Table 1. *Selected geometric parameters and hydrogen-bonding geometry (Å, °)*

Ir—N1	2.092 (3)	P—C31	1.832 (4)
Ir—N2	2.079 (3)	P—C41	1.825 (4)
Ir—C5	2.223 (4)	N1—C1	1.348 (5)
Ir—C6	2.211 (4)	N1—C2	1.429 (5)
Ir—C7	2.222 (3)	N2—C1	1.413 (5)
Ir—C8	2.210 (3)	N2—C3	1.349 (5)
Ir—C9	2.216 (4)	O1—C1	1.250 (5)
Ir—P	2.3001 (9)	O2—C3	1.236 (5)
P—C21	1.833 (4)	C3—C4	1.512 (6)
N1—Ir—P	87.84 (9)	C3—N2—C1	129.9 (3)
N2—Ir—P	88.79 (9)	O1—C1—N1	128.2 (4)
N2—Ir—N1	62.08 (12)	O1—C1—N2	129.5 (4)
C1—N1—Ir	98.5 (2)	O2—C3—N2	121.3 (4)
C2—N1—Ir	137.7 (3)	O2—C3—C4	120.6 (4)
C1—N2—Ir	97.0 (2)	N1—C1—N2	102.3 (3)
C3—N2—Ir	132.6 (3)	N2—C3—C4	118.1 (4)
C1—N1—C2	123.8 (3)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C50—H50*A*···O1	0.99	2.01	2.958 (6)	159

A single molecule of chloroform of crystallization was located from residual electron-density maps and was refined anisotropically. A reasonable hydrogen bond exists between the chloroform carbon (C50) and the O1 atom [2.958 (6) Å]. The maximum residual peak lies 1.37 Å from C45 and the minimum peak lies 0.89 Å from the Ir atom.

Data collection: *SMART* (Siemens, 1994*a*). Cell refinement: *SAINT* (Siemens, 1994*a*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *SHELXTL* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1247). Services for accessing these data are described at the back of the journal.

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Triaqua(2,2′-bipyridyl-*N*,*N*′)(thiosulfato-*S*)nickel(II) dihydrate and triaqua(1,10-phenanthroline-*N*,*N*′)(thiosulfato-*S*)nickel(II) monohydrate

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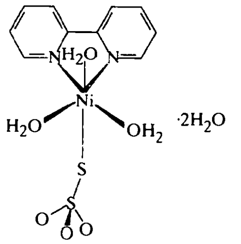
Abstract

In the title compounds, $[Ni(S_2O_3)(C_{10}H_8N_2)(H_2O)_3]\cdot 2H_2O$ and $[Ni(S_2O_3)(C_{12}H_8N_2)(H_2O)_3]\cdot H_2O$, the Ni^{II} ion displays a distorted octahedral coordination provided by the two N atoms of the organic ligand, one S atom from the thiosulfate anion and three water molecules. The bipyridine complex has two independent moieties in the asymmetric unit related by a non-crystallographic pseudosymmetry center. The thiosulfate anions are quite regular, in contrast with other similar sulfur-coordinated thiosulfates in the literature.

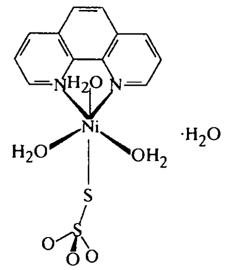
Comment

The thiosulfate group has been shown to be a most versatile ligand, able to coordinate in many different ways, depending both on the characteristics of the cations involved as well as on the environmental conditions. Thus, among the *ca* 50 structures containing the anion which are included in the October 1998 version of the Cambridge Structural Database (CSD; Allen & Kennard, 1993), there are examples where the thiosulfate binds in a mono-, bi- or even tridentate fashion, both in monomeric species as well as in one-, two- or three-dimensional polymers. At the same time, nickel(II) appears to be a rather interesting metal center for thiosulfate complexing because, as a borderline acid ion in the Pearson classification scheme (Pearson, 1973), it would not be expected to exhibit a preference for binding to the hard (O) or the soft (S) end of the thiosulfate group, leading to a potentially great variety of coordination geometries, each specific case depending on complementary external factors such as crystal-field stabilization, the shapes of accompanying ligands, hydrogen bonding, van der Waals interactions *etc.*

