Absorption correction:
 ψ scan (*XEMP* in *SHELXTL/PC*; Sheldrick, 1991)
 $T_{min} = 0.70$, $T_{max} = 0.84$
7932 measured reflections
6211 independent reflections

$R_{int} = 0.088$
$\theta_{max} = 25°$
$h = -27 \rightarrow 24$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 29$
2 standard reflections
 every 98 reflections
 intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.204$
$S = 1.328$
6041 reflections
486 parameters
H atoms: C—H riding
$w = 1/[\sigma^2(F_o^2) + 115.5136P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.487$ e Å^{-3}
$\Delta\rho_{min} = -0.563$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å)*

Zn1—N1*C*	2.134 (5)	Zn1—N2*C*	2.183 (5)
Zn1—N2*A*	2.141 (5)	S1—O2	1.458 (5)
Zn1—N1*B*	2.161 (5)	S1—O3	1.469 (5)
Zn1—N2*B*	2.164 (5)	S1—O1	1.472 (5)
Zn1—N1*A*	2.166 (5)	S1—S2	1.990 (2)

Refinement was performed with *SHELXL*93 (Sheldrick, 1993) on F^2, using the whole data set. H atoms bonded to C atoms were added at their expected positions and not refined, but allowed to ride. Those from water molecules could not be found in the final ΔF synthesis and were accordingly ignored. Two water molecules out of the seven independent ones in the structure appeared slightly disordered, though fully occupied. Refinement of the site-occupation factor for the other five, lying on single crystallographic sites, led to three of them being only partially occupied. This was taken as an explanation for some decay taking place in the appearance of the crystal after the diffractometric measurement had been performed. No effect on the diffracting power could be detected, however, as estimated by the regular check of two standard reflections.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL/PC*. Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* in *SHELXL*93, *PARST* (Nardelli, 1983) and *CSD* (Allen, Kennard & Taylor, 1983).

The authors would like to thank Fundación Andes for the purchase of the single-crystal diffractometer currently operating at the Universidad de Chile.

Supplementary data and a packing diagram for this paper are available from the IUCr electronic archives (Reference: HA1190). Services for accessing these data are described at the back of the journal.

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A Nickel Complex with an Asymmetric N_2OS Schiff Base Ligand

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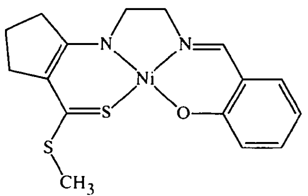
Abstract

In the structure of the title complex, {methyl 2-{2-[(2-hydroxyphenyl)methyleneamino]ethylamino}-1-cyclopentenedithiocarboxylato-*O*,*N*,*N'*,*S*}nickel(II), [Ni($C_{16}H_{18}N_2OS_2$)], the Ni^{II} atom is coordinated by S, O and two N atoms in a nearly planar environment. The two inequivalent N atoms, coordinated in a *cis* manner, show virtually identical bond lengths and angles indicating that the NS ligand fragment coordinates as a Schiff base ligand, with the N atom behaving as an imine and the S atom having a strong thiolate character.

Comment

The present compound, (I), was obtained as part of a systematic study on the effect of the ligand characteristics (coordination sphere and substituents) on the physical and chemical properties of nickel complexes, especially on the factors that influence the accessibility of several oxidation states for nickel (de Castro, Gomes & Pereira, 1997; Azevedo *et al.*, 1994). Details of synthetic procedures and physicochemical characterization will be published elsewhere (de Castro, Gomes & Pereira, 1997).



(I)

The structure revealed the existence of an asymmetric N_2OS coordination sphere around the Ni^{II} atom, with an almost planar geometry, only slightly tetrahedrally distorted. Maximum deviation of atoms from the least-squares plane of coordination (Ni, N1, N2, O1 and S1) is 0.055 (2) Å, and the dihedral angle between the Ni, N1, O1 and Ni, N2, S1 planes is 4.40 (17)°. The ethylene bridge shows a twisted conformation, with C8 and C9 displaced by 0.258 (8) and 0.249 (8) Å, respectively, on opposite sides of the best coordination plane. Metal–ligand bond lengths are within the expected range for NiN_2O_2 and NiN_2S_2 complexes, but are indicative that, upon coordination, the π-electron density of the NS ligand fragment (Bordas, Sohar, Matolcsy & Berencsi, 1972) is redistributed in such a way that the N-atom donor acquires imine character and the S-atom donor gains some thiolate character. This is corroborated by analysis of bond lengths and angles for this fragment of the ligand which shows that double-bond character is essentially located at N2—C10 and C14—C15, and explains the similarity of the two inequivalent Ni—N bond lengths.

