

The 1:1 Molecular Adduct of Triphenyltin Chloride with 2-(*m*-Methylphenyliminomethyl)phenol, [SnCl(C₆H₅)₃(C₁₄H₁₃NO)]

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Abstract. Chloro[2-(*m*-methylphenyliminomethyl)phenol]triphenyltin, $M_r = 596.72$, triclinic, $P\bar{1}$, $a = 9.705$ (2), $b = 10.758$ (1), $c = 15.201$ (3) Å, $\alpha = 85.20$ (1), $\beta = 73.54$ (1), $\gamma = 66.98$ (1)°, $V = 1400.2$ (6) Å³, $Z = 2$, $D_x = 1.415$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.03$ mm⁻¹, $F(000) = 604$, $T = 295$ K, $R = 0.0550$ for 4606 observed reflections. The geometry about the Sn atom is trigonal bipyramidal. The three phenyl rings are bonded to Sn in a trigonal plane [angles subtended at Sn vary from 114.5 (2) to 122.5 (2)°] while the Cl and O atoms of the ligand occupy the *trans* positions [176.9 (1)°].

Introduction. The coordination interactions of inorganic tin and organotin(IV) compounds with *N*-salicylideneaniline and its *meta*-substituted derivatives have been studied. From infrared spectral studies, Kogan, Osipov, Minkin & Sokolov (1965), Srivastava & Chauhan (1977*a*) and Dwivedi, Bhatnagar & Srivastava (1986) deduced that in the adducts obtained from such interactions, the Sn atom coordinates to the azomethine N atom. Recent X-ray crystallographic studies on the tin complexes of *N*-salicylideneaniline and related Schiff bases (Kamwaya & Khoo, 1985; Khoo, Charland, Gabe & Smith, 1987) have shown that only the phenolic oxygen of the ligand is involved in bonding to the Sn atom. In view of the above, we carried out the synthesis and full structural investigation of the title adduct.

Experimental. Reagents were used without further purification. Preparation of the title adduct was carried out according to the procedure of Srivastava & Chauhan (1977*b*). The yellow-to-red crystalline product was recrystallized in dichloromethane. Preliminary data obtained from Weissenberg and Buerger precession photographs yielded approximate cell dimensions and showed a triclinic system. Data collection on a crystal 0.4 × 0.2 × 0.3 mm was obtained

with a Syntex P2₁ diffractometer using the $2\theta/\theta$ mode in the index range $0 < h < 10$, $-10 < k < 10$, $-16 < l < 16$ to the 2θ limit of 53°. A variable scan speed of 5.0–29.3° min⁻¹ was used. Lattice parameters refined using 25 reflections in the range $38 < 2\theta < 45^\circ$. Standard reflection 01 $\bar{1}$ checked every 50 reflections; no significant deviation. The data were corrected for Lorentz and polarization effects. 5448 reflections were collected, 5129 unique ($R_{\text{int}} = 0.0651$), of which 4606 observed reflections with $I > 2.5\sigma(I)$ were used for refinement of the structure. The space group was confirmed as $P\bar{1}$ from successful solution and refinement. Structure solved using SHELXS86 (Sheldrick, 1986) with $R(E) = 0.24$ and refined using SHELX76 (Sheldrick, 1976). Scattering factors for all atoms inlaid in SHELX76.

Structure determination and refinement performed on IBM4361/4381. Refinement by full-matrix least squares based on F with idealized riding H atoms (C—H 0.96 Å); anisotropic refinement for non-H atoms, isotropic refinement for H atoms. In order to correct the observed structure factors for absorption effects, ABSORB (Ugozzoli, 1987) was used (correction factors min.–max.: 0.9154–1.1442). The final agreement factors were $R = 0.0550$, $wR = 0.0575$. Weight for every observed structure factor calculated according to $w = 5.0910/[\sigma^2(F) + 0.0006F^2]$, $(\Delta/\sigma)_{\text{max}} = 0.063$, $\Delta\rho_{\text{max}} = 0.864$ and $\Delta\rho_{\text{min}} = -1.181$ e Å⁻³. Geometrical calculations performed with XANADU (Roberts & Sheldrick, 1975) and illustrations drawn with ORTEP (Johnson, 1965). The final atomic coordinates are given in Table 1† while selected bond lengths and angles are listed in Table 2. A perspective view of the title complex is given in Fig. 1.

