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STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

XXIV *. TRIMETHYLTIN 2-PYRIDYLCARBOXYLATE MONOHYDRATE

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Summary

The crystal and molecular structure of the title compound has been determined by Patterson and Fourier techniques from diffractometer data using 4266 independent non-zero reflections. Crystals are orthohombic, space group $Pca2_1$ with a 27.015(6), b 13.471(3), c 14.028(4) Å, $Z = 4$. The geometry at all four crystallographically independent tin atoms resembles that in $Me_3SnO_3SPh.H_2O$ and $Me_3SnNO_3.H_2O$, with trigonal bipyramidal coordination and planar (Me_3Sn) units. Axial coordination sites are occupied by an unidentate 2-pyridylcarboxylate group (mean Sn—O 2.18(2) Å) and a water molecule (mean Sn—O 2.43(3) Å). The crystal structure differs from that of the analogous phenylsulphonate and nitrate in possessing a three-, rather than a one-dimensional, network of hydrogen-bonds involving the pyridyl nitrogen atom, the carbonyl oxygen atom, and the water molecule.

Introduction

We have previously reported the synthesis and properties of a number of triorganotin derivatives of 2-pyridylcarboxylic acid [1]. The 2-pyridylcarboxylate group is a potentially terdentate ligand, and as such could give rise to six-coordinated triorganotin derivatives, at present uncharacterised. An unequivocal choice between possible five- and six-coordinated geometries is not possible in the absence of crystallographic data. Attempts to obtain crystals of $Me_3SnO_2CC_5H_4N$ afforded a crystalline sample of the monohydrate, the structure of which should also be of interest due to the extra possibility of hydrogen-bonding.

The observed Mössbauer quadrupole splitting for the monohydrate (3.93

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[*] For part XXIII see ref. 7.

mm s^{-1}) is very similar to that of the anhydrous material (3.89 mm s^{-1}) indicating a possible similarity in geometry at tin. The infra-red spectrum of the hydrated material exhibits a very broad band centred at ca. 3380 cm^{-1}, indicative of a strongly coordinated water molecule which probably is engaged in hydrogen-bonding. The C=O stretching mode appears at 1620 cm^{-1}, higher than in the anhydrous material (1598 cm^{-1}), but lower than in the free ligand (ca. 1700 cm^{-1}), suggesting coordination via the carbonyl group, although not of the same type as in the anhydrous material. The tin—carbon stretching region exhibits only one band at 552 cm^{-1}, which may be assigned to the antisymmetric (SnC_3) stretching vibration. The absence of the corresponding symmetric mode is indicative of a planar (Me_3Sn) unit as often found in structures containing trigonal-bipyramidal five-coordinated tin. If this is so, the carbonyl group cannot be acting as a bridging ligand directly to neighbouring tin atoms, though it could participate in hydrogen-bonding. To clarify the ambiguities and uncertainties produced by the spectroscopic data, we have determined the X-ray crystal structure of the monohydrate.

Experimental

Crystal Preparation

Trimethyltin 2-pyridylcarboxylate was prepared by the azeotropic dehydration of a 1/1 molar ratio of trimethyltin hydroxide and 2-pyridylcarboxylic acid in boiling benzene [1]. The white powder produced by evaporating off the solvent in vacuo was recrystallised from methanol open to the atmosphere to afford a crystalline sample of the monohydrate. Found: C, 35.37; H, 4.85; N, 4.71%. $C_9H_{15}NO_3Sn$ calcd.: C, 35.43; H, 4.96; N, 4.59%. A crystal of suitable dimensions ($0.3 \times 0.2 \times 0.4$ mm^3) was selected, mounted on a fine glass fibre, and used to obtain the cell parameters and intensity data.

Crystal data

$C_9H_{15}NO_3Sn$, M = 268.82, orthorhombic, a 27.015(6), b 13.471(3), c 14.028(4) Å, V 5104.9 $Å^3$, $Z = 4$, $F(000) = 2496$, $D_c = 1.32$, Mo-K_α radiation ($\lambda = 0.7106$ Å), μ(Mo-K_α) = 19.99 cm^{-1}, space group $Pca2_1$.

Cell measurements and data collection

The space group and initial cell dimensions were determined from oscillation and zero- and first-layer Weissenberg photographs. Accurate unit cell parameters were obtained by least-squares refinement of data for 25 reflections. The intensities of 4321 independent reflections in the range $0 < \theta < 24.8°$ were collected on a Hilger and Watts Y290 four-circle diffratometer. Those with a corrected count $I < 3\sigma(I)$ were considered as unobserved, reducing the total number of reflections to 4266. Corrections were made for Lorentz and polarisation effects, but no correction was applied for absorption due to the low μ value.

