

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

 Bis[(*E*)-4-bromo-2-(methoxyimino-methyl)phenolato- κ^2 N,O¹]copper(II)

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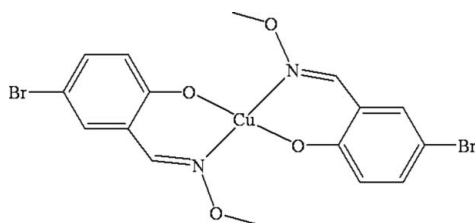
Received 5 November 2009; accepted 12 November 2009

 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.032; wR factor = 0.053; data-to-parameter ratio = 13.1.

In the title centrosymmetric mononuclear copper(II) complex, $[\text{Cu}(\text{C}_8\text{H}_7\text{BrNO}_2)_2]$, 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 $\text{C}-\text{H}\cdots\text{O}$ 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 $\pi-\pi$ 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

 $[\text{Cu}(\text{C}_8\text{H}_7\text{BrNO}_2)_2]$
 $M_r = 521.65$
 Monoclinic, $C2/c$
 $a = 24.691$ (3) Å
 $b = 3.8623$ (5) Å
 $c = 20.260$ (2) Å
 $\beta = 117.453$ (2)°

 $V = 1714.4$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 5.96$ mm⁻¹
 $T = 298$ K
 $0.40 \times 0.12 \times 0.11$ mm

Data collection

 Siemens SMART 1000 CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.199$, $T_{\text{max}} = 0.560$

 3981 measured reflections
 1521 independent reflections
 1128 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$

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
 $\Delta\rho_{\text{max}} = 0.54$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cu1—O2	1.910 (2)	Cu1—N1	2.000 (3)
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Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C1—H1C \cdots 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).

References

- Chaudhuri, P. (2003). *Coord. Chem. Rev.* **243**, 143–168.
 Dong, W.-K., Chen, X., Wang, S.-J., He, X.-N., Wu, H.-L. & Yu, T.-Z. (2007*a*). *Synth. React. Inorg. Met. Org. Nano-Chem.* **37**, 229–233.
 Dong, W.-K., Duan, J.-G., Liu, G.-L., Shi, J.-Y. & Yu, T.-Z. (2007*b*). *Synth. React. Inorg. Met. Org. Nano-Chem.* **37**, 627–631.
 Dong, W.-K., Zhang, Y.-P., Zhao, C.-Y., Tang, X.-L., Lv, Z.-W. & Zou, Z. (2008). *Chin. J. Chem.* **26**, 1821–1825.
 Dong, W.-K., Zhao, C.-Y., Sun, Y.-X., Tang, X.-L. & He, X.-N. (2009). *Inorg. Chem. Commun.* **12**, 234–236.
 Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Wang, J.-S., Jiang, Y.-L., Dong, W.-K., Xu, L. & Kong, A.-P. (2008). *Acta Cryst.* **E64**, o1794.
 Zhao, L., Dong, W.-K., Wu, J.-C., Sun, Y.-X. & Xu, L. (2009). *Acta Cryst.* **E65**, o2462.

supporting information

Acta Cryst. (2009). E65, m1599 [doi:10.1107/S1600536809047989]

Bis[(*E*)-4-bromo-2-(methoxyiminomethyl)phenolato- κ^2 N,O¹]copper(II)

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S1. 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*-CuN₂O₂ 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).

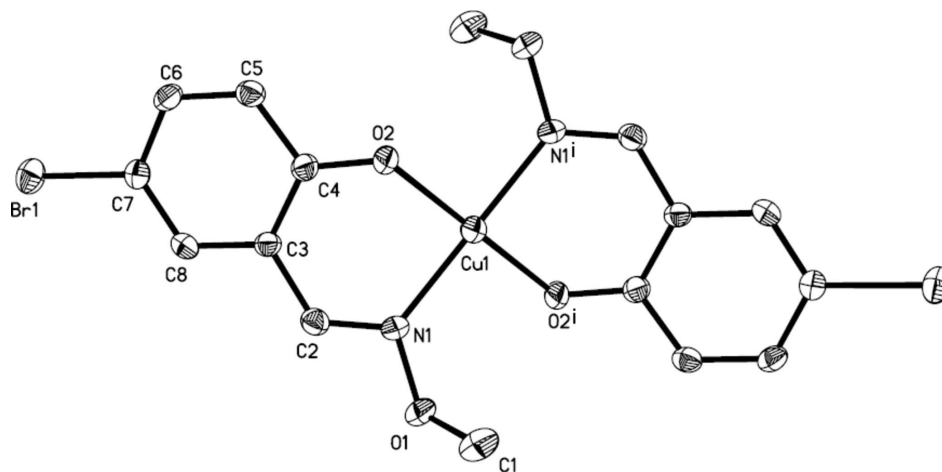
In the crystal structure, intermolecular C1—H1C...O1 hydrogen bonds link neighbouring molecules into a one-dimensional supramolecular structure, with an *R*₂²(14) ring motif (Table 2 and Fig. 2). The one-dimensional structure is further stabilized by weak π – π stacking interactions between the adjacent benzene rings [centroid–centroid distance = 3.862 (1) Å] (Fig. 2).

