

[*N,N'*-Bis(5-bromosalicylidene)-1,3-diaminopropane]nickel(II) and [*N,N'*-bis(5-chlorosalicylidene)-1,3-diaminopropane]copper(II)

Ayhan Elmali,^{a*†} C. Tuğrul Zeyrek,^a Yalçın Elerman^{a†} and Ingrid Svoboda^b

^aDepartment of Engineering Physics, Faculty of Sciences, University of Ankara, 06100 Beşevler, Ankara, Turkey, and ^bStrukturforschung, Fachbereich Materialwissenschaft, Technische Universität Darmstadt, Petersenstrasse 23, D-64287, Darmstadt, Germany

Correspondence e-mail: elmali@science.ankara.edu.tr

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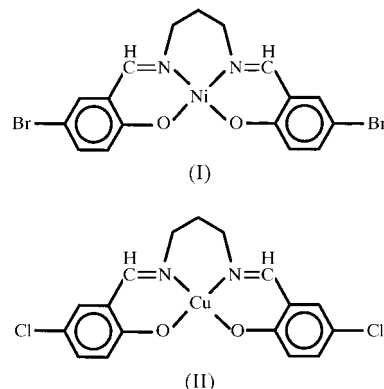
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The title compounds, {4,4'-dibromo-2,2'-[1,3-propanediylbis(nitrilomethylidene-*N*)]diphenolato-*O,O'*}nickel(II), [Ni(C₁₇H₁₄Br₂N₂O₂)], and {4,4'-dichloro-2,2'-[1,3-propanediylbis(nitrilomethylidene-*N*)]diphenolato-*O,O'*}copper(II), [Cu(C₁₇H₁₄Cl₂N₂O₂)], lie on crystallographic twofold axes. In both structures, the metal coordination sphere is a tetrahedrally distorted square plane formed by the four-coordinate N₂O₂ donor set of the Schiff base imine–phenol ligands. In the Ni compound, the Ni–O and Ni–N distances are 1.908 (3) and 1.959 (4) Å, respectively, while in the Cu compound, the Cu–O and Cu–N distances are 1.907 (2) and 1.960 (2) Å, respectively. The two Schiff base moieties, which themselves are nearly planar, are inclined at an angle of 29.26 (7)° for the Ni compound and 29.26 (5)° for the Cu compound.

Comment

Metal derivatives of Schiff bases have been extensively studied, and nickel(II) and copper(II) complexes play a major role in both synthesis and structural research (Garnovskii *et al.*, 1993). Several complexes of salicylideneiminato (Kessissoglou *et al.*, 1987, 1992; Bhatia *et al.*, 1981; Chen *et al.*, 1989; Calligaris *et al.*, 1972; Yao *et al.*, 1997) and 2-hydroxy-1-naphthaldimine derivatives (Elerman *et al.*, 1996; Elerman, Elmali, Svoboda & Fuess, 1998; Cariati *et al.*, 1985) have been studied. Recently, we studied the structure of the copper(II) complex of *N,N'*-bis(5-bromo-2-hydroxybenzylidene)-1,3-propanediamine (Kabak *et al.*, 1999). We report here the results of the reactions of nickel(II) with the tetradentate ligand *N,N'*-bis(5-bromo-2-hydroxybenzylidene)-1,3-propanediamine and copper(II) with the tetradentate ligand *N,N'*-

bis(5-chloro-2-hydroxybenzylidene)-1,3-propanediamine, to form monomeric Schiff base complexes of nickel(II) and copper(II).



The structures of [Ni(C₁₇H₁₄Br₂N₂O₂)], (I), and [Cu(C₁₇H₁₄Cl₂N₂O₂)], (II), are isomorphous. Both compounds have crystallographic twofold axes passing through the metal ions. The C9 atoms of compounds (I) and (II) are disordered about the twofold axis and not at the special position. The disorder observed in compounds (I) and (II) was also observed in similar monomer compounds (Kabak *et al.*, 1999; Akhtar & Drew, 1982). The molecules of (I) and (II) have the *cis* form as imposed by the geometry of the tetradentate ligand. In both structures, the metal ion has a tetrahedrally distorted square-planar coordination geometry. The dihedral angles between the MN₂ plane and the MO₂ plane (*M* = Ni or Cu) are 36.1 (2)° for (I) and 36.19 (16)° for (II). In compound (I), the two distances Ni–O of 1.908 (3) Å and Ni–N of 1.959 (4) Å are both larger than the comparable distances of 1.829 (mean Ni–O) and 1.859 Å (mean Ni–N) in *N,N'*-ethylenebis(salicylideneiminato)nickel (Shkol'nikova *et al.*, 1970) and 1.849 (2) (mean Ni–O) and 1.840 (2) Å (mean Ni–N) for *N,N'*-ethylenebis[2-hydroxy-1-naphthyl)methaniminato]nickel(II) (Akhtar, 1981). In compound (II), the Cu–O bond length of 1.907 (2) Å is in good agreement with values found in similar structures (Akhtar & Drew, 1982; Yao *et al.*, 1997). The Cu–N bond, 1.960 (2) Å, is longer than the Cu–O distances and a similar difference was noted in the structure of bis(*N*-methylsalicylideneiminato)copper (Lingafelter *et al.*,