Determination and refinement of the structure

The space group of the crystal was originally assigned as *Pbcm*, which was subsequently found to be incorrect and the reflections were re-indexed for the

TABLE 1

FINAL FRACTIONAL ATOMIC COORDINATES IN $(CH_3)_3SnO_2\ CC_5H_4N \cdot H_2O$

Atom	*x/a*	*y/b*	*z/c*
Sn(1)	0.25037(10)	0.22771(15)	0.16235(19)
Sn(2)	0.39816(9)	−0.01252(18)	−0.01655(18)
Sn(3)	0.35040(9)	0.54033(19)	0.37626(18)
Sn(4)	0.50242(10)	0.30178(16)	0.18363(20)
O(1)	0.2589(7)	0.0650(13)	0.1539(16)
O(2)	0.2340(8)	0.0421(16)	0.3021(16)
O(3)	0.4777(7)	0.0072(16)	0.0011(16)
O(4)	0.4970(9)	−0.0278(17)	−0.1474(17)
O(5)	0.2732(7)	0.5148(14)	0.3470(12)
O(6)	0.2539(8)	0.5334(14)	0.5025(16)
O(7)	0.4949(8)	0.4635(14)	0.2018(16)
O(8)	0.5179(10)	0.4979(19)	0.0487(20)
O(9)	0.2428(8)	0.4084(14)	0.1610(18)
O(10)	0.3088(8)	−0.0306(15)	−0.0300(17)
O(11)	0.4384(8)	0.5652(17)	0.3900(19)
O(12)	0.5150(8)	0.1225(17)	0.1883(22)
N(1)	0.2668(12)	−0.1292(20)	0.1206(20)
N(2)	0.5724(10)	0.0404(21)	0.0497(21)
N(3)	0.1759(10)	0.4713(19)	0.3090(19)
N(4)	0.4862(12)	0.6552(25)	0.2412(24)
C(1)	0.1697(13)	0.2192(27)	0.1732(33)
C(2)	0.3051(16)	0.2464(32)	0.2840(32)
C(3)	0.2837(14)	0.2428(28)	0.0149(28)
C(4)	0.2487(18)	0.0127(23)	0.2278(24)
C(5)	0.2453(12)	−0.1000(21)	0.2077(22)
C(6)	0.2189(17)	−0.1540(34)	0.2799(35)
C(7)	0.2143(19)	−0.2656(38)	0.2607(39)
C(8)	0.2441(18)	−0.3001(31)	0.1648(33)
C(9)	0.2628(20)	−0.2251(38)	0.1010(37)
C(10)	0.3910(15)	0.1127(31)	−0.1215(33)
C(11)	0.3883(14)	0.0230(27)	0.1339(27)
C(12)	0.4029(13)	−0.1742(34)	0.0559(31)
C(13)	0.4902(14)	0.0000(36)	0.0656(28)
C(14)	0.5606(12)	0.0057(25)	0.0456(24)
C(15)	0.5945(15)	0.0266(29)	0.1124(32)
C(16)	0.6504(20)	0.0093(43)	0.0742(40)
C(17)	0.6637(18)	0.0265(36)	0.0142(37)
C(18)	0.6213(15)	0.0437(30)	0.0755(30)
C(19)	0.3635(15)	0.5189(29)	0.2231(27)
C(20)	0.3504(16)	0.5403(29)	0.3762(35)
C(21)	0.3376(16)	0.6948(39)	0.4237(38)
C(22)	0.2428(11)	0.5182(17)	0.4170(21)
C(23)	0.1899(11)	0.5040(22)	0.3999(22)
C(24)	0.1538(16)	0.4636(30)	0.4631(34)
C(25)	0.1034(16)	0.5097(34)	0.4415(29)
C(26)	0.0893(18)	0.4815(36)	0.3452(34)
C(27)	0.1306(15)	0.4567(30)	0.2836(30)
C(28)	0.4670(16)	0.2888(33)	0.3250(32)
C(29)	0.5834(14)	0.3136(29)	0.1722(36)
C(30)	0.4506(17)	0.2861(34)	0.0419(36)
C(31)	0.5081(16)	0.5209(26)	0.1315(25)
C(32)	0.5079(15)	0.6289(34)	0.1517(32)
C(33)	0.5260(18)	0.6891(36)	0.0884(36)
C(34)	0.5267(14)	0.8001(39)	0.1132(27)
C(35)	0.5079(14)	0.8936(25)	0.2043(31)
C(36)	0.5117(14)	0.7519(28)	0.2672(28)

