Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis[(*E*)-4-bromo-2-(methoxyiminomethyl)phenolato-κ^2N,O^1]copper(II)

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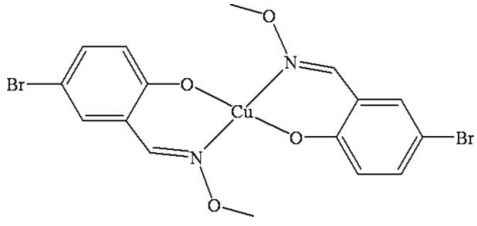
Received 5 November 2009; accepted 12 November 2009

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.006 Å; R factor = 0.032; wR factor = 0.053; data-to-parameter ratio = 13.1.

In the title centrosymmetric mononuclear copper(II) complex, $[Cu(C_8H_7BrNO_2)_2]$, the Cu^{II} atom, lying on an inversion centre, is four-coordinated in a *trans*-CuN_2O_2 square-planar geometry by two phenolate O atoms and two oxime N atoms from two symmetry-related *N*,*O*-bidentate oxime-type ligands. Intermolecular C—H···O hydrogen bonds link neighbouring molecules into a one-dimensional supramolecular structure with an $R_2^2(14)$ ring motif. This structure is further stabilized by π–π stacking interactions between adjacent benzene rings [centroid–centroid distance = 3.862 (1) Å].

Related literature

For general background to oxime compounds, see: Chaudhuri (2003); Dong *et al.* (2007*a*, 2008). For related structures, see: Dong *et al.* (2007*b*, 2009). For the ligand synthesis, see: Wang *et al.* (2008); Zhao *et al.* (2009).



Experimental

Crystal data

$[Cu(C_8H_7BrNO_2)_2]$
M_r = 521.65
Monoclinic, $C2/c$
a = 24.691 (3) Å
b = 3.8623 (5) Å
c = 20.260 (2) Å
β = 117.453 (2)°
V = 1714.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 5.96 mm^{-1}
T = 298 K
0.40 × 0.12 × 0.11 mm

Data collection

Siemens SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.199, T_{max} = 0.560
3981 measured reflections
1521 independent reflections
1128 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.053
S = 1.04
1521 reflections
116 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—O2	1.910 (2)	Cu1—N1	2.000 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1*C*···O1^{i}	0.96	2.52	3.328 (5)	142

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL*.

This work was supported by the Foundation of the Education Department of Gansu Province (0904–11) and the 'Jing Lan' Talent Engineering Funds of Lanzhou Jiaotong University, which are gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2253).

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supplementary materials

Acta Cryst. (2009). E**65**, m1599 [**doi:10.1107/S1600536809047989**]

Bis[(*E*)-4-bromo-2-(methoxyiminomethyl)phenolato-κ^2N,O^1]copper(II)

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Comment

Oximes are a traditional class of chelating ligands widely used in coordination and analytical chemistry and extraction metallurgy (Chaudhuri, 2003; Dong *et al.*, 2007a,b, 2008, 2009). We report here the title mononuclear copper(II) complex with an oxime-type ligand.

The molecular structure of the title compound is shown in Fig. 1. The Cu^{II} ion, lying on an inversion centre is four-coordinated in a *trans*-CuN_2O_2 square-planar geometry, with two phenolate O atoms and two oxime N atoms from two N,O-bidentate oxime-type ligands. Bond lengths and angles are within normal ranges (Table 1). The Cu—O and Cu—N bond lengths are 1.910 (2) Å and 2.000 (3) Å, respectively, which are slightly longer than those observed in a similar Schiff base copper(II) complex [the mean bond lengths of Cu—O and Cu—N are 1.894 (2) and 1.990 (3) Å] (Dong *et al.*, 2009).

In the crystal structure, intermolecular C1—H1C···O1 hydrogen bonds link neighbouring molecules into a one-dimensional supramolecular structure, with an $R_2^2(14)$ ring motif (Table 2 and Fig. 2). The one-dimensional structure is further stabilized by weak π–π stacking interactions between the adjacent benzene rings [centroid–centroid distance = 3.862 (1) Å] (Fig. 2).