So far, however, the possibilities of nickel(II) as a coordination center for thiosulfate complexes have not been adequately explored, as only a single structure of this type has been fully reported, *viz.* tetrakis(thiourea-*S*)(thiosulfato-*O*,*S*)nickel(II) monohydrate (Gasparri *et al.*, 1969), where the ligand binds in a rather unusual bidentate fashion. As part of a short series of structural studies of nickel thiosulfates, we report here the crystal structures of two novel complexes of this type, *i.e.* triaqua(2,2′-bipyridyl-*N*,*N*′)(thiosulfato-*S*)nickel(II) dihydrate, $[Ni(S_2O_3)(bpy)(H_2O)_3]\cdot 2H_2O$, (I), and triaqua(1,10-phenanthroline-*N*,*N*′)(thiosulfato-*S*)nickel(II) monohydrate, $[Ni(S_2O_3)(phen)(H_2O)_3]\cdot H_2O$, (II) (bpy is 2,2′-bipyridine and phen is 1,10-phenanthroline).



(I)



(II)

Both compounds are monomeric (Figs. 1 and 2) and present similar distorted octahedral environments around the Ni^{2+} ions [range of and average [s.u.] deviations from ideal values: 0.30–11.20° and 4.9 [34]° for (I); 0.3–10.5° and 4.1 [29]° for (II)]. The coordination positions are occupied by the terminal S atom from the thiosulfate group, three water molecules and two N atoms from the organic ligand, acting in the usual bidentate mode, which subtend the smallest coordination angle to the cation.

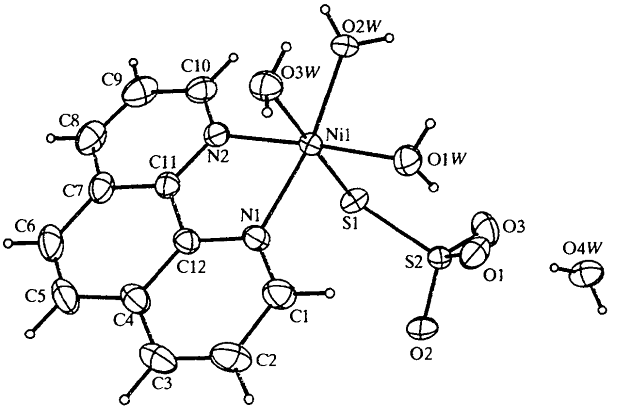


Fig. 2. The molecular diagram for (II). Displacement ellipsoids are drawn at the 50% probability level.

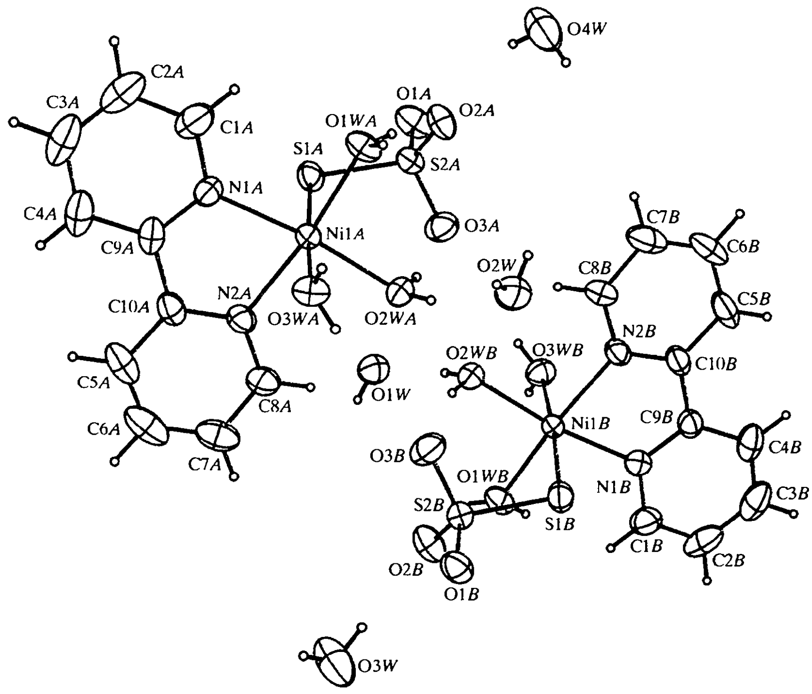


Fig. 1. The molecular diagram for (I). Note the pseudosymmetry center across the two independent molecules. Displacement ellipsoids are drawn at the 50% probability level.

