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Synthesis, characterization and *in vitro* cytotoxic activity of bis(triorganotin) 2,6-pyridinedicarboxylates

Abstract: Two bis(triorganotin) 2,6-pyridinedicarboxylates, 2,6-$C_5H_3N(COOSnR_3)_2$ (R=C_6H_{11}-*c*, **1**; $C_6H_5C(CH_3)_2CH_2$, **2**), have been synthesized by the reaction of 2,6-pyridinedicarboxylic acid with triorganotin hydroxide in toluene-ethanol and characterized by means of elemental analysis, FT-IR, ^{1}H NMR spectroscopy, and single crystal X-ray diffraction analysis. In the compounds, a 2,6-pyridinedicarboxylate dianion binds two triorganotin units in a monodentate manner and both tin atoms exist in a distorted tetrahedral environment. Bioassay results have shown that the compounds possess good *in vitro* cytotoxic activity against two human tumor cell lines, Hela and MCF-7.

Keywords: 2,6-pyridinedicarboxylic acid; crystal structure; cytotoxic activity; organotin.

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Introduction

In recent years, organotin carboxylates have been receiving considerable attention due to their structural interest and varied applications (Tiekink, 1994; Davies et al., 2008). Some studies found their wide use as catalysts and stabilizers, and certain derivatives are employed as biocides, as antifouling agents and as wood preservatives (Davies et al., 2008; Seter et al., 2012; Kaur et al., 2013; Dong et al., 2014). In addition, it has been observed that some di- and triorganotin carboxylates show potential as antineoplastic agents (Hadjikakou and Hadjiliadis, 2009; Amir et al., 2014; Carraher and Roner, 2014). The organotin moiety and the ligand appear to play an important role in determining their antitumor activity (Hadjikakou and Hadjiliadis, 2009; Amir et al., 2014). The design and synthesis of new organotin carboxylates by selecting ligands and organotin substrates has been encouraged in order to achieve efficacy. 2,6-pyridinedicarboxylic acid (Scheme 1) is a dicarboxylic acid containing an aromatic N donor atom, and some of its di- and trioganotin derivatives such as $R_2Sn(2,6\text{-}C_5H_3N)(COO)_2(H_2O)$ (R=Me, *n*-Bu) (Szorcsik et al., 2004a; Azadmeher et al., 2008), $R_2Sn(2,6\text{-}C_5H_3N)(COO)_2$ (R=*t*-Bu, Ph, Et) (Gielen, 2002; Szorcsik et al., 2004b), 2,6-$C_5H_3N(COOSnBu\text{-}n_3)_2$ (Yin et al., 2007), 2,6-$C_5H_3N(COOSnBu\text{-}n_3)_2$(4,4′-bpy) (Chandrasekhar et al., 2012) have been studied. In order to continue to expand the chemistry and therapeutic potential of the triorganotin/2,6-pyridinedicarboxylic acid compounds, we synthesized two new bis(triorganotin) 2,6-pyridinedicarboxylates from 2,6-pyridinedicarboxylic acid and triorganotin hydroxide and determined their *in vitro* cytotoxic activity.

Results and discussion

Synthesis

Compounds **1** and **2** were prepared by azeotropic removal of water from the reaction between triorganotin hydroxide and 2,6-pyridinedicarboxylic acid in the molar ratio 2:1 in toluene-ethanol.

$$2\,R_3SnOH + 2,6\text{-}C_5H_3N(COOH)_2 \rightarrow 2,6\text{-}C_5H_3N(COOSnR_3)_2 + H_2O$$
R = *c*-C_6H_{11} (**1**), $C_6H_5C(CH_3)_2CH_2$ (**2**)

Both compounds **1** and **2** are white solids and soluble in benzene and in common polar organic solvents such as methanol, trichloromethane, acetonitrile, and N,N-dimethylformamide.

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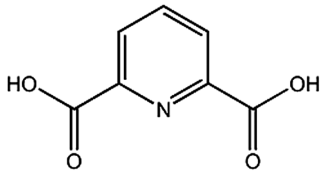

Scheme 1 The structure of the ligand.

