

Synthesis, Structural Elucidation and X-Ray Analysis of Triphenyltin(IV) [2-(2,3-dimethylanilino)nicotinate]

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(Received 27 June 2008, Accepted 24 October 2008)

Triphenyltin(IV) [2-(2,3-dimethylanilino)nicotinate] was prepared by the interaction of triphenyltin(IV) hydroxide and 2-(2,3-dimethylanilino)nicotinic acid in 1:1 ratio. This compound was characterized by elemental analyses, IR, multinuclear NMR spectroscopy (¹H and ¹³C) and mass spectrometry. The structure of title compound was confirmed by single crystal X-ray crystallography. The coordination around the tin atom was studied both in solution and solid state. The geometry around tin is trigonal bipyramidal in solid state while it is tetrahedral in solution. The compound belongs to Monoclinic system, having space group P 21/c with unit cell dimensions $a = 17.002(8)$ Å, $b = 9.0793(3)$ Å, $c = 18.2616(9)$ Å, $\alpha = 90$ (°) $\beta = 107.381(4)$ (°), $\gamma = 90$ (°).

Keywords: Triphenyltin(IV) derivative, NMR, X-Ray analysis, Pentacoordinated geometry

INTRODUCTION

Organotin(IV) compounds of the carboxylic acids are being extensively studied with special reference to their methods of synthesis, structural elucidation, and biological studies [1-2]. Generally, these compounds are well-characterized by multinuclear NMR (¹H, ¹³C and ¹¹⁹Sn), X-ray analysis, and ^{119m}Sn Mössbauer spectroscopy [3-4]. In recent years, organotin(IV) carboxylates have attracted much attention due to their potential biocidal activity, cytotoxicity and anticancer studies against different cell lines [5-6]. Many of the di-*n*-butyltin(IV), tri-*n*-butyltin(IV), and triphenyltin(IV) complexes display interesting antitumor activity. Another aspect of major interest in organotin carboxylates is their structural diversity. Both diorganotin and triorganotin esters of

various carboxylic acids show rich and diverse structural chemistry, as cited in reviews [7-8].

Keeping in view the structural and biological diversity of organotin(IV) carboxylates, and in connection with our interest in coordination chemistry of organotin compounds with different carboxylic acids [9-12], here we report the synthesis and characterization of triphenyltin(IV) [2-(2,3-dimethylanilino)nicotinate].

EXPERIMENTAL

Chemicals

2,3-Dimethylaniline, NaOH (97%), triphenyltin(IV) hydroxide and 2-chloronicotinic acid were purchased from Aldrich, Fluka and Alfa-Aesar (Johnson Matthey Chemical Company). The organic solvents *e.g.*, toluene, chloroform and benzene were of Merck (Germany) and dried *in situ* using

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standard procedures [13].

Instrumentation

Melting point was determined in a capillary tube using electrothermal melting point apparatus model MPD Mitamura Riken Kogyo (Japan). The infrared absorption spectrum was recorded as solid KBr pellet on a Bio-Rad Excalibur FT-IR model in the frequency range 4000-400 cm^{-1} . Multinuclear NMR (^1H and ^{13}C) spectra were recorded on a Bruker 300 MHz, FT-NMR Spectrometer, Switzerland, using deuterated chloroform as internal reference (δ ^1H CDCl_3 = 7.24 ppm, δ ^{13}C = 77 ppm). The elemental analyses were made on CHNS-932 Elemental Analyzer, Leco Corporation (USA). The mass spectrometric analyses were carried out on MAT-312, mass spectrometer. The m/z values were evaluated assuming that H = 1, C = 12, N = 14, O = 16, Cl = 35 and Sn = 120.

Synthesis of 2-(2, 3-Dimethylanilino)nicotinic Acid (Scheme 1)

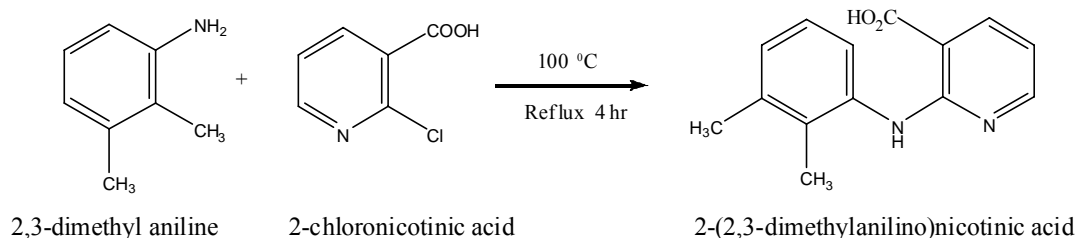
The ligand acid was prepared by using procedure as reported [14]. The 2-chloronicotinic acid (9.0 g, 57 mmol) and 2,3-dimethylaniline (7.1 ml, 57 mmol) were stirred and heated at 160-180 $^\circ\text{C}$ for 2 h, cooled and equilibrated between benzene (100 ml) and two 100 ml portions of 2 N NaOH. Neutralization of the aqueous solution with concentrated HCl yielded a light yellow precipitate which was collected by

