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Synthesis and Structure of Di-*n*-Butyltin Pyridine-2-phosphonate-6-carboxylate

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The crystal structure of di-*n*-butyltin pyridine-2-phosphonate-6-carboxylate, $[C_{14}H_{24}NO_6PSn]_2$, features centrosymmetric dimers disposed about a central Sn_2O_2 core. The phosphonate carboxylate dianion is μ_2-tetradentate, coordinating one tin atom via one of the phosphonate oxygen atoms, the pyridine nitrogen atom, and one of the carboxylate oxygen atoms; the latter atom also coordinates the second tin atom of the dimer. The remaining positions in the seven-coordinate, distorted pentagonal bipyramidal geometry are occupied by a water molecule and two *n*-butyl groups that occupy axial positions. The lattice is stabilized by hydrogen-bonding contacts leading to an arrangement of parallel, orthogonally related chains of dimeric units. In methanol solution, the dimer is involved in a dissociation equilibrium that is fast on the NMR time scale.

Introduction

Some diorganotin pyridine-2,6-dicarboxylates[1] exhibit interesting crystal structures.[1a,2,3] The tin atom is always seven-coordinate, with the two organic groups occupying the axial positions of the pentagonal bipyramidal structure. In diphenyltin pyridine-2,6-dicarboxylate,[1a] the equatorial plane comprises the tridentate pyridine-2,6-dicarboxylate ligand, a coordinated water molecule, and a carbonyl oxygen atom of an adjacent molecule, resulting in a polymeric zigzag chain. In the dimethyltin,[2a] di-*n*-butyltin,[2a] and ethylphenyltin[2b] analogues, the 2,6-pyridinedicarboxylate ligand exhibits a similar chelation mode with, in addition, one of the oxygen atoms already coordinated bridging a centrosymmetrically related tin atom. This arrangement leads to a Sn_2O_2 core. A coordinated water molecule completes the pentagonal plane about the tin atom.

In dicyclohexylammonium bis(2,6-pyridinedicarboxylato)dibutylstannate,[3] tin is again seven-coordinate, one pyridinedicarboxylate being tridentate, as in the above compounds, and the second one, bidentate through a single chelating carboxylate; the second pendant carboxylate interacts directly with the dicyclohexylammonium countercation.

The structure of other organotin compounds with a seven-coordinate tin ligated by carboxylate and nitrogen moieties has been described,[4] e.g., $Me_2Sn(picolinate)_2$,[4a] and several nitrogen-containing dicarboxylates,[4b] among which a recent repetition of dimethyltin pyridinedicarboxylate described earlier.[2a] On the other hand, apart from the compounds just described,[4] organotin compounds with a water molecule in the coordination sphere remain rare.[5] Organotin molecules with phosphonate coordination are likewise not so numerous.[6]

Dihydrogen pyridine-2-phosphonate-6-carboxylate has been synthesized recently.[7] Given the structural diversity of diorganotin pyridine-2,6-dicarboxylates, the purpose of the present study is to find out whether diorganotin compounds change their structural coordination properties when the pyridine-2,6-dicarboxylate ligand is replaced by the pyridine-2-phosphonate-6-carboxylate ligand, in particular with regard to water coordination. The crystal structure of di-*n*-butyltin

