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Synthesis and structural characterization of diorganotin(IV) complexes with 2,6-pyridinedicarboxylic acid

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Two new diorganotin(IV) derivatives of 2,6-pyridinedicarboxylic acid, {[$Ph_2Sn(2,6\text{-}C_5H_3N)(COO)_2$][$Na(2,6\text{-}C_5H_3N)(COOH)(COO)(CH_3OH)_2$]} (1) and [$Me_2Sn(2,6\text{-}C_5H_3N)(COO)_2(H_2O)$]•$H_2O$ (2) were synthesized by the reaction of Ph_3SnCl and $PhMe_2SnI$ with 2,6-pyridinedicarboxylic acid, respectively in the presence of sodium methoxide or potassium *iso*-propoxide. The prepared compounds were characterized by mass spectrometry, IR, ^1H, ^{13}C and ^{119}Sn NMR spectroscopies. The molecular structures of both complexes were determined by a single-crystal X-ray analysis. The X-ray structure revealed pentagonal bipyramidal geometry around the tin atom for compound 1, which is incorporated with a hexacoordinated monosodium derivative of 2,6-pyridinedicarboxylic acid. Complex 2 adopts a monomeric structure with two carboxylate oxygen atoms coordinated to tin in monodenate form from equatorial positions, and the coordination number is raised to six as the oxygen of water and pyridine nitrogen occupies the other equatorial positions of octahedron.

Keywords: organotin; 2,6-pyridinedicarboxylic acid; X-ray; sodium methoxide; potassium propoxide

Introduction

The structural diversity of organotin carboxylates is well recognized and a wide variety of coordination geometries has been reported.[1,2] Among various organotin carboxylates, di- and triorganotin pyridinedicarboxylates have been the subject of extensive investigations because of their biological activity and potential antineoplastic and antituberculosis activity.[3–9] Various synthetic pathways for the preparation of di- and tri-organotin(IV) 2,6-pyridinedicarboxylates have been used and, depending on the reaction conditions, diverse structures formed.[10–13] Such a divinyltin(IV) derivative has been prepared from divinyltin(IV) dichloride and 2,6-pyridinedicarboxylic acid in the presence of triethylamine, and X-ray crystallography showed it to be a centrosymmetric dimer held together by intermolecular interactions.[10] In contrast, the *t*-Bu_2Sn(IV) derivative prepared by reacting sodium 2,6-pyridinedicarboxylate to dibutyltin(IV) dichloride resulted in the formation of a monomeric species.[11] The trimethyltin(IV), triphenyltin(IV) and tribenzyltin(IV) derivatives were also prepared in the presence of triethylamine; interestingly, a single crystal structure determination of the trimethyltin(IV) derivative revealed a trinuclear structure in the form of a two-dimensional supramolecular structure, as a result of the coordination of water molecules via hydrogen bonds to the pendant oxygen atoms of the carbonyl groups and the nitrogen atoms of the pyridine ring.[12] The reaction of dimethyltin(IV) dichloride and 2,6-pyridinedicarboxylic acid in methanol under solvothermal conditions at 150 °C produced a cyclic trimer, whereas, at room temperature, a centrosymmetric dimer was formed in which two $Me_2Sn(2,6\text{-}C_5H_3N)$(MeOH) units were linked together by two asymmetric Sn–O–Sn bridges.[13] The reaction of di-*n*-butyltin oxide with 2,6-pyridinedicarboxylic acid in ethanol in the presence of dicyclohexylamine resulted in the formation of bis(dicyclohexylammonium) bis(2,6-pyridinedicarboxylato)dibutylstannate, in which two 2,6-pyridinedicarboxylato ligands were covalently linked to the tin atom.[14] The last mentioned complex is an ionic species, and contains a seven-coordinated tin atom, and its anhydrous form exhibits a higher *in vitro* cytotoxic activity compared with carboplatin and cisplatin against breast, colon and ovarian cancers, renal carcinoma and melanoma. The higher activity has been attributed to the presence of the second 2,6-pyridinedicarboxylato entity in the molecule.[14] The influence of the diorganotin moiety of di-organotin(IV) 2,6-pyridinedicarboxylates on the MCF-7 and WiDr, two tumour cell lines of human origin, has been recently reviewed.[3] Five- and seven-fold coordinations at tin have been reported for the tri-*n*-butyltin and di-*n*-butyltin 2,6-pyridinedicarboxylates.[15]

The diversity observed in the organotin(IV) derivatives of 2,6-pyridinedicarboxylic acid shows the significant influence of the preparation route on the structure of the final material. Considering that the biochemical activity of organotin(IV) carboxylates is influenced by the molecular structure and coordination status of the tin atom,[16,17] the synthesis of organotin(IV) derivatives of 2,6-pyridinedicarboxylic acid with new structures should be beneficial.