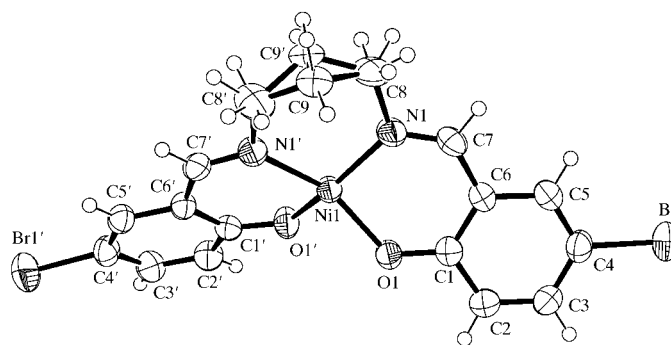


Figure 1
The molecular structure and atomic labelling scheme of (I). Displacement ellipsoids are plotted at the 50% probability level and all disordered atoms are shown (ORTEP-3; Farrugia, 1997).

[†] Alexander von Humboldt Fellow.

1961). The slight increase in metal-to-nitrogen bond distances in (I) and (II) may be attributed to the steric hindrance of the bulkier trimethylene group between the N atoms.

The atoms with the greatest deviation from the coordination planes [N1, O1, N1ⁱ and O1ⁱ; symmetry code: (i) $1 - x, y, \frac{1}{2} - z$] are O1 at 0.458 (3) Å for (I) and 0.460 (2) Å for (II). The unique half of the Schiff base ligands of compounds (I) and (II) are reasonably planar. In (I), the maximum deviation from the plane defined by atoms O1, N1, C1–C9 and Br is 0.297 (5) Å for the N1 atom. In (II), the maximum deviation from the plane defined by atoms O1, N1, C1–C9 and Cl is 0.295 (3) Å for the N1 atom. However, the whole ligands are not planar, since the two halves are twisted with respect to one another. The least-squares planes through each half of the molecules are inclined at an angle of 29.26 (7)° for (I) and 29.26 (5)° for (II). In the free ligand of compound (I), the same interplanar angle is 66.17 (7)° (Elerman, Elmali, Kabak & Svoboda, 1998).

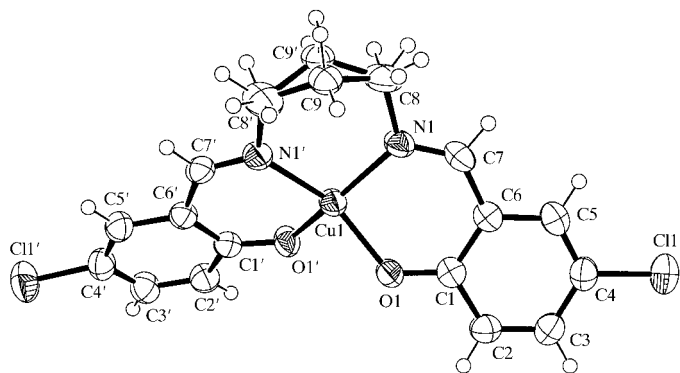


Figure 2

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

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

Experimental

N,N'-Bis(5-bromo-2-hydroxybenzylidene)-1,3-propanediamine was prepared by condensation of 5-bromosalicylaldehyde (10 mmol, 2.01 g) and 1,3-diaminopropane (5 mmol, 0.37 g) in ethanol (70 ml). The reaction mixture was stirred for 3 h and the yellow precipitate was collected by filtration and then washed with cold ethanol. Next, nickel(II) acetate tetrahydrate (1 mmol, 0.249 g) in methanol (50 ml) and *N,N'*-bis(5-bromo-2-hydroxybenzylidene)-1,3-propanediamine (1 mmol, 0.263 g) in methanol (70 ml) were mixed and heated under reflux for 30 min. The resulting product was recrystallized from acetonitrile by slow evaporation of the solvent at room temperature. Compound (II) was prepared from solutions of copper(II) acetate monohydrate (0.5 mmol, 0.099 g) in methanol (25 ml) and *N,N'*-bis(5-chloro-2-hydroxybenzylidene)-1,3-propanediamine (0.5 mmol, 0.230 g) in dioxane (50 ml). The solutions were mixed and the reaction mixture heated under reflux for 30 min. Single crystals of the product were obtained on cooling.