space group $Pca2_1$. The approximate positions of the four tin atoms in the asymmetric unit were calculated using a three-dimensional Patterson synthesis. These coordinates were used to phase the initial structure factor calculation and one cycle of block-diagonal, isotropic least-squares refinement on the coordinates produced an R-value of 0.209. A further four cycles of least-squares refinement, combined with the use of difference Fourier maps, yielded the positions of 25 of the non-hydrogen light atoms and reduced the R-value to 0.129. A total of 48 light atoms were found after eight cycles of refinement with the R-value being 0.117. At this point the tin atom parameters were

TABLE 2

FINAL ANISOTROPIC AND ISOTROPIC TEMPERATURE FACTORS [a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	2.09(14)	3.83(9)	3.91(11)	−0.07(14)	0.40(16)	0.06(13)
Sn(2)	4.99(13)	6.06(15)	3.42(11)	0.23(13)	−0.23(15)	−0.32(15)
Sn(3)	5.19(14)	6.91(16)	3.15(11)	−0.35(15)	0.09(15)	0.08(14)
Sn(4)	7.65(17)	4.61(11)	3.74(12)	0.31(14)	0.32(15)	−0.25(14)

Atom	U	Atom	U
O(1)	4.84(55)	C(19)	6.7(12)
O(2)	5.69(67)	C(20)	8.3(12)
O(3)	5.31(58)	C(21)	11.4(24)
O(4)	6.55(74)	C(22)	3.6(7)
O(5)	3.52(52)	C(23)	3.7(8)
O(6)	5.50(60)	C(24)	8.9(13)
O(7)	4.90(60)	C(25)	6.5(12)
O(8)	8.23(90)	C(26)	8.6(16)
O(9)	6.28(59)	C(27)	6.9(11)
O(10)	6.35(63)	C(28)	8.4(14)
O(11)	7.27(74)	C(29)	9.8(12)
O(12)	8.09(75)	C(30)	8.3(15)
N(1)	6.4(10)	C(31)	5.5(10)
N(2)	3.5(8)	C(32)	8.1(13)
N(3)	3.7(7)	C(33)	8.2(15)
N(4)	7.3(10)	C(34)	10.1(11)
C(1)	8.7(10)	C(35)	9.6(11)
C(2)	7.2(14)	C(36)	11.1(11)
C(3)	7.2(19)		
C(4)	5.0(9)		
C(5)	4.1(8)		
C(6)	9.4(14)		
C(7)	11.3(16)		
C(8)	13.6(15)		
C(9)	12.3(18)		
C(10)	8.5(13)		
C(11)	6.8(12)		
C(12)	7.4(13)		
C(13)	4.3(10)		
C(14)	5.2(9)		
C(15)	8.1(12)		
C(16)	10.6(19)]		
C(17)	10.6(16)		
C(18)	66.4(12)		

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[a] Values multiplied by 10^2 (U_{ij} are of the form: $\exp - 2\pi^2(h^2U_{11}a^{\star 2} + k^2U_{22}b^{\star 2} + l^2U_{33}c^{\star 2} + 2hkU_{12}a^\star b^\star + 2hlU_{13}a^\star c^\star + 2klU_{23}b^\star c^\star)$.

refined anisotropically, with the light atom parameters still being refined isotropically, leading to a reduction in the R-value to 0.094. A further four cycles of block-diagonal, mixed least-squares refinement enabled the coordinates of the remaining 4 light atoms to be calculated. Two cycles of refinement using all 56 atoms yielded an R-value of 0.061. The refinement and structure determination were stopped at this stage with no weighting scheme applied. The scattering factors used were those for neutral atoms [2] and refinement was carried out using the "X-ray'70" suite of programs. The determined atomic

TABLE 3

INTERATOMIC BOND DISTANCES IN $(CH_3)_3SnO_2CC_5H_4N\cdot H_2O$ [a]