Compound (I) has two independent molecules in the asymmetric unit (space group *Pc*). The molecules are very closely related to each other by a non-crystallographic symmetry center at [0.000 (1), 0.687 (1), 0.000 (1)]. The positioning of this 'center' (clearly incompatible with any space group of higher symmetry), as well as the distribution of the hydration water molecules (significantly out of the centrosymmetric pattern), are proof of the 'pseudo' character of the operation. However, the relationship linking the two units is amazingly good, as can be assessed by the r.m.s. deviation of the least-squares overlap of the two units [0.036 (4) Å]. The largest departures (0.06 Å) are found for some of the thiosulfate O atoms.

As a result of this relationship, the two independent molecules in (I) show quite similar bond lengths and angles around the central atom; the Ni—S bond distances are 2.477 (2) and 2.491 (2) Å, while the Ni—N distances range from 2.041 (6) to 2.071 (5) Å, which are typical values for octahedral nickel(II) complexes. The Ni—O distances split into two well differentiated groups, *i.e.* those which are *cis* to the thiosulfate anion [shorter, mean value 2.067 (5) Å] and those which are *trans* [significantly longer, mean value 2.121 (5) Å]. The same effect is observed in (II) where the *trans* Ni—O distance is 2.1125 (15) Å *versus* a mean of 2.0717 (14) Å for the *cis* Ni—O distances. The other distances in the coordination sphere of both compounds are quite comparable (Tables 1 and 3).

Contradicting a general feature observed in S-bonded thiosulfate complexes with other metal ions (Baggio *et al.*, 1996, and references therein), coordination does not seem to affect the geometry of the thiosulfate group; the mean values of the S—S and S—O bond lengths are practically the same as those reported for the ionic unit (Teng *et al.*, 1984, and references therein). This is probably related to the weak character of the Ni—S bonds, with lengths at the longmost end of the normal range.

The molecules are strongly interconnected to each other through a very complex hydrogen-bonding scheme (Tables 2 and 4). The result is a densely woven network where all the water molecules present in the structures [except O4*W* in (II)] are doubly involved as donors, and where all the thiosulfate O atoms, as well as the hydration water molecules, in turn, act as acceptors. The strength of the interactions range from normal to weak, with no H···O distance being shorter than 1.80 Å.

Experimental

The title compounds were obtained by mixing water solutions of nickel nitrate and sodium thiosulfate with a methanolic solution of the corresponding organic ligand (molar ratio 1:3:1). On standing, crystals suitable for X-ray diffraction were obtained.

Compound (I)

Crystal data

$[Ni(S_2O_3)(C_{10}H_8N_2)(H_2O)_3]\cdot 2H_2O$
$M_r = 417.09$
Monoclinic
Pc
$a = 12.377 (3)$ Å
$b = 6.9740 (14)$ Å
$c = 19.822 (4)$ Å
$\beta = 102.82 (3)°$
$V = 1668.3 (6)$ Å^3
$Z = 4$
$D_x = 1.66$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5–15.0°$
$\mu = 1.45$ mm^{-1}
$T = 293 (2)$ K
Needle
0.40 × 0.15 × 0.10 mm
Light blue

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1988)
$T_{min} = 0.66$, $T_{max} = 0.83$
4225 measured reflections
3838 independent reflections (plus 170 Friedel-related reflections)

3610 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 27.51°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 9$
$l = -25 \rightarrow 25$
3 standard reflections every 150 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.099$
$S = 1.08$
4008 reflections
496 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 2.20P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max} = 0.85$ e Å^{-3}
$\Delta\rho_{min} = -0.87$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.047 (18)

