O1—Cu1—N1	88.40 (5)	O3—C5—C6	117.43 (15)
O1^{i}—Cu1—N1	91.60 (5)	C4—C5—C6	119.94 (15)
N1^{i}—Cu1—N1	180.0	C7—C6—C5	120.02 (15)
O1—Cu1—O2	57.60 (4)	C7—C6—H6	120.0
O1^{i}—Cu1—O2	122.40 (4)	C5—C6—H6	120.0
N1^{i}—Cu1—O2	86.83 (4)	C6—C7—C2	120.61 (15)
N1—Cu1—O2	93.17 (4)	C6—C7—H7	119.7
C1—O1—Cu1	102.35 (9)	C2—C7—H7	119.7
C1—O2—Cu1	77.78 (8)	N1—C8—C9	122.52 (15)
C5—O3—H3A	109.5	N1—C8—H8	118.7
C12—N1—C8	118.01 (13)	C9—C8—H8	118.7
C12—N1—Cu1	122.01 (10)	C8—C9—C10	119.02 (15)
C8—N1—Cu1	119.89 (10)	C8—C9—H9	120.5
O2—C1—O1	121.52 (14)	C10—C9—H9	120.5
O2—C1—C2	120.11 (14)	C11—C10—C9	118.72 (15)
O1—C1—C2	118.34 (13)	C11—C10—H10	120.6
C7—C2—C3	118.88 (14)	C9—C10—H10	120.6

C7—C2—C1	121.28 (14)	C10—C11—C12	119.01 (15)
C3—C2—C1	119.75 (14)	C10—C11—H11	120.5
C4—C3—C2	120.95 (15)	C12—C11—H11	120.5
C4—C3—H3	119.5	N1—C12—C11	122.69 (15)
C2—C3—H3	119.5	N1—C12—H12	118.7
C3—C4—C5	119.55 (15)	C11—C12—H12	118.7
C3—C4—H4	120.2		

O1^{i}—Cu1—O1—C1	−98 (46)	O1—C1—C2—C7	4.3 (2)
N1^{i}—Cu1—O1—C1	−90.19 (9)	O2—C1—C2—C3	2.7 (2)
N1—Cu1—O1—C1	89.81 (9)	O1—C1—C2—C3	−179.10 (14)
O2—Cu1—O1—C1	−4.95 (8)	C7—C2—C3—C4	1.1 (2)
O1—Cu1—O2—C1	5.02 (8)	C1—C2—C3—C4	−175.51 (14)
O1^{i}—Cu1—O2—C1	−174.98 (8)	C2—C3—C4—C5	0.7 (2)
N1^{i}—Cu1—O2—C1	98.93 (9)	C3—C4—C5—O3	177.74 (15)
N1—Cu1—O2—C1	−81.07 (9)	C3—C4—C5—C6	−2.2 (3)
O1—Cu1—N1—C12	−143.73 (12)	O3—C5—C6—C7	−178.07 (17)
O1^{i}—Cu1—N1—C12	36.27 (12)	C4—C5—C6—C7	1.9 (3)
N1^{i}—Cu1—N1—C12	0(100)	C5—C6—C7—C2	0.0 (3)
O2—Cu1—N1—C12	−86.30 (12)	C3—C2—C7—C6	−1.5 (3)
O1—Cu1—N1—C8	39.72 (12)	C1—C2—C7—C6	175.12 (17)
O1^{i}—Cu1—N1—C8	−140.28 (12)	C12—N1—C8—C9	−1.7 (2)
N1^{i}—Cu1—N1—C8	0(95)	Cu1—N1—C8—C9	175.01 (13)
O2—Cu1—N1—C8	97.15 (12)	N1—C8—C9—C10	1.3 (3)
Cu1—O2—C1—O1	−7.68 (13)	C8—C9—C10—C11	0.2 (3)
Cu1—O2—C1—C2	170.43 (13)	C9—C10—C11—C12	−1.2 (3)
Cu1—O1—C1—O2	9.84 (16)	C8—N1—C12—C11	0.6 (2)
Cu1—O1—C1—C2	−168.30 (11)	Cu1—N1—C12—C11	−176.06 (12)
O2—C1—C2—C7	−173.84 (15)	C10—C11—C12—N1	0.9 (3)

Symmetry codes: (i) −*x*+2, −*y*, −*z*+2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3A···O2^{ii}	0.84	1.87	2.7028 (16)	171

Symmetry codes: (ii) −*x*+1, *y*+1/2, −*z*+3/2.

Fig. 1

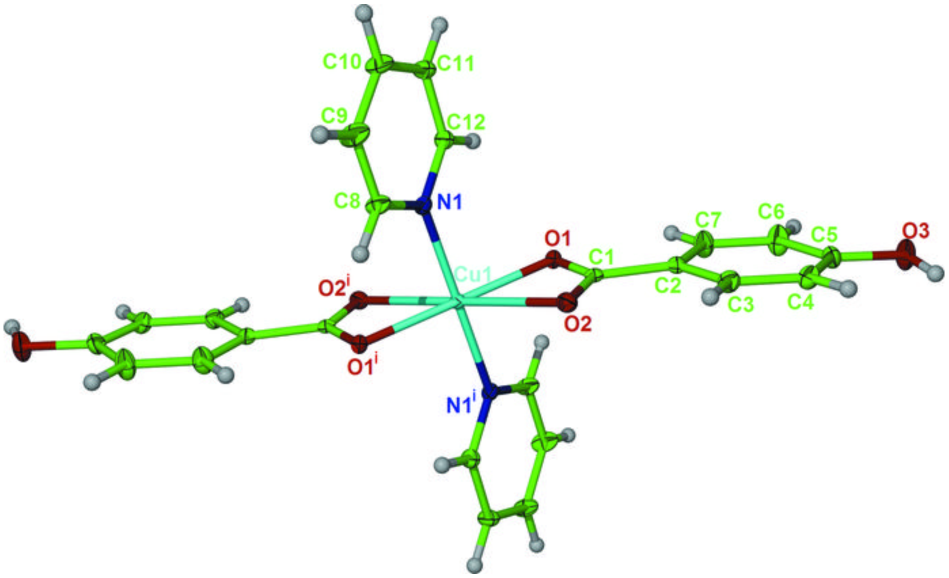

Fig. 2