ω scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.592$, $T_{\max} = 0.684$
5348 measured reflections
5007 independent reflections

$R_{\rm int} = 0.0117$
$\theta_{\max} = 24.97°$
$h = 0 \rightarrow 11$
$k = -10 \rightarrow 11$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: 5.5%

Refinement

Refinement on F^2
$R(F) = 0.0375$
$wR(F^2) = 0.1115$
$S = 1.166$
5004 reflections
280 parameters
H atoms: $U(\rm H) = 1.5U_{\rm eq}(\rm C)$
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 1.028P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.709$ e Å^{-3}
$\Delta\rho_{\min} = -0.281$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Sn1—C1	2.158 (4)	Sn1—C13	2.144 (5)
Sn1—C7	2.149 (4)	Sn1—O1	2.066 (3)
C1—Sn1—C7	110.1 (2)	C7—Sn1—C13	115.5 (2)
C1—Sn1—C13	114.6 (2)	C7—Sn1—O1	113.5 (2)
C1—Sn1—O1	95.2 (1)	C13—Sn1—O1	106.1 (2)

Data collection: *CAD*-4 *VAX/PC* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *VAX/PC*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1996). Software used to prepare material for publication: *SHELXL*93.

This research was supported by the University of Malaya (F102/96 and F677/96).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KH1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1988). *CAD*-4 *VAX/PC Fortran System. Operator's Guide to the Enraf–Nonius CAD-4 Diffractometer Hardware, its Software and the Operating System.* Enraf–Nonius, Delft, The Netherlands.

Hall, S. R. & Stewart, J. M. (1990). Editors. *Xtal*3.0 *Reference Manual.* Universities of Western Australia, Australia, and Maryland, USA.

Ng, S. W. & Kumar Das, V. G. (1991). *J. Organomet. Chem.* **409**, 143–156.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Tiekink, E. R. T. (1991). *Appl. Organomet. Chem.* **5**, 1–23.

Tiekink, E. R. T. (1994). *Trends Organomet. Chem.* **1**, 71–116.

Zsolnai, L. & Pritzkow, H. (1996). *ZORTEP. Molecular Graphics Program.* University of Heidelberg, Germany.

© 1997 International Union of Crystallography
Printed in Great Britain – all rights reserved

Acta Cryst. (1997). C**53**, 549-551

Bis[*N*-(4-bromophenyl)salicylaldimine]copper(II)

Yalçin Elerman[a] and Marcus Geselle[b]

[a]*Department of Engineering Physics, Faculty of Sciences, University of Ankara, 06100 Besevler, Ankara, Turkey, and* [b]*Struktur Forschung, FB-Materialwissenschaft, Technische Hochshule Darmstadt, Petersenstrasse 20, D-64287 Darmstadt, Germany. E-mail: elerman@eros.science.ankara.edu.tr*

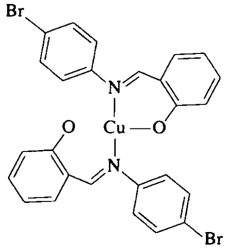
(*Received 16 February 1996; accepted 7 November 1996*)

Abstract

The title compound, bis[2-(4-bromophenyliminomethyl)-phenolato-*N*,*O*]copper(II), [Cu($C_{13}H_9BrNO$)$_2$], has crystallographic inversion symmetry. The Cu$^{\rm II}$ ion shows a slightly distorted square-planar coordination. The Cu—N and Cu—O distances are 2.019 (4) and 1.879 (4) Å, respectively.

Comment

Metal derivatives of Schiff bases have been extensively studied, and copper(II) and nickel(II) complexes play a major role in both synthetic and structural research. Schiff-base complexes are one of the most important stereochemical models in main group and transition metal coordination chemistry with their easy preparation and structural variation (Garnovskii, Nivorozhkin & Minkin, 1993). Copper(II) and nickel(II) ions react with tridentate anionic Schiff bases, giving dimerized complexes with square-planar configurations (Maggio, Pizzino & Romano, 1974). We report here the results of the reaction of copper(II) with the bidentate ligand *N*-(4-bromophenyl)salicylaldimine, forming the title complex, (I).



(I)

The two bidentate ligands are coordinated as chelates to copper(II). The coordination of the Cu atom is necessarily square planar by symmetry. The Cu—O and Cu—N distances are 1.879 (4) and 2.019 (4) Å, respectively. These distances agree with values in other square-planar coordinated copper(II) complexes (Akhtar

& Drew, 1982; Labisbal, Romero, García-Vazquez, Sousa, Castellano & Zukerman-Schpector, 1994). The Cu atom lies 0.537 (5) Å below the plane formed by the O1, C1, C2, C3 and N1 atoms (chelate 1). The chelate plane is inclined at an angle of 23.1 (2)° with respect to the coordination plane. The valence angles at copper are hardly distorted from 90°. The N atom shows sp^2 hybridization, with a sum of bond angles of 359.8 (5)°. The angle between the planar organic groups within one ligand is 39.2 (2)°.