Bonded Atoms	Distance (Å)	Bonded Atoms	Distance (Å)
Molecule 1		Molecule 2	
Sn(1)—O(9)	2.44(4)	Sn(2)—O(10)	2.43(2)
Sn(1)—O(1)	2.21(1)	Sn(2)—O(3)	2.18(2)
Sn(1)—C(1)	2.18(1)	Sn(2)—C(10)	2.24(2)
Sn(2)—C(2)	2.27(2)	Sn(2)—C(11)	2.17(3)
Sn(1)—C(3)	2.26(2)	Sn(2)—C(12)	2.26(4)
C(4)—O(1)	1.29(3)	C(13)—O(3)	1.28(4)
C(4)—O(2)	1.18(3)	C(13)—O(4)	1.25(4)
C(4)—C(5)	1.55(4)	C(13)—C(14)	1.40(3)
C(5)—C(6)	1.42(3)	C(14)—C(15)	1.39(3)
C(6)—C(7)	1.53(3)	C(15)—C(16)	1.62(4)
C(7)—C(8)	1.63(2)	C(16)—C(17)	1.38(4)
C(8)—C(9)	1.44(4)	C(17)—C(18)	1.54(4)
C(9)—N(1)	1.32(2)	C(18)—C(19)	1.37(2)
N(1)—C(5)	1.41(3)	N(2)—C(14)	1.43(3)
Molecule 3		Molecule 4	
Sn(3)—O(11)	2.41(5)	Sn(4)—O(12)	2.44(2)
Sn(3)—O(5)	2.15(2)	Sn(4)—O(7)	2.20(2)
Sn(3)—C(19)	2.19(1)	Sn(4)—C(28)	2.21(4)
Sn(3)—C(20)	2.30(4)	Sn(4)—C(29)	2.20(3)
Sn(3)—C(21)	2.21(2)	Sn(4)—C(30)	2.24(2)
C(22)—O(5)	1.28(2)	C(31)—O(7)	1.30(2)
C(22)—O(6)	1.25(2)	C(31)—O(8)	1.23(2)
C(22)—C(23)	1.46(5)	C(31)—C(32)	1.48(4)
C(23)—C(24)	1.39(4)	C(32)—C(33)	1.29(3)
C(24)—C(25)	1.44(2)	C(33)—C(34)	1.53(4)
C(25)—C(26)	1.45(2)	C(34)—C(35)	1.46(4)
C(26)—C(27)	1.45(4)	C(35)—C(36)	1.42(3)
C(27)—N(3)	1.29(2)	C(36)—N(4)	1.56(4)
N(3)—C(23)	1.39(2)	N(4)—C(32)	1.43(3)
Intermolecular Hydrogen Bonding			
O(9)—O(6)'	2.79(3)	O(11)—O(8)'	2.66(4)
O(9)—N(3)	2.88(3)	O(11)—N(4)	2.74(4)
O(10)—O(2)'	2.74(4)	O(12)—O(4)	2.65(3)
O(10)—N(1)	2.80(3)	O(12)—N(2)	2.72(3)

The primed atoms are related by the symmetry operation $-x$, $-y$, $1/2 + z$

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[a] Standard deviations in parentheses.

TABLE 4

INTERATOMIC BOND ANGLES IN $(CH_3)_3SnO_2CC_5H_4N \cdot H_2O$ [a]