† Lists of structure factors, anisotropic thermal parameters, full lists of bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53977 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atomic coordinates ($\times 10^4$, $\times 10^5$ for Sn) and B_{eq} (\AA^2) values
$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	B_{eq}
Sn	11668 (4)	30256 (3)	22767 (2)	3.11 (2)
Cl	2118 (2)	4932 (2)	2176 (1)	4.94 (7)
O	216 (4)	1362 (3)	2321 (2)	3.53 (14)
C1	-284 (5)	678 (5)	3003 (3)	3.39 (21)
C2	-1005 (7)	1222 (6)	3902 (4)	4.46 (25)
C3	-1510 (8)	466 (7)	4596 (4)	5.08 (30)
C4	-1316 (8)	-835 (7)	4453 (4)	5.44 (32)
C5	-573 (8)	-1432 (6)	3591 (4)	4.99 (29)
C6	-91 (6)	-650 (5)	2861 (3)	3.75 (22)
C7	651 (6)	-1317 (5)	1984 (4)	3.87 (23)
N	1161 (5)	-737 (4)	1256 (3)	3.41 (17)
C8	1933 (5)	-1340 (5)	363 (3)	3.19 (19)
C9	2515 (6)	-2726 (5)	216 (3)	3.38 (20)
C10	3284 (5)	-3281 (5)	-662 (3)	3.55 (21)
C11	3476 (6)	-2411 (6)	-1370 (4)	4.09 (24)
C12	2908 (7)	-1037 (6)	-1218 (4)	4.37 (25)
C13	2116 (6)	-482 (5)	-348 (4)	3.89 (22)
C14	3880 (7)	-4786 (6)	-819 (5)	4.86 (28)
C21	-1086 (6)	4306 (5)	3041 (3)	3.90 (21)
C22	-2402 (7)	4268 (7)	2890 (5)	5.50 (29)
C23	-3877 (8)	5068 (8)	3403 (6)	6.76 (37)
C24	-4037 (10)	5880 (8)	4087 (6)	7.66 (41)
C25	-2769 (12)	5934 (9)	4261 (6)	8.55 (49)
C26	-1287 (9)	5160 (7)	3720 (4)	6.17 (34)
C31	2883 (5)	1691 (5)	2919 (3)	3.51 (20)
C32	3348 (6)	298 (6)	2832 (4)	4.48 (24)
C33	4482 (7)	-569 (7)	3216 (4)	5.59 (30)
C34	5173 (8)	-93 (9)	3677 (5)	6.63 (36)
C35	4736 (8)	1302 (9)	3767 (4)	6.25 (37)
C36	3597 (7)	2187 (7)	3378 (4)	4.79 (28)
C41	1776 (5)	2753 (4)	837 (3)	3.15 (19)
C42	703 (6)	3278 (5)	334 (4)	3.87 (22)
C43	1139 (7)	3176 (5)	-606 (4)	4.48 (26)
C44	2674 (8)	2497 (6)	-1071 (4)	4.97 (29)
C45	3766 (7)	1944 (6)	-588 (4)	5.01 (27)
C46	3344 (6)	2069 (5)	351 (4)	4.16 (23)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

