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Bis(2,4-dibromo-6-formylphenolato- κ^2O,O')copper(II)

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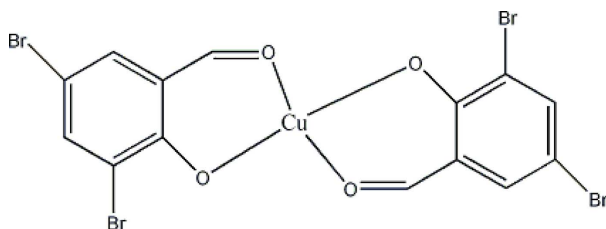
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(C-C) = 0.006$ Å; R factor = 0.028; wR factor = 0.068; data-to-parameter ratio = 13.4.

In the title compound, $[Cu(C_7H_3Br_2O_2)_2]$, the Cu^{II} atom, which lies on an inversion centre, is coordinated by four O atoms from two chelating bidentate 2,4-dibromo-6-formylphenolate ligands in a slightly distorted square-planar coordination geometry. In the crystal structure, short intermolecular $Br \cdots Br$ [3.516 (4) and 3.653 (4) Å] and $Cu \cdots Br$ [3.255 (1) Å] contacts together with $C-H \cdots O$ hydrogen bonds generate a three-dimensional network.

Related literature

The presence of halo substituents on aromatic compounds frequently results in stacking arrangements with a short (*ca* 4 Å) crystallographic axis (Cohen *et al.*, 1964; Zordan *et al.*, 2005; Zaman *et al.*, 2004; Zhang *et al.*, 2007).



Experimental

Crystal data

 $[Cu(C_7H_3Br_2O_2)_2]$ $M_r = 621.37$ Orthorhombic, *Pbca* $a = 8.2625$ (12) Å $b = 12.8216$ (14) Å $c = 15.229$ (2) Å $V = 1613.3$ (4) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 11.28$ mm⁻¹ $T = 298$ (2) K $0.58 \times 0.18 \times 0.14$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer

Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002) $T_{\min} = 0.059$, $T_{\max} = 0.301$
(expected range = 0.040–0.206)
6267 measured reflections1418 independent reflections
1049 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.028$ $wR(F^2) = 0.069$ $S = 1.02$

1418 reflections

106 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.64$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O2	1.892 (3)	Cu1—O1	1.959 (3)
O2—Cu1—O2 ⁱ	180	O2—Cu1—O1	92.91 (12)
O2—Cu1—O1 ⁱ	87.09 (12)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C7-H7 \cdots O1^{ii}$	0.93	2.54	3.475 (5)	178

Symmetry code: (ii) $-x - 1, y + \frac{5}{2}, -z + \frac{1}{2}$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2447).

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supplementary materials

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Bis(2,4-dibromo-6-formylphenolato- κ^2O,O')copper(II)

G. Z. Li, S. H. Zhang and Z. Liu

Comment

The packing arrangements of halogenated compounds, which Schmidt called the 'chloro effect', have been studied for many years. The presence of chloro substituents on aromatic compounds frequently results in stacking arrangements with a short (*ca* 4 Å) crystallographic axis (Cohen *et al.*, 1964; Zordan *et al.*, 2005; Zaman *et al.*, 2004; Zhang *et al.*, 2007). The title compound, (I), Fig. 1, contains the dibromo ligand 2,4-dibromo-6-formylphenolate with two Br atoms accessible at the periphery of each ligand.

In (I), the Cu^{II} atom is coordinated by four O atoms from two chelating, bidentate 3,5-2,4-dibromo-6-formylphenolate ligands, in a slightly distorted square planar geometry (Table 1). A weak Cu1 \cdots Br1ⁱ, 3.255 (1) Å contact (*i* = 1 + *x*, *y*, *z*) occurs in the axial coordination position with respect the coordination plane of the molecule. In addition there are short Br1ⁱⁱ–Br2ⁱⁱⁱ 3.516 (4) Å and Br1ⁱⁱ–Br2^{iv} 3.653 (4) Å [symmetry codes: ii = *x*, 1/2 - *y*, -1/2 + *z*; iii = -*x*, 1 - *y*, -*z*; iv = -1/2 - *x*, 1 - *y*, -1/2 + *z*] contacts. In the crystal structure these intermolecular Br \cdots Br and Cu \cdots Br contacts together with C7—H7 \cdots O1 hydrogen bonds generate a three-dimensional network (Fig. 2).

Experimental

An ethanol solution (30 ml) containing 3,5-dibromo-2-hydroxy-benzaldehyde (0.382 g, 2 mmol) was added to an aqueous solution containing amino-methanesulfonic acid(0.222 g, 2 mmol) and sodium hydroxide (0.080 g, 2 mmol). After stirring for 1 h, an aqueous solution of copper chloride (0.396 g, 2 mmol) was added to the resulting solution and stirred for 2 h. The green mixture solution was filtered. After 10 days, green block-like crystals of (I) were obtained by slow evaporation of the filtrate (yield: 49.2%, based on Cu).