Atom	Angle (°)	Atom	Angle (°)
Molecule 1			
O(9)—Sn(1)—O(1)	176.2(8)	O(1)—C(4)—O(2)	126.7(21)
O(9)—Sn(1)—C(1)	88.2(12)	O(1)—C(4)—C(5)	113.8(32)
O(9)—Sn(1)—C(2)	87.0(13)	O(2)—C(4)—C(5)	118.1(30)
O(9)—Sn(1)—C(3)	86.3(13)	C(4)—C(5)—C(6)	113.9(29)
C(1)—Sn(1)—C(2)	127.0(15)	C(4)—C(5)—N(1)	114.1(31)
C(1)—Sn(1)—C(3)	117.7(16)	C(6)—C(5)—N(1)	131.8(31)
C(2)—Sn(1)—C(3)	114.6(15)	C(5)—C(6)—C(7)	115.8(28)
O(1)—Sn(1)—C(1)	93.2(12)	C(6)—C(7)—C(8)	111.6(28)
O(1)—Sn(1)—C(2)	94.7(13)	C(7)—C(8)—C(9)	118.9(19)
O(1)—Sn(1)—C(3)	89.9(13)	C(8)—C(9)—N(1)	125.7(27)
Sn(1)—O(1)—C(4)	118.6(14)	C(9)—N(1)—C(5)	114.7(23)
Molecule 2			
O(10)—Sn(2)—O(3)	177.5(9)	O(3)—C(13)—O(4)	120.0(20)
O(10)—Sn(2)—C(10)	86.5(10)	O(3)—C(13)—C(14)	119.9(34)
O(10)—Sn(2)—C(11)	88.6(10)	O(4)—C(13)—C(14)	119.1(23)
O(10)—Sn(2)—C(12)	86.5(11)	C(13)—C(14)—C(15)	118.1(23)
C(10)—Sn(2)—C(11)	117.3(14)	C(13)—C(14)—N(2)	115.6(21)
C(10)—Sn(2)—C(12)	123.6(19)	C(15)—C(14)—N(2)	126.1(26)
C(11)—Sn(2)—C(12)	118.3(15)	C(14)—C(15)—C(16)	109.7(31)
O(3)—Sn(2)—C(10)	93.8(12)	C(15)—C(16)—C(17)	126.1(30)
O(3)—Sn(2)—C(11)	88.9(11)	C(16)—C(17)—C(18)	112.6(19)
O(3)—Sn(2)—C(12)	95.2(11)	C(17)—C(18)—N(2)	126.8(28)
Sn(2)—O(3)—C(13)	125.2(15)	C(18)—N(2)—C(14)	117.8(19)
Molecule 3			
O(11)—Sn(3)—O(5)	173.5(9)	O(5)—C(22)—O(6)	125.8(32)
O(11)—Sn(3)—C(19)	86.4(12)	O(5)—C(22)—C(23)	119.5(16)
O(11)—Sn(3)—C(20)	89.7(13)	O(6)—C(22)—C(23)	114.7(28)
O(11)—Sn(3)—C(21)	89.9(12)	C(22)—C(23)—C(24)	122.2(29)
C(19)—Sn(3)—C(20)	120.6(18)	C(22)—C(23)—N(3)	117.3(33)
C(19)—Sn(3)—C(21)	116.3(13)	C(24)—C(23)—N(3)	119.6(18)
C(20)—Sn(3)—C(21)	122.9(18)	C(23)—C(24)—C(25)	116.6(25)
O(5)—Sn(3)—C(19)	87.1(13)	C(24)—C(25)—C(26)	120.5(33)
O(5)—Sn(3)—C(20)	93.3(13)	C(25)—C(26)—C(27)	114.3(25)
O(5)—Sn(3)—C(21)	93.3(13)	C(26)—C(27)—N(3)	122.0(27)
Sn(3)—O(5)—C(22)	118.3(21)	C(27)—N(3)—C(23)	123.7(24)
Molecule 4			
O(12)—Sn(4)—O(7)	171.3(9)	O(7)—C(31)—O(8)	128.5(34)
O(12)—Sn(4)—C(28)	87.6(12)	O(7)—C(31)—C(32)	115.9(14)
O(12)—Sn(4)—C(29)	86.2(13)	O(8)—C(31)—C(32)	115.3(17)
O(12)—Sn(4)—C(30)	90.9(13)	C(31)—C(32)—C(33)	118.7(22)
C(28)—Sn(4)—C(29)	120.1(18)	C(31)—C(32)—N(4)	114.2(23)
C(28)—Sn(4)—C(30)	118.4(17)	C(33)—C(32)—N(4)	126.9(28)
C(29)—Sn(4)—C(30)	121.2(19)	C(32)—C(3)—C(34)	117.2(19)
O(7)—Sn(4)—C(28)	86.2(12)	C(33)—C(34)—C(35)	121.3(21)
O(7)—Sn(4)—C(29)	91.6(12)	C(34)—C(35)—C(36)	112.0(15)
O(7)—Sn(4)—C(30)	97.3(13)	C(35)—C(36)—N(4)	124.9(27)
Sn(4)—O(7)—C(31)	118.3(27)	C(36)—N(4)—C(31)	117.9(19)
Hydrogen bonding			
N(3)—O(9)—O(6)′	114.6(15)	N(2)—O(12)—O(4)′	119.6(114)
N(1)—O(10)—O(2)′	130.2(17)	N(4)—O(11)—O(8)′	124.7(16)

[a] Standard deviations in parentheses.

parameters are listed in Table 1 and the corresponding mixed thermal parameters in Table 2. Interatomic bond distances and angles are listed in Tables 3 and 4, respectively, and least-squares planes data is collected in Table 5. Fig. 1 shows the atomic labelling and coordination about each tin atom. Fig. 2 shows the arrangement of the four molecules in the asymmetric unit. The complex hydrogen bonding is illustrated in Fig. 3 which is an enlarged section of the unit cell projection onto the *ac* plane. A Table of observed and calculated structure factors is available from the authors on request.

