

[*N,N'*-Bis(5-bromosalicylidene)-*o*-phenylenediaminato]copper(II)Ayhan Elmali,^{a*} Yalçın Elerman^a and Ingrid Svoboda^b^aDepartment of Physics Engineering, Faculty of Sciences, University of Ankara, 06100 Besevler, Ankara, Turkey, and ^bStrukturforschung, Fachbereich Materialwissenschaft, Technische Universität Darmstadt, Petersenstrasse 23, D-64287 Darmstadt, Germany
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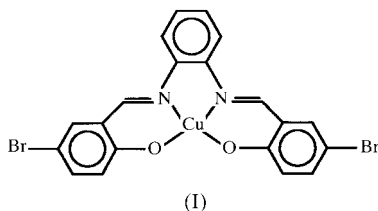
Received 5 November 1999

Accepted 24 December 1999

In the title compound, {4,4'-dibromo-2,2'-[*o*-phenylenebis(nitrilomethylidene)]diphenolato-*O,N,N',O'*}copper(II), [Cu(C₂₀H₁₂Br₂N₂O₂)], the Cu^{II} ion shows a slightly distorted square-planar geometry with the N₂O₂ atoms of the Schiff base imine-phenol tetradentate ligand.

Comment

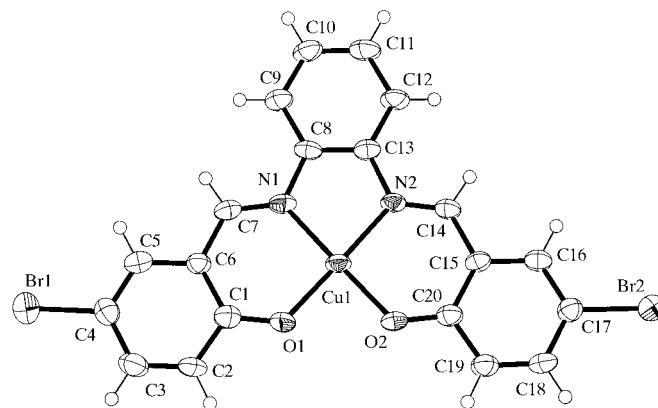
Schiff base complexes are some of the most important stereochemical models in transition metal coordination chemistry, with their ease of preparation and structural variation (Garnovskii *et al.*, 1993). Metal derivatives of Schiff bases have been studied extensively, and copper(II) and nickel(II) complexes play a major role in both synthetic and structural research. The geometry of the coordination sphere is usually planar in the case of Ni, but for Cu, a tetrahedral distortion is often observed (Garnovskii *et al.*, 1993). We have reported previously the crystal structures of several dimeric and monomeric Schiff base complexes of Cu^{II} (Elmali *et al.*, 1997; Elerman & Geselle, 1997; Elerman, Elmali & Özbey, 1998; Elerman, Elmali, Kabak & Svoboda, 1998). We report here the results of the reaction of copper(II) with the tetradentate ligand *N,N'*-bis(5-bromosalicylidene)-*o*-phenylenediamine, forming the title compound, (I).



Tetracoordinate Schiff base metal complexes may form *trans* or *cis* planar or tetrahedral structures. A strictly planar or slightly distorted coordination is characteristic for transition metal complexes of copper(II) with a CuN₂O₂ coordination sphere (Garnovskii *et al.*, 1993). In (I), the Cu atom is coordinated by two imine N atoms and two phenol O atoms from the imine-phenol ligand, in a slightly distorted square-planar

coordination. The N1—Cu1—N2, N1—Cu1—O1, O1—Cu1—O2 and O2—Cu1—N2 bond angles are 84.6 (2), 94.1 (2), 87.4 (2) and 93.9 (2)°, respectively. The Cu—N distances [1.936 (4) and 1.946 (4) Å] are longer than the Cu—O distances [1.887 (4) and 1.882 (3) Å]. These distances agree with values in other square-planar-coordinated copper(II) complexes (Akhtar & Drew, 1982; Labisbal *et al.*, 1994). The planar molecules are stacked in columns along the *b* axis, with Cu···Cu separations of 3.399 (1) Å. However, this Cu···Cu dimeric interaction is considerably shorter than the value of 3.613 (3) Å observed in *N,N'*-propylenebis[(2-hydroxy-1-naphthyl)methaniminato]copper(II) (Akhtar & Drew, 1982).