filtration, washed with a small amount of water, and recrystallized from aqueous ethanol. The expected product was obtained as needles Yield (8 g, 58%), m.p.: 242-243 $^\circ\text{C}$. Anal. %Calcd. (found) for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$: C, 69.4 (69.7); H, 5.8 (5.7); N, 11.6 (11.7). IR (KBr, cm^{-1}) $\nu(\text{COO})_{\text{asym}}$ 1678, $\nu(\text{COO})_{\text{sym}}$ 1468, $\Delta\nu$ [$\nu(\text{COO})_{\text{asym}}$ - $\nu(\text{COO})_{\text{sym}}$] 210, $\nu(\text{N-H})$ 3316. ^1H NMR (300 MHz, CDCl_3) 11.46 s 1H (Acidic proton), 9.99 s 1H (Nitrogen proton), 8.44 dd (7.2, 2.1) 1H, 8.35 d (6.6) 1H, 8.03 d (8) 1H (N-Heterocyclic protons), 7.17 d (7.8) 1H, 7.04 d (7.5) 1H, 6.78 d (6.6) 1H (Aromatic protons), 2.32 s 3H, 2.22, s, 3H (2,3-dimethyl protons).

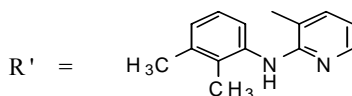
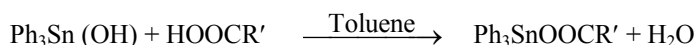
Synthesis of Triphenyltin(IV) [2-(2,3-Dimethylanilino)nicotinate] (Scheme 2)

The ligand acid (0.5 g, 1.85 mmol) and triphenyltin(IV) hydroxide (0.70 g, 1.86 mmol) were suspended in dry toluene (100 ml) in two necked round bottom flask (250 ml), equipped with a Dean-Stark apparatus, magnet bar and water condenser. The mixture was refluxed for 6-8 h, and water formed during the condensation reaction was removed at regular intervals. It was then cooled to room temperature and solvent was removed by rotary evaporator. The solid obtained was recrystallized from a mixture of chloroform and *n*-hexane (4:1).

Physical data; Mol. Formula $\text{C}_{32}\text{H}_{28}\text{O}_2\text{N}_2\text{Sn}$, Elemental analysis; %Calcd. (found): C, 65.06 (64.97); H, 4.74 (4.69); N,



Scheme 1. Reaction scheme for synthesis of ligand



Scheme 2. Reaction scheme for synthesis of triphenyltin(IV) derivative

4.74 (4.71). Yield 70%, m.p.: 158-160 °C, Recrystallization Chloroform/n-hexane (4:1) mixture. IR (KBr, cm^{-1}) $\nu(\text{COO})_{\text{asym}}$ 1608, $\nu(\text{COO})_{\text{sym}}$ 1427, $\Delta\nu$ [$\nu(\text{COO})_{\text{asym}}$ - $\nu(\text{COO})_{\text{sym}}$] 181, $\nu(\text{Sn-O})$ 473, $\nu(\text{N-H})$ 3314. ^1H NMR (300 MHz, CDCl_3) 10.34 s 1H (Nitrogen proton), 8.44 d (7.5) 1H, 7.94 bs 1H, 8.32 d (3) 1H (N-Heterocyclic protons), 7.32-7.84 m 15H, 7.17 d (7.5) 1H, 7.02 d (7.5) 1H, 6.68 d (7.2) 1H (Aromatic protons), 2.36 s 3H, 2.21, s, 3H (2,3-dimethyl protons). ^{13}C NMR (75 MHz, CDCl_3) 173 (Carbonyl carbon), 157.2, 153.4, 138.2, 112.1, 107.5 (N-Heterocyclic carbons), 141.9, 137.9, 137.3, 136.2, 130.5, 129.8, 129.0, 126.0, 125.6, 121.9 (Aromatic carbons), 20.9, 14.7 (Aromatic substituted methyl groups). Mass Spectral data $m/z(\%)$ [Ph_2SnCOO] $^+$ 306(5), [Ph_3Sn] $^+$ 351(60), [Ph_2Sn] $^+$ 274(7), [PhSn] $^+$ 195(37), [C_6H_4] $^+$ 77(456), [Sn] $^+$ 120(6), [OCOL_2] $^+$ 242(6), [$\text{C}_{13}\text{H}_{13}\text{N}_2$] $^+$ 197(100).

