

## Molecular Adduct of Dimethyltin Dichloride with 2-(*p*-Methoxyphenyliminomethyl)phenol, [SnCl<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>(C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub>)<sub>2</sub>]

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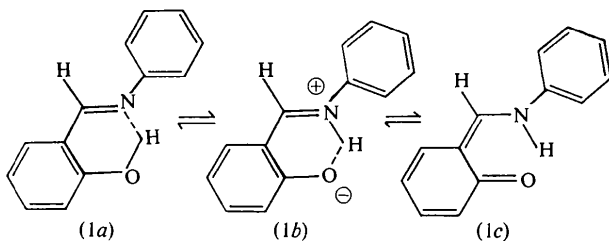
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**Abstract.**  $M_r = 674.2$ , monoclinic,  $P2_1/a$ ,  $a = 9.735$  (2),  $b = 21.000$  (5),  $c = 7.140$  (4) Å,  $\beta = 75.98$  (2)°,  $V = 1416$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.58$ ,  $D_x = 1.581$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 1.4$  mm<sup>-1</sup>,  $F(000) = 684$ , room temperature,  $R = 0.0417$  for 1232 observed reflexions. The coordination of the tin atom is octahedral, all *trans*, with bond distances Sn–Cl 2.610 (2), Sn–O 2.262 (4) and Sn–C 2.120 (7) Å. The two ligands are coordinated to Sn through the hydroxyl O atoms. The molecular configuration supports the existence of intramolecular hydrogen bonding, N(H)···O 2.622 (2) Å, the hydroxylic H atom probably having shifted to the N atom of the same molecule.

**Introduction.** Recently 1:2 adducts formed by tin tetrachloride and mono- and diorganotin halides with salicylideneanilines have been prepared and studied by infrared and Mössbauer spectroscopy. Kogan, Osipov, Minkin & Sokolov (1965) and Srivastava & Chauhan (1977) concluded from infrared spectral evidence that coordination occurs at the azomethine N atom found in the ligand present in the phenolimine form (1*a*). However, Saraswat, Srivastava & Mehrotra (1979) from essentially identical infrared results reported that only the phenolic O atoms from the ligands are coordinated in the complexes, indicating that the intermediate zwitterion (1*b*) is predominant in the phenolimine (1*a*)/ketoenamine (1*c*) equilibrium of Schiff bases. This is further substantiated by Bullock, Ladd, Povey & Tajmir-Riahi (1979) from the crystal structure and spectroscopic study of Schiff-base complexes of calcium nitrate.



In view of this unusual occurrence of the zwitterion of salicylideneaniline as a neutral ligand and the uncertainty in its mode of coordination with tin tetrachloride and organotin halides, a complete X-ray structural investigation of the title adduct was undertaken.

**Experimental.** Preparation according to procedure of Srivastava & Chauhan (1977), recrystallization in ethanol (95%) at room temperature, gave soft orange-red crystals that are reflexion twins. Approximate cell dimensions and space group from oscillation and Weissenberg photographs;  $D_m$  by flotation in potassium tetraiodomercurate solution. Intensity data collected from crystal  $0.35 \times 0.25 \times 0.65$  mm, Syntex  $P2_1$  diffractometer (Nicolet, 1975) of the School of Physics, USM. Mo  $K\alpha$  radiation with graphite monochromator. Cell dimensions by least-squares analysis of the setting angles of 15 reflexions (Nicolet, 1975); 1743 reflexions with positive net intensity collected with  $2 < \theta < 26^\circ$ ; standard reflexion showed no significant variation; 1232 reflexions considered observed with  $I > 2.5\sigma(I)$ . No absorption correction; Lorentz–polarization corrections applied; index range  $h \pm 10$ ,  $k 0/25$ ,  $l 0/8$ . Refinement and structure determination performed at the School of Physics, USM, on an IBM 370/4381 computer. Structure solved by *MULTAN80* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All non-hydrogen atoms located except methyl C bonded to Sn. Refinement with isotropic temperature factors by accelerated full-matrix least squares,  $F$  magnitudes, unit weights, with *SHELX76* (Sheldrick, 1976). After three cycles methyl C located; H atoms fixed at ideal positions with bond lengths 1.08 Å. Further refinement with anisotropic temperature factors for heavier atoms and isotropic temperature factors for H atoms reduced  $R$  to 0.0417,  $wR = 0.042$ . Final max. and min. electron densities 0.44 and  $-0.39$  e Å<sup>-3</sup>.  $\Delta/\sigma_{\max} = 0.06$ . Dihedral angles and non-contact distances calculated with *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic-scattering factors from *SHELX*.