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Interestingly, the structure of organotin(IV) carboxylates is not only dependent on the nature of the organic substituents bound to the tin and on the type of the carboxylate ligands, but also varies with the details of the preparation route. In continuation of the authors' interest in the synthesis of organotin(IV) carboxylates using potassium or sodium alkoxides, the synthesis, characterization and crystal structure determination of two new derivatives of 2,6-pyridinedicarboxylic acid are reported.

Experimental

Materials and methods

Triphenyltin(IV) chloride, diphenyltin(IV) dichloride, methyl iodide and 2,6-pyridinedicarboxylic acid were purchased from Merck and used without further purification. All solvents were dried and distilled under nitrogen prior to use according to a standard procedure. Dimethyldiphenyltin(IV) was prepared using a conventional Grignard synthesis with diphenyltin(IV) dichloride and methylmagnesium iodide and purified by vacuum distillation (b.p. 120 °C/0.5 torr, yield 75%).

Melting points were obtained with an Electrothermal 9200 melting point apparatus and were not corrected. Infrared spectra from 4000–400 cm^{-1} were recorded on a Shimadzu 470 FT-IR instrument, using KBr pellets. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded at room temperature in DMSO on a Bruker Avance 300 MHz operating at 300.3, 75.4 and 111.9 MHz, respectively. The NMR spectra are referenced to Me_4Si (^{1}H and ^{13}C) or Me_4Sn (^{119}Sn) as external standards. The mass spectrometry was performed on a Varian Matt 44 instrument (electron impact, 20 eV).

Crystallography

Intensity data for {$[Ph_2Sn(2,6\text{-}C_5H_3N)(COO)_2][Na(2,6\text{-}C_5H_3N)(COOH)(COO)(CH_3OH)_2$} (**1**) were collected on a STOE IPDS-II diffractometer with graphite monochromated Mo K_α radiation at room temperature using Stoe X-AREA software,[18] and for $[Me_2Sn(2,6\text{-}C_5H_3N)(COO)_2(H_2O)]\bullet H_2O$ (**2**), data were collected at 100 K (Oxford Cryosystems Cobra) on a Bruker APEX-II using APEX2.[19] A numerical absorption correction was applied in each case using X-RED[20] and X-SHAPE[21] software, respectively. The structures were solved by direct methods[22] and refined on F^2 using a full-matrix least-squares procedure with anisotropic displacement parameters.[23] The maximum residual peak of 2.07 e/Å^3 was located 0.93 Å from Sn1, whereas the minimum residual peak of −1.10 e/Å^3 was located 0.51 Å from O1W. Crystal data and refinement details are listed in Table 1.

Table 1. Crystal data and refinement details for **1** and **2**

	1	**2**
Formula	$C_{29}H_{29}N_2NaO_{11}Sn$	$C_9H_{13}NO_6Sn$
Formula weight	723.22	349.89
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$P2_1/c$
a (Å)	9.5836(10)	6.6805(2)
b (Å)	10.4547(11)	18.8494(4)
C (Å)	15.7127(16)	9.8111(2)
α (deg)	79.465(8)	90
β (deg)	87.694(9)	98.5750(10)
γ (deg)	80.919(8)	90
Z	2	4
Absorption coefficient (mm^{-1})	0.913	2.107
Crystal size (mm)	0.03 × 0.0 ×0.30	0.05 × 0.13 ×0.19
D_c (g cm^{-3})	1.572	1.902
θ range for data collection (deg)	2.0–28.0	2.2–28.7
Reflections collected	15 945	13 014
Unique reflections (R_{int})	7276 (0.028)	3138 (0.053)
Data with $I \geq 2\sigma(I)$	6713	2207
Goodness-of-fit on F^2	1.09	1.10
Final R indices [obs. data]	$R_1 = 0.030$ $wR_2 = 0.066$	$R_1 = 0.042$ $wR_2 = 0.078$
R indices (all data)	$R_1 = 0.034$ $wR_2 = 0.068$	$R_1 = 0.079$ $wR_2 = 0.089$
CCDC deposition no.	657 010	657 011

Synthesis of complexes

*Synthesis of {[$Ph_2Sn(2,6\text{-}C_5H_3N)(COO)_2$][$Na(2,6\text{-}C_5H_3N)(COOH)(COO)(CH_3OH)_2$]} (**1**)*