Discrete monomeric molecules are held together in the crystal by van der Waals interactions. The minimum distances between two non-H atoms in neighbouring molecules are C3···C6 and Cu1···C7 with values of 3.569 (7) and 3.573 (5) Å, respectively.

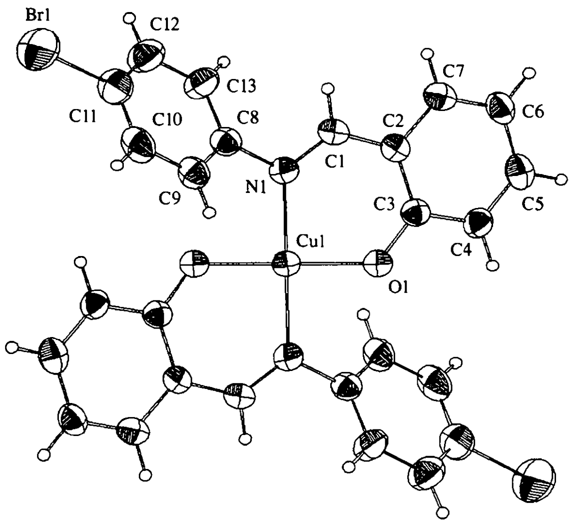


Fig. 1. The molecular structure of the title compound with 50% probability displacement ellipsoids.

Experimental

Solutions of 4-bromoaniline (0.5 mmol) and salicylaldehyde (0.5 mmol) in 50 ml acetonitrile and [Cu(O$_2$CCH$_3$)$_2$].4H$_2$O in 30 ml methanol were heated to boiling, mixed and refluxed for 2 d. Crystals of the product were obtained on cooling.

Crystal data

[Cu(C$_{13}$H$_9$BrNO)$_2$]
M_r = 613.78
Monoclinic
$P2_1/c$
a = 13.843 (2) Å
b = 10.683 (2) Å
c = 8.155 (2) Å
β = 99.13 (2)°
V = 1190.7 (3) Å^3
Z = 2
D_x = 1.712 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 3.3–12.6°
μ = 4.3 mm^{-1}
T = 293 (2) K
Plate
0.33 × 0.33 × 0.04 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Kopfmann & Huber, 1968; North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.25, $T_{\max}$ = 0.84
1656 measured reflections

1656 independent reflections
1229 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 22.98°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 11$
$l = -8 \rightarrow 8$
3 standard reflections
frequency: 120 min
intensity decay: 2.4%

Refinement

Refinement on F^2
$R(F)$ = 0.0434
$wR(F^2)$ = 0.1208
S = 1.117
1463 reflections
151 parameters
H-atom parameters were constrained to parent sites

$w = 1/[\sigma^2(F_o^2) + (0.0851P)^2 + 0.7231P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.813 e Å^{-3}
$\Delta\rho_{\min}$ = −0.408 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Cu1	1/2	1/2	1/2	0.0474 (3)
Br1	1.02545 (6)	0.35580 (13)	0.6921 (2)	0.1411 (6)
N1	0.5897 (3)	0.4277 (3)	0.6966 (5)	0.046 (1)
O1	0.4030 (3)	0.5303 (3)	0.6321 (4)	0.058 (1)
C1	0.5568 (4)	0.3860 (4)	0.8257 (6)	0.047 (1)
C2	0.4593 (4)	0.3904 (4)	0.8558 (6)	0.045 (1)
C3	0.3857 (4)	0.4614 (5)	0.7584 (6)	0.047 (1)
C4	0.2921 (4)	0.4608 (5)	0.8014 (7)	0.055 (1)
C5	0.2710 (5)	0.3924 (6)	0.9337 (7)	0.062 (1)
C6	0.3430 (5)	0.3242 (5)	1.0315 (7)	0.059 (1)
C7	0.4345 (4)	0.3236 (5)	0.9927 (6)	0.055 (1)
C8	0.6928 (4)	0.4100 (5)	0.6952 (6)	0.052 (1)
C9	0.7486 (5)	0.5092 (5)	0.6558 (7)	0.061 (1)
C10	0.8486 (5)	0.4942 (7)	0.6574 (7)	0.074 (2)
C11	0.8894 (5)	0.3780 (8)	0.6944 (8)	0.082 (2)
C12	0.8343 (5)	0.2785 (7)	0.730 (1)	0.087 (2)
C13	0.7363 (4)	0.2958 (5)	0.7322 (8)	0.068 (2)

Table 2. *Selected geometric parameters (Å, °)*

Cu1—N1	2.019 (4)	O1—C3	1.318 (6)
Cu1—O1	1.879 (4)	C1—C2	1.411 (7)
N1—C1	1.291 (6)		
O1—Cu1—N1	90.9 (2)	C8—N1—Cu1	122.0 (3)
C1—N1—C8	116.0 (4)	C3—O1—Cu1	125.9 (3)
C1—N1—Cu1	121.8 (3)	N1—C1—C2	127.0 (4)

Data were collected to $\theta_{\max}$ = 23°; only very weak reflections were observed at higher angles.

