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CRYSTAL AND MOLECULAR STRUCTURE OF DIMETHYLCHLOROTIN 2-PYRIDINECARBOXYLATE

IAN W. NOWELL [a], JOHN S. BROOKS [b], GARRY BEECH [b]

Departments of Chemistry [a] and Applied Physics [b], Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB (Great Britain)

and ROBIN HILL

International Tin Research Institute, Fraser Road, Greenford, Middlesex, UB6 7AQ (Great Britain)

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Summary

The crystal and molecular structure of the title compound has been determined using Patterson and Fourier techniques from diffractometer data. Crystals are monoclinic, space group $P2_1/c$ with a 10.805(7), b 20.292(15), c 10.804(8) Å, β 113.20(5)°, U 2177.37 Å^3. D_m 1.85, D_c 1.87 mg m^{-3} for $Z = 8$, with two independent molecules in the asymmetric unit. The structure has been refined using 1153 observed reflections to a final $R = 0.075$ and $R' = 0.080$. The 2-pyridinecarboxylate ligand bridges adjacent tin atoms to give a polymeric structure consisting of chains which run parallel to the a axis. The pyridine ring is orientated to facilitate a close approach of the nitrogen atom to tin and the Sn–N distances of 2.468(20), 2.505(25) Å indicate the presence of a significant interaction. The resulting coordination about each tin atom is that of a distorted octahedron.

Introduction

In an earlier paper [1] we reported the spectroscopic studies of mono- and di-organotin(IV) derivatives of pyridinecarboxylic acids. Of particular interest were the ^{119m}Sn Mössbauer parameters of the diorganochlorotin pyridinecarboxylates. The parameters observed for the dimethylchlorotin 4-pyridinecarboxylate were similar to other diorganotin halide carboxylates and indicated a pentacoordinate structure. However, dimethyl- and diphenyl-chlorotin 2-pyridinecarboxylate had parameters corresponding to an octahedral *trans*-R_2SnX_4 tin atom geometry. This was of interest as it suggested the involvement of the nitrogen atom in coordination with the tin when the nitrogen is in the 2-position in the phenyl ring, while this is not observed in the 4-position. To substantiate the involvement of the nitrogen atom, a single crystal X-ray structure determination of dimethylchlorotin 2-pyridinecarboxylate has been undertaken.

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TABLE 1

FRACTIONAL POSITIONAL PARAMETERS ($\times 10^4$) WITH e.s.d.'s FOR NON-HYDROGEN ATOMS IN PARENTHESES

Atom	*x*	*y*	*z*
Sn(1)	−537(3)	3345(1)	1805(2)
Sn(2)	4570(3)	4070(1)	2111(2)
Cl(1)	−1742(13)	2324(4)	1070(9)
Cl(2)	3520(15)	5145(5)	1888(12)
N(1)	−18(24)	4519(12)	2542(20)
N(2)	4605(26)	2854(10)	2179(17)
O(11)	−2258(27)	3736(8)	1931(18)
O(12)	−3386(28)	4517(13)	2427(22)
O(21)	2687(24)	3682(7)	1952(17)
O(22)	1412(27)	2821(10)	1762(19)
C(11)	428(30)	3118(15)	3850(21)
C(12)	−731(29)	3720(13)	−93(20)
C(13)	−2427(33)	4370(19)	2251(23)
C(101)	−1189(26)	4715(12)	2578(21)
C(102)	−1273(30)	5418(14)	2985(23)
C(103)	−57(29)	5742(17)	3244(26)
C(104)	1058(31)	5519(15)	3182(24)
C(105)	1062(31)	4857(16)	2818(25)
C(21)	5392(29)	4038(15)	4248(22)
C(22)	4273(31)	3950(16)	77(21)
C(23)	2359(28)	3079(16)	1929(20)
C(201)	3422(26)	2626(18)	1990(20)
C(202)	3445(30)	1914(10)	1960(21)
C(203)	4539(30)	1528(12)	2098(21)
C(204)	5602(30)	1882(13)	2284(23)
C(205)	5740(31)	2572(14)	2334(23)
H(111)	−177	3289	4377
H(112)	1399	3357	4529
H(113)	561	2591	3971
H(121)	−1614	4029	−496
H(122)	−828	3316	−775
H(123)	151	4006	24
H(102)	−2148	5639	3065
H(103)	−29	6252	3539
H(104)	1929	5831	3401
H(105)	1952	4636	2771
H(211)	6414	4220	4632
H(212)	5386	3536	4578
H(213)	4794	4342	4622
H(221)	4195	4428	−388
H(222)	3357	3676	−442
H(223)	5115	3685	18
H(202)	2518	1662	1816
H(203)	4518	996	2057
H(204)	6503	1608	2419
H(205)	6659	2832	2481