Discussion

The crystal structure of $(CH_3)_3SnO_2CC_5H_4N.H_2O$ shows the tin to be five-coordinated, with planar methyl-groups and the axial positions being occupied by oxygen from a unidentate carboxylate group and a water molecule, the resulting geometry being that of a trigonal bipyramid. Thus, the structure is similar,to two other hydrated tin compounds, $(CH_3)_3SnNO_3.H_2O$ [3] and $(CH_3)_3SnSO_3C_6H_5.H_2O$ [4], both of which have trigonal bipyramidally coordinated tin atoms and lattices composed of infinite chains of hydrogen-bonded molecular units. The four crystallographically independent molecules have the

TABLE 5

WEIGHTED LEAST-SQUARES PLANES AND DEVIATIONS FROM THE PLANES [a]

Equations of planes ($pX + qY + rZ = s$)

Plane	*p*	*q*	*r*	*s*
(1) C(1), C(2), C(3)	−0.10081	0.99490	0.00257	22.48209
(2) C(10), C(11), C(12)	0.99416	0.09477	0.05164	10.55716
(3) C(19), C(20), C(21)	0.98177	0.14833	0.11883	11.05078
(4) C(28), C(29), C(30)	−0.10391	0.99458	0.00253	2.57027
(5) C(5), C(6), C(7), C(8), C(9), N(1)	0.86598	0.13095	0.48264	18.98397
(6) C(14), C(15), C(16), C(17), C(18), N(2)	0.00899	0.93856	−0.34500	0.39164
(7) C(23), C(24), C(25), C(26), C(27), N(3)	−0.03005	0.93524	−0.35175	4.21860
(8) C(32), C(33), C(34), C(35), C(26), C(4)	0.90971	0.12895	0.39471	1.67337

Devaitions from planes (Å)

	Atom	Deviation		Atom	Deviation
Plane (1)	Sn(1)	−0.10630	Plane (3)	Sn(3)	−0.05050
Plane (2)	Sn(2)	0.16415	Plane (4)	Sn(4)	0.06914

Plane (5)		Plane (6)		Plane (7)		Plane (8)	
Atom	Deviation	Atom	Deviation	Atom	Deviation	Atom	Deviation
C(5)	0.03612	C(14)	0.03051	C(23)	−0.004431	C(32)	0.00554
C(6)	−0.01105	C(15)	−0.03858	C(24)	0.08604	C(33)	−0.00340
C(7)	−0.03770	C(16)	−0.00724	C(25)	−0.08762	C(34)	−0.04283
C(8)	0.07091	C(17)	0.03653	C(26)	0.04760	C(35)	−0.06163
C(9)	−0.05779	C(18)	−0.05335	C(27)	−0.00569	C(36)	0.17798
N(1)	−0.00048	N(2)	0.01765	N(3)	0.00398	N(4)	−0.07565

[a] According to ref. 8.

