Note

Synthesis and Crystal Structure of Bis[(2,6-pyridinedicarboxylato)(methanol)dibenzyltin(IV)]

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A novel seven-coordinate dimer bis[(2,6-pyridinedicarboxylato)(methanol)dibenzyltin(IV)] was synthesized by the reaction of $(PhCH_2)_3SnCl$ with 2,6-pyridine dicarboxylic acid in 1:1 molar ratio in methanol solution. The structure was characterized by elemental analysis, IR and ^1H NMR spectra, and the crystal structure was determined by X-ray single crystal diffraction analysis. The crystal belongs to monoclinic space group $P2_1/n$, $a = 0.96250(19)$ nm, $b = 1.0947(2)$ nm, $c = 1.9965(4)$ nm, $\beta = 92.31(3)°$, $Z = 2$, $V = 2.1019(7)$ nm^3, $D_c = 1.574$ g/cm^3, $\mu = 1.248$ mm^{-1}, $F(000) = 1000$, $R_1 = 0.0675$, $wR_2 = 0.0836$. In the crystals of the complex, each tin atom is seven-coordinated in a distorted bipyramidal structure.

Keywords organotin complex, 2,6-pyridinedicarboxylic acid, synthesis, crystal structure

Introduction

Diorganotin derivatives of 2,6-pyridinedicarboxylic acid exhibit high *in vitro* antitumour activities.[1-5] These compounds have been synthesized by the reaction of diorganotin dichlorides or diorganotin oxides with 2,6-pyridinedicarboxylic acid, but the reaction between triorganotin chlorides and 2,6-pyridinedicarboxylic acid has not been studied. This paper reported a new debenzylation reaction and crystal structure of an unexpected product bis[(2,6-pyridinedicarboxylato)(methanol) dibenzyltin(IV)] (**4**).

We expected to synthesize $(PhCH_2)_3SnO_2C(2,6\text{-}C_5H_3N)CO_2H$ (**3**) by the reaction of $(PhCH_2)_3SnCl$ (**1**) with $HO_2C(2,6\text{-}C_5H_3N)CO_2H$ (**2**) in 1:1 molar ratio in the presence of organic base Et_3N, however an unexpected complex was obtained as shown in Scheme 1:

Scheme 1

$$(PhCH_2)_3SnCl + HO_2C(2,6\text{-}C_5H_3N)CO_2H$$
1 **2**

Et_3N / MeOH

- ✗ → $(PhCH_2)_3SnO_2C(2,6\text{-}C_5H_3N)CO_2H$ (**3**)
- → $\{(PhCH_2)_2Sn[2,6\text{-}(O_2C)_2C_5H_3N](CH_3OH)\}_2$ (**4**)

Experimental

Starting materials and instruments

The triphenyltin chloride and 2, 6-pyridinedicarboxylic acid were of analytical grade. Melting points were determined with Kofler micro meting point apparatus and the thermometer was uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer in KBr. ^1H NMR spectra were measured on a JEOL-FX-90Q spectrometer using TMS as the internal standard and $CDCl_3$ as the solvent. Elemental analysis was performed on a Carlo-Erba 1106 elemental analyzer.

Synthesis of complex **4**

A 50 mL flask was charged with $HO_2C(2,6\text{-}$

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$C_5H_3N)CO_2H$ (**2**) (0.34 g, 2.0 mmol), $(PhCH_2)_3SnCl$ (**1**) (0.85 g, 2.0 mmol) and methanol (25 mL). The mixture was refluxed for 1 h, and then Et_3N (0.5 g, 5 mmol) was added and refluxed for another 1 h. The solvent was evaporated under vacuum to give a white solid. The product was recrystallized from methanol to give colorless crystals 0.71 g, yield 71%; m.p. 221—223 ℃; ^1H NMR ($CDCl_3$, 90 MHz) δ: 3.31 (t, J = 92.45 Hz, 4H, 2 × $SnCH_2$), 3.98 (s, 3H, OCH_3), 7.25—7.37 (m, 10H, 2 × C_6H_5), 8.26 (d, J = 6.8 Hz, 1H, 3-pyridine-H), 8.38(d, J = 6.8 Hz, 1H, 4-pyridine-H); IR (KBr) ν: 3445 (m, OH), 3082, 3043 (m, ArH), 2974, 2937, 2833, 2802 (s, CH), 1634, 1398 (s, CO_2), 582 (w, SnC), 469, (m, SnO), 490 (w, SnN) cm^{-1}. Anal. calcd for $C_{44}H_{42}N_2O_{10}Sn_2$ 996.18: C 53.05, H 4.25, N 2.81, Sn 23.83; found C 53.29, H 4.22, N 2.90, Sn 23.67.