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES

Symmetry code

none *x*, *y*, *z*; (′) 1 + *x*, *y*, *z*; (″) − 1 + *x*, *y*, *z*

Bond distances

Sn(1)–Cl(1)	2.409(9)	Sn(2)–Cl(2)	2.426(11)
Sn(1)–N(1)	2.505(25)	Sn(2)–N(2)	2.468(20)
Sn(1)–O(11)	2.076(29)	Sn(2)–O(21)	2.125(26)
Sn(1)–O(22)	2.375(28)	Sn(2)–O(12′)	2.285(30)
Sn(1)–C(11)	2.089(21)	Sn(2)–C(21)	2.123(22)
Sn(1)–C(12)	2.120(24)	Sn(2)–C(22)	2.107(24)
O(11)–C(13)	1.36(4)	O(21)–C(23)	1.27(4)
O(12)–C(13)	1.16(5)	O(22)–C(23)	1.10(4)
C(13)–C(101)	1.43(4)	C(23)–C(201)	1.45(5)
C(101)–N(1)	1.34(4)	C(201)–N(2)	1.30(4)
C(101)–C(102)	1.51(4)	C(201)–C(202)	1.45(4)
C(102)–C(103)	1.40(5)	C(202)–C(203)	1.38(4)
C(103)–C(104)	1.31(5)	C(203)–C(204)	1.30(4)
C(104)–C(105)	1.40(4)	C(204)–C(205)	1.41(4)
C(105)–N(1)	1.28(4)	C(205)–N(2)	1.30(4)

Bond angles

Cl(1)–Sn(1)–O(11)	88.2(6)	Cl(2)–Sn(2)–O(21)	86.0(6)
Cl(1)–Sn(1)–O(22)	88.7(6)	Cl(2)–Sn(2)–O(12′)	92.6(8)
Cl(1)–Sn(1)–C(11)	98.0(8)	Cl(2)–Sn(2)–C(21)	96.6(9)
Cl(1)–Sn(1)–C(12)	99.0(7)	Cl(2)–Sn(2)–C(22)	97.4(9)
O(11)–Sn(1)–N(1)	73.1(8)	O(21)–Sn(2)–N(2)	68.6(8)
O(11)–Sn(1)–C(11)	95.8(11)	O(21)–Sn(2)–C(21)	93.1(10)
O(11)–Sn(1)–C(12)	100.1(10)	O(21)–Sn(2)–C(22)	97.2(10)
N(1)–Sn(1)–O(22)	110.0(8)	N(2)–Sn(2)–O(12′)	112.9(9)
N(1)–Sn(1)–C(11)	85.2(9)	N(2)–Sn(2)–C(21)	86.6(9)
N(1)–Sn(1)–C(12)	83.7(9)	N(2)–Sn(2)–C(22)	84.8(10)
O(22)–Sn(1)–C(11)	81.1(10)	O(12′)–Sn(2)–C(21)	83.3(11)
O(22)–Sn(1)–C(12)	83.8(10)	O(12′)–Sn(2)–C(22)	86.7(11)
C(11)–Sn(1)–C(12)	157.0(12)	C(21)–Sn(2)–C(22)	163.2(12)
O(11)–Sn(1)–O(22)	175.3(8)	O(21)–Sn(2)–O(12′)	175.9(8)
Cl(1)–Sn(1)–N(1)	161.3(7)	Cl(2)–Sn(2)–N(2)	154.5(8)
Sn(1)–O(11)–C(13)	126.3(22)	Sn(2)–O(21)–C(23)	127.5(21)
O(11)–C(13)–O(12)	120.0(35)	O(21)–C(23)–O(22)	134.1(32)
O(11)–C(13)–C(101)	108.7(30)	O(21)–C(23)–C(201)	113.5(28)
O(12)–C(13)–C(101)	130.0(34)	O(22)–C(23)–C(201)	112.1(30)
C(13)–O(12)–Sn(2″)	138.1(25)	C(23)–O(22)–Sn(1)	124.0(22)
C(13)–C(101)–N(1)	130.6(26)	C(23)–C(201)–N(2)	119.6(30)
C(13)–C(101)–C(102)	112.3(27)	C(23)–C(201)–C(202)	130.6(28)
N(1)–C(101)–C(102)	117.1(24)	N(2)–C(201)–C(202)	109.6(27)
C(101)–C(102)–C(103)	110.2(28)	C(201)–C(202)–C(203)	125.9(27)
C(102)–C(103)–C(104)	129.5(32)	C(202)–C(203)–C(204)	111.8(24)
C(103)–C(104)–C(105)	116.8(30)	C(203)–C(204)–C(205)	129.0(30)
C(104)–C(105)–N(1)	118.4(31)	C(204)–C(205)–N(2)	110.7(28)
Sn(1)–N(1)–C(101)	101.3(16)	Sn(2)–N(2)–C(201)	110.4(21)
Sn(1)–N(1)–C(105)	130.7(23)	Sn(2)–N(2)–C(205)	116.5(20)
C(101)–N(1)–C(105)	128.0(27)	C(201)–N(2)–C(205)	133.0(26)

Experimental

Dimethylchlorotin 2-pyridinecarboxylate was prepared as previously described [1] and recrystallisation from methanol gave crystals suitable for single crystal X-ray studies.

