Chlorotriphenyl(pyridinium-2-carboxylato)tin(IV)*

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Abstract. $C_{24}H_{20}ClNO_2Sn$, monoclinic, $P2_1/n$, $a = 13\cdot618$ (1), $b = 15\cdot646$ (1), $c = 10\cdot332$ (1) Å, $\beta = 98\cdot35$ (1)°, $Z = 4$, $D_m = 1\cdot549$, $D_c = 1\cdot551$ g cm^{-3}. The final residual is $R_F = 0\cdot028$ on 3042 observed reflections. The coordination around the Sn atom is a distorted trigonal bipyramid, consisting of an O atom of the carboxyl group and a Cl atom in axial positions and three phenyl groups in the equatorial plane. The N atom of the pyridine ring is protonated and centrosymmetrically related molecules are hydrogen-bonded together.

Introduction. Many organotin complexes of the 2-pyridinecarboxylato group have been synthesized and investigated (Naik & Curran, 1971; Harrison & Phillips, 1975, 1979; Allen, Brooks, Formstone, Crowe & Smith, 1978; Crowe, Hill & Smith, 1981). However, it appears that the only complex so far reported between Sn and the zwitterion form of 2-pyridinecarboxylic acid itself is the title compound, which has shown promising fungicidal activity (Smith, Okioga & Khoo, 1980). In view of this unusual occurrence of the zwitterion as a ligand, a complete X-ray structural investigation of the complex was undertaken.

The complex was obtained in good yield by mixing hot ethanolic solutions containing stoichiometric quantities of triphenyltin chloride and 2-pyridinecarboxylic acid. The complex was recrystallized from ethanol as white crystals (m.p. 385–387 K). Microanalyses were carried out by the Australian Microanalytical Service, CSIRO, Melbourne, Australia. Composition: found (%): C 56·62, H 3·99, N 2·78, Sn 23·3; calculated (%) for $C_{24}H_{20}ClNO_2Sn$: C 56·68, H 3·96, N 2·75, Sn 23·3.

The diffraction intensities of a crystal (0·35 × 0·35 × 0·35 mm) of the title compound were measured at room temperature (299 K). Graphite-mono-

chromatized Mo $K\alpha$ radiation generated at 50 kV and 16 mA was used in a $\theta/2\theta$ scan with line-profile analysis (Grant & Gabe, 1978). A total of 4172 measurements were made, up to 50° in 2θ, giving 3863 unique reflections, of which 3042 had a net intensity larger than $3\sigma(I)$ based on counting statistics. Of the 165 measurements made of the systematic absences, 162 were found to be unobserved. The intensities were corrected for measured direct-beam polarization (Le Page, Gabe & Calvert, 1979), but not for absorption ($\mu = 13\cdot18$ cm^{-1}). The cell parameters were obtained by least-squares refinement of the setting angles of 52 reflections with 2θ larger than 40° [λ(Mo $K\alpha_1$) = 0·7093 Å].

The Sn atom was located in an E map obtained by application of *MULTAN* (Germain, Main & Woolfson, 1971) to the 414 largest E values. A subsequent heavy-atom-phased Fourier map revealed all the non-hydrogen atoms. The structure was refined anisotropically by block-diagonal least squares. In the process the H atoms were located in a difference map and these were refined isotropically. An extinction correction was included (Larson, 1970). The scattering curves for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The final residuals were $R_F = 0\cdot028$ and $R_{WF} = 0\cdot023$ for 3042 observed reflections with counting-statistics weights. $R_F = 0\cdot043$ and $R_{WF} = 0\cdot023$ for a total of 3863 reflections including unobserved reflections. The atomic positional and equivalent isotropic thermal parameters are listed in Table 1.†