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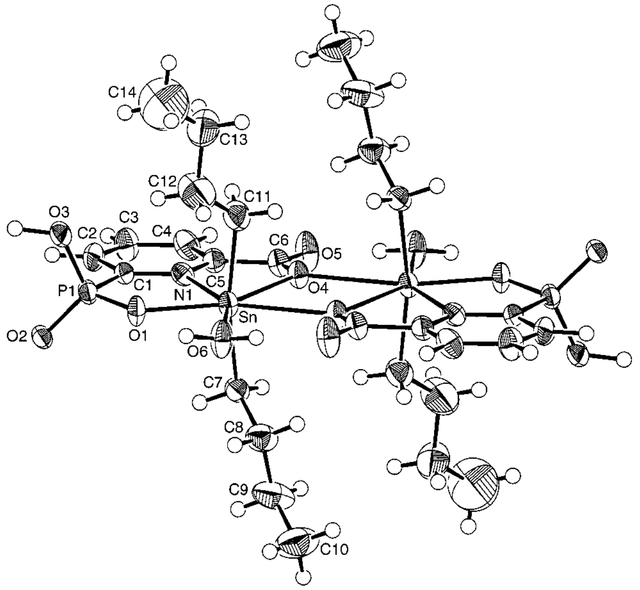
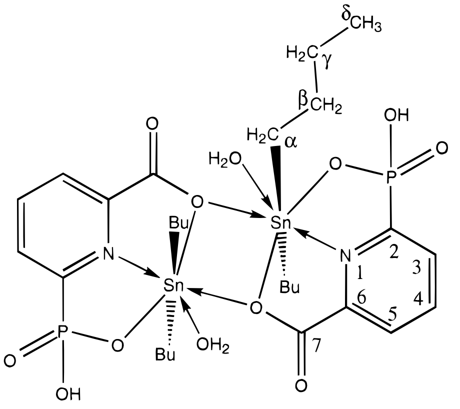


Figure 1. Molecular structure and atomic numbering scheme for $[C_{14}H_{24}NO_6PSn]_2$.

Scheme 1



pyridine-2-phosphonate-6-carboxylate is presented, and its solution state behavior is discussed.

Results and Discussion

Synthesis. Di-*n*-butyltin pyridine-2-phosphonate-6-carboxylate was synthesized using the procedure described by Davies.[8] It consists of preparing tetra-*n*-butyldi-*n*-propoxydistannoxane from di-*n*-butyltin oxide and *n*-propanol in refluxing benzene. The transient distannoxane obtained is subsequently reacted at room temperature with dihydrogen pyridine-2-phosphonate-6-carboxylate[7] in a tin/diacid molar ratio 1/1, to yield the desired condensation compound. Its structure, as evidenced by X-ray diffraction, is depicted in Scheme 1.

Table 1. Selected Interatomic (Å, deg) Parameters for $[C_{14}H_{24}NO_6PSn]_2$[a]

Sn−O(1)	2.144(4)	Sn−O(4)	2.539(4)
Sn−O(4)^i	2.602(4)	Sn−O(6)	2.270(4)
Sn−N(1)	2.380(5)	Sn−C(7)	2.121(7)
Sn−C(11)	2.124(8)	P(1)−O(1)	1.501(4)
P(1)−O(2)	1.501(4)	P(1)−O(3)	1.549(5)
P(1)−C(1)	1.798(7)	O(4)−C(6)	1.265(8)
O(5)−C(6)	1.229(7)		
O(1)−Sn−O(4)	140.0(2)	O(1)−Sn−O(4)^i	154.4(1)
O(1)−Sn−O(6)	75.8(2)	O(1)−Sn−N(1)	74.2(2)
O(1)−Sn−C(7)	95.1(2)	O(1)−Sn−C(11)	96.5(2)
O(4)−Sn−O(4)^i	65.6(2)	O(4)−Sn−O(6)	144.2(1)
O(4)−Sn−N(1)	65.8(2)	O(4)−Sn−C(7)	85.2(2)
O(4)−Sn−C(11)	84.4(2)	O(4)^i−Sn−O(6)	78.7(1)
O(4)^i−Sn−N(1)	131.3(2)	O(4)^i−Sn−C(7)	85.2(2)
O(4)^i−Sn−C(11)	85.4(2)	O(6)−Sn−N(1)	149.9(2)
O(6)−Sn−C(7)	91.5(2)	O(6)−Sn−C(11)	93.6(3)
N(1)−Sn−C(7)	89.5(2)	N(1)−Sn−C(11)	91.4(3)
C(7)−Sn−C(11)	168.2(3)	Sn−O(1)−P(1)	127.6(3)
Sn−O(4)−Sn^i	114.4(2)	Sn−O(4)−C(6)	119.4(4)
Sn−O(4)^i−C(6)^i	125.7(4)	Sn−N(1)−C(1)	119.0(4)
Sn−N(1)−C(5)	121.6(4)		

[a] Symmetry operation *i*: −*x*, −*y*, −*z*.