Experimental

(*E*)-5-Bromo-2-hydroxybenzaldehyde *O*-methyl oxime (H*L*) was synthesized according to an analogous method in literature (Wang *et al.*, 2008; Zhao *et al.*, 2009). A blue solution of copper(II) acetate monohydrate (1.7 mg, 0.008 mmol) in methanol (4 ml) was added dropwise to a solution of H*L* (4.1 mg, 0.016 mmol) in methanol (5 ml) at room temperature. The colour of the mixing solution turned to yellow immediately then turned to brown slowly. The mixture was allowed to stand at room temperature for several days. With evaporating of the solvent, dark-brown needle-like single crystals suitable for X-ray crystallographic analysis were obtained (yield 49.3%). IR: ν(C═N) 1607, ν(Ar—O) 1243, ν(Cu—N) 447, ν(Cu—O) 422 cm^{-1}. Analysis, calculated for $C_{16}H_{14}Br_2CuN_2O_4$: C 39.30, H 3.32, Cu 11.51, N 5.13%; found: C 39.21, H 3.39, Cu 11.64, N 4.85%.

Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.96 (CH_3) and 0.93 Å (CH) and with U_{iso}(H) = 1.2(1.5 for methyl)U_{eq}(C).

Figures

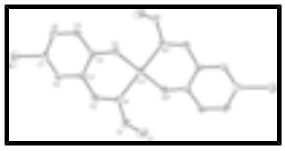

Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted. [Symmetry code: (i) 1-x, 1-y, 1-z.]

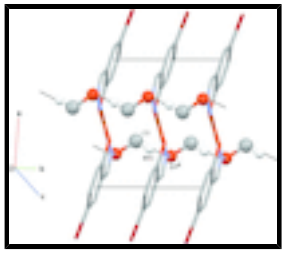

Fig. 2. Packing diagram for the title compound, showing the one-dimensional supramolecular structure formed by intermolecular C—H···O hydrogen bonds (dashed lines) and π–π stacking interactions (dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry code: (ii) x, 1+y, z.]

Bis[(*E*)-4-bromo-2-(methoxyiminomethyl)phenolato- κ^2N,O^1]copper(II)

Crystal data

$[Cu(C_8H_7BrNO_2)_2]$	F_{000} = 1020
M_r = 521.65	D_x = 2.021 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 1233 reflections
a = 24.691 (3) Å	θ = 2.2–23.4º
b = 3.8623 (5) Å	μ = 5.96 mm^{-1}
c = 20.260 (2) Å	*T* = 298 K
β = 117.453 (2)º	Needle-like, dark-brown
V = 1714.4 (3) Å^3	0.40 × 0.12 × 0.11 mm
Z = 4	

Data collection

Siemens SMART 1000 CCD diffractometer	1521 independent reflections
Radiation source: fine-focus sealed tube	1128 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.040
T = 298 K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 1.9º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	*h* = −21→28
T_{min} = 0.199, T_{max} = 0.560	*k* = −4→4
3981 measured reflections	*l* = −24→23