Triphenyltin(IV) chloride (0.77 g, 2 mmol) was treated with sodium methoxide (0.1 g, 2 mmol) in methanol (10 ml) to produce triphenyltin(IV) methoxide and sodium chloride. The sodium chloride precipitate was removed by filtration and then 2,6-pyridinedicarboxylic acid (0.33 g, 2 mmol) in methanol (20 ml) was added to the filtrate; the solution was refluxed for 3 h. Evaporation of the solvent yielded a colorless solid, which was purified by recrystallization from methanol at 4 °C to furnish colorless crystals (m.p. above 300 °C). Anal. found: C, 47.84; H, 3.92; N, 4.12; calcd for $C_{29}H_{29}N_2O_{11}NaSn$: C, 48.15; H, 4.00; N, 3.87. IR (KBr, cm^{-1}): 3450, 2836, 1660, 1618, 1598, 1548, 1473, 1425, 1388, 1333, 1215, 1159, 1073, 733, 696, 563, 486, 451. ^{1}H NMR (DMSO, ppm): 3.39 (9H, s. CH_3O), 7.13–8.16 (16H, m, C_6H_5 and C_6H_3N). ^{13}C NMR (DMSO, ppm): 49.0 (CH_3OH), 125.9 (C_6H_5, C_{meta}), 128.7 (C_6H_5, C_{para}), 129.0 (C_6H_5, C_{ortho}, $^{2}J^{119/117}Sn\text{-}^{13}C$, 80 Hz), 134.4 ($C_6H_5$, C_{ipso}, $^{1}J^{119/117}Sn\text{-}^{13}C$, 505 Hz), 129.5 ($C_5H_3N$, C_{meta}), 142.1 (C_5H_3N, C_{ortho}), 147.6 (C_5H_3N, C_{para}), 171.5 (COO). ^{119}Sn NMR (DMSO, ppm): -563.2. Mass spectrum data, tin bearing fragment: *m/e* 197 $[SnPh]^+$, 274 $[SnPh_2]^+$, 439 $[Ph_2Sn(C_5H_3N)(COO)_2]^+$. Mass numbers are based on ^{1}H, ^{12}C, ^{14}N, ^{16}O and ^{120}Sn.

*Synthesis of $[Me_2Sn(2,6\text{-}C_5H_3N)(COO)_2(H_2O)]\bullet H_2O$ (**2**)*

Dimethylphenyltin(IV) iodide was prepared according to the published procedure.[24] This reagent (0.70 g, 2 mmol) was added to a solution of potassium *iso*-propoxide (0.19 g, 2 mmol) in *iso*-propanol (20 ml). A white precipitate was formed which was removed by filtration, and the resulted solution was reacted to 2,6-pyridinedicarboxylic acid (0.33 g, 2 mmol) in *iso*-propanol. The reaction mixture was refluxed for 3 h, and then the solvent was removed under reduced pressure to give a white solid. The white solid was recrystallized from a methanol–acetonitrile mixture (1 : 1 v/v) at 4 °C to yield colorless crystals (m.p. above 300 °C). Anal. found: C, 31.35; H, 3.81; N, 3.83; calcd for $C_9H_{13}NO_6Sn$: C, 30.89; H, 3.71; N, 4.00. IR (KBr, cm^{-1}): 3380, 2944, 2833, 1668, 1546, 1465, 1419, 1392, 1284, 1156, 1036, 679, 489, 451. ^{1}H NMR (DMSO, ppm): 0.44–0.82 (6H, s, CH_3, $^{2}J^{117/119}Sn\text{-}H$, 108.0 Hz), 4.12 (b, H, H_2O), 8.42 (t, 1H, C_5H_3N), 8.25 (d, 2H, C_5H_3N). ^{13}C NMR (DMSO, ppm): 11.1 (CH_3, $^{1}J^{119/117}Sn\text{-}^{13}C$, 958.3 Hz), 126.4 ($C_5H_3N$, C_{meta}), 142.1 (C_5H_3N, C_{ortho}), 146.1, (C_5H_3N, C_{para}), 167.1 (COO). ^{119}Sn NMR (DMSO, ppm): −396.5. Mass spectrum data, tin bearing fragment:

m/e 120 $[Sn]^+$, 135 $[SnMe]^+$, 300 $[SnMe(C_5H_3N)(COO)_2]^+$. Mass numbers are based on ^1H, ^{12}C, ^{14}N, ^{16}O and ^{120}Sn.