Spectroscopic analysis

The infrared data of organotin carboxylates are usually used to predict their solid-state structures. The infrared spectra of **1** and **2** do not show a strong band at ~3300 cm^{-1} assigned to ν(OH), indicating the deprotonation of the carboxylic hydroxyl group of the ligand due to the formation of the oxygen-tin (Sn-O) bond. Furthermore, the presence of Sn-O vibrations for both complexes at ~480 cm^{-1} also confirms the coordination of carboxylate groups to tin (Rehman et al., 2005). In organotin carboxylates, IR spectroscopy can provide useful information concerning the coordination mode of the carboxylate group. Generally, the difference between the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ bands, $\Delta\nu(CO_2)$, of bidentate carboxylate group is below 200 cm^{-1}, while unidentate carboxylate is above 200 cm^{-1} and is larger than that observed for ionic compounds (Deacon and Phillips, 1980). The magnitudes of $\Delta\nu(CO_2)$ in **1** and **2** (317 and 308 cm^{-1}) and in the Na(I) salts of the ligand (221 cm^{-1}) indicate that the carboxylate group harbors a monodentate coordination to tin in the solid state (Szorcsik et al., 2004a), which is in agreement with the solid state structure of **2**·H_2O shown below.

The ^{1}H NMR spectra show the expected integration and peak multiplicities. A single resonance of -OH in the spectra of the free ligand is absent in the spectra of the complexes indicating the replacement of the carboxylic acid protons by an organotin moiety on complex formation. The proton resonances of the pyridine ring appear at 8.15 (H-4, triplet) and 8.35 (H-3 and H-5, triplet). The complex multiplets in the range of 1.30–2.12 ppm are assigned to the cyclohexyl protons. In **2**, the SnCH_2 protons appear at 1.30 ppm as a singlet and the spin-spin coupling between the methylene proton and the tin nucleus (^2J) is 50 Hz.

Structure analysis of 2·H_2O

The molecular structure of **2**·H_2O is shown in Figure 1. Selected bond lengths and bond angles are listed in Table 1. This compound crystallizes in monoclinic space group $P2_1/n$, and is a di-nuclear tin complex in which each tin atom is four-coordinated and possesses a distorted C_3SnO tetrahedral geometry. The four coordination atoms of the tin atom come from three carbon atoms of 2-methyl-2-phenylpropyl groups and a carboxylate oxygen atom which is monodentate to tin, respectively. Bond dimensions, particularly the covalent Sn-O distance (2.064(3) and 2.072(3) Å), are similar to those found in the tris(2-methyl-2-phenylpropyl)tin carboxylate structures, such as phthalate (Tian et al., 2005a), 2-phenyl-1,2,3-triazole-4-carboxylate (Tian et al., 2005b), and 2,3-pyridinedicarboxylate (Tian et al., 2006). The Sn(1)-O(2) and Sn(2)- O(4) separation of 2.958(3) and 3.029(3) Å, respectively, are not indicative

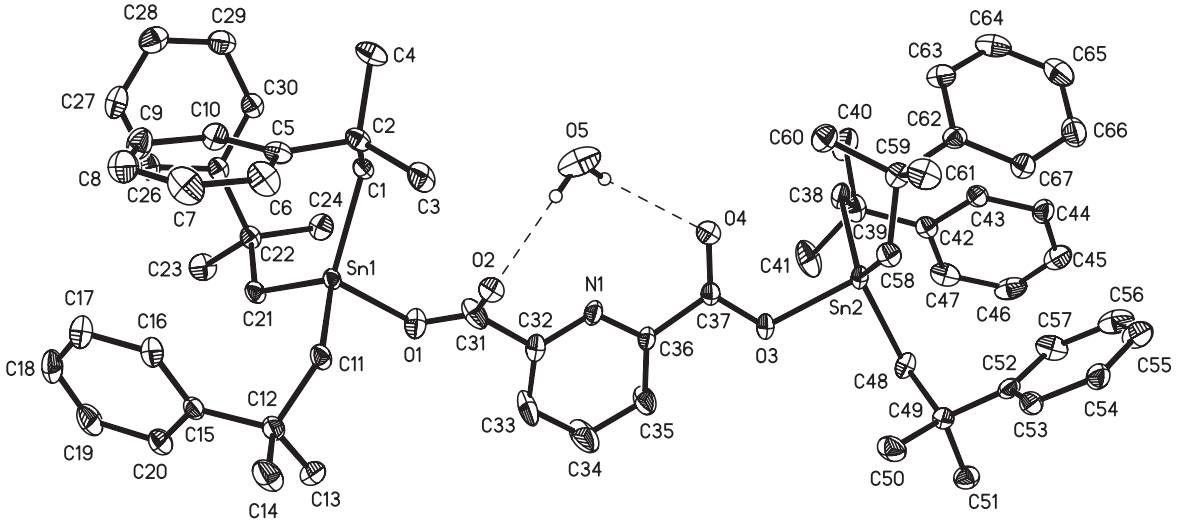

Figure 1 The molecular structure of **2**·H_2O with ellipsoids at the 30% probability level; except H atoms of water, the other H atoms are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for **2**·H_2O.