RESULTS AND DISCUSSION

Infrared Spectroscopy

Infrared spectroscopy is an important technique used for the characterization of organotin(IV) compounds and hence plays a key role in the preparative organotin chemistry. IR spectrum of the compound has been recorded as KBr pellet in the range 4000-400 cm^{-1} . The characteristic absorption frequencies *e.g.*, $\nu(\text{COO})$, $\nu(\text{Sn-O})$, and $\nu(\text{N-H})$ provide valuable information about the formation of complex and coordination mode of ligand.

Assignment of different vibration bands have been made by the comparison of free acid spectrum with the triphenyltin(IV) derivative. The absence of broad band due to $\nu(\text{OH})$ stretching frequency in the organotin(IV) derivative and the presence of $\nu(\text{Sn-O})$ stretching at 473 cm^{-1} is indicative of complex formation [15].

The explicit feature observed in the spectrum of the compound is the absence of broad band in the range 3424-3034 cm^{-1} , which appears in the free ligand acid as $\nu(\text{O-H})$ vibration, thus indicating metal-ligand bond formation through carboxylate group.

The values of IR stretching vibration frequencies of carboxylic group [$\nu(\text{COO}_{\text{asym}})$ and $\nu(\text{COO}_{\text{sym}})$] in organotin(IV) carboxylate are helpful in elucidation of the structure and bonding behaviour of the ligand [16-17]. The

carboxylate group in the organotin(IV) derivative generally adopt a bridged structure in the solid state unless the organic substituents at tin are bulky or unless the carboxylates groups are branched at the α -carbon.

Coordination of the ligand to tin atom is based on the $\Delta\nu$, difference between $\nu(\text{COO})_{\text{asym}}$ and $\nu(\text{COO})_{\text{sym}}$ and on the corresponding band position [18].

Various attempts have been made to correlate the values of characteristic vibration frequencies with their precursors and literature reports predict the structures of synthesized compound [19], when the structure changes from four to five- or higher coordinated symmetry, the ($\nu\text{COO}_{\text{asym}}$) frequencies shift to lower and ($\nu\text{COO}_{\text{sym}}$) to higher frequencies which cause decrease in the $\Delta\nu$ value in compounds [20]. Thus, a decrease in the $\Delta\nu$ value is observed in this complex compared to the corresponding free acid which indicates penta coordinated geometry around metal atom. It is proposed that the carboxylate group acts as a bidentate ligand in this compound.

^1H NMR Spectroscopy

The characteristic resonance peaks in the ^1H NMR spectra for triphenyltin(IV) complex recorded in CDCl_3 are given in experimental section. The expected resonances are assigned by their peak multiplicity, intensity pattern and integration. The integration of spectrum shows good agreement with the composition of the compound.

The ^1H NMR spectral data of the ligand show single resonance at 11.46 ppm, which is absent in the spectrum of the triphenyltin(IV) derivative, indicating the replacement of the carboxylic acid proton by the organotin moiety. In addition, the resonance appearing at 10.03 ppm as a singlet is attributed to the N-H proton and aromatic protons appearing in the expected region as doublets, triplets and multiplets. The splitting due to the coupling of aromatic and heterocyclic protons in almost the same region makes it hard to allocate the proper position to protons. However, heterocyclic protons appear at relatively downfield shift value at the range 7.94-8.44 ppm, while three protons of aromatic ring of ligand appear as doublets and a triplet at 7.16, 7.02 and 6.68 ppm with 3J (^1H , ^1H) 7.5, 7.5 and 7.2 Hz, respectively.

The phenyl groups attached the metal atom come into view as multiplet 7.32-7.84 ppm. In such complex conditions, it is

difficult to indicate the geometry around tin atom in solution state because splitting due to coupling of aromatic protons with each other overlaps the smaller satellites.