Results and Discussion

Synthesis

Organotin carboxylates are usually prepared by reacting organotin hydroxides or dialkyltin oxides with carboxylic acids. However, organotin hydroxides or oxides with mixed alkyl or aryl groups are not known, and other routes are needed for the synthesis of organotin carboxylates, specifically organotin carboxylates with mixed alkyl and aryl groups. As mentioned earlier, the structures of organotin(IV) 2,6-pyridinedicarboxylates are diverse and the nature of the final compound strongly depends on synthetic route. In the present study, sodium methoxide or potassium *iso*-propoxide was reacted with triphenyltin chloride and, in a subsequent reaction, with 2,6-pyridinedicarboxylic acid, yielding two new diorganotin(IV) derivatives, 2,6-pyridinedicarboxylates, whose structures differ from the compounds reported earlier. In contrast to earlier reports,[12] one of the phenyl groups bound to tin was cleaved and, instead of a triorganotin(IV) compound, a diorganotin(IV) derivative was formed. It appears that in the synthesis of complex **1,** when sodium methoxide reacted with triphenyltin(IV) chloride, an equilibrium between sodium methoxide and triphenyltin(IV) methoxide is established, in spite of the majority of sodium chloride being removed from the reaction mixture. Consequently, by addition of 2,6-pyridinedicarboxylic acid to the reaction mixture, both sodium methoxide and triphenyltin(IV) methoxide reacted with the acid and resulted in the formation of diphenyltin(IV) 2,6-pyridinedicarboxylate. The cleavage of the phenyl–tin bonds by various reagents is well known.[25] Cleavage of the phenyl group has also been observed in the authors' earlier study when potassium *iso*-propoxide and methyldiphenyltin(IV) iodide were used as reagents in synthesis.[26]

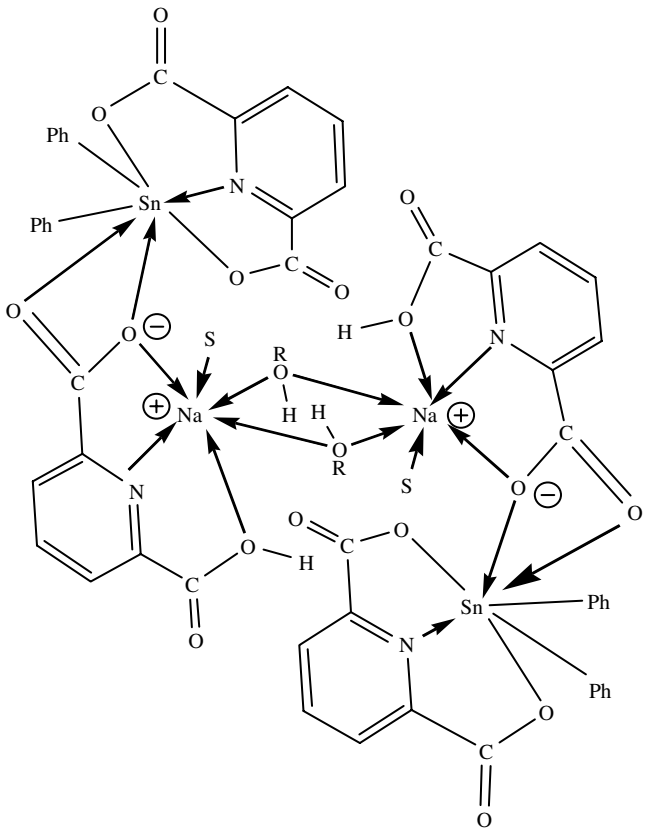
General characterization

Infrared spectroscopy

The infrared data of organotin carboxylates are usually used to predict their solid-state structures. The bridging carboxylate in organotin compounds is simply characterized by infrared spectroscopy by the shift of $\upsilon(CO_2)$ bands, as compared with the parent carboxylic acid. In the infrared spectra of $\{[Ph_2Sn(2,6\text{-}C_5H_3N)(COO)_2][Na(2,6\text{-}C_5H_3N)(COOH)(COO)(CH_3OH)_2]\}$ (**1**) and $Me_2Sn(2,6\text{-}C_5H_3N)(COO)_2(H_2O)]^{\bullet}H_2O$ (**2**), the $\upsilon_{asym}(CO_2)$ and the $\upsilon_{sym}(CO_2)$ stretchings appear at 1660, 1548, 1388; 1333, 1688 and 1392 cm^{-1}, respectively. The shift of those bands to the red for both compounds with respect to the free acid confirms the formation of organotin carboxylates. According to Deacon, the magnitude of $\Delta\upsilon[\upsilon_{asym} - \upsilon_{sym}]$ can be attributed to the coordination status of carboxylate group.[27] For complex **1** (Scheme 1), these $\Delta\upsilon$ values indicate that both bridging bi- and mono-dentate coordination modes of the carboxylate groups are present, while for complex **2** the presence of only mono-dentate coordination mode is detected. Furthermore, the presence of Sn–O vibrations for both complexes at 451 cm^{-1} also confirms the coordination of carboxylate groups to tin. The presence of a single Sn–C stretching vibration at 486 and 489 cm^{-1} in the infrared spectra of **1** and **2**, respectively, indicates that the C–Sn–C bond angle is close to 180°. The aforementioned conclusions were confirmed by single-crystal structure determination.

