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Structural chemistry of organotin carboxylates

VII *. Synthesis of triorganostannate esters of dicarboxylic acids. Crystal structure of dicyclohexylammonium 2,6-pyridinedicarboxylatotributylstannate

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Abstract

The dicyclohexylammonium 2,6-pyridinedicarboxylatotriorganostannates, $[(c\text{-}C_6H_{11})_2NH_2]$-$[R_3Sn((O_2C)_2C_5H_3N)]$, ($R = n\text{-}C_4H_9$, C_6H_5) have been prepared from di-c-hexylamine, 2,6-pyridinedicarboxylic acid and bis(tributyltin)oxide ($R = n\text{-}C_4H_9$) or triphenyltin hydroxide ($R = C_6H_5$). On the basis of Mössbauer quadrupole splittings the tin atoms are assigned five-coordinate geometries. An X-ray analysis of the R = n-butyl compound shows that the structure is polymeric with neighbouring triorganotin centres being linked by dicarboxylate ligands. Each carboxylate moiety is involved in coordination to a Sn atom via one O atom only which has the result that the Sn atoms are five-coordinate and exist in trigonal bipyramidal geometries with the O atoms in axial positions; Sn–O(1) 2.31(1), Sn–O(3′) 2.26(1) Å and O(1)–Sn–O(3′) 173.2(6)°. The pyridine N atom is not involved in coordination to tin.

Introduction

As the 1/1 reaction of a dicarboxylic acid, $(HO_2C)_2R'$, with bis(triorganotin)oxide could proceed beyond the $R_3SnO_2CR'CO_2H$ stage, an amine added to the reaction mixture should convert the half ester to an ammonium compound. The resultant product, a triorganostannate, would be expected to be somewhat soluble in water, a desirable factor in the biocidal applications of triorganotin compounds. This strategy

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* For part VI, see ref. 1.

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is only partially realized, however, when dicyclohexylamine is used in the condensation between oxalic acid and bis(tributyltin)oxide where, as expected, the $[(c\text{-}C_6H_{11})_2NH_2][(n\text{-}C_4H_9)_3Sn(O_2CCO_2)]$ compound is formed along with half a mole of bis(tributyltin)oxalate [2]. These studies have now been extended using the dianion derived from 2,6-pyridinedicarboxylic acid.

Results and discussion

The reaction of bis(tributyltin)oxide with two molar equivalents each of 2,6-pyridinedicarboxylic acid and dicyclohexylamine gave $[(c\text{-}C_6H_{11})_2NH_2][(n\text{-}C_4H_9)_3Sn((O_2C)_2C_5H_3N)]$. The triphenyltin analogue, $[(c\text{-}C_6H_{11})_2NH_2][(C_6H_5)_3Sn((O_2C)_2C_5H_3N)]$ was prepared from the equimolar reaction between the amine, the dicarboxylic acid and triphenyltin hydroxide. The positions of the asymmetric carbonyl bands in the infrared spectra ($R = n\text{-}C_4H_9$: 1623, 1569; $R = C_6H_5$: 1623, 1569 cm^{-1}) of the compounds relative to those found for the free acid (1696, 1573 cm^{-1}) indicate that neither carboxyl group in each of the 2,6-pyridine-dicarboxylatotriorganostannate compounds is bridging [3]. A chelating mode for the dianion, giving rise to six-coordinate Sn centres, is excluded on the basis of the magnitudes of the Mössbauer quadrupole splittings for the compounds (see Experimental) which are typical of five-coordinate, *trans*-trigonal bipyramidal triorganotin compounds [4]. Unambiguous assignment of the structure for the $R = n\text{-}C_4H_9$ compound is afforded by an X-ray analysis which confirms the spectroscopic observations.

Crystals of $[(c\text{-}C_6H_{11})_2NH_2][(n\text{-}C_4H_9)_3Sn((O_2C)_2C_5H_3N)]$ were invariably twinned which precluded an accurate structure analysis, however, the gross stereochemical features of the compound have been determined reliably. Selected interatomic bond distances and angles are listed in Table 1 and the numbering scheme employed is shown in Fig. 1. As can be seen from Fig. 1(b) the structure is polymeric in the solid state owing to the presence of bridging 2,6-pyridinedicarboxylate dianions.