Crystal data. $C_8H_{10}ClNO_2Sn$, M_r 306.3, monoclinic, $P2_1/c$, $a = 10.805(7)$, b 20.292(15), c 10.804(8) Å, β 113.20(5)°, U 2177.37 Å^3, $Z = 8$, $D_c = 1.87$, $D_m = 1.85$ mg m^{-3}, μ(Mo-K_α) 2.37 mm^{-1}, $F(000) = 1184$.

Data collection and reduction. A crystal of approximate dimensions $0.15 \times 0.21 \times 0.36$ mm was used for data collection and was mounted with the a-axis coincident with the rotation (ω) axis of a Stöe Stadi-2 two circle diffractometer. 3083 unique reflections were collected, of which 1153 had $I \geqslant 3\sigma(I)$ and were considered as observed and used for subsequent analysis. Corrections were made for Lorentz and polarisation effects, but no correction was applied for absorption.

Structure determination and refinement. The approximate positions of the two independent tin atoms were calculated using a three-dimensional Patterson synthesis. The remaining atoms were located from successive difference Fourier maps. The hydrogen atoms were located, but given ideal geometry (C–H 1.08 Å). Scattering factors were calculated using an analytical approximation [2] and the weighting scheme adopted was $w = 1.000/[\sigma^2(F_0) + 0.0176(F_0)^2]$. The methyl and pyridine hydrogen atoms were given common isotropic temperature factors which refined to final values of 0.232(4) and 0.102(4) Å^2, respectively. Apart from C(201), all other atoms were given anisotropic temperature factors and full matrix least-squares refinement gave the final $R = 0.075$ and $R' = 0.080$. The final positional parameters are given in Table 1, bond distances and angles in Table 2. Lists of structure factors, thermal parameters and least-squares planes data are available on request from the authors (I.W.N.).

Discussion

Dimethylchlorotin 2-pyridinecarboxylate is found to be polymeric in the solid state with the carboxylate group bridging adjacent tin centres and giving rise to chains running along the a-direction (Fig. 1). In addition, the orientation of the 2-pyridinecarboxylate ligand is such as to allow the close approach of the nitrogen atom to tin. The resulting Sn–N distances of 2.468 and 2.505 Å for the two independent tin atoms is indicative of a significant interaction for while the values are greater than the sum of the covalent radii (2.15 Å), they are considerably smaller than the sum of the Van der Waals' radii of tin and nitrogen (3.75 Å). The Sn–N bond distances observed in the present study indicate a stronger intramolecular Sn–N interaction than those found in triphenyltin quinoline-8-thiolate (2.592(9), 2.611(8)Å [3]) and in the 2-pyridinethiolate complexes $Bu_2Sn(SC_5H_3N\text{-}2, NO_2\text{-}5)_2$ (2.77(1)Å [4]), $(p\text{-}MeC_6H_4)_3Sn(SC_5H_4N\text{-}2)$ (2.73(3), 2.74(3)Å [5]). The significantly shorter Sn–N distances of 2.256(9) and 2.271(9) Å found in dichlorotin bis(2-pyridinethiolate) [6] may well be attributable to the absence of aryl or alkyl substituents at tin. In $Ph_3Sn(SC_5H_4N\text{-}4)$ the 4-mercaptopyridine ligand gives rise to an intermolecular N → Sn coordination, the Sn–N distance being 2.62(2) Å [7]. It is interesting to note that in contrast to the present study, no Sn–N interaction is

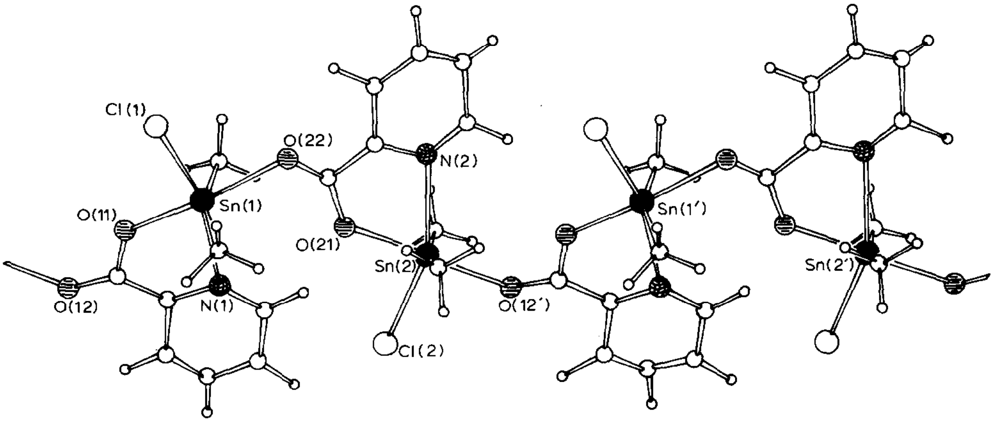

Fig. 1. Projection down the *c* axis showing part of one polymeric chain running in the *a* direction.