Table 1. *Selected bond lengths (Å) for (I)*

Ni1*A*—N1*A*	2.052 (6)	Ni1*B*—N1*B*	2.041 (6)
Ni1*A*—N2*A*	2.071 (5)	Ni1*B*—N2*B*	2.065 (5)
Ni1*A*—O1*WA*	2.069 (4)	Ni1*B*—O1*WB*	2.075 (4)
Ni1*A*—O2*WA*	2.062 (5)	Ni1*B*—O2*WB*	2.064 (5)
Ni1*A*—O3*WA*	2.110 (5)	Ni1*B*—O3*WB*	2.133 (5)
Ni1*A*—S1*A*	2.4772 (18)	Ni1*B*—S1*B*	2.4914 (18)
S1*A*—S2*A*	2.027 (2)	S1*B*—S2*B*	2.030 (2)
S2*A*—O1*A*	1.453 (5)	S2*B*—O1*B*	1.463 (5)
S2*A*—O2*A*	1.467 (5)	S2*B*—O2*B*	1.468 (5)
S2*A*—O3*A*	1.464 (5)	S2*B*—O3*B*	1.459 (5)

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*WA*—H1*A*1···O1*A*^{i}	0.81 (4)	1.86 (4)	2.676 (7)	178 (4)
O1*WA*—H1*A*2···O2*A*	0.80 (7)	1.95 (6)	2.735 (7)	165 (6)
O2*WA*—H2*A*1···O2*W*	0.78 (7)	2.02 (7)	2.795 (8)	167 (6)
O2*WA*—H2*A*2···O3*A*	0.83 (7)	1.93 (7)	2.762 (8)	167 (5)
O3*WA*—H3*A*1···O1*W*^{i}	0.80 (5)	1.94 (5)	2.750 (6)	174 (6)
O3*WA*—H3*A*2···S1*A*^{i}	0.81 (7)	2.49 (7)	3.284 (5)	163 (7)

O1*WB*—H1*B*1· · ·O2*B*	0.82 (10)	2.15 (13)	2.725 (7)	126 (9)
O1*WB*—H1*B*2· · ·O1*B*^{ii}	0.82 (15)	2.08 (19)	2.715 (7)	133 (13)
O2*WB*—H2*B*1· · ·O3*B*	0.84 (6)	1.93 (5)	2.758 (8)	163 (5)
O2*WB*—H2*B*2· · ·O1*W*	0.81 (8)	1.99 (9)	2.807 (8)	173 (7)
O3*WB*—H3*B*1· · ·S1*B*^{ii}	0.79 (5)	2.51 (5)	3.279 (5)	160 (5)
O3*WB*—H3*B*2· · ·O2*W*^{ii}	0.80 (5)	1.98 (5)	2.772 (6)	164 (6)
O1*W*—H11· · ·O4*W*^{iii}	0.78 (9)	1.87 (8)	2.656 (10)	174 (8)
O1*W*—H12· · ·O3*B*^{ii}	0.80 (7)	2.09 (6)	2.894 (8)	174 (6)
O2*W*—H21· · ·O3*A*^{i}	0.82 (8)	2.08 (7)	2.911 (8)	172 (7)
O2*W*—H22· · ·O3*W*^{iv}	0.79 (5)	1.91 (5)	2.709 (10)	170 (5)
O3*W*—H31· · ·O1*B*	0.82 (6)	2.08 (7)	2.873 (10)	159 (5)
O3*W*—H32· · ·O2*A*^{v}	0.82 (8)	2.11 (8)	2.942 (10)	176 (8)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $x, y - 1, z$; (iii) $x, 1 - y, z - \frac{1}{2}$; (iv) $x, 2 - y, \frac{1}{2} + z$; (v) $x, 2 - y, z - \frac{1}{2}$.