Bond lengths (Å)			
Sn(1)-O(1)	2.064(3)	Sn(2)-C(48)	2.146(4)
Sn(1)-C(1)	2.144(4)	Sn(2)-C(58)	2.144(4)
Sn(1)-C(11)	2.143(4)	C(31)-O(1)	1.289(7)
Sn(1)-C(21)	2.143(4)	C(31)-O(2)	1.197(6)
Sn(2)-O(3)	2.072(3)	C(37)-O(3)	1.287(5)
Sn(2)-C(38)	2.158(4)	C(37)-O(4)	1.198(5)
Bond angles (°)			
O(1)-Sn(1)-C(1)	106.83(16)	O(3)-Sn(2)-C(38)	104.22(16)
O(1)-Sn(1)-C(11)	101.24(17)	O(3)-Sn(2)-C(48)	91.65(16)
O(1)-Sn(1)-C(21	95.35(17)	O(3)-Sn(2)-C(58)	103.65(16)
C(1)-Sn(1)-C(11)	118.05(16)	C(38)-Sn(2)-C(48)	115.60(18)
C(1)-Sn(1)-C(21)	116.14(15)	C(38)-Sn(2)-C(58)	119.41(19)
C(11)-Sn(1)-C(21)	114.67(15)	C(48)-Sn(2)-C(58)	116.12(17)

of a significant interaction between these atoms. The distortion of the tetrahedral geometry is reflected by the C(1)-Sn(1)-C(11), C(38)-Sn(2)-C(58), O(1)-Sn(1)-C(21), and O(3)-Sn(2)-C(48) bond angles of 118.05(16)°, 119.41(19)°, 95.35(17)°, and 91.65(16)°, respectively. The monodentate mode of coordination of the two carboxylate groups is reflected in the disparate C(31)-O(1) (1.289(7) Å) and C(31)-O(2) (1.197(6) Å), and C(37)-O(3) (1.287(5) Å) and C(37)-O(4) (1.198(5) Å). In triorganotin 2,6-pyridinedicarboxylate complexes such as [(*c*-$C_6H_{11})_2NH_2$][2,6-$C_5H_3N(CO_2)_2Sn$(*n*-$C_4H_9)_3$] (Ng et al., 1991), [(C_6H_5)(CH_3)NH_2][2,6-$C_5H_3N(CO_2)_2Sn$(*n*-$C_4H_9)_3$] (Ng et al., 2000), 2,6-C_5H_3N(COOSn(*n*-$C_4H_9)_3)_2(H_2O)$ (Yin et al., 2007), and 2,6-C_5H_3N(COOSnBu-*n*$_3)_2$(4,4′-bpy) (Chandrasekhar et al., 2012), the Sn atoms are five-coordinate and exist in a trigonal bipyramidal geometry. The tetrahedral nature of tris(2-methyl-2-phenylpropyl)tin compound **2** arises from the crowding of the three organic groups bound to tin. In **2**·H_2O, the carboxylate groups and pyridine ring are not in the same plane, and the dihedral angle between the pyridine ring and the two carboxylate planes is 41.15(16)° and 18.33(16)°, respectively, and the dihedral angle between the two carboxylate planes is 55.40(14)°. In the crystal, a $R_2^2(10)$ hydrogen-bond formed by a solvated water and the two carbonyl groups of the pyridinedicarboxylate ligand [O(5)-H(5A)-O(4) (3.148(8) Å, 150.13(39)°) and O(5)- H(5B)- O(2) (3.059(8) Å, 176.75(45)°)] is observed (Figure 1).