Refinement

All H atoms bound to C atoms were positioned geometrically and refined as riding atoms, with C–H distances of 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Figures

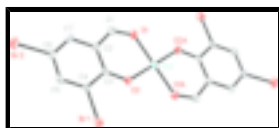


Fig. 1. A view of (I), showing 30% probability displacement ellipsoids. Atoms labelled A are related to other atoms by the symmetry operation $-x + 1, -y + 2, -z$.

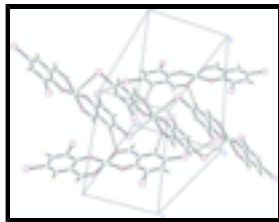


Fig. 2. Part of the packing of (I) showing the three-dimensional network; broken lines indicate short Br...Br and M...Br contacts and C-H...O hydrogen bonds.

Bis(2,4-dibromo-6-formylphenolato- $\kappa^2 O, O'$)copper(II)

Crystal data

[Cu(C₇H₃Br₂O₂)₂]

$M_r = 621.37$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 8.2625$ (12) Å

$b = 12.8216$ (14) Å

$c = 15.229$ (2) Å

$V = 1613.3$ (4) Å³

$Z = 4$

$F_{000} = 1164$

$D_x = 2.558$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2295 reflections

$\theta = 2.7$ – 26.8°

$\mu = 11.28$ mm⁻¹

$T = 298$ (2) K

Block, green

$0.58 \times 0.18 \times 0.14$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298$ (2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2002)

$T_{\min} = 0.059$, $T_{\max} = 0.301$

6267 measured reflections

1418 independent reflections

1049 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$

$\theta_{\text{max}} = 25.0^\circ$

$\theta_{\text{min}} = 2.7^\circ$

$h = -9 \rightarrow 9$

$k = -15 \rightarrow 14$

$l = -10 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.069$

$S = 1.02$

1418 reflections

106 parameters

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2]$

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

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

$\Delta\rho_{\text{max}} = 0.64$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.40$ e Å⁻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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	1.0000	0.0000	0.0343 (2)
O1	0.3788 (4)	1.1291 (2)	-0.0202 (2)	0.0401 (9)
O2	0.3351 (3)	0.9426 (2)	0.0713 (2)	0.0353 (8)
Br1	0.15473 (6)	0.79703 (4)	0.19008 (4)	0.04386 (18)
Br2	-0.32171 (5)	1.11175 (5)	0.16575 (4)	0.04679 (19)
C1	0.2415 (6)	1.1486 (3)	0.0101 (3)	0.0387 (12)
H1	0.1983	1.2133	-0.0044	0.046*
C2	0.1438 (5)	1.0839 (3)	0.0638 (3)	0.0290 (11)
C3	0.1976 (5)	0.9837 (3)	0.0916 (3)	0.0259 (11)
C4	0.0877 (5)	0.9270 (3)	0.1451 (3)	0.0277 (11)
C5	-0.0614 (5)	0.9652 (4)	0.1676 (3)	0.0323 (12)
H5	-0.1302	0.9262	0.2031	0.039*
C6	-0.1097 (5)	1.0627 (4)	0.1372 (3)	0.0318 (11)
C7	-0.0094 (5)	1.1223 (3)	0.0878 (3)	0.0301 (11)
H7	-0.0418	1.1884	0.0698	0.036*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0233 (4)	0.0325 (5)	0.0469 (6)	-0.0004 (4)	0.0076 (4)	0.0068 (4)
O1	0.0293 (18)	0.0369 (19)	0.054 (2)	0.0031 (15)	0.0131 (16)	0.0149 (17)
O2	0.0215 (16)	0.0349 (18)	0.049 (2)	0.0036 (14)	0.0069 (16)	0.0080 (16)
Br1	0.0395 (3)	0.0338 (3)	0.0583 (4)	-0.0038 (2)	0.0016 (3)	0.0118 (3)
Br2	0.0286 (3)	0.0583 (4)	0.0534 (4)	0.0058 (3)	0.0100 (2)	-0.0060 (3)
C1	0.033 (3)	0.033 (3)	0.050 (3)	0.001 (2)	-0.001 (3)	0.010 (3)
C2	0.025 (2)	0.032 (3)	0.030 (3)	-0.004 (2)	0.003 (2)	0.000 (2)
C3	0.023 (2)	0.027 (3)	0.028 (3)	-0.0062 (19)	-0.003 (2)	0.000 (2)
C4	0.025 (2)	0.027 (2)	0.030 (3)	-0.006 (2)	-0.006 (2)	0.002 (2)
C5	0.029 (3)	0.037 (3)	0.031 (3)	-0.010 (2)	0.007 (2)	-0.001 (2)
C6	0.021 (2)	0.039 (3)	0.035 (3)	0.000 (2)	0.003 (2)	-0.005 (2)
C7	0.026 (2)	0.030 (3)	0.035 (3)	0.005 (2)	0.000 (2)	-0.001 (2)