NMR spectroscopy

For the determination of structural features of organotin carboxylates in solution, their ^1H, ^{13}C and ^{119}Sn were recorded. The ^1H NMR spectrum of both complexes shows the expected aliphatic and/or aromatic peaks with the right integration and multiplicities. For complex **2**, the $^2J(^{117/119}Sn-C-^1H)$ value, 108.0 Hz, implies an almost linear alignment of C_2Sn skeleton and octahedral geometry. The estimated value of the C–Sn–C angle from tin–proton (108.0 Hz) and tin–carbon (958.3 Hz) coupling constants,[28] 158° and 161°, is in good agreement with the one found in the solid-state structure However, it should be noted that the NMR spectra due to the low solubility in $CDCl_3$ have been recorded in DMSO; consequently, the question of the solid-state structure retention in the solution is not conclusive. The observation of only one carboxyl resonance in the ^{13}C NMR spectra of complex **1,** 171.5 ppm, suggests that the four carboxyl groups of two 2,6-pyridinedicarboxylato ligands are equivalently linked to the tin atom. An alternative explanation would be a dynamic model and a rapid equilibrium,[14] which are involved between a mono-dentate ligand that binds through a carboxyl oxygen and a tridentate ligand that chelates to tin atom. Another possibility is the coincidental magnetic equivalence of the carbonyl carbon atoms or that the separations between resonances are too small to be resolved. A single resonance was also observed for the COO group in the ^{13}C NMR spectrum of $[Me_2Sn(2,6\text{-}C_5H_3N)(COO)_2]_2(MeOH)_2$.[13] As observed previously, the ^{13}C NMR downfield shifts of the resonance of the C_p atom were attributed to the Sn–N bonds.[13] The solution ^{119}Sn NMR spectrum of both complexes consists of only one resonance, the chemical shifts of compounds **1** and **2**,



Scheme 1. $\{[Ph_2Sn(2,6\text{-}C_5H_3N)(COO)_2][Na(2,6\text{-}C_5H_3N)(COOH)(COO)(CH_3OH)_2]\}_2$ (**1**), S = CH_3OH.

−563.2 and −396.5 ppm, falling within the range of seven- and six-coordinated compounds, respectively.[29,30] These results are consistent with the X-ray crystal structures.

Crystal structures

*Crystal structure of {[$Ph_2Sn(2,6\text{-}C_5H_3N)(COO)_2$][Na(2,6-$C_5H_3N$)(COOH)(COO) ($CH_3OH$)$_2$]} (**1**)*

Selected bond angles and distances for complex **1** are given in Table 2 and the molecular structure is shown in Fig. 1. In complex **1**, which is unique among organotin 2,6-pyridinedicarboxylic acid derivatives, the tin atom is coordinated by two monodentate carboxylate groups and the pyridine–nitrogen atom of a dinegative 2,6-pyridinedicarboxylate ligand. At the same time, the tin atom is chelated by a carboxylate ligand derived from a uninegative 2,6-pyridinedicarboxylate ligand that coordinates a sodium cation in a tridentate mode. The geometry around the tin atom can best be described as a distorted pentagonal bipyramidal in which the two phenyl groups are *trans* to each other, defining a C–Sn–C angle of 167.52(8)°. Two methanol molecules link the aforementioned tin/sodium aggregates into a centrosymmetric dimer. The four Sn–O bond lengths around are not equal. As expected, the Sn1–O6 bond length of 2.4511(15) Å is longer than the Sn1–O5 distance due to simultaneous coordination of O6 to tin and sodium. Interestingly, the Sn1–O1 bond length of 2.3624(15) Å is significantly longer than the Sn1–O4 distance of 2.1717(15) Å. The Sn–O bond lengths are similar to the bond length found in [$Me_2Sn(2,6\text{-}C_5H_3N)(COO)_2]_2(MeOH)_2$ and [$Me_2Sn(2,6\text{-}C_5H_3N)(COO)_2]_3$.[13] Furthermore, the C–O bond lengths of non-coordinating oxygen atoms, i.e. C1–O2 = 1.246(3) Å and C7–O3 = 1.228(3) Å, are somewhat shorter than the coordinating C–O bond lengths: C1–O2 = 1.246(3) Å and C7–O4 = 1.292(3) Å. The Sn–N bond length, 2.2631(17) Å, is almost identical to those found in [$Me_2Sn(2,6\text{-}C_5H_3N)(COO)_2]_3$,[13] [$MePhSn(2,6\text{-}C_5H_3N)(COO)_2(H_2O)]_2$[26] and slightly longer than in [$EtPhSn(2,6\text{-}C_5H_3N)(COO)_2(H_2O)]_2$.[31]