Crystal Structure of $[C_{14}H_{24}NO_6PSn]_2$. The molecular structure of $[C_{14}H_{24}NO_6PSn]_2$ is shown in Figure 1, and selected interatomic parameters are listed in Table 1. The structure is dimeric, being disposed about a crystallographic center of inversion. The tin atom is coordinated by O(1), derived from the phosphonate group, the pyridine N(1) atom, and the O(4) atom of the carboxylate residue. The O(4) atom also bonds to the centrosymmetrically related tin atom, thereby generating a Sn_2O_2 four-membered ring. The coordination mode of the dianion is μ_2-tetradentate. The remaining sites in each tin atom environment are occupied by two *n*-butyl groups and a water molecule. The overall tin geometry is based on a pentagonal bipyramid with the two organic substituents occupying trans positions; C−Sn−C = 168.2(3)°. The tin atom lies 0.0193(4) Å above the least-squares plane through the NO_4 donor set (max. deviation 0.023(5) Å for N(1), mean deviation 0.011 Å) in the direction of the C(11) atom. The Sn−O(1) bond distance of 2.144(4) Å is significantly shorter than the $Sn-O_{water}$ bond distance of 2.270(4) Å and the two Sn−O(4), O(4)^i distances of 2.539(4) and 2.602(4) Å, respectively; symmetry operation *i*: −*x*, −*y*, −*z*. The overall geometry, including the spread of Sn−ligand distances, found for $[C_{14}H_{24}NO_6PSn]_2$ is in agreement with the analogous pyridine-2,6-dicarboxylate structures.[2] It thus appears that the structural diversity of this type of compound is more determined by the organic substituents than by the nature of the chelating acid residue.

The lattice of $[C_{14}H_{24}NO_6PSn]_2$ is stabilized by a number of hydrogen-bonding contacts (O−H atoms were located in the X-ray study). Hydrogen bonds formed between the O(3)H and O(2) atoms of symmetry-related phosphonate groups (O(3)H···O(2)^{ii} = 1.45 Å, O(3)···O(2)^{ii} = 2.503(6) Å, and O(3)−H···O(2)^{ii} = 175°; symmetry operation *ii*: 0.5 − *x*, 0.5 − *y*, *z*) lead to the formation of chains composed of connected $[C_{14}H_{24}NO_6PSn]_2$ units. The planes of rods thus formed are aligned parallel to the crystallographic *ab* plane and are interspersed by similar planes of rods but which are orientated orthogonally. Links between alternate planes of rods in the *c*-direction are provided by O(6)H···O(2) interactions (O(6)H(2o)···O(2)^{iii} = 1.70 Å, O(6)···O(2)^{iii} = 2.782(6) Å, and O(6)−H(2o)···O(2)^{iii} = 173°; *iii*: 0.5 − *x*, *y*, *z* − 0.5). This arrangement of hydrogen bonds leads to the formation of square columns that are occupied by the *n*-butyl groups. The O*H*(1o) atom does not form an intermolecular contact but forms an in-

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Table 2. ^1H and ^{13}C NMR Data from a CD_3OD Solution of Di-*n*-butyltin Pyridine-2-phosphonate-6-carboxylate[a,b]

	2	3	4	5	6	7	α	β	γ	δ
^1H		ddd 8.37 (7.5, **6.2**, 1.5)	ddd 8.61 (7.6, 7.6, **3.3**)	ddd 8.56 (7.7, **1.5**, 1.5)			t 1.72 (8) [90][c]	m 1.13−1.29		t 0.75 (7)
^{13}C	156.1 **188**	131.2 **16**	145.1 **9**	128.1 **2**	147.0 **12**	169.3	30.9 [856/822]	28.2 [47][c]	27.3 [162][c]	13.9

[a] Chemical shifts in ppm, $^nJ(^1H-^1H)$ coupling constants in Hz in parentheses, $^nJ(^1H-^{31}P)$, $^nJ(^{13}C-^{31}P)$ coupling constants in bold, $^nJ(^1H-^{119/117}Sn)$ and $^nJ(^{13}C-^{119/117}Sn)$ coupling constants in Hz in brackets. [b] Abbreviations: d = doublet; t = triplet; m = complex pattern. [c] Unresolved coupling satellites.

tramolecular contact of 1.67 Å with the noncoordinating O(5) atom (O(6)−H(1o)···O(5) is 152°).