Cl—Sn	2.535 (1)	C12—C11	1.375 (8)
O—Sn	2.301 (3)	C13—C12	1.377 (7)
C21—Sn	2.122 (5)	C22—C21	1.376 (9)
C31—Sn	2.146 (5)	C26—C21	1.361 (8)
C41—Sn	2.113 (4)	C23—C22	1.384 (9)
Cl—O	1.312 (5)	C24—C23	1.350 (12)
C2—Cl	1.403 (7)	C25—C24	1.353 (13)
C6—Cl	1.394 (7)	C26—C25	1.395 (10)
C3—C2	1.376 (8)	C32—C31	1.392 (8)
C4—C3	1.365 (9)	C36—C31	1.371 (8)
C5—C4	1.375 (8)	C33—C32	1.376 (8)
C6—C5	1.420 (7)	C34—C33	1.341 (11)
C7—C6	1.422 (7)	C35—C34	1.398 (11)
N—C7	1.295 (6)	C36—C35	1.389 (9)
C8—N	1.420 (6)	C42—C41	1.380 (7)
C9—C8	1.385 (7)	C46—C41	1.408 (7)
C13—C8	1.379 (7)	C43—C42	1.371 (7)
C10—C9	1.383 (7)	C44—C43	1.375 (9)
C11—C10	1.386 (7)	C45—C44	1.375 (9)
C14—C10	1.506 (7)	C46—C45	1.371 (8)
O—Sn—Cl	176.9 (1)	C14—C10—C11	122.4 (5)
C21—Sn—Cl	90.5 (1)	C12—C11—C10	121.8 (5)
C31—Sn—Cl	88.2 (2)	C13—C12—C11	120.3 (5)
C41—Sn—Cl	93.9 (1)	C12—C13—C8	118.4 (5)
C31—Sn—O	89.2 (2)	C22—C21—Sn	121.1 (4)
C31—Sn—C21	122.5 (2)	C26—C21—Sn	121.4 (5)
C41—Sn—Cl	93.5 (1)	C26—C21—C22	117.5 (6)
C41—Sn—O	84.9 (1)	C23—C22—C21	121.6 (7)
C41—Sn—C21	122.4 (2)	C24—C23—C22	119.5 (8)
C41—Sn—C31	114.5 (2)	C25—C24—C23	120.5 (7)
Cl—O—Sn	131.5 (3)	C26—C25—C24	119.7 (8)
C2—Cl—O	122.5 (5)	C25—C26—C21	121.2 (8)
C6—Cl—O	120.5 (4)	C32—C31—Sn	120.2 (4)
C6—Cl—C2	117.0 (5)	C36—C31—Sn	120.9 (4)
C3—C2—Cl	120.5 (5)	C36—C31—C32	118.9 (5)
C4—C3—C2	122.3 (5)	C33—C32—C31	120.7 (6)
C5—C4—C3	119.7 (5)	C34—C33—C32	120.8 (7)
C6—C5—C4	118.7 (6)	C35—C34—C33	119.5 (6)
C5—C6—Cl	121.8 (5)	C36—C35—C34	120.2 (7)
C7—C6—Cl	122.0 (4)	C35—C36—C31	119.9 (6)
C7—C6—C5	116.1 (5)	C42—C41—Sn	122.7 (3)
N—C7—C6	123.1 (5)	C46—C41—Sn	119.7 (4)
C8—N—C7	126.4 (4)	C46—C41—C42	117.5 (4)
C9—C8—N	121.6 (4)	C43—C42—C41	121.8 (5)
C13—C8—N	116.8 (4)	C44—C43—C42	119.9 (6)
C13—C8—C9	121.6 (4)	C45—C44—C43	119.6 (5)
C10—C9—C8	120.0 (5)	C46—C45—C44	120.8 (5)
C11—C10—C9	117.9 (5)	C45—C46—C41	120.3 (5)
C14—C10—C9	119.7 (5)		

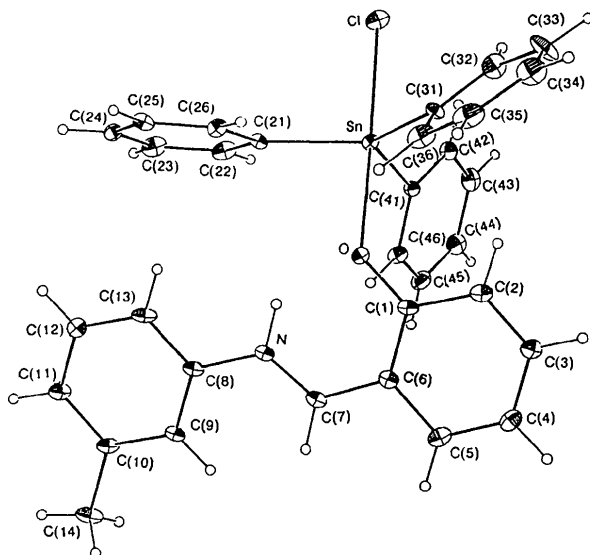


Fig. 1. A perspective view of the molecule.