Each dianion bridges two Sn centres via only one O atom of each carboxylate moiety and the resulting polymer is aligned along the crystallographic *c*-axis

Table 1

Selected interatomic parameters (Å; deg) for $[(c\text{-}C_6H_{11})_2NH_2][(n\text{-}C_4H_9)_3Sn((O_2C)_2C_5H_3N)]$

Sn–O(1)	2.31(1)	Sn–O(3′)	2.26(1)
Sn···O(2)	3.37(1)	Sn···O(4)	3.37(1)
Sn–C(11)	2.10(2)	Sn–C(21)	2.14(3)
Sn–C(31)	2.17(2)	C(1)–O(1)	1.32(2)
C(1)–O(2)	1.22(2)	C(4)–O(3)	1.29(2)
C(4)–O(4)	1.21(2)		
O(1)–Sn–O(3′)	173.2(6)	O(1)–Sn–C(11)	89.8(7)
O(1)–Sn–C(21)	84.7(8)	O(1)–Sn–C(31)	94.0(7)
O(3′)–Sn–C(11)	96.9(7)	O(3′)–Sn–C(21)	90.9(8)
O(3′)–Sn–C(31)	83.5(8)	C(11)–Sn–C(21)	122.8(9)
C(11)–Sn–C(31)	120.0(9)	C(21)–Sn–C(31)	117.2(9)
Sn–O(1)–C(1)	120(1)	Sn–O(3)–C(4)	122(1)
O(1)–C(1)–O(2)	126(1)	O(3)–C(4)–O(4)	127(1)
O(1)–C(1)–C(2)	123(1)	O(3)–C(4)–C(3)	112(1)
O(2)–C(1)–C(2)	123(1)	O(4)–C(4)–C(3)	122(1)

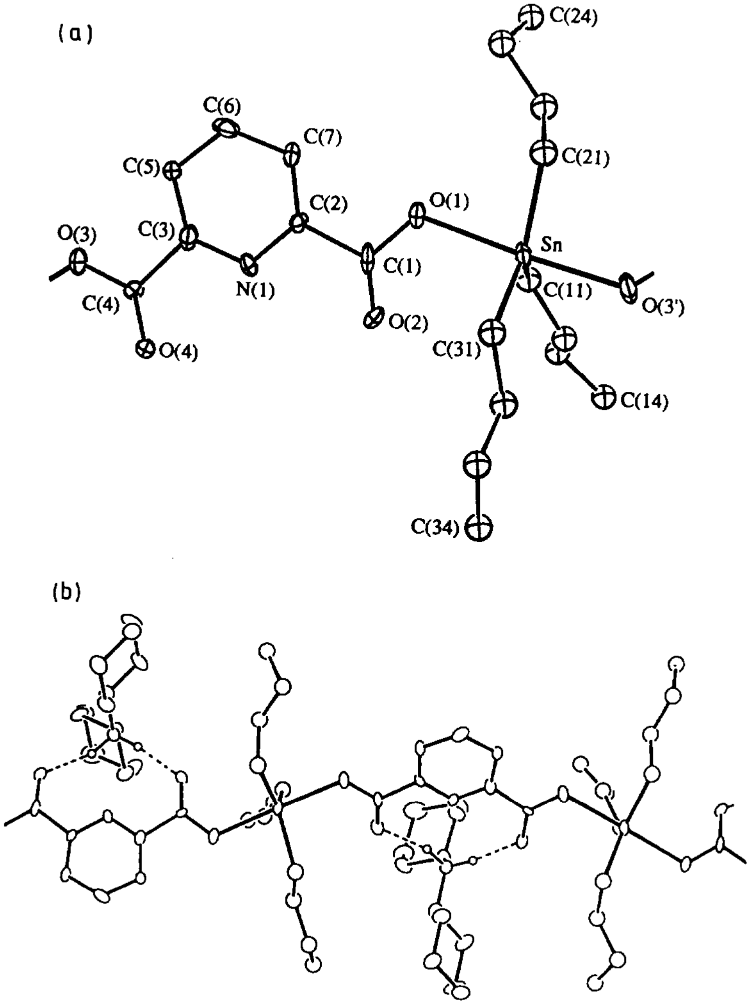

Fig. 1. (a) Molecular structure and crystallographic numbering scheme employed for $[(c\text{-}C_6H_{11})_2NH_2][(n\text{-}C_4H_9)_3Sn((O_2C)_2C_5H_3N)]$ and (b) the polymeric chain and mode of association between anions and cations in the lattice.