In vitro cytotoxicity

Under the experimental conditions, the results of the cytotoxic assay of the compounds against Hela (cervix tumor cell) and MCF-7 (mammary tumor cell) are shown in Table 2. Compounds **1** and **2** displayed potent *in vitro* activity, and are more active than the clinically used *cis*-platin. The activity of **1** is better than that of **2**, which is comparable to that of the reported diorganoltin 2,6-pyridinedicarboxylates (Gielen, 2002), bis(triorganoltin) 2,3-pyridinedicarboxylates (Tian et al., 2006), and triorganoltin 2-phenyl-1,2,3-triazole-4-carboxylates (Tian et al., 2005b). Apparently, the numbers and type of the alkyl group on tin atom and the ligand play an important role in the antiproliferative action of the compounds.

Table 2 *In vitro* cytotoxicity (IC_{50}, μg/mL) of the compounds.

Compound	Hela	MCF-7
1	0.087	0.136
2	0.579	0.932
cis-platin	1.443	5.457

Conclusion

In summary, two new bis(triorganotin) 2,6-pyridinedicarboxylates have been synthesized and characterized. Both are di-nuclear tin complexes in which each tin atom is four-coordinated and possesses a distorted C_3SnO tetrahedral geometry. The compounds have good *in vitro* cytotoxic activity against two human tumor cell lines, i.e., Hela and MCF-7, and were better than the clinically used *cis*-platin. They can be considered as antitumor compounds to study further with possible modification of their structure.

Experimental

General

The tris(2-phenyl-2-methylpropyl)tin hydroxide was prepared according to the literature procedure (Reichle, 1966). All other chemicals (Sinopharm Chemical Reagent Company Limited, Shanghai, China) were of reagent grade and were used without further purification. Carbon and hydrogen analyses were determined using a Perkin Elmer 2400 Series II elemental analyzer (Perkin Elmer, Waltham, MA, USA). IR spectra were recorded on a Nicolet Nexus 470 FT-IR spectrophotometer using KBr discs in the range 4000–400 cm^{-1} (Thermo Nicolet Corporation, Madison, WI, USA). ^1H NMR spectral data were collected using a Bruker Avance DPX300 NMR spectrometer (Bruker Corporation, Switzerland) with $CDCl_3$ as solvent and TMS as internal standard.

Synthesis of bis(triorganotin) 2,6-pyridinedicarboxylates

Bis(tricyclohexyltin) 2,6-pyridinedicarboxylate (1) To a suspension of tricyclohexyltin hydroxide (0.770 g, 2 mmol) in 60 mL of

toluene-ethanol (3:1, V/V) was added 2,6-pyridinedicarboxylic acid (0.167 g, 1 mmol). The reaction mixtures were refluxed for 5 h with a Dean-Stark separator, and then allowed to cool to room temperature. The solution was filtered and the solvent was removed under reduced pressure by a rotary evaporator. The resulting white solid was recrystallized from methanol-trichloromethane (1:1, V/V) and dried in a vacuum dryer for 24 h at room temperature. Yield: 0.699 g (77.6%), melting point: 161–162°C. Anal. Found: C, 57.12; H, 7.59; N, 1.56. Calcd for $C_{43}H_{69}NO_4Sn_2$: C, 57.29; H, 7.72; N, 1.55%. Selected IR (KBr) cm^{-1}: 1650 [$\nu(COO^-)_{as}$)], 1333 [($\nu(COO^-)_s$)], 1599, 1571, 1445 (pyridine ring). ^1H NMR δ: 1.30–2.12 (m, 66H, C_6H_{11}), 8.15 (t, J=6.8 Hz, 1H, C_5H_3N), 8.36 (d, J=6.8 Hz, 2H, C_5H_3N).

Bis[tris(2-methyl-2-phenylpropyl)tin] 2,6-pyridinedicarboxylate (2) This compound was prepared in the same way as **1**, by adding tris(2-methyl-2-phenylpropyl)tin hydroxide (1.070 g, 2 mmol) to 2,6-pyridinedicarboxylic acid (0.167 g, 1 mmol). The colorless crystals were obtained with a yield of 1.012 g (84.2%). Melting point: 127–128°C. Anal. Found: C, 67.04; H, 6.68; N, 1.19. Calcd for $C_{67}H_{81}NO_4Sn_2$: C, 66.96; H, 6.79; N, 1.17%. Selected IR (KBr) cm^{-1}: 1654 [$\nu(COO^-)_{as}$)], 1346 [($\nu(COO^-)_s$)], 1599, 1578, 1450 (pyridine ring). ^1H NMR δ: 1.26 (s, 36H, CH_3), 1.30 (s, 12H, CH_2Sn), 7.09–7.29 (30H, m, C_6H_5), 8.16 (t, J=6.8 Hz, 1H, C_5H_3N), 8.38 (d, J=6.8 Hz, 2H, C_5H_3N).