No unusual bond distances are observed in the salen derivative of (I); average distances and angles include C—C = 1.391 (8) Å, C—O = 1.294 (6) Å, C—N = 1.420 (6) and C=N = 1.292 (6) Å, and phenyl C—C—C = 120.3 (3)°. These values are within the expected ranges for coordinated salen derivatives (Riley *et al.*, 1986; Zamian *et al.*, 1995; Schmidt *et al.*, 1996).

**Figure 1**

The molecular structure and atom-labelling scheme of (I). Displacement ellipsoids are plotted at the 50% probability level and H atoms are drawn as spheres of arbitrary radii (ORTEP-3 for Windows; Farrugia, 1997).

Experimental

Suitable crystals were obtained directly from the synthesis of compound (I). The preparation of *N,N'*-bis(5-bromosalicylidene)-1,2-diaminobenzene followed the process described recently by Elerman, Elmali, Kabak & Svoboda (1998). Two solutions, *N,N'*-bis(5-bromosalicylidene)-1,2-diaminobenzene (0.5 mmol) in tetrahydrofuran (50 ml) and [Cu(O₂CCH₃)₂·4H₂O] in methanol (30 ml), were prepared and heated to boiling point. The mixture of the two solutions was then refluxed for 4 h. Crystals of (I) were obtained after 2 d.

Crystal data

[Cu(C₂₀H₁₂Br₂N₂O₂)]
M_r = 535.70
 Monoclinic, *P*2₁/*n*
a = 12.1140 (10) Å
b = 8.095 (2) Å
c = 18.538 (6) Å
 β = 106.300 (10)°
V = 1744.8 (7) Å³
Z = 4

D_x = 2.039 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 2.34–10.25°
 μ = 5.851 mm⁻¹
T = 299 (2) K
 Prism, brown
 0.30 × 0.13 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.045$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 25.97^\circ$
Absorption correction: empirical via ψ scans (North <i>et al.</i> , 1968)	$h = -14 \rightarrow 9$
$T_{\text{min}} = 0.421$, $T_{\text{max}} = 0.752$	$k = -9 \rightarrow 0$
6199 measured reflections	$l = -22 \rightarrow 22$
3399 independent reflections	3 standard reflections
1973 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: -3.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.115$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.073$	$\Delta\rho_{\text{max}} = 0.81 \text{ e } \text{\AA}^{-3}$
3399 reflections	$\Delta\rho_{\text{min}} = -1.08 \text{ e } \text{\AA}^{-3}$
245 parameters	Extinction correction: <i>SHELXL93</i>
H atoms constrained	(Sheldrick, 1993)
	Extinction coefficient: 0.0001 (3)

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1—O1	1.291 (6)	C17—Br2	1.899 (5)
C4—Br1	1.898 (5)	C20—O2	1.296 (6)
C7—N1	1.298 (6)	N1—Cu1	1.936 (4)
C8—N1	1.423 (6)	N2—Cu1	1.946 (4)
C13—N2	1.416 (6)	O1—Cu1	1.887 (4)
C14—N2	1.286 (6)	O2—Cu1	1.882 (3)
O1—C1—C2	119.4 (5)	C7—N1—C8	122.0 (4)
O1—C1—C6	124.2 (5)	C7—N1—Cu1	125.4 (3)
C5—C4—Br1	119.4 (4)	C8—N1—Cu1	112.6 (3)
C3—C4—Br1	120.0 (4)	C14—N2—C13	122.6 (4)
N1—C7—C6	125.0 (4)	C14—N2—Cu1	125.0 (3)
C9—C8—N1	125.4 (5)	C13—N2—Cu1	112.4 (3)
C13—C8—N1	115.1 (4)	C1—O1—Cu1	127.9 (3)
C12—C13—N2	125.5 (5)	C20—O2—Cu1	127.9 (3)
C8—C13—N2	115.4 (4)	O2—Cu1—O1	87.4 (2)
N2—C14—C15	125.9 (5)	O2—Cu1—N1	178.4 (2)
C16—C17—Br2	120.9 (4)	O1—Cu1—N1	94.1 (2)
C18—C17—Br2	119.1 (4)	O2—Cu1—N2	93.9 (2)
O2—C20—C19	118.8 (5)	O1—Cu1—N2	178.5 (2)
O2—C20—C15	124.3 (4)	N1—Cu1—N2	84.6 (2)

Data collection: *CAD-4 Diffractometer Control Software* (Enraf–Nonius, 1993); cell refinement: *CAD-4 Diffractometer Control Software*; data reduction: *REDU4* (Stoe & Cie, 1991); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1068). Services for accessing these data are described at the back of the journal.

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