(generated by the symmetry operation $x, \frac{1}{2} - y, \frac{1}{2} + z$). As a result of the bidentate mode of coordination of the dicarboxylic acid, each Sn centre is five-coordinate and exists in a trigonal bipyramidal geometry with the O atoms occupying the axial sites; Sn–O(1) 2.31(1), Sn–O(3′) 2.26(1) Å and O(1)–Sn–O(3′) 173.2(6)°. The Sn atom lies 0.020(1) Å out of the trigonal plane defined by the three n-butyl groups (the sum of the trigonal angles is 360°) in the direction of the O(3′) atom. Significantly, the pyridine N atom does not participate in coordination to the Sn atom. Despite the rather high estimated standard deviations in the C–O bond distances a clear trend in these parameters may be discerned. As expected the C–O bond distances associated with the non-coordinating O atoms are significantly shorter than the other two C–O bond distances. Other geometric parameters are as expected, the six-membered ring is planar to within ±0.02(2) Å and the two carboxyl groups $C(1)O_2$ and $C(4)O_2$ form dihedral angles of 0.8 and 7.5°, respectively with this plane. The intramolecular Sn ··· O(2) and Sn ··· O(4) separations of 3.37(1) and 3.37(1) Å, respectively are not indicative of bonding interactions between these atoms. Although not involved in coordination to Sn, the O(2) and O(4) atoms form significant intermolecular contacts in the crystal lattice.

Associated with the polymeric chain, via hydrogen bonding contacts, are the di-c-hexylammonium cations as shown in Fig. 1(b). The ammonium bound H atoms hydrogen-bond to the pendant O atoms, O(2) and O(4), such that the O(2) ··· Hn(1) and O(4) ··· Hn(2) separations are 1.82 and 1.83 Å, respectively and the N(100)–Hn(1) ··· O(2) and N(100)–Hn(2) ··· O(4) angles are 160 and 170°, respectively.

The structure adopted by $[(c\text{-}C_6H_{11})_2NH_2][(n\text{-}C_4H_9)_3Sn((O_2C)_2C_5H_3N)]$ is unprecedented in organotin carboxylate chemistry although there are several structure determinations of organotin complexes with dicarboxylic acids [5]. Particularly relevant to this study are the structures of the diorganotin species with the 2,6-pyridine-carboxylate dianion: i.e. $[R_2Sn((O_2C)_2C_5H_3N)(OH_2)]_2$ (R = Me and ^{n}Bu [6]) and $[Ph_2Sn((O_2C)_2C_5H_3N)(OH_2)]_n$ [7]. In the dimeric compounds [6], the dianion is effectively tetradentate, however, employs only three donor atoms in coordination to the Sn atoms. Each ligand in these compounds coordinates one Sn atom via one O atom of each carboxylate group as well as the pyridine N atom and, at the same time, bridges a centrosymmetrically related Sn atom via one of the O atoms already involved in coordination to the first Sn atom. The coordination polyhedron about the Sn atom is based on a distorted pentagonal bipyramidal geometry owing to the presence of a coordinated water molecule which occupies the fifth site in the basal plane; the organic substituents occupy the axial positions in this description. In the polymeric compound, $[Ph_2Sn((O_2C)_2C_5H_3N)]_n$ [7], the dianion is again tetradentate but in this case utilizes four donor atoms. The dianion coordinates one Sn atom as described above for the dimeric compounds, however, the intermolecular links in this example now involve the second O atom of one of the carboxylate groups such that only one of the five potential donor atoms is not involved in coordination to Sn. The coordination geometry about the Sn atom in the polymeric compound is similar to that described for the dimeric compounds.