supplementary materials

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

Cu1—O2	1.892 (3)	C1—H1	0.9300
Cu1—O2 ⁱ	1.892 (3)	C2—C7	1.407 (5)
Cu1—O1 ⁱ	1.959 (3)	C2—C3	1.424 (6)
Cu1—O1	1.959 (3)	C3—C4	1.420 (6)
O1—C1	1.249 (5)	C4—C5	1.370 (6)
O2—C3	1.290 (5)	C5—C6	1.391 (6)
Br1—C4	1.885 (4)	C5—H5	0.9300
Br2—C6	1.912 (4)	C6—C7	1.355 (6)
C1—C2	1.418 (6)	C7—H7	0.9300
O2—Cu1—O2 ⁱ	180.0	O2—C3—C2	124.9 (4)
O2—Cu1—O1 ⁱ	87.09 (12)	C4—C3—C2	115.6 (4)
O2 ⁱ —Cu1—O1 ⁱ	92.91 (12)	C5—C4—C3	122.4 (4)
O2—Cu1—O1	92.91 (12)	C5—C4—Br1	119.3 (3)
O2 ⁱ —Cu1—O1	87.09 (12)	C3—C4—Br1	118.2 (3)
O1 ⁱ —Cu1—O1	180.000 (1)	C4—C5—C6	119.7 (4)
C1—O1—Cu1	125.1 (3)	C4—C5—H5	120.1
C3—O2—Cu1	127.8 (3)	C6—C5—H5	120.1
O1—C1—C2	127.8 (4)	C7—C6—C5	121.1 (4)
O1—C1—H1	116.1	C7—C6—Br2	120.1 (3)
C2—C1—H1	116.1	C5—C6—Br2	118.9 (3)
C7—C2—C1	117.3 (4)	C6—C7—C2	119.8 (4)
C7—C2—C3	121.3 (4)	C6—C7—H7	120.1
C1—C2—C3	121.4 (4)	C2—C7—H7	120.1
O2—C3—C4	119.5 (4)		
O2—Cu1—O1—C1	-0.4 (4)	C1—C2—C3—C4	-179.9 (4)
O2 ⁱ —Cu1—O1—C1	179.6 (4)	O2—C3—C4—C5	-178.7 (4)
O1 ⁱ —Cu1—O1—C1	125 (100)	C2—C3—C4—C5	0.8 (6)
O2 ⁱ —Cu1—O2—C3	-37.4 (17)	O2—C3—C4—Br1	4.0 (6)
O1 ⁱ —Cu1—O2—C3	-179.0 (4)	C2—C3—C4—Br1	-176.5 (3)
O1—Cu1—O2—C3	1.0 (4)	C3—C4—C5—C6	0.4 (7)
Cu1—O1—C1—C2	-0.5 (7)	Br1—C4—C5—C6	177.8 (4)
O1—C1—C2—C7	-178.3 (4)	C4—C5—C6—C7	-2.1 (7)
O1—C1—C2—C3	1.1 (8)	C4—C5—C6—Br2	177.5 (3)
Cu1—O2—C3—C4	178.7 (3)	C5—C6—C7—C2	2.5 (7)
Cu1—O2—C3—C2	-0.7 (6)	Br2—C6—C7—C2	-177.2 (3)
C7—C2—C3—O2	179.0 (4)	C1—C2—C7—C6	178.3 (4)
C1—C2—C3—O2	-0.4 (7)	C3—C2—C7—C6	-1.1 (7)
C7—C2—C3—C4	-0.5 (6)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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C7—H7 \cdots O1ⁱⁱ

0.93

2.54

3.475 (5)

178

Symmetry codes: (ii) $-x-1, y+5/2, -z+1/2$.

Fig. 1

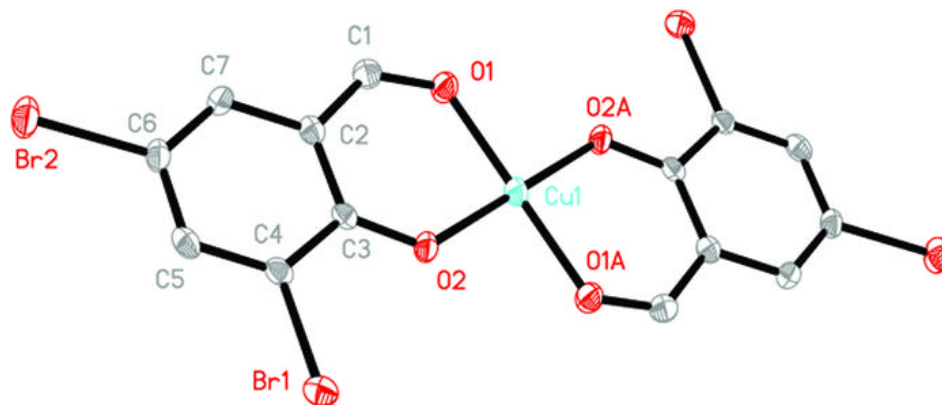


Fig. 2