Table 2. Selected bond lengths (Å) and angles (deg) for {[$Ph_2Sn(2,6\text{-}C_5H_3N)(COO)_2$][Na(2,6-$C_5H_3N$)(COOH)(COO)($CH_3OH$)$_2$]} (**1**)

Bond lengths			
O1–C2	1.246(3)	Sn1–O1	2.3624(15)
O1–C1	1.274(3)	Sn1–O6	2.4511(15)
N1–C2	1.334(3)	O6–Na1	2.3896(18)
N1–C6	1.337(3)	O7–Na1	2.6674(18)
O3–C7	1.228(3)	O9–Na1	2.411(2)
O4–C7	1.292(3)	O9–Na1#1	2.500(2)
Sn1–C8	2.134(2)	O10–Na1	2.266(2)
Sn1–O4	2.1717(15)	N2–Na1	2.494(2)
Sn1–N1	2.2631(17)	Na1–O9#1	2.500(2)
Sn1–O5	2.2953(15)	Na1–Na1#1	3.7607(18)
Bond angles			
C8–Sn1–O4	93.94(7)	C20–O6–Na1	120.16(13)
C14–Sn1–O4	97.01(8)	C20–O6–Sn1	87.68(12)
C14–Sn1–N1	92.83(7)	Na1–O6–Sn1	150.43(7)
C8–Sn1–N1	96.26(7)	Na1–O9–C27	107.40(17)
O4–Sn1–N1	71.90(6)	Na1–O9–Na1#1	99.92(7)
C8–Sn1–O5	89.98(7)	Na1–O10–C28	135.5(2)
C14–Sn1–O5	85.91(7)	C2–N1–C6	121.35(18)
O4–Sn1–O5	80.65(6)	O10–Na1–O6	116.01(9)
N1–Sn1–O5	152.17(6)	O10–Na1–O9	120.01(9)
C8–Sn1–O1	88.38(7)	O10–Na1–N2	99.12(9)
C14–Sn1–O1	86.88(7)	O6–Na1–N2	67.09(6)
O4–Sn1–O1	141.01(5)	O10–Na1–O9#1	95.24(8)
N1–Sn1–O1	69.16(6)	O6–Na1–O9#1	80.21(6)
O5–Sn1–O1	138.32(5)	N2–Na1–O9#1	147.30(7)
C8–Sn1–O6	84.29(7)	O6–Na1–O7	127.52(6)
C14–Sn1–O6	83.67(7)	O9–Na1–O7	77.70(6)
O4–Sn1–O6	136.07(5)	N2–Na1–O7	61.00(6)
N1–Sn1–O6	152.01(6)	O9#1–Na1–O7	151.09(7)
O5–Sn1–O6	55.51(5)	O9–Na1–Na1#1	40.91(5)
C1–O1–Sn1	118.67(13)	N2–Na1–Na1#1	147.72(6)
C7–O4–Sn1	121.61(13)	O9#1–Na1–Na1#1	39.17(5)

Symmetry operation: (#1) 1 − *x*, 2 − *y*, −*z*.