In previous contributions in this area, the effect on an organotin carboxylate structure by the presence of an additional donor atom, such as N, O or S, residing on the R group of a uninegative carboxylate ligand has been examined [1,8]. Our studies have shown that in general when a N-donor atom is available for coordination, it does so, in keeping with other structures available in the literature [5]. There are, however, no examples where potential O- and S-donor atoms residing on the carboxylate R group are involved in coordination to Sn. Exceptions to these generalizations are found in the organotin structures with dinegative carboxylates, e.g. $[Ph_3Sn(O_2C_6H_4S)SnPh_3]$ [9] and $[^nBu_2Sn((O_2CCH_2)_2N(CH_2CH_2OH))]$ [10]. The structure of $[(c\text{-}C_6H_{11})_2NH_2][(n\text{-}C_4H_9)_3Sn((O_2C)_2C_5H_3N)]$ represents a rare example of an organotin carboxylate structure in which a pyridine N atom that is available for bonding to the Sn atom does not do so. Other examples are found in the structures of $[Me_3Sn(O_2CC_5H_4N) \cdot H_2O]$ [11] and $[Ph_3(O_2CCH_2(8\text{-}C_9H_6NO) \cdot H_2O]_n$ [12], however, we note that there are significant hydrogen bonding contacts between the pyridine N atom and solvent water molecules of crystallization in both crystal lattices.

In a recent survey of organotin carboxylate structures it was noted that the Sn atom in the triorganotin compounds was either four- or five-coordinate [5]. The higher coordination number was found to predominate and the Sn atom invariably had a distorted trigonal bipyramidal geometry. No triorganotin carboxylate structures have been reported in which the Sn atom exists in a six-coordinate geometry. This being the case, the Sn atom in $[(c\text{-}C_6H_{11})_2NH_2][(n\text{-}C_4H_9)_3Sn((O_2C)_2C_5H_3N)]$ has a maximum of two sites available for coordination and it is not surprising that the two negatively-charged O atoms fill this role precluding coordination of the pyridine N atom.

Experimental

Preparation of compounds

$[(c\text{-}C_6H_{11})_2NH_2][(n\text{-}C_4H_9)_3Sn((O_2C)_2C_5H_3N)]$. One molar equivalent of bis(tributyltin)oxide was added to an ethanol solution containing two molar equivalents each of 2,6-pyridinedicarboxylic acid and dicyclohexylamine which gave an immediate precipitate which was filtered off. Anal. Found: C, 58.40; H, 8.71; N, 4.31. $C_{31}H_{54}N_2O_4Sn$ calcd.: C, 58.40; H, 8.53; N, 4.39% The solid is sparingly soluble in most organic solvents but is sufficiently soluble in boiling ethanol for needle-shaped crystals to be grown by the slow evaporation of this solvent. Tin-119m Mössbauer data: isomer shift (IS) 1.40, quadrupole splitting (QS) 3.51 mm s^{-1}. Infrared data: CO_2 (asymmetric) 1623, 1569; (symmetric) 1267 cm^{-1}.

$[(c\text{-}C_6H_{11})_2NH_2][(C_6H_5)_3Sn((O_2C)_2C_5H_3N)]$. Triphenyltin hydroxide, the acid and the amine in equimolar amounts when similarly reacted as described above gave this stannate. Anal. Found: C, 63.70; H, 6.13; N, 4.06. $C_{37}H_{42}N_2O_4Sn$ calcd.: C, 63.71; H, 6.06; N, 4.01%. Mössbauer IS 1.18, QS 3.12 mm^{-1}; infrared CO_2 (asymmetric) 1623, 1569; (symmetric) 1267 cm^{-1}.

Crystallography

Intensity data were measured at room-temperature on an Enraf-Nonius CAD-4F diffractometer fitted with Mo-K_α radiation, $\lambda = 0.7107$ Å. The $\omega:2\theta$ scan technique was employed to measure the intensities of 5646 reflections up to a maximum Bragg angle of 22.5°. Corrections were applied for Lorentz and polarization effects but not for absorption. Crystal data are listed in Table 2.