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.032$	H-atom parameters constrained
$wR(F^2) = 0.053$	$w = 1/[\sigma^2(F_o^2) + (0.0126P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
1521 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
116 parameters	$\Delta\rho_{min} = -0.40$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.5000	0.5000	0.5000	0.0478 (2)
Br1	0.169435 (18)	0.60817 (11)	0.35138 (2)	0.04703 (16)
N1	0.46014 (14)	0.4521 (8)	0.56593 (15)	0.0359 (8)
O1	0.48859 (12)	0.2994 (7)	0.63799 (13)	0.0454 (7)
O2	0.43631 (11)	0.8108 (7)	0.43906 (13)	0.0459 (8)
C1	0.54119 (19)	0.4966 (11)	0.6868 (2)	0.0563 (13)
H1A	0.5672	0.5306	0.6638	0.084*
H1B	0.5632	0.3737	0.7328	0.084*
H1C	0.5284	0.7173	0.6964	0.084*
C2	0.40218 (17)	0.4722 (9)	0.54291 (19)	0.0353 (10)
H2	0.3870	0.3956	0.5747	0.042*
C3	0.35910 (16)	0.6052 (9)	0.47123 (18)	0.0303 (9)
C4	0.37870 (17)	0.7699 (10)	0.42340 (19)	0.0337 (10)
C5	0.33223 (17)	0.9004 (10)	0.35507 (19)	0.0357 (10)
H5	0.3434	1.0184	0.3232	0.043*
C6	0.27127 (17)	0.8574 (9)	0.33473 (19)	0.0358 (10)
H6	0.2418	0.9423	0.2894	0.043*
C7	0.25404 (16)	0.6861 (9)	0.3825 (2)	0.0308 (9)
C8	0.29692 (16)	0.5679 (9)	0.45035 (19)	0.0323 (9)
H8	0.2847	0.4628	0.4826	0.039*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0365 (4)	0.0708 (6)	0.0413 (4)	0.0207 (4)	0.0224 (4)	0.0218 (4)
Br1	0.0330 (3)	0.0476 (3)	0.0530 (3)	−0.0031 (2)	0.0134 (2)	−0.0005 (2)
N1	0.035 (2)	0.044 (2)	0.0273 (18)	0.0067 (17)	0.0131 (15)	0.0089 (15)
O1	0.0378 (17)	0.057 (2)	0.0334 (15)	0.0074 (14)	0.0095 (13)	0.0140 (14)
O2	0.0311 (17)	0.064 (2)	0.0454 (16)	0.0148 (15)	0.0198 (13)	0.0245 (14)
C1	0.057 (3)	0.060 (3)	0.037 (2)	0.003 (2)	0.009 (2)	−0.001 (2)
C2	0.038 (3)	0.036 (3)	0.036 (2)	0.001 (2)	0.020 (2)	0.0039 (18)
C3	0.034 (2)	0.032 (2)	0.026 (2)	0.0051 (19)	0.0140 (18)	0.0016 (19)
C4	0.034 (2)	0.037 (2)	0.030 (2)	0.007 (2)	0.015 (2)	0.0004 (19)
C5	0.043 (3)	0.036 (2)	0.033 (2)	0.008 (2)	0.0216 (19)	0.004 (2)
C6	0.036 (3)	0.038 (3)	0.027 (2)	0.009 (2)	0.0097 (19)	0.003 (2)

C7	0.031 (2)	0.024 (2)	0.036 (2)	0.0008 (18)	0.0148 (19)	−0.0039 (18)
C8	0.039 (2)	0.032 (2)	0.034 (2)	0.000 (2)	0.0224 (19)	0.0001 (19)

Geometric parameters (Å, °)