Compound (II)

Crystal data

$[Ni(S_2O_3)(C_{12}H_8N_2)(H_2O)_3]\cdot H_2O$
$M_r = 423.10$
Triclinic
$P\overline{1}$
$a = 8.434$ (2) Å
$b = 8.782$ (2) Å
$c = 11.344$ (2) Å
$\alpha = 90.47$ (3)°
$\beta = 91.27$ (3)°
$\gamma = 104.23$ (3)°
$V = 814.2$ (3) Å^3
$Z = 2$
$D_x = 1.73$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5–15.0°$
$\mu = 1.49$ mm^{-1}
$T = 293$ (2) K
Plate
0.45 × 0.25 × 0.12 mm
Light blue

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Molecular Structure Corporation, 1988)
$T_{\min} = 0.65$, $T_{\max} = 0.87$
3982 measured reflections
3738 independent reflections
3566 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 27.49°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 11$
$l = -14 \rightarrow 14$
3 standard reflections every 150 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.071$
$S = 1.09$
3738 reflections
250 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 0.460P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.59$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected bond lengths (Å) for (II)*

Ni1—N1	2.0695 (14)	Ni1—S1	2.4488 (10)
Ni1—N2	2.0658 (15)	S1—S2	2.0031 (9)
Ni1—O1*W*	2.0634 (14)	S2—O1	1.4865 (15)
Ni1—O2*W*	2.0800 (14)	S2—O2	1.4570 (14)
Ni1—O3*W*	2.1125 (15)	S2—O3	1.4757 (15)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H· · ·*A*	*D*—H	H· · ·*A*	*D*· · ·*A*	*D*—H· · ·*A*
O1*W*—H1*WA*· · ·O3^{i}	0.76 (3)	2.02 (3)	2.783 (2)	175 (3)
O1*W*—H1*WB*· · ·O1	0.86 (2)	1.82 (2)	2.679 (2)	170 (3)
O2*W*—H2*WA*· · ·O1^{i}	0.86 (2)	2.02 (2)	2.880 (2)	170 (2)
O2*W*—H2*WB*· · ·O2^{ii}	0.80 (3)	1.92 (3)	2.714 (2)	168 (3)
O3*W*—H3*WA*· · ·O4*W*^{iii}	0.81 (3)	1.99 (3)	2.795 (2)	170 (2)
O3*W*—H3*WB*· · ·O4*W*^{i}	0.78 (3)	2.05 (3)	2.816 (2)	164 (2)
O4*W*—H4*WA*· · ·O1^{iv}	0.82 (3)	2.06 (3)	2.869 (2)	167 (3)
O4*W*—H4*WB*· · ·O3	0.84 (2)	1.90 (3)	2.723 (2)	165 (3)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x - 1, y, z$; (iii) $x - 1, y - 1, z$; (iv) $2 - x, 1 - y, 1 - z$.

Those H atoms attached to carbon and unequivocally defined by the stereochemistry were placed at their calculated positions and allowed to ride on their host atoms (C—H 0.96 Å). Those corresponding to water molecules were found in difference Fourier synthesis and subsequently refined with a (refinable) restrained O—H distance. The final ΔF map for compound (I) showed rather large peaks and troughs (≈0.90 e Å^{-3}) in the vicinity (≈0.85 Å) of the Ni atom, suggesting perhaps an absorption effect not fully accounted for by the empirical correction performed. The remainder of the map appeared rather featureless with peaks below 0.55 e Å^{-3}.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983) and *CSD* (Allen & Kennard, 1993) for (I); *PARST* (Nardelli, 1983) and CSD (Allen & Kennard, 1993) for (II).

This work was partially supported by a CONICET grant (PIP 0470/98). We thank the Spanish Research Council (CSIC) for providing us with a free-of-charge license to the CSD system. EF is a grateful recipient of a scholarship from CONICET.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1471). Services for accessing these data are described at the back of the journal.

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{[μ-Bis(salicylidene)-1,3-propanediaminato]copper(II)}dibromomercury(II)

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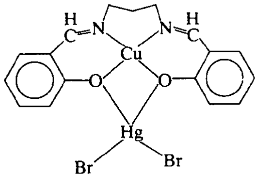
Abstract

In the title complex, dibromo-$2\kappa^2Br$-μ-{2,2′-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato}-$1\kappa^4N,N',O,O'$:$2\kappa^2O,O'$-copper(II)mercury(II), [$Cu(C_{17}H_{16}N_2O_2)\{HgBr_2\}$], the Cu^{II} and Hg^{II} atoms are doubly bridged by the two O atoms of the *N*,*N*′-bis(salicylidene)-1,3-propanediaminate ($SALPD^{2-}$) ligand, and the two N atoms of this ligand complete the distorted square-planar coordination around the Cu^{II} atom. The coordination around the Hg^{II} atom is distorted tetrahedral, involving two bridging O atoms and two Br atoms. The bond angles in the $HgCuO_2$ bridging plane are in the range 61.4 (1)–108.0 (2)°. The Cu···Hg distance is 3.523 (3) Å.