X-ray crystallography

The colorless single crystal of **2**·H_2O was obtained from methanol-chloroform (1:1, V/V) by slow evaporation at room temperature. Diffraction measurements were performed on a Bruker Smart Apex imaging-plate area detector fitted with graphite monochromatized Mo-Kα radiation (0.71073 Å) using the φ and ω scan technique. The structures were solved by direct-methods and refined by a full-matrix least squares procedure based on F^2 using SHELXL-97 (Sheldrick, 2008). The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at calculated positions (C-H=0.93 Å and $U_{iso}(H)=1.2U_{eq}(C)$ for the aromatic H atoms, C-H=0.96 Å and $U_{iso}(H)=1.5U_{eq}(C)$ for the methyl H atoms, and C-H=0.97 Å and $U_{iso}(H)=1.2U_{eq}(C)$ for the methylene H atoms). The water H-atoms were located in a different Fourier map and were refined with an O-H distance restrained to 0.85 (1) Å and with $U_{iso}(H)=1.5U_{eq}(O)$. Crystal data, collection procedures and refinement results are shown in Table 3. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre with supplementary publication number CCDC 1020069.

Table 3 Crystallographic and refinement data of **2**·H_2O.

Empirical formula	$C_{67}H_{83}NO_5Sn_2$
Formula weight	1219.72
Crystal system	Monoclinic
Space group	*P*21/n
a/Å	18.2714(11)
b/Å	18.4599(11)
c/Å	19.4979(12)
β/(°)	108.741(1)
Volume/Å^3	6227.7(7)
Z	4
D_c/(g·cm^{-3})	1.301
μ/mm^{-1}	0.849
F(000)	2528
Crystal size/mm	0.25×0.24×0.18
θ range/(°)	1.33–26.00
Tot. reflections	47 856
Uniq. reflections	12 202 (R_{int}=0.0315)
Reflections with $I>2\sigma(I)$	9979
GOF on F^2	1.054
R indices [$I>2\sigma(I)$]	*R*=0.0479, *wR*=0.1156
R indices (all data)	*R*=0.0604, *wR*=0.1236
$\Delta\rho_{min}$, $\Delta\rho_{max}$/(e·Å^{-3})	-0.822, 0.992

In vitro cytotoxicity

Cytotoxic activity was assayed against two human tumor cell lines, Hela (cervix tumor cell) and MCF-7 (mammary tumor cell). The samples (200 mg/L stock solutions) were prepared by dissolving the test compounds in DMSO and by diluting the resultant solutions with free-serum DMEM (Dulbecco's modified eagle medium) solution. In the assays, the final concentration of DMSO was <0.1% (the concentration used was found to be non-cytotoxic against tumor cells). *In vitro* cytotoxic activity of the compounds was measured by the MTT assay according to the literature (Denizot and Lang, 1986). All cells cultured in DMEM were supplemented with 10% heat-inactivated new-born calf serum at 37°C in a humidified 5% CO_2 incubator and were seeded into each well of a 96-well plate and were fixed for 24 h. The following day, different concentrations of the test compounds (0.125, 0.250, 0.500, and 1.000 μg/mL) were added. After incubation with various concentrations of test compounds for 72 h, the inhibition on cell proliferation was measured. Briefly, 100 μL of MTT working solution (1 mg/mL) were into each well of the 96-well plate. The plate was incubated at 37°C for 4 h and then the medium was removed. The converted dye formazan was solubilized with 150 μL acidic isopropanol. The results were read on the absorbance microplate readers (Model 680, Bio-Rad) with a wavelength of 570 nm. Different concentrations of *cis*-platin and 0.1% of DMSO were used as positive and negative control for the cytotoxicity study of the test compounds *in vitro*. The experiments were conducted in triplicate for each tested concentration. The dose causing 50% inhibition of cell growth (IC_{50}) was calculated as previously described (Zheng et al., 2004).

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