^{13}C NMR Spectroscopy

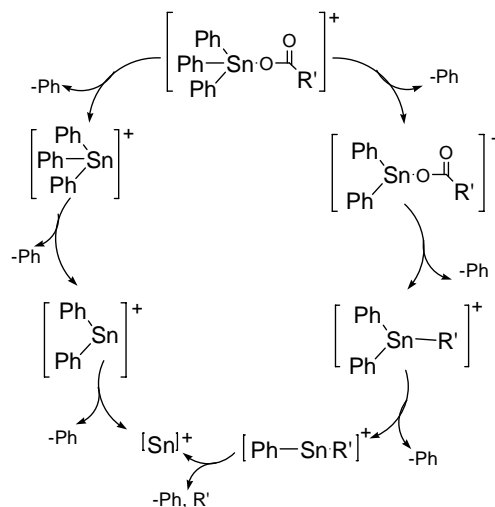
The characteristic resonance peaks in the ^{13}C NMR spectrum of the complex recorded in CDCl_3 are reported in experimental section. The ^{13}C NMR spectral data for the phenyl groups attached to the tin atom were assigned by comparison with related analogues as model compounds [21-22]. The positions of the phenyl carbons of ligands signals undergo a minor variation in the complex as compared to those observed in free acid. The carboxylate carbon does not shift to a very lower field region in the complex, indicating no contribution of the carboxylic group (COO) in coordination to tin(IV). The N-Heterocyclic carbons appear at very downfield shift value at 157.2 and 153.4 ppm due to deshielding by nitrogen atom while all the other carbons of aromatic ring appear at the normal range which makes it very difficult to assign the proper position of each carbon.

The complex pattern of signals in aromatic regions makes it difficult to calculate the magnitude for nJ [^{119}Sn , ^{13}C] coupling value. However, a very slight shift value of carbonyl carbon indicates the monodentate nature of carbonyl group and geometry around tin atom is assumed to be tetrahedral.

Mass Spectrometry

The fragment ions with their m/z (%) values for compound have been already reported in experimental part. As tin has ten naturally occurring isotopes, each ion appears in the mass spectrum as a series of peaks close to each other. However, mass spectrometry may be applied conveniently to the structure elucidation and theoretical interpretation of the organotin compound. It has been observed that large organotin molecules suffer considerable fragmentation in the mass spectrometer, while small organotin molecules often show the molecular ion peaks.

Molecular ion peak is observed for the reported complex. The primary decomposition is due to either loss of phenyl group or ligand, while secondary decomposition is a consequence of loss of either phenyl group or CO_2 molecules [23]. However, the latter is more frequent and probable pathway. Peaks for $[\text{Ph}_3\text{Sn}]^+$, $[\text{Ph}_2\text{Sn}]^+$ and $[\text{PhSn}]^+$ have either



Scheme 3. Fragmentation pattern of Triphenyltin(IV) carboxylates

very low intensities or are absent, thus indicating that fragmentation through these species is not favourable. The general fragmentation pattern proposed for the title compound is given in Scheme 3.

X-Ray Crystallographic Analysis

The crystal data and refinement parameters are shown in Table 1. The solid state structure of the reported compound shows that ligand is coordinated through carbonyl oxygen to tin atom. The bond lengths C1-O1 and C1-O2 are 1.311(2) Å and 1.241(3) Å, respectively, which specify a delocalized bonding at carboxylic group indicating that carbonyl oxygen interacts with tin, making distorted trigonal bipyramidal geometry around tin atom. The bond angles around tin are O1-Sn1-C23 111.21(7), O1-Sn1-C29 107.67(7), C23-Sn1-C17 110.02(8), C29-Sn1-C17 108.70(8) C23-Sn1-C29 120.98(8), O1-Sn1-C17 95.17(7) (°), which show that metal is penta coordinated. This distortion is due to the bulky phenyl groups attached to tin atom as well as bulky ligand acid. Intramolecular hydrogen bonding as well as intermolecular hydrogen bonding by N-H hydrogen is also observed. The selected bond lengths and bond angles are given in Tables 2 and 3.

Table 1. Crystallographic Data and Structure Refinement Parameters for Title Compound

Crystal parameters	Compound
Empirical formula	C ₃₂ H ₂₈ N ₂ O ₂ Sn
Formula weight	591.25
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	
a(Å)	17.0022(8)
b(Å)	9.0793(3)
c(Å)	18.2616(9)
α(°)	90
β(°)	107.381(4)
γ(°)	90
V(Å ³)	2690.3(2) Å ³
Z	4
Crystal size (mm)	0.50 × 0.40 × 0.20
F(000)	1196
Reflections measured	51029
R indices (all data)	R1 = 0.0345, wR2 = 0.0813
Final R indices [I > 2σ(I)]	R1 = 0.0282, wR2 = 0.0788
Goodness-of-fit	1.037
Theta range for data collection (°)	2.30 to 29.24 deg