The structures of the nickel complexes of the corresponding symmetric ligands, salen (Manfredotti & Guastini, 1983) and cd_2en [*N*,*N*′-ethylenebis(methyl-2-amino-1-cyclopentenedithiocarboxylate; Martin, Bereman & Singh, 1991], are also approximately square planar, thus allowing a direct comparison between bond lengths and angles of these three related complexes. Essentially, all bond lengths and angles within the ligand skeleton are similar to those of Ni(salen) and Ni(cd_2en), and there are only minor differences in metal–ligand bond lengths, with a small decrease in Ni—N1 and Ni—O, and a small increase in Ni—N2 and Ni—S bond lengths. These differences indicate that while the NO fragment behaves as a weaker ligand, the NS fragment seems to be more tightly bound to the metal ion than in the corresponding symmetric complex, and may be related to the different steric requirements of O and S donors. This is in agreement with the spectroscopic characteristics of the complex reported here (de Castro, Gomes & Pereira, 1997) which is more similar to the complex with an N_2S_2 coordination sphere (Martin & Bereman, 1991) than to [Ni(salen)] (Holm, 1960).

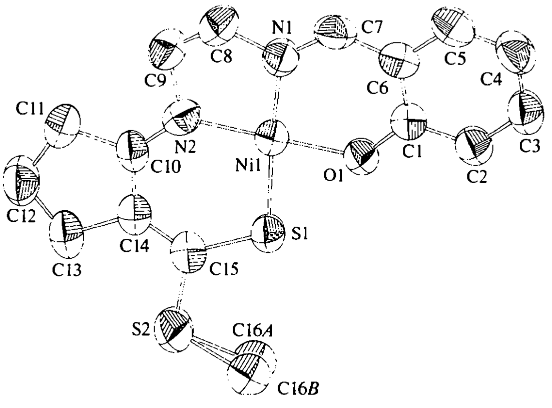


Fig. 1. The molecular structure of [Ni($C_{16}H_{18}N_2OS_2$)] with the atom-labelling scheme. Displacement ellipsoids are plotted at the 50% probability level. H atoms have been omitted for clarity.

Experimental

The title compound was prepared by addition of $Ni(CH_3COO)_2.4H_2O$ (0.01 mol/10 ml) to a stoichiometric amount of the protonated ligand in methanol–chloroform (20 ml, 1:1 *v*/*v*). The solution immediately turned light green and a green powder was obtained by allowing the solution to stand for a few hours. The complex was recrystallized from acetonitrile. Slow evaporation of a 1,4-dioxane–dichloromethane solution afforded prismatic single crystals of diffractometric quality. Analysis: C 50.50, H 5.47, N 7.48%; $C_{10}H_{18}N_2NiOS_2$ requires C 50.96, H 5.35, N 7.43%.

Crystal data

[Ni($C_{16}H_{18}N_2OS_2$)]
$M_r = 377.13$
Triclinic
$P\overline{1}$
$a = 7.567 (11)$ Å
$b = 9.297 (13)$ Å
$c = 12.281 (14)$ Å
$\alpha = 72.00 (8)°$
$\beta = 80.21 (8)°$
$\gamma = 81.04 (8)°$
$V = 804.8 (19)$ Å^3
$Z = 2$
$D_x = 1.556$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 397 reflections
$\theta = 9.5–56.3°$
$\mu = 1.435$ mm^{-1}
$T = 293 (2)$ K
Transparent block
0.3 × 0.1 × 0.1 mm
Bright green

Data collection

Stoe Image plate detector system
Area detector scans
Absorption correction: none
9660 measured reflections
3603 independent reflections

1960 reflections with $I > 2\sigma(I)$
$R_{int} = 0.097$
$\theta_{max} = 28.29°$
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.216$
$S = 1.091$
3001 reflections
211 parameters
H atoms: see below