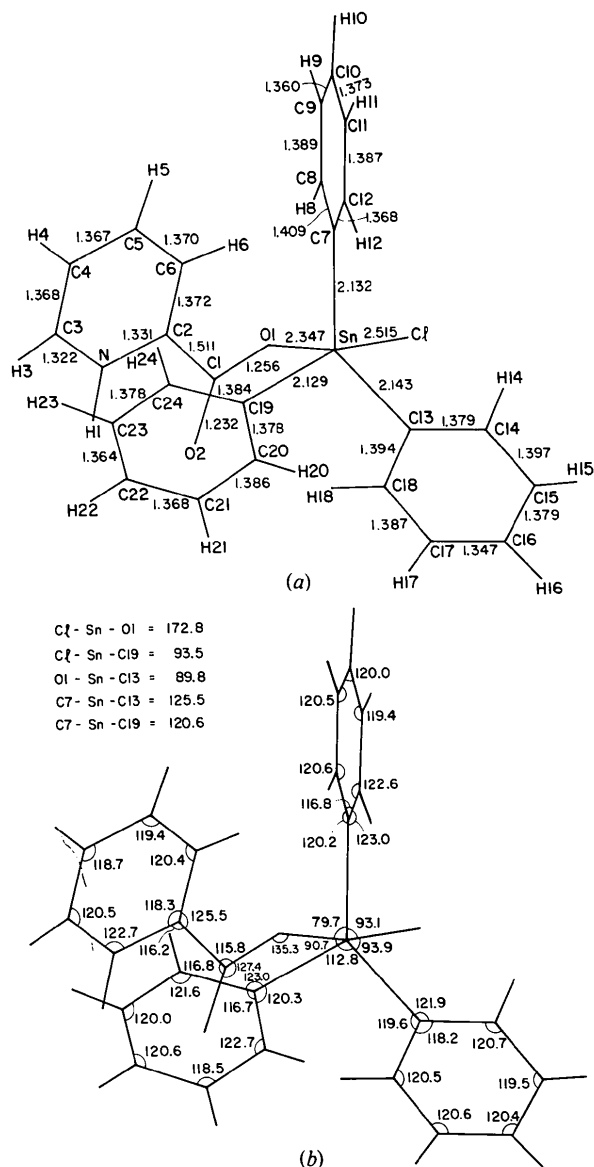All calculations were performed using the NRC PDP8-E system of programs (Larson & Gabe, 1978).

