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[*N*,*N*′-Bis(5-bromosalicylidene)-1,3-diaminopropane]copper(II)†

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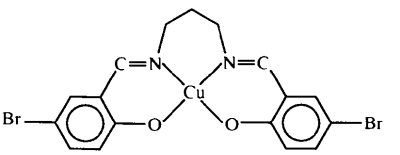
Abstract

The title compound, $[Cu(C_{17}H_{14}Br_2N_2O_2)]$, has a crystallographic twofold axis. The coordination geometry about the Cu^{II} centre is a tetrahedrally distorted square plane formed by the four-coordinate N_2O_2 donor set of the Schiff base imine–phenol ligand. The Cu—N and Cu—O distances are 1.967 (5) and 1.914 (4) Å, respectively.

Comment

Schiff base complexes are considered to be among the most important stereochemical models in main-group and transition metal coordination chemistry due to their preparative accessibility and structural variety (Garnovskii *et al.*, 1993). Transition metal Schiff base complexes are of interest in catalysis (Jacobsen *et al.*, 1991) and in small-molecule binding (Jones *et al.*, 1979; Chen & Martell, 1987). We have reported previously the structures of several dimeric and monomeric Schiff base complexes of copper(II) (Elmali *et al.*, 1993, 1995, 1997; Elerman *et al.*, 1995; Elerman & Geselle, 1997). We report here the results of the reaction of copper(II) with the tetradentate ligand *N*,*N*′-bis(5-bromo-2-hydroxybenzylidene)-1,3-propanediamine, to form a monomeric Schiff base complex of copper(II), (I).



(I)

The bond lengths and angles around the Cu atom are in good agreement with the values found in other tetracoordinated copper complexes with similar ligands (Baker *et al.*, 1970; Labisbal *et al.*, 1994; Yao *et al.*, 1997; Lo *et al.*, 1997). The Cu atom is coordinated by two imine N atoms and two phenol O atoms from the imine–phenol ligand in a distorted square-planar coordination geometry. The atom with the greatest deviation from the coordination plane [Cu1, N1, O1, $N1^i$ and $O1^i$; symmetry code: (i) $-x, y, -\frac{1}{2}-z$] is O1 at 0.458 (4) Å. The unique half of the Schiff base ligand of the title compound is reasonably planar, with the maximum deviation from the plane defined by atoms O1, N1, C1–C9 and Br1 being 0.168 (4) Å for the O1 atom. However, the entire ligand is not planar, as the two halves are twisted with respect to one another. The least-squares planes through each half of the molecule are inclined at an angle of 35.6 (1)°. In the free ligand, the same interplanar angle is 66.17 (7)° (Elerman *et al.*, 1998); besides, the torsion angle of −41.2 (13)° for N1—C8—C9—$C8^i$ supports the non-planarity of the molecule. It is possible that the Cu atom plays an important role in the planarity of the whole molecule.

The bond distances and angles in the chelating moieties of the molecule are significantly different from those present in the free ligand. In particular, the distances C1—O1 and C6—C7 [1.302 (7) and 1.436 (9) Å, respectively] are shorter than those found in the free ligand [1.342 (7) and 1.448 (8) Å, respectively; Elerman *et al.*, 1998], while the N1—C7 distance [1.288 (8) Å] is longer [1.269 (7) Å for the free ligand]. This trend, which has been observed already in some other complexes (Calligaris *et al.*, 1972; Pahor *et al.*, 1978), shows that an extended conjugation is present in the coordinated ligand.

All bond distances and angles in the title compound are within the ranges found for related derivatives (Riley *et al.*, 1986; Zamian *et al.*, 1995; Schmidt *et al.*, 1996).

† Systematic name: {4,4′-dibromo-2,2′-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato-*O*,*N*,*N*′,*O*′}copper(II).

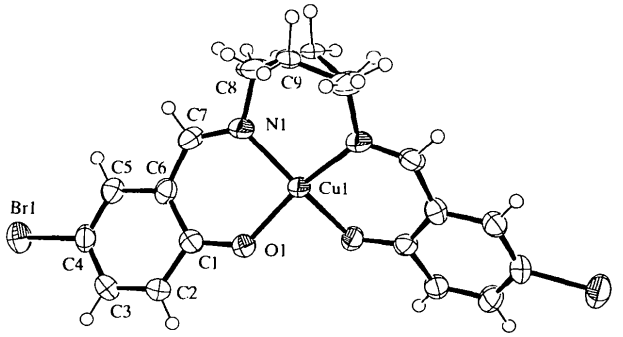


Fig. 1. The molecular structure and atomic labelling scheme of the title compound (*ORTEP*-3; Farrugia, 1997). Displacement ellipsoids are plotted at the 50% probability level and all disordered atoms are shown.

Experimental

The title compound was prepared from solutions of copper(II) acetate monohydrate (0.099 g, 0.5 mmol) in methanol (25 ml) and *N*,*N*′-bis(5-bromo-2-hydroxybenzylidene)-1,3-propanediamine (0.235 g, 0.5 mmol) in dioxane (50 ml). The solutions were mixed and the reaction mixture was heated under reflux for 30 min. Single crystals of the product were obtained on cooling.