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.484$ e Å^{-3}
$\Delta\rho_{min} = -0.508$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.043 (11)

$w = 1/[\sigma^2(F_o^2) + (0.0822P)^2 + 0.3787P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ni1—O1	1.860 (4)	C8—N1	1.442 (7)
Ni1—N2	1.867 (5)	C8—C9	1.485 (9)
Ni1—N1	1.872 (5)	C9—N2	1.476 (7)
Ni1—S1	2.163 (3)	C10—N2	1.313 (7)
S1—C15	1.725 (6)	C10—C14	1.440 (8)
C1—O1	1.311 (7)	C10—C11	1.517 (8)
C1—C2	1.412 (8)	C13—C14	1.509 (8)
C6—C7	1.410 (9)	C14—C15	1.343 (8)
C7—N1	1.295 (7)	C15—S2	1.775 (7)
O1—Ni1—N2	178.1 (2)	C15—S1—Ni1	110.3 (2)
O1—Ni1—N1	94.0 (2)	O1—C1—C6	124.4 (5)
N2—Ni1—N1	86.3 (2)	N1—C7—C6	127.0 (6)
O1—Ni1—S1	81.87 (15)	N1—C8—C9	109.0 (5)
N2—Ni1—S1	98.0 (2)	N2—C9—C8	109.1 (5)
N1—Ni1—S1	174.09 (14)	N2—C10—C14	127.3 (5)

Data was corrected for Lorentz–polarization effects. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares techniques. All H atoms were calculated for geometric idealized positions, except for H7 and H11 which were located in the difference Fourier map. H atoms, when calculated in idealized positions, were riding in the refinement with site-occupancy factors and U (or U^{ij}) fixed, but with coordinates free to refine. Structural calculations were carried out on an IBM-PC.

Data collection: Stoe IPDS software. Cell refinement: Stoe IPDS software (*CELL*). Data reduction: Stoe IPDS software (*INTEGRATE*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1482). Services for accessing these data are described at the back of the journal.

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(Ketoprofenato)trimethyltin(IV)†

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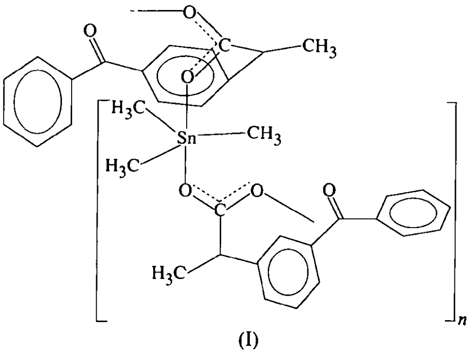
Abstract

In the title compound, $[Sn(CH_3)_3(C_{16}H_{13}O_3)]$, the Sn atom has fivefold coordination involving three methyl C atoms defining the equatorial plane of a trigonal bipyramid and two O atoms from two carboxylate groups occupying the axial positions. The Sn—C bond lengths [2.106 (6), 2.110 (5) and 2.116 (5) Å] are very similar. The two carboxylate O atoms have notably different distances to the metal atom [2.184 (3) and 2.433 (4) Å], with an O—Sn—O angle of 174.0 (1)°. Bidentate bridging of the carboxylate ligands *via* trimethyltin groups forms a polymeric structure.

Comment

There are basically two major structure types for compounds with the general formula $[R_3Sn(O_2CR')]$ (Tiekink, 1994). The *trans*-R_3SnO_2 structure in which the bidentate carboxylate ligand bridges two Sn atoms in a distorted trigonal-bipyramidal coordination is polymeric (Danish *et al.*, 1995; Stocco *et al.*, 1996; Basu Baul & Tiekink, 1996; Ng & Kumar Das, 1996; Tahir *et al.*, 1997). The second most frequent structure type is monomeric, with an essentially fourfold coordinated Sn atom involving a secondary interaction with a second O atom (Tiekink, 1994). The title compound, (I), is a new example of a *trans* type of structure.



(I)

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† Alternative name: *catena*-poly[trimethyltin(IV)-μ-(3-benzoyl-α-methylbenzeneacetato-O^1,$O^{1'}$)].

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