S2. Experimental

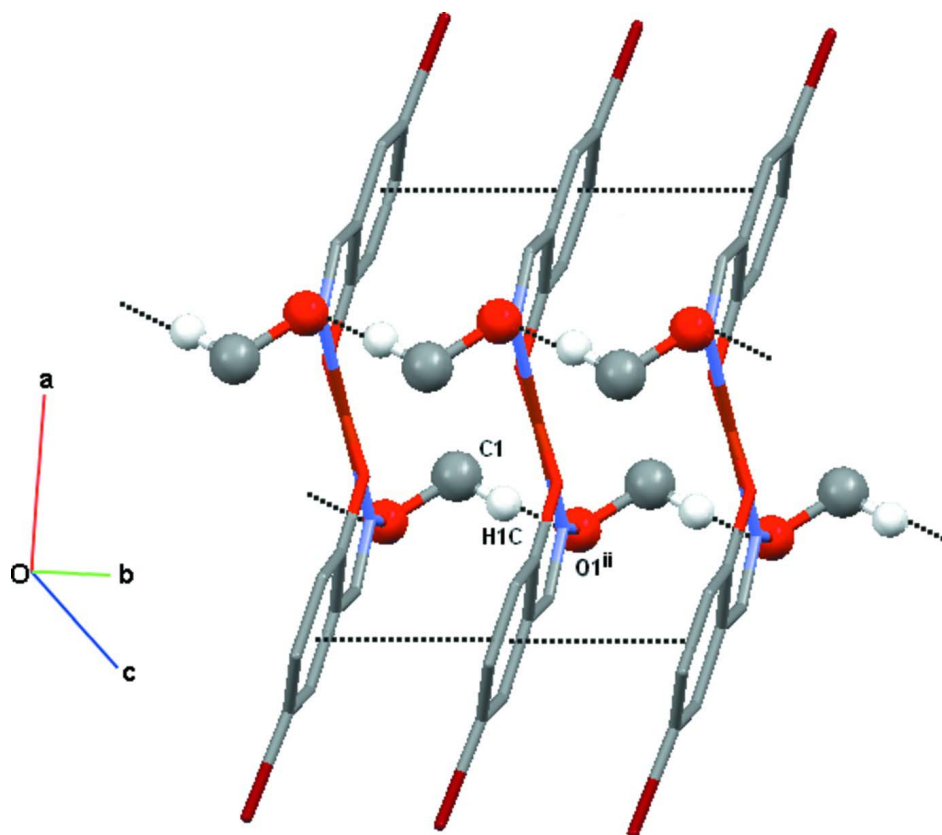
(*E*)-5-Bromo-2-hydroxybenzaldehyde *O*-methyl oxime (HL) was synthesized according to an analogous method in literature (Wang *et al.*, 2008; Zhao *et al.*, 2009). A blue solution of copper(II) acetate monohydrate (1.7 mg, 0.008 mmol) in methanol (4 ml) was added dropwise to a solution of HL (4.1 mg, 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 C₁₆H₁₄Br₂CuN₂O₄: 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%.

S3. Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.96 (CH₃) and 0.93 Å (CH) and with $U_{\text{iso}}(\text{H}) = 1.2(1.5 \text{ for methyl})U_{\text{eq}}(\text{C})$.

**Figure 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) $1-x, 1-y, 1-z$.]

**Figure 2**

Packing diagram for the title compound, showing the one-dimensional supramolecular structure formed by intermolecular C—H \cdots 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(C₈H₇BrNO₂)₂] $M_r = 521.65$ Monoclinic, *C2/c*

Hall symbol: -C 2yc

 $a = 24.691$ (3) Å $b = 3.8623$ (5) Å $c = 20.260$ (2) Å $\beta = 117.453$ (2)° $V = 1714.4$ (3) Å³ $Z = 4$ $F(000) = 1020$ $D_x = 2.021$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1233 reflections

 $\theta = 2.2$ – 23.4 ° $\mu = 5.96$ mm⁻¹ $T = 298$ K

Needle-like, dark-brown

 $0.40 \times 0.12 \times 0.11$ mm*Data collection*

Siemens SMART 1000 CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\min} = 0.199$, $T_{\max} = 0.560$

3981 measured reflections

1521 independent reflections

1128 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.040$ $\theta_{\text{max}} = 25.0$ °, $\theta_{\text{min}} = 1.9$ ° $h = -21 \rightarrow 28$ $k = -4 \rightarrow 4$ $l = -24 \rightarrow 23$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.032$ $wR(F^2) = 0.053$ $S = 1.04$

1521 reflections

116 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

 $w = 1/[\sigma^2(F_o^2) + (0.0126P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.54$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{Cq}}$
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 (Å²)

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

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C1—H1C \cdots O1 ⁱⁱ	0.96	2.52	3.328 (5)	142

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