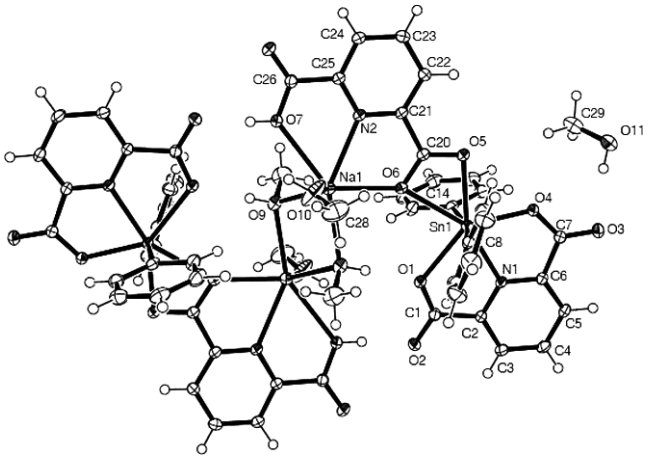


Figure 1. Molecular structure of {[$Ph_2Sn(2,6\text{-}C_5H_3N)(COO)_2$][$Na(2,6\text{-}C_5H_3N)(COOH)(COO)(CH_3OH)_2$]} (**1**).

The hexa-coordinated sodium derivative of 2,6-pyridinedicarboxylic acid, which is connected to the organotin moiety, is also of interest. In addition to the pyridine–nitrogen, one carboxylate coordinates in the monodentate form and the other is chelating while simultaneously bridging the tin atom (Fig. 1). The coordination is completed by two bridging methanol molecules. Although the sodium atom is hexa-coordinate, the sum of the O9–Na1–O9 [120.01(9)°], O10–Na1–O6 [116.01(9)°] and O6–Na1–O9 [121.72(7)°] angles of 357.7°, and the O9#1–Na1–O7 angle of 151.09(7)°, define a distorted trigonal bipyramid geometry. The nitrogen atom is added to the O7O6O10 plane and coordination number raised to six, leading to a heavily distorted trigonal bipyramid geometry. The sodium–nitrogen bond length of compound **2** is almost identical to that in the hepta-coordinated sodium in the only other crystallographically characterized sodium 2,6-pyridinedicarboxylate species.[32]

*Crystal structure of [$Me_2Sn(2,6\text{-}C_5H_3N)(COO)_2(H_2O)$]•$H_2O$ (**2**)*

Compound **2**, shown in Fig. 2, has a distorted octahedral geometry; selected bond lengths and angles are given in Table 3. Two carboxylate oxygen atoms and nitrogen of the dinegative 2,6-pyridinedicarboxylate ligand are coordinated to the dimethyltin entity in equatorial positions and the coordination number is raised to six as a water molecule occupies a position *trans* to the pyridine–nitrogen. In contrast to the majority of crystal structures of organotin derivatives of 2,6-pyridinedicarboxylate, which feature seven-coordinate geometries in the form of oligomeric

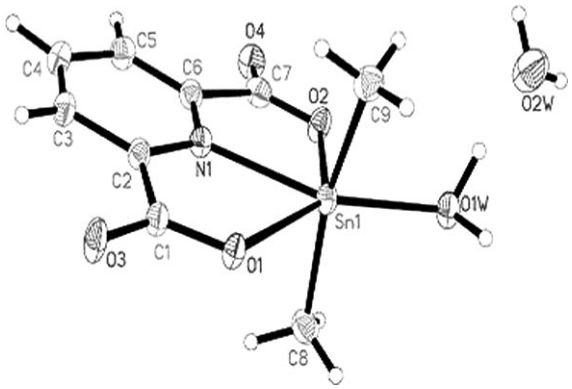


Figure 2. Molecular structure of $[Me_2Sn(2,6\text{-}C_5H_3N)(COO)_2(H_2O)]\bullet H_2O$ (**2**).

Table 3. Selected bond lengths (Å) and angles (deg) for $[Me_2Sn(2,6\text{-}C_5H_3N)(COO)_2(H_2O)]\bullet H_2O$ (**2**)

Bond lengths			
Sn1–C8	2.092(5)	O1–C1	1.274(5)
Sn1–C9	2.085(5)	O2–C7	1.286(6)
Sn1–O2	2.182(3)	O3–C1	1.243(5)
Sn1–N1	2.287(4)	O4–C7	1.224(6)
Sn1–O1W	2.300(3)	N1–C2	1.331(6)
Sn1–O1	2.435(3)	N1–C6	1.336(6)
Bond angles			
C1–O1–Sn1	118.9(3)	C9–Sn1–O2	97.54(17)
C2–N1–C6	121.0(4)	C9–Sn1–C8	164.8(2)
C2–N1–C6	121.0(4)	C7–O2–Sn1	121.7(3)
C2–N1–Sn1	122.5(3)	O1W–Sn1–O1	145.29(11)
C6–N1–Sn1	116.4(3)	O2–Sn–N1	71.68(13)
C8–Sn1–N1	96.70(17)	O2–Sn1–O1W	75.50(12)
C9–Sn1–N1	95.02(18)	O2–Sn1–O1	139.14(11)
C8–Sn1–O1	87.71(16)	O3–C1–O1	125.6(4)
C8–Sn1–O2	95.24(18)	O3–C1–C2)	118.5(4)
C8–Sn1–O1W	86.19(16)	N1–Sn1–O1W	147.18(13)
C9–Sn1–O1W	89.17(17)	N1–Sn1–O1	67.50(12)
C9–Sn1–O1	87.93(16)		