Table 1. *Positional parameters and isotropic thermal parameters*

E.s.d.'s refer to the last digit given. For non-hydrogen atoms B_{iso} is the arithmetic mean of the principal axes of the thermal ellipsoid.
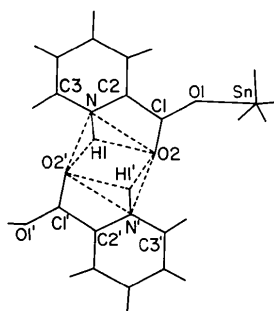
	x	y	z	B_{iso} (Å^2)
Sn	0·218737 (20)	0·261333 (15)	0·191583 (23)	3·121 (9)
Cl	0·37739 (8)	0·34564 (6)	0·20995 (10)	4·75 (5)
O(1)	0·07144 (18)	0·18559 (14)	0·20267 (21)	3·96 (12)
O(2)	0·03360 (20)	0·09754 (15)	0·03291 (21)	4·49 (13)
N	−0·06577 (22)	−0·00566 (17)	0·1723 (3)	3·52 (14)
C(1)	0·0298 (3)	0·12145 (21)	0·1457 (3)	3·39 (17)
C(2)	−0·0321 (3)	0·06820 (20)	0·2253 (3)	3·04 (16)
C(3)	−0·1197 (3)	−0·05914 (23)	0·2318 (4)	4·71 (21)
C(4)	−0·1448 (3)	−0·0394 (3)	0·3517 (4)	5·37 (23)
C(5)	−0·1128 (3)	0·03637 (25)	0·4089 (4)	5·08 (22)
C(6)	−0·0546 (3)	0·08922 (22)	0·3465 (3)	4·24 (19)
C(7)	0·21561 (25)	0·26434 (20)	0·3972 (3)	3·00 (15)
C(8)	0·3035 (3)	0·25177 (24)	0·4853 (3)	4·33 (18)
C(9)	0·3023 (3)	0·2534 (3)	0·6195 (3)	5·36 (20)
C(10)	0·2163 (3)	0·26896 (24)	0·6681 (3)	5·14 (20)
C(11)	0·1295 (3)	0·28119 (24)	0·5844 (3)	4·90 (21)
C(12)	0·1306 (3)	0·27778 (21)	0·4505 (3)	3·84 (18)
C(13)	0·1394 (3)	0·34642 (20)	0·0511 (3)	3·16 (16)
C(14)	0·1628 (3)	0·43205 (22)	0·0468 (3)	4·04 (19)
C(15)	0·1151 (3)	0·48463 (24)	−0·0521 (4)	5·32 (23)
C(16)	0·0456 (3)	0·4500 (3)	−0·1482 (4)	5·34 (22)
C(17)	0·0217 (3)	0·3666 (3)	−0·1451 (3)	4·85 (21)
C(18)	0·0680 (3)	0·31378 (23)	−0·0469 (3)	3·98 (19)
C(19)	0·2795 (3)	0·15445 (21)	0·1033 (3)	3·29 (17)
C(20)	0·3346 (3)	0·16637 (23)	0·0030 (4)	4·37 (19)
C(21)	0·3720 (3)	0·0989 (3)	−0·0620 (4)	5·59 (24)
C(22)	0·3541 (3)	0·01736 (25)	−0·0238 (4)	5·92 (25)
C(23)	0·2997 (4)	0·00289 (23)	0·0749 (4)	5·88 (24)
C(24)	0·2637 (3)	0·07083 (23)	0·1387 (4)	4·61 (21)
H(1)	−0·040 (3)	−0·0184 (21)	0·082 (3)	8·3 (11)
H(3)	−0·1370 (23)	−0·1081 (18)	0·187 (3)	5·6 (9)
H(4)	−0·1764 (21)	−0·0744 (17)	0·392 (3)	4·1 (8)
H(5)	−0·133 (3)	0·0569 (22)	0·493 (3)	8·9 (12)
H(6)	−0·0329 (22)	0·1398 (17)	0·374 (3)	4·6 (8)
H(8)	0·3673 (21)	0·2438 (18)	0·455 (3)	4·7 (8)
H(9)	0·361 (3)	0·2446 (21)	0·674 (3)	9·4 (12)
H(10)	0·214 (3)	0·2741 (19)	0·771 (3)	7·7 (10)
H(11)	0·0671 (24)	0·2903 (18)	0·615 (3)	5·5 (9)
H(12)	0·0752 (23)	0·2903 (18)	0·394 (3)	5·8 (9)
H(14)	0·2197 (22)	0·4530 (18)	0·114 (3)	4·7 (8)
H(15)	0·137 (3)	0·5407 (21)	−0·048 (3)	7·5 (11)
H(16)	0·014 (3)	0·4917 (21)	−0·215 (3)	8·3 (11)
H(17)	−0·0237 (22)	0·3389 (17)	−0·196 (3)	4·8 (8)
H(18)	0·0511 (22)	0·2522 (18)	−0·047 (3)	4·9 (8)
H(20)	0·3485 (20)	0·2144 (15)	−0·0201 (24)	3·2 (7)
H(21)	0·415 (3)	0·1096 (20)	−0·125 (3)	6·8 (10)
H(22)	0·3845 (24)	−0·0291 (19)	−0·066 (3)	6·0 (9)
H(23)	0·289 (3)	−0·0532 (20)	0·108 (3)	7·1 (10)
H(24)	0·2182 (23)	0·0583 (18)	0·207 (3)	5·6 (9)
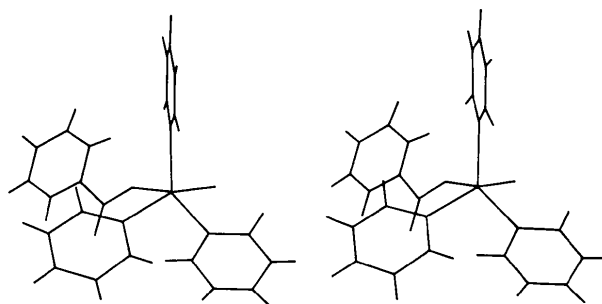
Fig. 1. Stereoscopic pair of the molecule seen approximately along the |100| direction.