Data collection: *Enraf–Nonius SDP-Plus* (Frenz, 1985). Cell refinement: *Enraf–Nonius SDP-Plus*. Data reduction: *Enraf–Nonius SDP-Plus*. Program(s) used to solve structure: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *Xtal*3.0.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Akhtar, B. & Drew, M. G. B. (1982). *Acta Cryst.* **B38**, 1149–1154.

Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Garnovskii, A. D., Nivorozhkin, A. L. & Minkin, V. I. (1993). *Coord. Chem. Rev.* **126**, 1–42.

Hall, S. R. & Stewart, J. M. (1990). Editors. *Xtal3.0 Reference Manual*. Universities of Western Australia, Australia, and Maryland, USA.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kopfmann, G. & Huber, R. (1968). *Acta Cryst.* **A24**, 348–351.

Labisbal, E., Romero, J., García-Vasquez, J. A., Sousa, A., Castellano, E. E. & Zukerman-Schpector, J. (1994). *Acta Cryst.* **C50**, 1043–1044.

Maggio, F., Pizzino, T. & Romano, V. (1974). *Inorg. Nucl. Chem. Lett.* **10**, 1005–1008.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1997). C53, 551–554

Sodium Bis(2,9-dimethyl-1,10-phenanthroline)-μ-hydroxo-di(thiosulfato)dizinc(II) Pentahydrate Methanol Solvate

SERGIO BAGGIO,[a] MARIA I. PARDO,[a] RICARDO BAGGIO[b] AND MARIA TERESA GARLAND[c]

[a]Universidad Nacional de la Patagonia, Sede Puerto Madryn and CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina, [b]División Física del Sólido, Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina, and [c]Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 487-3, Santiago de Chile, Chile. E-mail: baggio@cnea.edu.ar

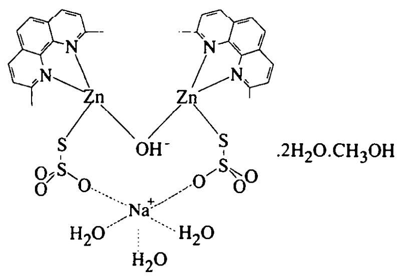
(Received 24 July 1996; accepted 12 December 1996)

Abstract

The title complex, triaqua-1κ^3O-bis(2,9-dimethyl-1,10-phenanthroline)-2κ^2N,N';3κ^2N,N'-μ-hydroxo-2:3κ^2O-di-μ-thiosulfato-1:2κ^2O:S;1:3κ^2O:S-sodiumdizinc(II) dihydrate methanol solvate, $[Zn_2(C_{14}H_{12}N_2)_2(\mu\text{-}OH)(\mu\text{-}S_2O_3)_2Na(H_2O)_3].2H_2O.CH_3OH$, presents an unusual ten-membered ring containing three different metal centers, two zinc and one sodium, bridged by one hydroxo and two thiosulfate groups. The thiosulfate groups bridge through S and O atoms, with a mean S—S bond length which is longer than that found in the free anion, with the corresponding S—O distances shorter. Both zinc coordination spheres are tetrahedral, while that of the pentacoordinate sodium is distorted trigonal bipyramidal. The monomeric units are linked by strong hydrogen-bonding interactions into chains parallel to **z**, which in turn are held together by hydrogen-bonding contacts through some not fully occupied solvate molecule sites, as well as by van der Waals interactions.

Comment

Zn^{II} complexes including the thiosulfate ion as a ligand are not common. The few structures reported so far (Andreetti, Cavalca, Domiano & Musatti, 1968; Baggio, Baggio & de Perazzo, 1974; Baggio, Baggio, Pardo & Garland, 1996) invariably display very interesting coordination geometries, a characteristic shared by many d^{10} ions, where the coordination number is strongly influenced by the ligands involved, as well as by crystal-packing interactions and hydrogen-bonding forces. As part of a structural study of complexes of d^{10} ions containing the thiosulfate group, we report here the structure of $[Zn_2(dmph)_2(\mu\text{-}OH)(\mu\text{-}S_2O_3)_2Na(H_2O)_3].2H_2O.CH_3OH$ (where dmph is 2,9-dimethyl-1,10-phenanthroline), (I).



(I)

The molecule of (I) with the numbering scheme used is shown in Fig. 1. A striking feature in the compound is the presence of a ten-membered ring containing three metal atoms (Zn1, Zn2 and Na). The two independent Zn atoms in the cycle have a similar distorted tetrahedral environment, provided in each case by two N atoms from a dmph molecule, one S atom from a thiosulfate group and a bridging OH group, which is shared by the two Zn atoms. This type of Zn—(OH)—Zn bridge has already been reported in other compounds. The mean 'bridge' Zn—OH distance in the present structure [1.910 (3) Å] is at the shorter end of the reported range [shortest is 1.869 (6) Å (Guseinov *et al.*, 1987) and longest

© 1997 International Union of Crystallography
Printed in Great Britain – all rights reserved

ISSN 0108-2701
© 1997