Cu1—O2	1.910 (2)	C2—H2	0.9300
Cu1—N1	2.000 (3)	C3—C8	1.399 (5)
Br1—C7	1.907 (4)	C3—C4	1.418 (5)
N1—C2	1.287 (4)	C4—C5	1.422 (5)
N1—O1	1.424 (3)	C5—C6	1.375 (5)
O1—C1	1.435 (4)	C5—H5	0.9300
O2—C4	1.316 (4)	C6—C7	1.391 (5)
C1—H1A	0.9600	C6—H6	0.9300
C1—H1B	0.9600	C7—C8	1.370 (5)
C1—H1C	0.9600	C8—H8	0.9300
C2—C3	1.442 (5)		
O2^{i}—Cu1—O2	180.000 (2)	C3—C2—H2	117.7
O2^{i}—Cu1—N1	91.27 (11)	C8—C3—C4	120.8 (3)
O2—Cu1—N1	88.73 (11)	C8—C3—C2	117.7 (3)
O2^{i}—Cu1—N1^{i}	88.73 (11)	C4—C3—C2	121.5 (3)
O2—Cu1—N1^{i}	91.27 (11)	O2—C4—C3	124.1 (3)
N1—Cu1—N1^{i}	180.000 (1)	O2—C4—C5	119.3 (3)
C2—N1—O1	109.7 (3)	C3—C4—C5	116.6 (3)
C2—N1—Cu1	124.0 (2)	C6—C5—C4	122.0 (4)
O1—N1—Cu1	124.1 (2)	C6—C5—H5	119.0
N1—O1—C1	110.4 (3)	C4—C5—H5	119.0
C4—O2—Cu1	123.8 (2)	C5—C6—C7	119.5 (3)
O1—C1—H1A	109.5	C5—C6—H6	120.2
O1—C1—H1B	109.5	C7—C6—H6	120.2
H1A—C1—H1B	109.5	C8—C7—C6	120.9 (4)
O1—C1—H1C	109.5	C8—C7—Br1	120.0 (3)
H1A—C1—H1C	109.5	C6—C7—Br1	119.0 (3)
H1B—C1—H1C	109.5	C7—C8—C3	120.1 (3)
N1—C2—C3	124.5 (3)	C7—C8—H8	120.0
N1—C2—H2	117.7	C3—C8—H8	120.0
O2^{i}—Cu1—N1—C2	−148.5 (3)	C8—C3—C4—O2	−179.3 (3)
O2—Cu1—N1—C2	31.5 (3)	C2—C3—C4—O2	1.1 (6)
O2^{i}—Cu1—N1—O1	13.2 (3)	C8—C3—C4—C5	1.5 (5)
O2—Cu1—N1—O1	−166.8 (3)	C2—C3—C4—C5	−178.1 (3)
C2—N1—O1—C1	−133.0 (3)	O2—C4—C5—C6	178.2 (3)
Cu1—N1—O1—C1	63.0 (3)	C3—C4—C5—C6	−2.6 (5)
N1—Cu1—O2—C4	−38.8 (3)	C4—C5—C6—C7	1.0 (6)
N1^{i}—Cu1—O2—C4	141.2 (3)	C5—C6—C7—C8	1.8 (5)
O1—N1—C2—C3	−178.3 (3)	C5—C6—C7—Br1	−176.9 (3)
Cu1—N1—C2—C3	−14.3 (5)	C6—C7—C8—C3	−2.8 (5)
N1—C2—C3—C8	171.7 (3)	Br1—C7—C8—C3	175.9 (3)
N1—C2—C3—C4	−8.6 (6)	C4—C3—C8—C7	1.1 (5)

Cu1—O2—C4—C3	29.8 (5)	C2—C3—C8—C7	−179.2 (3)
Cu1—O2—C4—C5	−151.0 (3)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1C···O1^{ii}	0.96	2.52	3.328 (5)	142

Symmetry codes: (ii) *x*, *y*+1, *z*.

Fig. 1

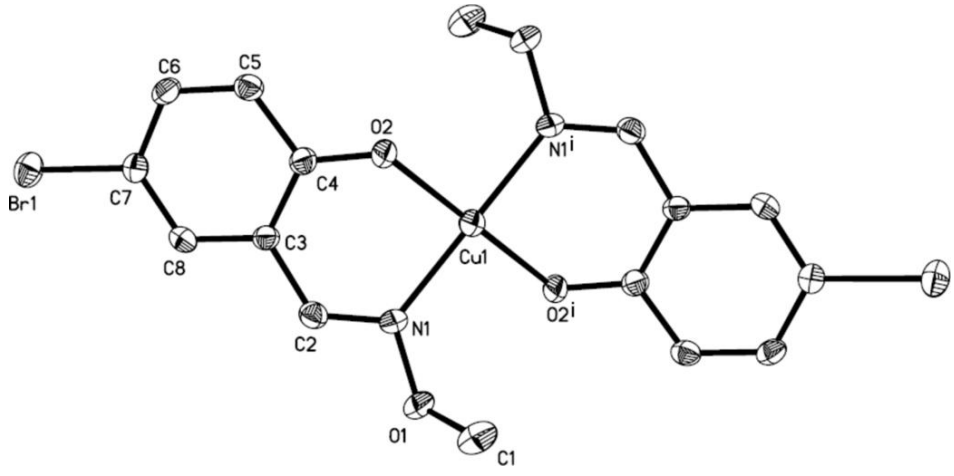

Fig. 2