**Discussion.** Atom parameters are given in Table 1,\* bond lengths and angles in Table 2. Fig. 1 is a view of the unit cell along *c*.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42107 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic temperature factors

*B*<sub>eq</sub> calculated according to Willis & Pryor (1975).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
C(1)	0.6678 (8)	-0.2900 (3)	0.6019 (12)	4.8 (1)
O(1)	0.7449 (5)	-0.2327 (2)	0.5615 (9)	4.8 (1)
C(2)	0.6715 (6)	-0.1765 (3)	0.6110 (10)	2.9 (1)
C(3)	0.7461 (5)	-0.1215 (3)	0.5767 (9)	3.6 (1)
C(4)	0.6824 (6)	-0.0634 (3)	0.6259 (11)	4.0 (2)
C(5)	0.5354 (6)	-0.0605 (3)	0.7201 (10)	3.3 (1)
C(6)	0.4602 (6)	-0.1158 (3)	0.7466 (10)	3.8 (1)
C(7)	0.5240 (6)	-0.1753 (3)	0.6966 (11)	4.2 (1)
N	0.4640 (4)	-0.0033 (2)	0.7715 (7)	3.0 (1)
C(8)	0.5100 (6)	0.0548 (3)	0.7666 (9)	3.2 (1)
C(9)	0.4228 (5)	0.1092 (3)	0.8202 (9)	3.5 (1)
C(10)	0.4876 (5)	0.1701 (3)	0.7960 (10)	3.5 (1)
C(11)	0.4086 (6)	0.2234 (3)	0.8498 (10)	3.1 (1)
C(12)	0.2559 (6)	0.2188 (3)	0.9173 (9)	3.4 (1)
C(13)	0.1954 (6)	0.1600 (3)	0.9332 (10)	4.1 (1)
C(14)	0.2723 (5)	0.1048 (3)	0.8875 (8)	2.9 (1)
O(2)	0.2138 (4)	0.0479 (2)	0.9059 (9)	2.2 (1)
Sn	0.0000	0.0000	1.0000	2.8 (1)
Cl	-0.1319 (2)	0.0864 (1)	0.8470 (3)	4.5 (1)
C(15)	0.0531 (8)	-0.0506 (3)	0.7354 (11)	4.5 (1)

Table 2. Bond lengths (Å) and angles (°) and intramolecular distances (Å) and angles (°)