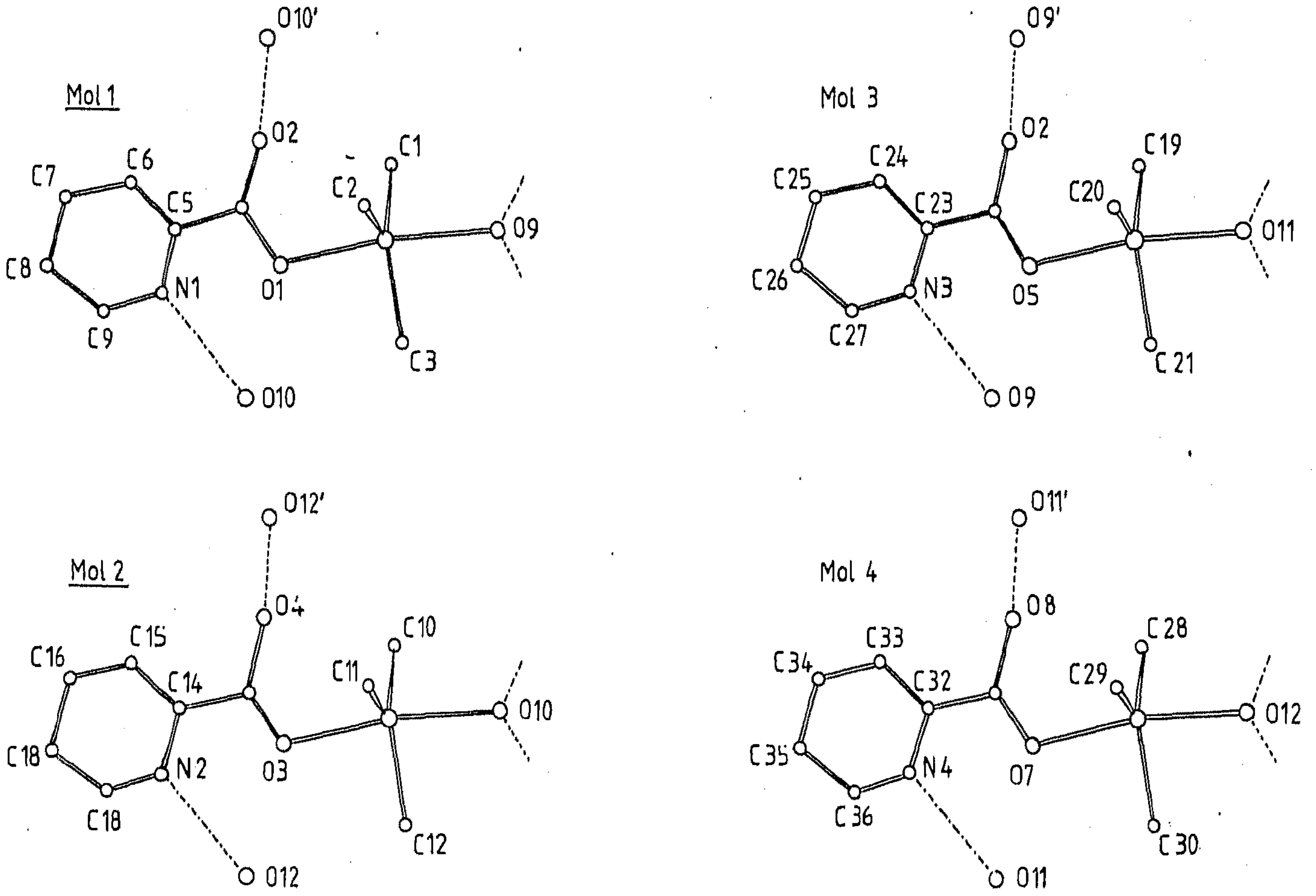

Fig. 1. Molecular geometry and atomic labelling in the four crystallographically independent $Me_3SnO_2CC_5H_4N.H_2O$ molecules.

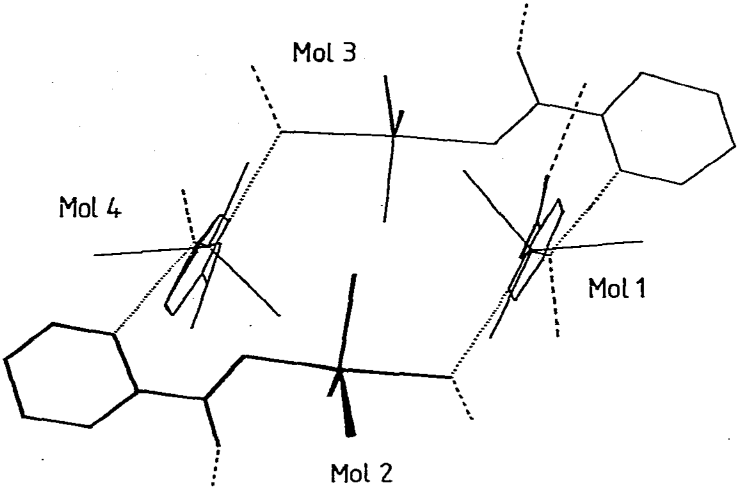

Fig. 2. The asymmetric unit of $Me_3SnO_2CC_5H_4Sn.H_2O$.

same basic geometry, and only differ in the degree of distortion from the ideal geometry. The tin—carbon distances are similar in all four molecules (2.18—2.30 Å), however, they are longer than the average bond distance (2.13 Å) found in trimethyltin compounds generally, and in particular the nitrate hydrate (mean 2.11 Å) and the sulphonate hydrate (mean 2.16 Å). As expected from the infra-red, the trimethyltin unit is almost planar with largest deviation of the tin atom out of the plane of the carbon atoms being 0.16 Å, in the case of molecule 2. The mean Sn—O(H_2) bond distance (2.43 Å) is of similar magni-