Determination of crystal structure

A single crystal having approximate dimensions of 0.30 mm × 0.20 mm × 0.20 mm was mounted on a fiber. All measurements were made on a Bruker smart-1000 CCD diffractometer with graphite monochromated Mo Kα (0.071073 nm) radiation. The data were collected at temperature of 293(2) K to maximum θ value of 25.03°. The crystal belongs to monoclinic space group $P2_1/n$, a = 0.96250(19) nm, b = 1.0947(2) nm, c = 1.9965 (4) nm, β = 92.31(3)°, Z = 2, V = 2.1019(7) nm^3, D_c = 1.574 g/cm^3, μ = 1.248 mm^{-1}, $F(000)$ = 1000, S = 0.826. The structure was solved by direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined by full-matrix least-squares calculation to R_1 = 0.0675, wR_2 = 0.0836 $\{w = 1/[\sigma^2 \cdot (F_0^2 + 0.0000P)^2 + 0.00P]$, $P = \text{Max} \times (F_0^2, 0) + (2 \times F_c^2)/3\}$ for 2464 independent reflections with $I \geqslant 2\sigma(I)$ (R_{int} = 0.1500). In the final difference map, the residuals are 594 and −618 e/nm^3, respectively.

Results and discussion

Reaction mechanism

A possible mechanism was given in Scheme 2.

Scheme 2

$(PhCH_2)_3SnCl + HO_2C(2,6\text{-}C_5H_3N)CO_2H$

1 **2**

↓

$(PhCH_2)_3SnO_2C(2,6\text{-}C_5H_3N)COOH + HCl$

↓ $-C_6H_5CH_3$

$(PhCH_2)_2Sn(Cl)O_2C(2,6\text{-}C_5H_3N)COOH$

↓ NEt_3

$(PhCH_2)_2Sn(Cl)O_2C(2,6\text{-}C_5H_3N)C\overset{\ominus}{O}_2\overset{\oplus}{N}HEt_3$

↓

$(PhCH_2)_2Sn[2,6\text{-}(O_2C)_2C_5H_3N]$

↓ CH_3OH

$(PhCH_2)_2Sn[2,6\text{-}(O_2C)_2C_5H_3N](CH_3OH)$

↓

$\{(PhCH_2)_2Sn[2,6\text{-}(O_2C)_2C_5H_3N](CH_3OH)\}_2$

4

Crystal structure

Table 1 gives the atomic coordinates and equivalent isotropic thermal parameters of **4**. The selected bond lengths and angles were listed in Table 2. The molecular structure of $\{(PhCH_2)_2Sn[2,6\text{-}(O_2C)_2C_5H_3N](CH_3OH)\}_2$ was shown in Fig. 1. Fig. 2 shows the packing of the molecules in the unit cell as seen in a projection on to its face. The molecule possesses a dimeric structure, but this structure differs from that of $\{[R_2Sn\text{-}(O_2CR)]_2O\}_2$.[6] Each tin atom is seven-coordinated in a pentagonal bipyramidal structure. Each central tin atom is surrounded equatorially by four oxygen atoms, one nitrogen atom and axially by two carbon atoms of the benzyl groups. The complex can be viewed as a centrosymmetric dimer, where one half of the molecule comprises the crystallographic asymmetric unit and the other half is generated by an inversion center located at the center of the oxo-bridging parallel quadrilateral $(SnO)_2$ ring. The atoms Sn(1), Sn(1)#, O(3) and O(3)# are coplanar to within ±0.00112 nm. The atoms Sn(1), Sn(1)#, O(3), O(3)#, O(1), O(1)#, O(5), O(5)#, N(1) and N(1)# are coplanar to within ±0.00223 nm.