C(1)—O(1)	1.411 (9)	N—C(8)	1.297 (8)
O(1)—C(2)	1.381 (8)	C(8)—C(9)	1.418 (9)
C(2)—C(3)	1.354 (9)	C(9)—C(10)	1.418 (8)
C(3)—C(4)	1.375 (9)	C(10)—C(11)	1.360 (9)
C(4)—C(5)	1.428 (9)	C(11)—C(12)	1.451 (8)
C(5)—C(6)	1.362 (8)	C(12)—C(13)	1.360 (9)
C(6)—C(7)	1.402 (9)	C(13)—C(14)	1.376 (8)
C(7)—C(2)	1.418 (8)	C(14)—C(9)	1.430 (7)
C(5)—N	1.393 (8)	C(14)—O(2)	1.317 (7)
C(1)—O(1)—C(2)	117.4 (5)	N—C(8)—C(9)	124.7 (5)
O(1)—C(2)—C(3)	117.5 (5)	C(8)—C(9)—C(10)	118.2 (5)
C(3)—C(2)—C(7)	120.4 (6)	C(8)—C(9)—C(14)	122.4 (5)
O(1)—C(2)—C(7)	122.1 (6)	C(9)—C(10)—C(11)	120.2 (5)
C(2)—C(3)—C(4)	121.4 (5)	C(10)—C(9)—C(14)	119.2 (5)
C(3)—C(4)—C(5)	119.9 (5)	C(10)—C(11)—C(12)	120.2 (5)
C(4)—C(5)—C(6)	118.2 (6)	C(11)—C(12)—C(13)	118.5 (5)
N—C(5)—C(6)	118.9 (5)	C(12)—C(13)—C(14)	123.0 (5)
C(4)—C(5)—N	122.7 (5)	C(13)—C(14)—C(9)	118.7 (5)
C(5)—C(6)—C(7)	122.4 (5)	C(13)—C(14)—O(2)	122.9 (5)
C(6)—C(7)—C(2)	117.7 (5)	C(9)—C(14)—O(2)	118.4 (5)
C(5)—N—C(8)	131.1 (5)		
Sn...O(2)	2.262 (4)	Sn...O(2)—C(14)	141.1 (4)
Sn—Cl	2.610 (2)	O(2)...Sn—Cl	94.4 (1)
Sn—C(15)	2.120 (7)	O(2)...Sn—C(15)	87.1 (2)
N...O(2)	2.622 (2)	C(15)—Sn—Cl	90.8 (2)
H(N)...O(2)	2.312		
O(2)...Cl	3.583 (1)		
O(2)...C(15)	3.021 (1)		
Cl...C(15)	3.385 (1)		

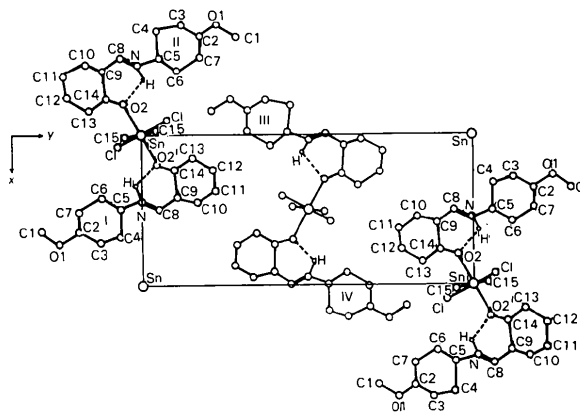


Fig. 1. View of the unit cell along *c*.

The Sn atom is bonded to two Cl atoms, two methyl groups and the phenolic O atom of two ligands giving an all-*trans* octahedral geometry. The coordination bond angles involving the equivalent *trans* ligands are 180° by symmetry and the other angles range from 87 to 94°. The Sn—O bond length is close to those found in the Me<sub>2</sub>SnCl<sub>2</sub>salicylideneamine adduct (2.22 Å) (Randaccio, 1973). The torsion angle N—C(8)—C(9)—C(14) 1.1 (1)° is *cis*, suggestive of the presence of an intramolecular hydrogen bond between N and O(2), and the distance N...O(2) compares well with that reported for 2-bromo-*N*-salicylideneaniline (Burr & Hobson, 1969) for the intramolecular case [2.62 (8) Å]. It was not easy to locate the H atom at a fairly reasonable distance between N and O. A peak near O could be found but at a separation of 1.831 Å from Sn. A trial calculation of H near O was not successful. This peak was considered as a spurious background ripple from Sn. On the other hand, a lone peak was found in the vicinity of N and C(5), away from O. This was interpreted as the H atom being sought. H was, therefore, assumed to be near N, and fixed at a distance of 1.08 Å from N. Convergence for the structure became faster. The distance H(N)...O(2) of 2.312 (2) Å is indicative of only a weak hydrogen bond and this may well account for the indecision by several workers as to whether or not the hydrogen bond is retained.