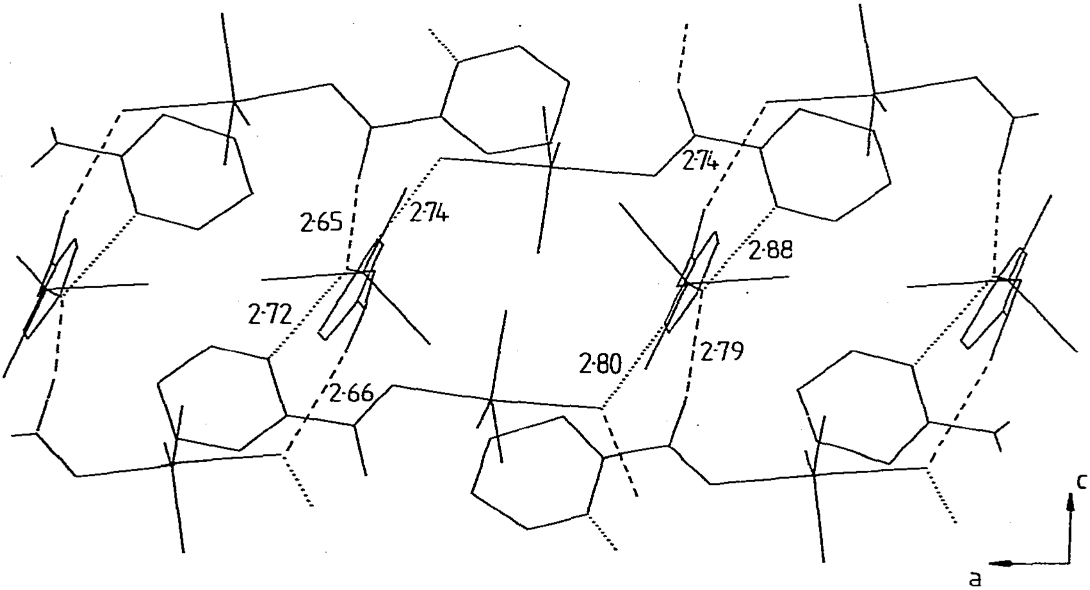

Fig. 3. Part of the unit cell of $Me_3SnO_2CC_5H_4N.H_2O$ projected on to the *ac* plane, illustrating N· · · · · ·O_{water} and (C=)O- - - - - -O_{water} hydrogen bonds.

tude to that in the nitrate (2.47 Å) but is much longer than that in the sulphonate (2.30 Å). The carboxylate oxygen—tin bond distance (mean 2.185 Å) is of similar length to the corresponding distance in $(CH_3)_3SnO_2CCF_3$ (2.177 Å) [5] but much longer than that in $(C_6H_5CH_2)_3SnO_2CCH_3$ (2.14 Å) [6], both of which have oxygen-bridged structures. However, the corresponding distance in $(C_6H_{11})SnO_2CCH_3$ (2.12 Å) is much shorter and in this case the carboxylate group is unidentate [6]. The C=O bond distances range from 1.18 to 1.25 Å (mean 1.23 Å), which, apart from the very short value of 1.18 Å, compare well with the bond distances found in simple carbonyls (1.23 Å), $(C_6H_{11})_3SnO_2CCH_3$ (125 Å) [6] and $(CH_3)_3SnO_2CCH_3$ (1.24 Å) [5], even though the latter compound contains a bridging carbonyl group and the compound under discussion does not. Thus, the hydrogen-bond to the carbonyl-oxygen does not seem to have any significant effect on the C=O bond. The bond distances and angles within the pyridine rings all have usual values, and require no comment.

As Fig. 3 illustrates, the lattice is strongly hydrogen-bonded, In all four independent molecules the water molecule participates in the formation of two hydrogen-bonds. One of these hydrogen-bonds is formed between the water molecule and the pyridyl nitrogen of a neighbouring molecule within the asymmetric unit (Fig. 2 and 3). The other hydrogen-bond is formed between the oxygen of the water molecule and the carbonyl oxygen of the symmetry related neighbouring molecule. Thus, each $Me_3SnO_2CC_5H_4N.H_2O$ molecule is connected by four hydrogen bonds to four neighbouring molecules in the crystal lattice. It is interesting to note that for both types of hydrogen-bond there appear to be two distinct distances. The distance for the N···O(water) interaction in molecules 1 and 2 are 2.88 and 2.80 Å, respectively, but are only 2.74 and 2.72 Å, respectively, in molecules 3 and 4. Similarly, molecules 1 and 2 exhibit (C=)O···O(water) distance of 2.79 and 2.74 Å, respectively, whilst, again, the corresponding distances in molecules 3 and 4 are shorter, at 2.66 and 2.65 Å, respectively. The reason for this is not clear, and is probably due to crystal packing since in molecules 3 and 4 the $O—Sn—O_{water}$ bond angle deviates more from linearity than in the other two molecules, and thus the contact distance, for both types of interaction, will be shortened. In trimethyltin nitrate monohydrate the O···O contact distance is 2.72 Å, which is approximately intermediate between the two extremes (2.79 and 2.65 Å) in trimethyltin 2-pyridylcarboxylate monohydrate.

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