The large value of the Mössbauer quadrupole splitting (QS = 4.30 mm/s; IS = 1.49; $\Gamma_1 = 1.12$; $\Gamma_2 = 1.08$ mm/s) is in agreement with the crystal structure[1a,c] and characteristic for pentagonal bipyramidal seven-coordinate geometries.[9] The infrared data in KBr, as outlined in the Experimental Section, likewise conform to this structure.

Solution NMR Studies. The ^1H and ^{13}C NMR data are given in Table 2. The ^1H and ^{13}C NMR spectra of the compound were recorded in CD_3OD because of its low solubility in most common organic solvents. The dibutyltin protons were assigned from multiplicities and integration ratios. The overlapping β and γ proton complex pattern resonances were identified by $^1H-^{13}C$ correlations from 2D HMQC and HMBC NMR spectra.[9,10] The aromatic protons and carbons were assigned from their $^nJ(^1H-^{31}P)$, $^nJ(^{13}C-^{31}P)$, and $^nJ(^{117}Sn-^{13}C)$ ($1 \leq n \leq 5$) coupling constants as well as from $^1H-^{13}C$ correlations in the HMQC and HMBC NMR spectra.

The ^{119}Sn NMR spectrum in CD_3OD solution exhibits a single $^2J(^{119}Sn-O-^{31}P)$ doublet shifting from −306.4 (5 mg/0.5 mL) through −330.9 (25 mg/0.5 mL) to −345.9 ppm (55 mg/0.5 mL) upon increasing the concentration. These data are in agreement with the dimeric structure of Scheme 1 being involved in a dimer−monomer dissociation equilibrium which is fast on the ^{119}Sn NMR time scale. The concentration-independent $^2J(^{119}Sn-O-^{31}P)$ coupling constant of 166 (±1) Hz indicates that the latter equilibrium does not modify fundamentally the bonding characteristics of the tin phosphonate unit. The compound is weakly soluble in DMSO. Under concentration conditions of 5 mg/0.5 mL DMSO-d_6, the same coupling constant is observed, while the ^{119}Sn doublet is found at lower frequency (−343.1 ppm) as compared to CD_3OD. This suggests a slight but significant contribution of the solvent to the coordination sphere around tin, suggesting substitution of the water molecule observed in the crystalline state for a solvent molecule, coordination being stronger with DMSO than with methanol. The small difference of ca. 2 ppm between the ^{31}P chemical shifts in DMSO (1.9 ppm) and CD_3OD (3.8 ppm) (5 mg/0.5 mL) is uninformative in this respect. On the other hand, the ^1H NMR spectrum of the compound in DMSO displays a very broad signal extending from 2 to 3 ppm, arising from the crystal water, the spectrum having been recorded with fresh dry DMSO-d_6 from a sealed ampule. This observation suggests exchange between free and bound water. An attempt to observe the coordinated water through a $^1H-^{119}Sn$ correlation in a $^1H-^{119}Sn$ HMQC spectrum between the bound water proton signal and the ^{119}Sn resonance unfortunately failed. This indicates either that no water coordination to tin exists in solution or, if it does, that the coordination is so weak that free/bound water exchange is sufficiently fast on the $^1H-^{119}Sn$ HMQC time scale to make its preexchange lifetime much shorter than the HMQC evolution delay.[10c] This necessarily precludes the cross-peak observation and thus evidence for water coordination in solution.

Experimental Section

Synthesis. A 0.24 g (0.98 mmol) portion of dibutyltin oxide and an excess (4 mL) of propanol were refluxed in 100 mL of benzene for 3 h. The ternary azeotrope benzene/water/propanol was distilled off using a Dean−Stark apparatus. The reaction mixture was cooled to room temperature; a solution of 0.20 g (0.98 mmol) of pyridine-6-phospho-2-carboxylic acid in 15 mL of dry methanol was added dropwise, and the mixture was stirred for one night at room temperature. The solvent was removed under reduced pressure. The residue obtained was crystallized from methanol. Yield: 84%, mp 208−210 °C. Anal. Calcd for $C_{28}H_{48}N_2O_{12}P_2Sn_2$ (MM = 904.02): H 5.4; C 37.2; N 3.1. Found H 5.4; C 37.4; N 3.1.