found in either trimethyltin 2-pyridinecarboxylate monohydrate [8] or in chlorotriphenyltin 2-pyridiniumcarboxylate [9].

The tridentate character of the 2-pyridinecarboxylate ligands leads to similarly distorted octahedral arrangements about the two independent tin atoms in which the methyl groups are *trans* to each other, as are the oxygen atoms from differing carboxylate groups (Figs. 2,3). While the O–Sn(n)–O groupings are almost linear (175.3, 175.9°; $n = 1, 2$), the Cl(n)–Sn(n)–N(n) and C(n1)–Sn(n)–C(n2) arrangements are considerably distorted, the bond angles being 161.3, 154.5° ($n = 1, 2$) and 157.0, 163.2° ($n = 1, 2$), respectively. The two Sn–O distances associated with each metal atom fall in the range of reported values (e.g. 8–10); however, they differ

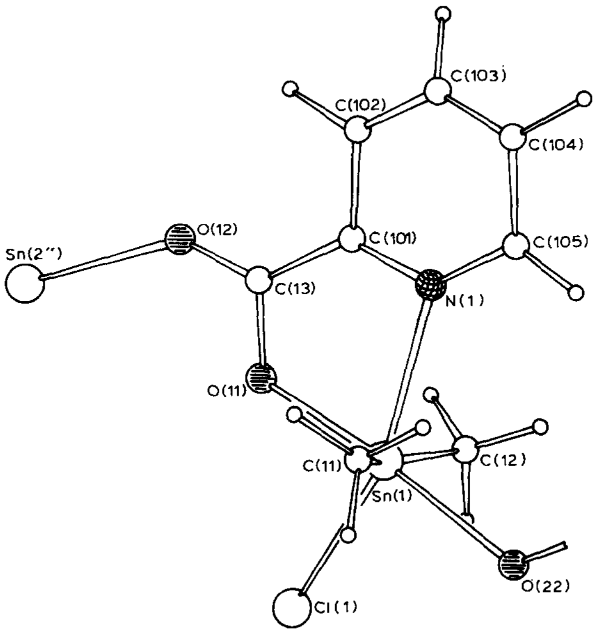

Fig. 2. Coordination about Sn(1).

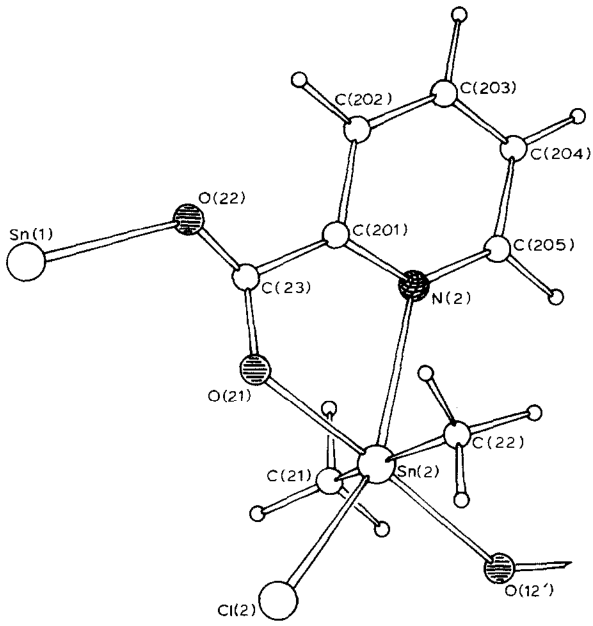

Fig. 3. Coordination about Sn(2).

significantly. Thus the oxygen atom which comprises part of the five-membered chelate ring gives rise to the shorter of the two Sn–O distances (2.076, 2.375 Å, Sn(1); 2.125, 2.285 Å, Sn(2)). For each tin atom the O_2NClSn grouping is approximately co-planar (Figs. 2, 3) and the dihedral angle between these units on adjacent metal atoms is 18.5°. The polymer chains thus consist of an approximately planar $ClSn(C_5H_3N,CO_2\text{-}2)_\infty$ strip running parallel to the *a*-axis with methyl groups located above and below it.

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