Table 2

Crystal data and refinement details for $[(c\text{-}C_6H_{11})_2NH_2][(n\text{-}C_4H_9)_3Sn((O_2C)_2C_5H_3N)]$

Formula	$C_{31}H_{54}N_2O_4Sn$	D_c, (g cm^{-3})	1.221
Mol. wt.	637.5	$F(000)$	1344
Crystal system	monoclinic	μ, cm^{-1}	15.47
Space group	$P2_1/c$	θ limits (°)	1.5–22.5
a, Å	9.201(3)	No. of data collected	5646
b, Å	17.128(5)	No. of unique data	4256
c, Å	22.12(2)	No. of unique reflections used	
β, deg.	95.94(4)	with $I \geqslant 3.0\sigma(I)$	2254
Vol., Å^3	3467.3	R	0.086
Z	4	Residual ρ_{max} (e Å^{-3})	0.67

Table 3

Fractional atomic coordinates ($\times 10^4$) for $[(c\text{-}C_6H_{11})_2NH_2][(n\text{-}C_4H_9)_3Sn((O_2C)_2C_5H_3N)]$

Atom	*x*	*y*	*z*
Sn	2944(1)	7521(1)	9427(1)
O(1)	2735(15)	8122(8)	8487(5)
O(2)	3967(16)	7178(9)	8033(6)
O(3)	2856(17)	8067(9)	5338(6)
O(4)	3795(17)	7080(8)	5909(6)
N(1)	3127(15)	7832(7)	6928(6)
C(1)	3189(25)	7758(13)	8013(8)
C(2)	2689(18)	8187(10)	7419(7)
C(3)	2652(22)	8158(13)	6395(8)
C(4)	3150(20)	7692(9)	5840(8)
C(5)	1826(21)	8824(11)	6299(8)
C(6)	1361(21)	9159(12)	6830(10)
C(7)	1829(25)	8838(12)	7409(8)
C(11)	5217(22)	7698(13)	9503(10)
C(12)	6187(34)	7080(20)	9808(17)
C(13)	7812(37)	7243(25)	9775(18)
C(14)	8810(54)	6775(32)	10211(23)
C(21)	1440(27)	8399(15)	9659(12)
C(22)	2298(44)	9175(20)	9712(21)
C(23)	1539(61)	9842(28)	9370(27)
C(24)	2611(53)	10416(29)	9678(23)
C(31)	2028(24)	6425(13)	9075(11)
C(32)	3203(31)	5784(17)	9137(15)
C(33)	2672(42)	5020(22)	8859(24)
C(34)	4025(37)	4516(22)	8839(17)
N(100)	4799(15)	6423(9)	7027(6)
C(111)	4103(18)	5625(14)	7096(9)
C(112)	2424(22)	5704(13)	6967(11)
C(113)	1617(26)	4950(14)	7034(12)
C(114)	2152(30)	4329(15)	6613(12)
C(115)	3868(33)	4226(14)	6757(14)
C(116)	4685(28)	5006(14)	6681(12)
C(211)	6410(20)	6455(13)	7124(9)
C(212)	6998(24)	6218(13)	7750(10)
C(213)	8707(25)	6298(15)	7828(13)
C(214)	9151(28)	7116(18)	7698(15)
C(215)	8585(29)	7345(20)	7054(14)
C(216)	6848(22)	7280(12)	6989(11)

The structure was solved from the Patterson synthesis and refined by a full-matrix least squares procedure based on *F* [13]. The n-butyl groups were found to be disordered and were hence refined with constrained C–C bond distances of 1.52(2) Å and individual isotropic thermal parameters. The remaining non-H atoms were refined anisotropically and H atoms were included in the model at their calculated positions. The analysis of variance showed no special features and hence unit weights were employed throughout the refinement which converged with $R = 0.086$. Final details are listed in Table 2. Fractional atomic coordinates are given in Table 3 and the numbering scheme for the anion is given in Fig. 1 which was drawn at 15% probability ellipsoids with ORTEP [14]. Refinement was performed on a SUN4/280 computer with SHELX76 [13]. Lists of thermal parameters, H-atom parameters, all bond distances and angles, and observed and calculated structure factors are available from E.R.T.T.

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