Electrospray Mass Spectrometry. $[(C_{14}H_{22}NO_5PSn)+H]^+$: 436 (base peak). $[(C_{28}H_{44}N_2O_{10}P_2Sn_2)+H]^+$: 869 (29%). The electrospray mass spectra were recorded in the cationic mode on a Micromass Quattro II instrument coupled with a Masslynx system (ionization in an electric field of 3.5 kV; source temperature 80 °C; source pressure 1 atm; analyzer pressure 10^{-5} mbar).[11]

IR Spectroscopy.[12] KBr (cm^{-1}): ∼3300 (very broad, w) HOH; 2330 (m) PO−H; 1624 (s) C═O; 1582 (s); 1376 (s); 1275 (s) P═O; 1139 (bs); 953 (s); 874 (s); 772 (s); 671 (s). The spectrum has been recorded on a Perkin-Elmer FT-IR 1720X spectrometer.

Crystal and Molecular Structure of $[C_{14}H_{24}NO_6PSn]_2$. Intensity data for a crystal 0.19 × 0.27 × 32 mm were measured at 200 K on a Rigaku AFC6R diffractometer fitted with graphite-monochromatized Mo Kα radiation, $\lambda = 0.710\,73$ Å. The ω:2θ scan technique was employed to measure 4949 data up to a maximum Bragg angle of 27.5°. The data set was corrected for Lorentz and polarization effects,[13] and an empirical absorption correction was applied.[14] Relevant crystal data are given in Table 3.

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Table 3. Crystallographic Data for $[C_{14}H_{24}NO_6PSn]_2$

formula	$C_{28}H_{48}N_2O_{12}P_2Sn_2$
fw	904.0
cryst size, mm	0.19 × 0.27 × 0.32
cryst syst	orthorhombic
space group	Pccn
a, Å	15.245(9)
b, Å	23.762(4)
c, Å	10.680(5)
V, Å^3	3868(2)
Z	4 (dimers)
D_{cacld}, g cm^{-3}	1.552
F(000)	1824
μ, cm^{-1}	14.28
transmission factors	0.554−1
no. of data colld	4949
no. of unique data with $I \geq 3.0\sigma(I)$	2733
R	0.046
R_w	0.060
resd electron dens, e Å^{-3}	0.74

The structure was solved by direct methods employing DIRDIF[13] and refined by a full-matrix least-squares procedure based on *F*.[13] Non-H atoms were refined with anisotropic displacement parameters, and H atoms were included in the model in their calculated positions; the three O−H atoms were located from a difference map, but their positions were not refined. The refinement was continued until convergence employing σ weights (i.e. $1/\sigma^2(F)$) for 2733 data with $I \geq 3.0\sigma(I)$. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied. Final refinement details are collected in Table 3, and the numbering scheme employed is shown in Figure 1 (drawn with ORTEP[16] at 50% probability ellipsoids). The teXsan[13] package, installed on an Iris Indigo workstation, was employed for all calculations.

NMR Spectroscopy. The NMR spectra were recorded from $CDCl_3$ solutions on a Bruker AC250 spectrometer, using a QNP probe tuned at 250.13, 62.93, and 89.15 MHz for ^1H, ^{13}C, and ^{117}Sn nuclei, respectively. ^1H and ^{13}C resonances were referenced to the solvent peak at 7.24 and 77.0 ppm, respectively, while $\Xi(^{117}Sn) = 35.632\,295$[17] was used for the ^{117}Sn resonances. The standard 1D ^{119}Sn spectra and the 2D gradient-enhanced $^1H-^{13}C$ HMQC and HMBC spectra were recorded on a Bruker AMX500 instrument, as described elsewhere.[9]

Mössbauer Spectroscopy. Mössbauer spectra were obtained as previously described.[18]

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Supporting Information Available: Further details of the structure determination including atomic coordinates, bond distances and angles, thermal parameters, and a diagram of the unit cell contents (5 pages). Ordering information is given on any current masthead page.

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