Comment

The title complex, (I), was synthesized in the process of extending our structural studies on doubly oxygen-bridged dimeric homonuclear metal complexes to heteronuclear complexes (Ülkü *et al.*, 1998, and references therein).



(I)

As can be seen from Fig. 1, the distorted square-planar coordination around the Cu^{II} atom involves two O and two N atoms from the *N*,*N*′-bis(salicylidene)-1,3-propanediaminate ($SALPD^{2-}$) ligand. The Cu^{II} atom is located −0.0261 (7)° from the best plane of the coordinating O1, O2, N2 and N1 atoms. The bond angles within the coordination plane around the Cu^{II} atom range from 82.0 (2) (O1—Cu—O2) to 170.7 (2)° (O1—Cu—N2). In the bridging plane, the two Cu—O distances [1.919 (4) and 1.921 (3) Å] are equal within experimental error and compare well with values reported previously (Baker *et al.*, 1970; Ülkü *et al.*, 1997; Tahir *et al.*, 1996), but the Hg—O bond lengths [2.418 (4) (Hg—O1) and 2.519 (3) Å (Hg—O2)] are slightly different. The Cu···Hg distance is 3.523 (3) Å.

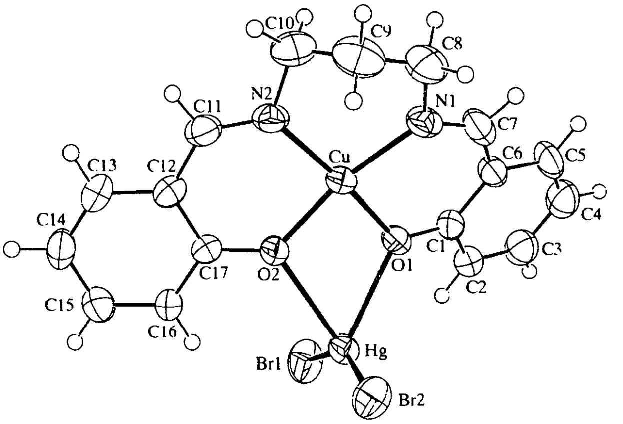


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound with the atomic numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii.

The coordination around the Hg^{II} atom is distorted tetrahedral consisting of two bridging O atoms and two Br atoms. The smallest bond angle of the distorted tetrahedron around the Hg^{II} atom is 61.4 (1)° (O1—Hg—O2) and the largest bond angle is 152.25 (3)° (Br1—Hg—Br2). The dihedral angle between the O1/Hg/O2 and Br1/Hg/Br2 moieties is 87.2 (1)°. The distances of the *para*-positioned Cu and C9 atoms of the Cu/N1/C8/C9/C10/N2 chelate ring from the plane of the other four atoms are 0.185 (1) and 0.648 (7) Å, respectively. In the Cu/N2/C11/C12/C17/O2 chelate ring, the Cu^{II} atom has the greatest deviation of 0.0695 (7) Å from the best plane, while the greatest deviation from the best plane of the Cu/N1/C7/C6/C1/O1 chelate ring is for the O1 atom [0.178 (4) Å].

Experimental

Ammonia solution (20 ml) was added to a solution of *N*,*N*′-bis(salicylidene)-1,3-propanediamine (2.82 g, 10 mmol) in hot ethanol (30 ml) and the mixture was heated. A solution of $CuCl_2\cdot 2H_2O$ (1.70 g, 10 mmol) in hot water (30 ml) was added and the resulting mixture was set aside. After 2 h, the resulting copper complex, *i.e.* [$Cu(C_{17}H_{16}N_2O_2)$], was filtered off and dried. This complex (0.343 g, 1 mmol) was dissolved in hot dioxane (50 ml) and a solution of $HgBr_2$ (0.360 g, 1 mmol) in

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