Table 2. Selected Bond Lengths of Compound

Bond angle	(°)	Bond angle	(°)
O(1)-Sn(1)-C(23)	111.21(7)	C(23)-Sn(1)-C(29)	120.98(8)
O(1)-Sn(1)-C(29)	107.67(7)	O(1)-Sn(1)-C(17)	95.17(7)
C(23)-Sn(1)-C(17)	110.02(8)	C(29)-Sn(1)-C(17)	108.70(8)
C(1)-O(1)-Sn(1)	105.54(13)	O(2)-C(1)-O(1)	119.40(19)
O(2)-C(1)-C(2)	123.95(18)	N(1)-C(5)-C(4)	125.07(19)
C(5)-N(1)-C(6)	118.19(17)	N(1)-C(6)-N(2)	119.36(15)

Table 3. Selected Bond Angles of Compound

Bond length	[Å]	Bond length	[Å]
Sn(1)-O(1)	2.0736(15)	Sn(1)-C(23)	2.114(2)
Sn(1)-C(29)	2.122(2)	Sn(1)-C(17)	2.133(2)
O(1)-C(1)	1.311(2)	O(2)-C(1)	1.241(3)
C(1)-C(2)	1.472(3)	C(2)-C(3)	1.384(3)
N(2)-C(7)	1.410(2)	C(6)-N(20)	1.362(2)
N(1)-C(6)	1.342(2)	N(2)-H(2A)	0.8800

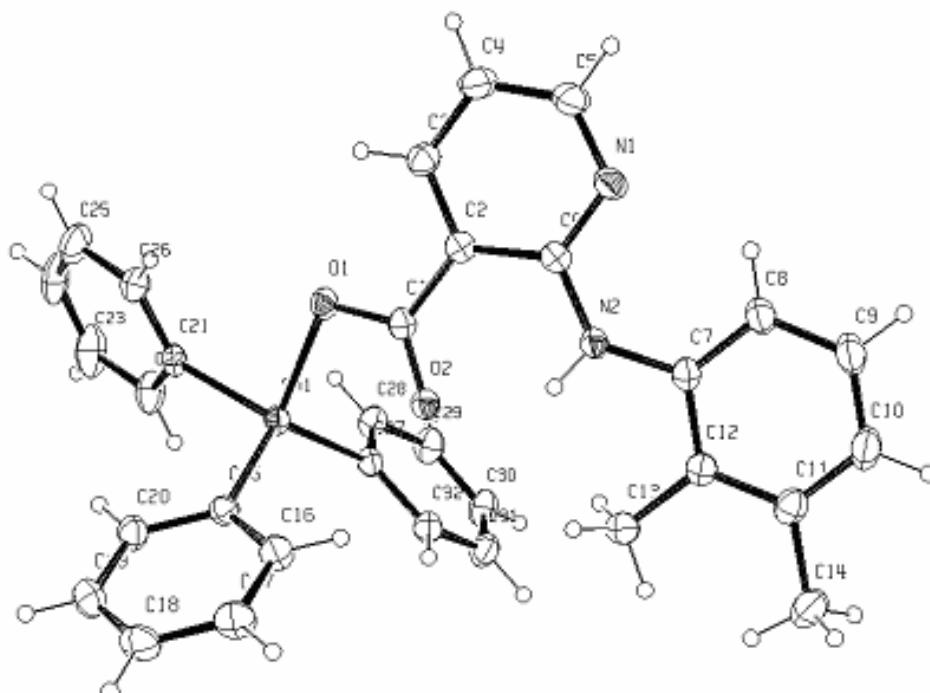


Fig. 1. Ortep drawing of title compound.

CONCLUSIONS

Triphenyltin(IV) [2-(2,3-dimethylanilino)nicotinate] was synthesized, its structure was studied in solid and solution state by using instrumental techniques like, FTIR, multinuclear (^1H , ^{13}C) NMR spectroscopy, mass spectrometry and x-ray analysis. Solid state studies show that geometry around the tin is distorted trigonal bipyramidal while tin is tetra coordinated in solution state.

ACKNOWLEDGMENTS

M. Hussain and M. Hanif are grateful to Higher Education Commission of Pakistan for the financial support [041-212152c-030].

SUPPLEMENTARY MATERIALS

Crystallographic data for the structural analysis has been deposited with Cambridge Crystallographic Data Centre, CCDC Nos. 691272 for title compound. Copies of information

may be obtained free from the Director, CCDC, 12 Union Road, Cambridge, CB2IEZ, UK. Email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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