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## Structure of the *cis*-Facial Isomer of Bis[2,2'-iminodi(acetamide oxime)-*N,N',N''*]nickel(II) Dichloride, $[\text{Ni}(\text{C}_4\text{H}_{11}\text{N}_5\text{O}_2)_2]\text{Cl}_2$

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**Abstract.**  $M_r = 451.95$ , monoclinic,  $C2/c$ ,  $a = 10.427$  (3),  $b = 14.738$  (4),  $c = 11.438$  (3) Å,  $\beta = 91.62$  (2)°,  $V = 1757.0$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.70$ ,  $D_x = 1.708$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 14.52$  cm<sup>-1</sup>,  $F(000) = 936$ ,  $T = 297$  K, final  $R = 0.024$  for 1483 observed reflections. The complex cation,  $[\text{Ni}\{\text{HN}(\text{CH}_2\text{C}(=\text{NOH})\text{NH}_2)_2\}_2]^{2+}$ , has a twofold axis through the nickel ion, which bisects the N(3)–Ni–N(3') and the N(5)–Ni–N(5') angles. The two terdentate ligands are attached to opposite faces of the distorted nickel(II) octahedron through the amino nitrogen and the two oxime nitrogens; the amino nitrogens of the two ligands are *cis* to each other.

**Introduction.** The ligand 2,2'-iminodi(acetamide oxime), *ibo*, forms only two isomers with nickel(II) chloride. The structure of the *cis*-facial (*fac*) isomer is reported here, and the structure of the *trans*-facial (*fac*) isomer was reported earlier (Cullen, Lingafelter & Eddy, 1970). In aqueous solution the *cis*-facial isomer isomerizes to the less-soluble *trans*-facial isomer; we suggest the isomerization mechanism is the Bailar twist. After this isomerization became known to us, slow evaporation of an aqueous solution of the *cis*-facial isomer was avoided, and crystals for the present study were obtained quickly from solution to avoid isomerization.

**Experimental.** Concentrated aqueous solutions of ligand and nickel(II) chloride were mixed at room temperature; the violet *trans*-facial crystals that immediately formed were filtered off; the purple solution was passed through a Sephadex G-10 column, and elution with water washed out first the violet isomer then the desired purple *cis*-facial isomer. Saturated aqueous potassium chloride solution was added to the purple eluate to speed crystallization; purple crystals of suitable size were formed overnight.  $D_m$  measured using pycnometer with toluene as covering liquid (Berman, 1939). Purple crystal 0.20 × 0.22 × 0.25 mm with well-defined faces and edges, glass-fiber mount, extinguished plane-polarized light. Syntex P2<sub>1</sub> automated four-circle diffractometer, graphite-monochromated Mo  $K\alpha$  radiation. Cell parameters by least-squares fit of 15  $2\theta$  values ( $20.2 < 2\theta < 23.1^\circ$ ).  $hkl$  and  $\bar{h}kl$  reflections with  $2\theta$  from 3 to 55° measured; range of  $hkl$ :  $h -13$  to  $+12$ ,  $k 0$  to  $19$ ,  $l 0$  to  $14$ . Intensity data collected by  $2\theta/\theta$  scan technique, variable scan rate 2.0 to 29.3° min<sup>-1</sup>, range from 0.8°  $2\theta$  below calc.  $K\alpha_1$  peak to 1.0° above calc.  $K\alpha_2$  peak positions. Corrections for Lorentz and polarization effects and absorption (Busing & Levy, 1957), max. and min. absorption corrections to intensities 0.780 and 0.738. 2290 reflections collected, which include standards and non-unique data; 2039 unique; 1483 with  $I > 3\sigma$ , used in structure refinement; 248 unobserved reflections with  $I < 3\sigma$ . Internal consistency index  $R_{\text{int}} = 0.021$ .

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