or polymeric aggregates, compound **2** is a six-coordinated monomeric complex. The Sn–N bond length, 2.287(4) Å, is very close to that of complex **1**, and is similar to the bond length in the other diorganotin complex of 2,6-pyridinedicarboxylic acid.[26] The two O–Sn–N bite angles, 67.50(12)° and 71.68(13)°, are similar to those of compound **1** and are non-equivalent. The N1–Sn1–O1w angle, 147.18(13)°, is the largest angle among angles in the equatorial plane, and indicates the extent of distortion from the ideal geometry. Another structural feature of complex **2** is the significant difference in the O2–Sn1–O1w and O1–Sn1–O1w bond angles. Although the carbon–tin–carbon skeleton is bent, 164.8(2)°, the sum of oxygen–tin–oxygen angles (359.7°) is consistent with the ideal value of 360°. Furthermore, the torsion angles of O1w–Sn1–O1–C1 and O1w–Sn1–O2–C7 with values of 179.7(3) and 176.6(4)° show that the coordinated water is almost co-planar with the plane through the 2,6-pyridinedicarboxylato ligand. An analysis of the crystal packing shows intermolecular OH···H hydrogen bonds exist between the oxygen atoms of coordinated water and carboxylato groups and oxygen atoms of solvated water (Fig. 3). Furthermore, there is a face-to-face

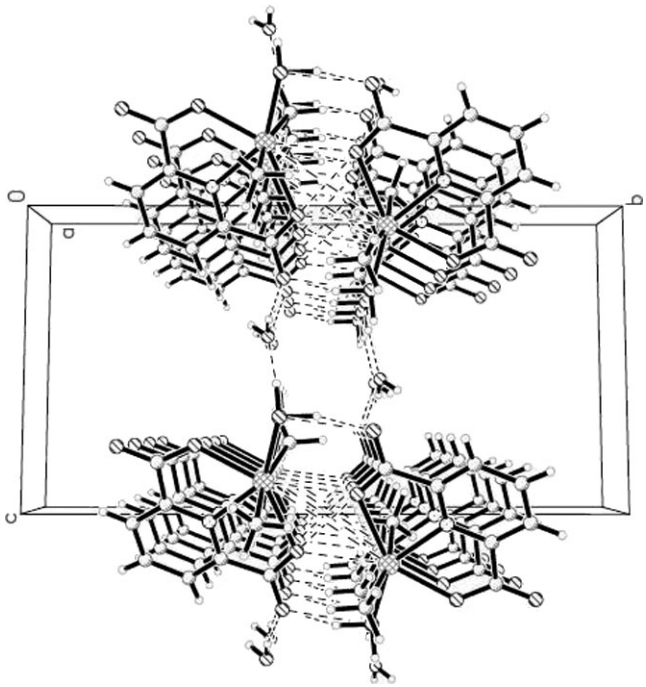


Figure 3. The molecular packing of $[Me_2Sn(2,6\text{-}C_5H_3N)(COO)_2(H_2O)]\bullet H_2O$ (**2**).

$\pi - \pi$ stacking interaction between pyridyl rings. Consequently, the monomeric molecules are assembled into three-dimensional supramolecular packing through hydrogen bonding and aromatic stacking interactions, which generate one-dimensional channels along the *a*-direction.

Conclusion

This paper shows that the preparation of 2,6-pyridinedicarboxylic acid derivatives of organotin compounds in the presence of alkaline alkoxides results in the formation of new derivatives, of which the structures are entirely different from the earlier reported compounds. The preparation of triphenyltin(IV) or dimethylphenltin(IV) 2,6-pyridinedicarboxylates in the presence of an alkaline alkoxide results in the formation of diorganotin(IV) derivatives through cleavage of one of the phenyl groups. This synthetic approach can be adopted for the preparation of diorganotin(IV) carboxylates with alkyl and aryl groups on tin from triorganotin(IV) halides.

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