metal-organic compounds

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

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In the title compound, [Cu(C₇H₃Br₂O₂)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-formyl-phenolate ligands in a slightly distorted square-planar coordination geometry. In the crystal structure, short intermolecular Br···Br [3.516 (4) and 3.653 (4) Å] and Cu···Br [3.255 (1) Å] contacts together with C—H···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).
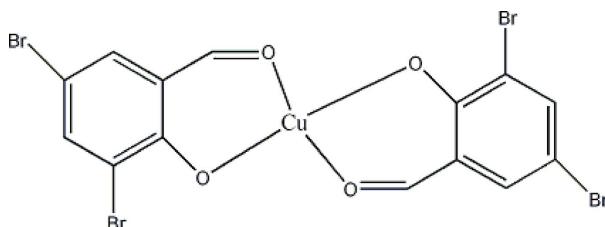
Experimental

Crystal data

[Cu(C₇H₃Br₂O₂)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 reflections

1418 independent reflections
1049 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$

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
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ 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···A	D—H	H···A	D···A	D—H···A
C7—H7···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.

References

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supporting information

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

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S1. 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···Br1^{i}, 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 Br1^{ii}–Br2^{iii} 3.516 (4) Å and Br1^{ii}–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···Br and Cu···Br contacts together with C7—H7···O1 hydrogen bonds generate a three-dimensional network (Fig. 2).

S2. 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).

S3. 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_{iso}(H) = 1.2 U_{eq}(C).
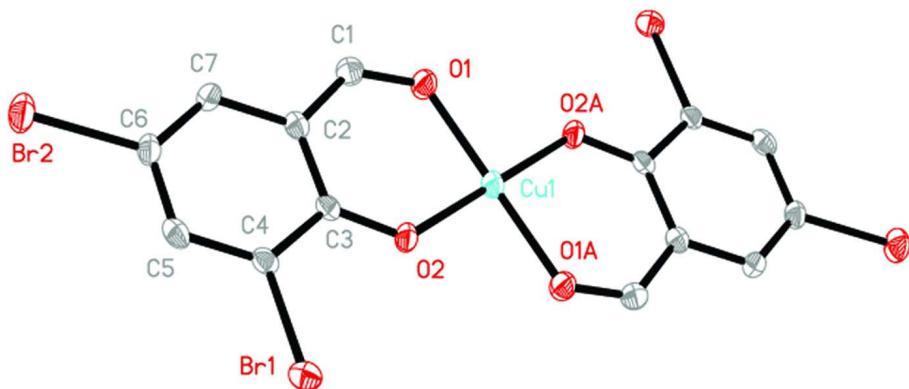
Figure 1

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.
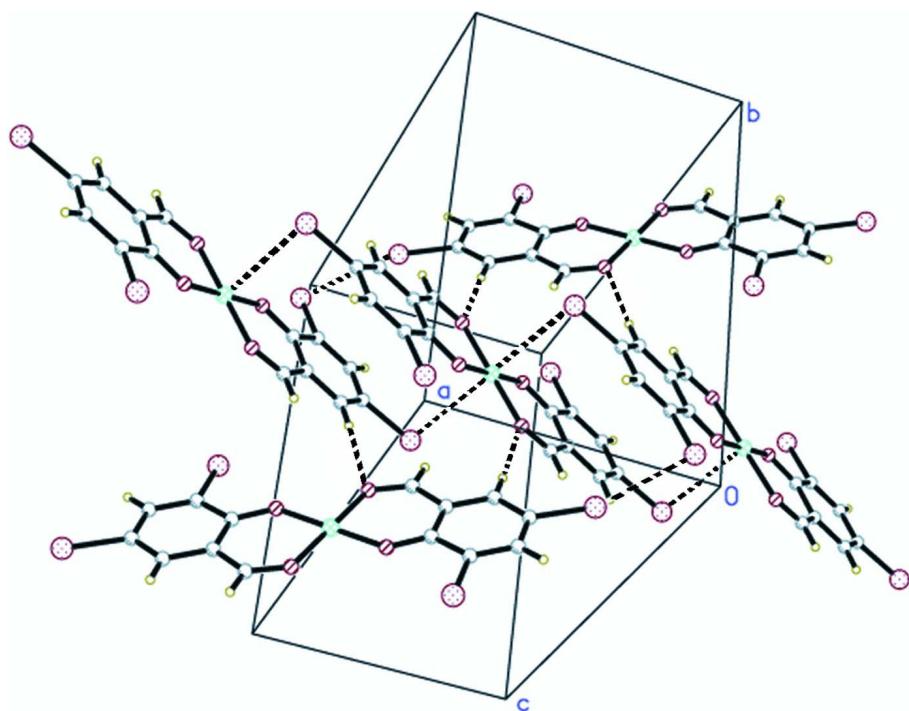
Figure 2

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-κ^2O,O')copper(II)

Crystal data

[Cu(C$_7$H$_3$Br$_2$O$_2$)$_2$]	c = 15.229 (2) Å
M_r = 621.37	V = 1613.3 (4) Å^3
Orthorhombic, *Pbca*	Z = 4
Hall symbol: -P 2ac 2ab	$F(000)$ = 1164
a = 8.2625 (12) Å	D_x = 2.558 Mg m^{-3}
b = 12.8216 (14) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 2295 reflections	$T = 298$ K
$\theta = 2.7–26.8°$	Block, green
$\mu = 11.28$ mm^{-1}	$0.58 \times 0.18 \times 0.14$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer	6267 measured reflections
	1418 independent reflections
Radiation source: fine-focus sealed tube	1049 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.058$
φ and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.7°$
Absorption correction: multi-scan	$h = -9 \rightarrow 9$
(*SADABS*; Sheldrick, 2002)	$k = -15 \rightarrow 14$
$T_{min} = 0.059$, $T_{max} = 0.301$	$l = -10 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.028$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.069$	
$S = 1.02$	H-atom parameters constrained
1418 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2]$
106 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.64$ e Å^{-3}
	$\Delta\rho_{min} = -0.40$ 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	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 (Å²)

	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)

Geometric parameters (Å, º)

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)

O2ⁱ—Cu1—O1—C1	179.6 (4)	O2—C3—C4—C5	−178.7 (4)
O1ⁱ—Cu1—O1—C1	125 (100)	C2—C3—C4—C5	0.8 (6)
O2ⁱ—Cu1—O2—C3	−37.4 (17)	O2—C3—C4—Br1	4.0 (6)
O1ⁱ—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 code: (i) −*x*+1, −*y*+2, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···O1ⁱⁱ	0.93	2.54	3.475 (5)	178

Symmetry code: (ii) −*x*−1, *y*+5/2, −*z*+1/2.