Discussion. The present compound crystallizes in a ligand:organotin ratio of 1:1, unlike the 3:2 stoichiometry reported for the triphenyltin complexes of similar Schiff bases (Khoo *et al.*, 1987).

The geometry about the Sn atom is trigonal bipyramidal. The three phenyl rings are bonded to Sn in

a trigonal plane [angles subtended at Sn vary from 114.5 (2) to 122.5 (2) $^\circ$] while Cl and O occupy the *trans* positions [176.9 (1) $^\circ$]. Coordination of the Schiff base to the Sn atom takes place *via* the phenolic O atom in contrast to the Sn—N coordinating mode reported earlier for the adducts formed by tin(II) and tin(IV) halides and organotin(IV) halides with salicylidene-*meta*-substituted anilines (Kogan *et al.*, 1965; Srivastava & Chauhan, 1977b; Dwivedi *et al.*, 1986).

The phenolic proton of the ligand has shifted to the imine N atom; the H(N)···O distance of 1.834 \AA indicates a weak hydrogen bond. This phenomenon of intramolecular hydrogen bonding was well substantiated by Bullock, Ladd, Povey & Tajmir-Riahi (1979) and by Kamwaya & Khoo (1985) in the tin complexes of salicylideneanilines mentioned earlier.

The Sn—O bond distance [2.301 (3) \AA] is in accord with those found in the Ph₃SnCl:salicylideneaniline adduct [2.280 (4) \AA] (Khoo *et al.*, 1987). The bond lengths and bond angles for the phenyl rings are

normal and the respective values are in the ranges 1.361–1.408 Å and 117.5–121.6°. The three phenyl rings are non-coplanar; each of them is rotated so that they may be bonded to tin in the trigonal plane.

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Structure of a Nickel Complex with *p*-Nitrophenylazothiomethyl-*N*-phenylcarboximide Anion Radical

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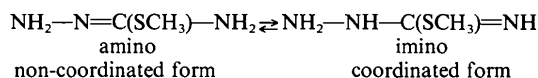
Abstract. Ni[NO₂C₆H₄NNC(SCH₃)NC₆H₅]₂, *M_r* = 659.3, monoclinic, *P*2₁/*c*, *a* = 11.660 (8), *b* = 19.428 (6), *c* = 13.025 (6) Å, β = 90.47 (2)°, *V* = 2950 (3) Å³, *Z* = 4, *D_x* = 1.484 g cm⁻³, Cu *K*α radiation, λ = 1.54178 Å, μ = 26.42 cm⁻¹, *F*(000) = 1360, *T* = 295 K, *R* = 0.0470, *wR* = 0.0533 for 4264 reflections, *I* ≥ 2σ(*I*). The coordination of the Ni atom is tetrahedral. This is the first case of such a coordination polyhedron for nickel complexes with ligands derived from *S*-alkylisothiosemicarbazide.

Introduction. *S*-Alkylisothiosemicarbazides, *R*₁*R*₂-N(1)—N(2)=C(3)(SCH₃)—N(4)*R*₃*R*₄ (*L*), behave differently from those with a non-substituted sulfur atom *R*₁*R*₂—N—NH—CS—N*R*₃*R*₄. While the latter are coordinated by the metal *via* the S and N(1) atoms, the former use the N atoms N(1) and N(4)

(Malinowskii, Simonov, Gerbeleu, Yampol'skaya, Revenko & Shova, 1985).

It is known that the Ni^{II} complexes can form two types of coordination geometry with the *L* ligands: octahedral high-spin neutral or cationic complexes, such as [NiL₂(NO₂)₂] (Bourosh, Revenko, Simonov, Gerbeleu, Dvorkin & Malinowski, 1987) and [NiL₂im₂]₂ (Revenko, Bourosh, Gerbeleu, Simonov, Virtosu & Malinowskii, 1989) and square-planar low-spin cationic complexes, such as [NiL₂]*X*₂ (Leovac, Babin, Canic & Gerbeleu, 1980) where *R*₁ = *R*₂ = *R*₃ = *R*₄ = H; *X* = Cl, Br, I.

In all these cases *L* is neutral and after coordination assumes the imino form



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