In this complex, the Sn atom exists in distorted pentagonal bipyramidal coordination environments in which

one methanol molecule, one multidentate coordinated 2,6-pyridinedicarboxylate ligand, and two trans benzyl groups have assembled around each Sn center. Each of the two 2,6-pyridinedicarboxylate ligands bridges a pair of Sn atoms utilizintg one O atom of carboxylate group to give rise to slightly different Sn(1)—O(3) and Sn(1)#—O(3) bond distances [0.2409(6) nm and 0.2538(5) nm, respectively], to form a seven-coordinate dimer.

Each of tin atoms show *trans*-pentagonal bipyramidal coordination [Sn(1)—C(15), 0.2179(14) nm; Sn(1)—C(8), 0.2140(10) nm; C(15)-Sn(1)-C(8), 161.2(5)°; $\Sigma_{\text{equatorial plane}}$ 359.8° (Fig. 1)]. Two 2,6-pyridine-dicarboxylato ligands chelate to two tin atoms through its O, N, O ends [Sn(1)—O(1), 0.2147(6) nm; Sn(1)—O(3), 0.2409(6) nm; Sn(1)—N(1), 0.2181(12) nm], and the two carboxylate groups of each 2,6-pyridinedicarboxylate ligand coordinate to tin atom in monodentate fashion.

The absorption at 1634 and 1398 cm^{-1} were assigned $\nu_{as(co_2)}$ and $\nu_{s(co_2)}$ bands, respectively. The magnitude of $\Delta\nu$ [$\nu_{as(co_2)} - \nu_{s(co_2)}$], 236 cm^{-1}, indicates that the carboxylate groups function as monodentate ligands,[7] in agreement with the crystal structure as mentioned above.

Table 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^5$ nm^2) of **4**

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
Sn(1)	1332(1)	5198(1)	9122(1)	58(1)	C(9)	3211(14)	7021(14)	9733(7)	83(5)
N(1)	890(10)	7040(10)	8754(5)	79(4)	C(10)	2599(19)	8157(17)	9969(7)	111(6)
O(1)	2655(7)	5495(9)	8296(3)	64(3)	C(11)	2977(18)	9330(20)	9760(11)	133(8)
O(2)	3390(8)	6820(9)	7527(3)	90(3)	C(12)	4060(20)	9441(15)	9359(10)	120(6)
O(3)	-436(7)	6154(7)	9762(3)	56(2)	C(13)	4871(13)	8383(15)	9177(6)	81(5)
O(4)	-1739(9)	7858(8)	9833(4)	90(3)	C(14)	4480(13)	7213(15)	9364(6)	88(5)
O(5)	2625(11)	3354(9)	9148(4)	106(3)	C(15)	-214(13)	4133(11)	8547(6)	70(4)
C(1)	2718(13)	6512(13)	8008(6)	68(4)	C(16)	-972(14)	4875(12)	8125(6)	72(5)
C(2)	1606(12)	7488(10)	8233(6)	66(4)	C(17)	-2217(13)	5364(17)	8274(6)	81(5)
C(3)	1414(14)	8671(15)	7971(6)	85(5)	C(18)	-2964(16)	6128(18)	7864(8)	107(6)
C(4)	403(15)	9396(13)	8208(7)	93(5)	C(19)	-2580(16)	6430(13)	7174(7)	88(5)
C(5)	-366(15)	8890(12)	8738(7)	99(6)	C(20)	-1326(18)	5879(18)	6992(9)	113(7)
C(6)	-171(13)	7781(12)	8958(6)	68(4)	C(21)	-570(16)	5133(14)	7450(6)	79(5)
C(7)	-845(13)	7242(13)	9564(6)	67(4)	C(22)	3916(14)	3028(15)	8860(7)	99(6)
C(8)	2810(11)	5734(14)	9895(5)	67(4)					