Cℓ- Sn - Ol = 172.8
Cℓ- Sn -Cl9 = 93.5
Ol - Sn -Cl3 = 89.8
C7 - Sn -Cl3 = 125.5
C7 - Sn -Cl9 = 120.6

(a)

(b)

Fig. 2. (*a*) Atom names and bond distances (Å) (uncorrected for thermal motion). The e.s.d.'s on bond distances are Sn–Cl = 0·001, Sn–O and Sn–C = 0·003 Å, and on the others 0·005 Å. (*b*) Angles (°). The e.s.d.'s on angles involving Sn are 0·1°, and on the others 0·4°.

Discussion. A stereoscopic view of the molecule is shown in Fig. 1. The atom names, distances and angles are indicated on Fig. 2.

The Sn atom is coordinated to the Cl atom, the three phenyl groups and one of the O atoms |O(1)| of the 2-pyridinecarboxylic acid zwitterion. The three phenyl C atoms are in the equatorial plane, with Cl and O(1) in the axial positions of a trigonal pyramid. It was expected that the 2-pyridinecarboxylic acid molecule would act as a bidentate chelating ligand with Sn coordinated to the N atom of the pyridine ring and an

N- O2 = 2.661   N -Hl.....O2 = 106.0
N- O2' = 2.651   Cl-O2.....N' = 163.0
O2-Hl = 2.17   N'-Hl'....O2 = 143.0
O2'-Hl = 1.73

Fig. 3. Hydrogen bonding. Distances are in Å (e.s.d.'s: N—O 0·005, O—H and N—H 0·03 Å) and angles in degrees (e.s.d.'s 0·4°).

O atom of the carboxyl group. However, this is not so and it appears as though an Sn atom with three Sn—C(Ph) bonds is incapable of having a coordination number of more than five. This effect was also seen in the structures of aquachlorotriphenyl(2,2':6',2''-terpyridyl)tin(IV) (TAPC) (Prasad, Lee, Le Page & Smith, 1982) and aquaisothiocyanatotriphenyl-(2,2':6',2''-terpyridyl)tin(IV) (TAPI) (Prasad & Smith, 1982), where the Sn atom with three Sn—C(Ph) bonds does not bond to the terpyridyl group and is only five-coordinated.

The average Sn—C(Ph) distance of 2·135 (3) Å is within the range [2·105 (5)–2·16 (2) Å] of Sn—C(Ph) distances reported in the literature (Harrison, King & Richards, 1974). The C—C bond lengths in the phenyl groups are all normal.

The Sn—Cl distance of 2·515 (1) Å is comparable to the Sn—Cl distance of 2·518 (1) Å in TAPC and is within the range of Sn—Cl distances (2·32–2·58 Å) in other chloro complexes (Harrison, King & Richards, 1974). The Sn—O distance of 2·347 (2) Å is longer than the Sn—O distances of 2·25 (2) Å in dichloro-dimethylbis(pyridine N-oxide)tin(IV) (Blom, Penfold & Robinson, 1969), 2·317 (2) Å in TAPC and 2·252 (2) Å in TAPI. The elongation of the Sn—O distance is probably partially due to the double-bond character of the C—O bonds.

The acidic proton is bonded to the N atom of the pyridine ring and is involved in hydrogen bonding

between pairs of centrosymmetrically related molecules (Fig. 3). The hydrogen bond is bifurcated, there being an intramolecular hydrogen bond between N and O(2) and an intermolecular hydrogen bond between N and O(2'). The relevant distances and angles are shown in Fig. 3. Pairs of hydrogen-bonded molecules are held together in the crystal by van der Waals forces.

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