Crystal data

$[Cu(C_{17}H_{14}Br_2N_2O_2)]$
M_r = 501.65
Monoclinic
$C2/c$
a = 21.432 (4) Å
b = 8.158 (1) Å
c = 9.515 (2) Å
β = 92.95 (2)°
V = 1661.4 (6) Å^3
Z = 4
D_x = 2.006 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 20.13–29.93°
μ = 6.14 mm^{-1}
T = 293 (2) K
Plate
0.20 × 0.10 × 0.10 mm
Dark brown

Data collection

Rigaku AFC-7*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.512, T_{max} = 0.541
1957 measured reflections
1906 independent reflections

1013 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 27.49°
h = 0 → 27
k = 0 → 10
l = −12 → 12
3 standard reflections every 150 reflections
intensity decay: −0.31%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.154
S = 1.160

1906 reflections
116 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0700P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.97 e Å^{-3}
$\Delta\rho_{min}$ = −1.23 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Br1—C4	1.899 (6)	C1—C6	1.415 (8)
Cu1—O1	1.914 (4)	C2—C3	1.364 (9)
Cu1—N1	1.967 (5)	C3—C4	1.389 (9)
O1—C1	1.302 (7)	C4—C5	1.368 (9)
N1—C7	1.288 (8)	C5—C6	1.419 (8)
N1—C8	1.475 (9)	C6—C7	1.436 (9)
C1—C2	1.410 (9)	C8—C9	1.463 (8)
O1—Cu1—O1^i	87.0 (3)	N1^i—Cu1—N1	97.9 (3)
O1—Cu1—N1^i	153.8 (2)	C1—O1—Cu1	128.0 (4)
O1—Cu1—N1	93.2 (2)	C8—C9—C8^i	120.9 (9)

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

The C9 atom is disordered about a twofold axis and geometrical restraints were applied to the C8—C9 distance to prevent anomalous bond distances in the propanediamine chelate ring. The maximum and minimum residual electron-density regions were within 1.0 Å of the Br atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *ORTEP*-3 (Farrugia, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1075). Services for accessing these data are described at the back of the journal.

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Bis{(μ-nitrato)[μ-bis(salicylidene)-1,3-propanediaminato]copper(II)}zinc(II)†

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Abstract

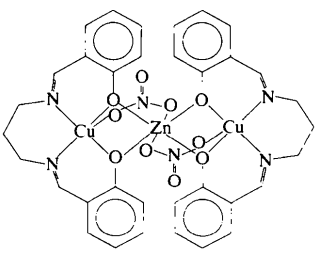
The title compound, $[Zn\{Cu(NO_3)(C_{17}H_{16}N_2O_2)\}_2]$, has the central Zn^{2+} ion located on an inversion centre, with four bridging O atoms from two *N*,*N*′-bis(salicylidene)-1,3-propanediaminate ($SALPD^{2-}$) ligands and one O atom from each bridging nitrate group as nearest neighbours. This arrangement constitutes a distorted octahedral coordination around the Zn^{2+} ion. The inversion-related terminal Cu^{2+} ions have irregular square-pyramidal coordinations involving two O and two N atoms of a $SALPD^{2-}$ ligand and one O atom from a nitrate group in the axial position. The Zn—Cu pairs are triple bridged by the $SALPD^{2-}$ O atoms and by the O—N—O atoms of the nitrate groups. The Zn···Cu bridging distance is 3.0017 (6) Å.

† Alternative name: bis(μ-nitrato)-1:3$\kappa^2O:O'$;2:3$\kappa^2O:O'$-bis{μ-2,2′-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato}-1κ^4N,N',O,O':-3κ^2O,O';2κ^4N,N',O,O':3κ^2O,O'-zinc(II)dicopper(II).

Comment

The structure and magnetic properties of the trinuclear complex $[Zn\{Cu(CH_3CO_2)(SALPD)\}_2]$ have been reported previously (Fukuhara *et al.*, 1990). Similar examples of trihomo- and heteronuclear complexes have been prepared in our laboratory using different metal ions, acetate or nitrite groups, and the ligand *N*,*N*′-bis(salicylidene)-1,3-propanediamine. The structures of these complexes have also been described (Ülkü, Tahir *et al.*, 1997; Ülkü, Ercan *et al.*, 1997; Ercan *et al.*, 1998; Tahir *et al.*, 1998; Atakol *et al.*, 1999). These triple-bridged linear complexes are of interest because of their magnetic properties.

We report here a new heterometallic trinuclear complex, $[Zn\{Cu(NO_3)(C_{17}H_{16}N_2O_2)\}_2]$, (I), which, in addition to the two O-atom bridges between a pair of metal ions, has a third bridge provided by an NO_3 group. In our previously reported complexes, the third bridge was either an acetate or a nitrite group.



(I)

The central Zn^{2+} ion, located on an inversion centre, has a distorted octahedral coordination involving four bridging O atoms from two $SALPD^{2-}$ ligands in the equatorial plane [O1, O2, O1^i and O2^i; symmetry code: (i) $-x$, $-y$, $-z$] and an O atom from each of the two bridging nitrate groups occupying the apical positions (Fig. 1). The Zn—O1, Zn—O2 and Zn—O3 bond lengths are 2.063 (2), 2.055 (2) and 2.188 (2) Å, respectively. The O—Zn—O bond angles within the distorted octahedra range from 76.04 (9) to 93.74 (9)°. Owing to the inversion centre, the Zn^{2+} ion is in the equatorial plane.

The coordination around the terminal Cu^{2+} ions, related by the inversion centre, is an irregular square pyramid. The basal plane, defined by the O1, O2, N1 and N2 atoms, consists of two N and two bridging O atoms from a $SALPD^{2-}$ ligand. The axial position of the square pyramid is occupied by an O atom of the bridging NO_3 group. The two Cu—O bond lengths [1.945 (2) and 1.941 (2) Å], as well as the two Cu—N distances [1.964 (3) and 1.959 (3) Å] in the basal plane, are equal among themselves within experimental error. The Cu—O4 distance along the pyramidal axis is considerably longer [2.355 (3) Å] than those observed in the basal plane. The bond angles in the five coordinated polyhedra have values between 81.5 (1) (O1—Cu—O2)