Table 2 Selected bond lengths (nm) and angles (°) of **4**

Sn(1)—C(15)	0.2179(14)	Sn(1)—O(3)	0.2409(6)	Sn(1)—O(3)#	0.2538(5)
Sn(1)—C(8)	0.2140(10)	Sn(1)—O(5)	0.2370(10)	O(4)···O(5)#	0.2601
Sn(1)—O(1)	0.2147(6)	Sn(1)—N(1)	0.2181(12)		
C(15)-Sn(1)-C(8)	161.2(5)	N(1)-Sn(1)-O(5)	152.8(3)	C(2)-N(1)-Sn(1)	119.5(7)
C(15)-Sn(1)-O(3)	91.7(3)	C(15)-Sn(1)-O(1)	95.2(4)	C(7)-O(3)-Sn(1)	116.4(6)
C(8)-Sn(1)-O(3)	87.8(4)	O(5)-Sn(1)-O(1)#	79.6(3)	C(1)-O(1)-Sn(1)	121.8(8)
C(6)-N(1)-Sn(1)	125.5(7)	O(3)-Sn(1)-O(3)#	64.2(4)	C(22)-O(5)-Sn(1)	131.7(8)
C(15)-Sn(1)-N(1)	101.4(4)	O(3)-Sn(1)-O(1)#	142.6(3)	C(9)-C(8)-Sn(1)	105.7(10)
C(8)-Sn(1)-N(1)	96.0(5)	O(3)-Sn(1)-O(1)	142.7(3)	C(16)-C(15)-Sn(1)	110.1(9)
O(1)-Sn(1)-N(1)	73.5(3)	N(1)-Sn(1)-O(3)	69.2(3)	C(8)-Sn(1)-O(3)#	87.7(6)
C(15)-Sn(1)-O(5)	84.4(4)	O(5)-Sn(1)-O(1)	79.6(3)	C(15)-Sn(1)-O(3)#	91.7(1)
C(8)-Sn(1)-O(5)	83.4(5)	C(8)-Sn(1)-O(1)	96.6(4)	N(1)-Sn(1)-O(3)#	133.2(1)
O(3)-Sn(1)-O(5)	137.7(3)	O(5)-Sn(1)-O(3)#	73.3(1)		

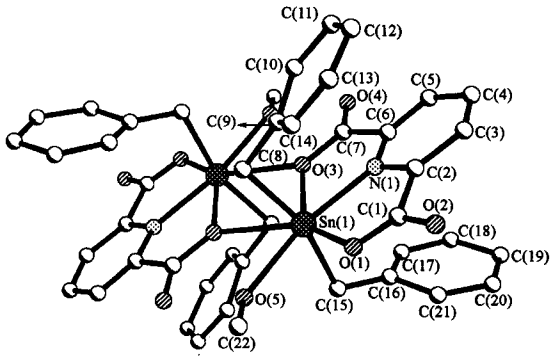

Fig. 1 Molecular structure of bis[(2,6-pyridinedicarboxylato)-(methanol)dibenzyltin(IV)] (**4**).

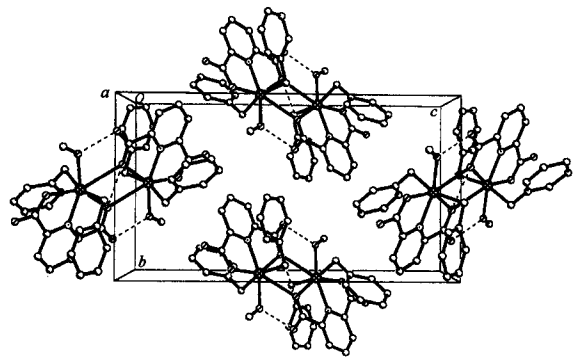

Fig. 2 Projection of the unit cell of **4**.

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