Compound (I)

Crystal data

[Ni(C₁₇H₁₄Br₂N₂O₂)]
M_r = 496.83
 Monoclinic, *C*2/*c*
a = 21.466 (3) Å
b = 8.1670 (10) Å
c = 9.495 (3) Å
 β = 93.07 (2)°
V = 1662.2 (6) Å³
Z = 4

D_x = 1.985 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 2.65–13.28°
 μ = 5.99 mm⁻¹
T = 293 (2) K
 Needle, dark blue
 0.40 × 0.05 × 0.03 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 T_{\min} = 0.75, T_{\max} = 0.84
 2249 measured reflections
 1628 independent reflections
 1016 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.027
 θ_{\max} = 25.97°
 $h = -26 \rightarrow 26$
 $k = -10 \rightarrow 0$
 $l = -11 \rightarrow 3$
 3 standard reflections
 frequency: 120 min
 intensity decay: 2.0%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.085$
 $S = 0.966$
 1628 reflections
 114 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0349P)^2 + 4.1291P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.71 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.38 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °) for (I).

Ni1–O1	1.908 (3)	C1–C6	1.414 (6)
Ni1–N1	1.959 (4)	C2–C3	1.365 (6)
Br1–C4	1.897 (4)	C3–C4	1.383 (6)
O1–C1	1.300 (5)	C4–C5	1.371 (6)
N1–C7	1.289 (6)	C5–C6	1.410 (6)
N1–C8	1.480 (6)	C6–C7	1.436 (6)
C1–C2	1.415 (6)	C8–C9	1.473 (7)
O1 ⁱ –Ni1–O1	87.23 (18)	N1–Ni1–N1 ⁱ	97.4 (2)
O1 ⁱ –Ni1–N1	153.75 (14)	C1–O1–Ni1	127.8 (3)
O1–Ni1–N1	93.39 (14)	C8 ⁱ –C9–C8	123.4 (7)

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

Compound (II)

Crystal data

[Cu(C₁₇H₁₄Cl₂N₂O₂)]
M_r = 412.74
 Monoclinic, *C*2/*c*
a = 21.022 (3) Å
b = 8.140 (2) Å
c = 9.416 (3) Å
 β = 94.06 (2)°
V = 1607.2 (7) Å³
Z = 4

D_x = 1.706 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 1.94–15.86°
 μ = 1.70 mm⁻¹
T = 293 (2) K
 Needle, blue
 0.30 × 0.08 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 T_{\min} = 0.79, T_{\max} = 0.87
 1946 measured reflections
 1568 independent reflections
 1274 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.017
 θ_{\max} = 25.98°
 $h = -25 \rightarrow 25$
 $k = -10 \rightarrow 0$
 $l = -11 \rightarrow 2$
 3 standard reflections
 frequency: 90 min
 intensity decay: 3.0%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.106$
 $S = 1.127$
 1568 reflections
 114 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 0.4477P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.57 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.51 \text{ e } \text{Å}^{-3}$

Table 2

Selected geometric parameters (Å, °) for (II).

Cu1—O1	1.907 (2)	C1—C2	1.422 (4)
Cu1—N1	1.960 (2)	C2—C3	1.361 (4)
C1—C4	1.749 (3)	C3—C4	1.391 (5)
O1—C1	1.298 (4)	C4—C5	1.361 (4)
N1—C7	1.284 (4)	C5—C6	1.409 (4)
N1—C8	1.478 (4)	C6—C7	1.439 (4)
C1—C6	1.420 (4)	C8—C9	1.471 (6)
O1 ⁱ —Cu1—O1	87.44 (12)	N1—Cu1—N1 ⁱ	97.51 (14)
O1 ⁱ —Cu1—N1	153.63 (10)	C1—O1—Cu1	127.66 (18)
O1—Cu1—N1	93.27 (10)	C8 ⁱ —C9—C8	123.7 (4)

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

Geometrical restraints were applied to the C8—C9 distance to prevent anomalous bond distances in the propanediamine chelate ring in (I) and (II). All H atoms were fixed at ideal positions with isotropic displacement parameters constrained to be $1.2U_{\text{eq}}$ of the parent C atom for the phenyl H atoms and $1.5U_{\text{eq}}$ for the methylene H atoms.

For both compounds, 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: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1285). Services for accessing these data are described at the back of the journal.

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