

Synthesis and Characterization of Some Diorganotin (IV) Complexes of Benzamidoacetic Acid

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Abstract: New diorganotin(IV) complexes of the type Ph_2SnL_2 , Bu_2SnL_2 and Me_2SnL_2 of the ligand benzamidoacetic acid (L_H). Ligand formed by reaction of benzoyl chloride with glycine in presence of sodium hydroxide. The prepared complexes were characterized by elemental analysis, infrared and nuclear magnetic resonance (^1H NMR and ^{13}C NMR). From the spectral measurements, monomer structures for the complexes were proposed. Octahedral geometry was proposed for the complex prepared.

Key words: diorganotin(IV), carboxylates

INTRODUCTION

The interest in organotin compounds in general and organotin carboxylates in particular continues to grow because of their biological activity and potential antineoplastic and antituberculosis agents (Zhang *et al.*, 2007, Tian *et al.*, 2005 and Nathm *et al.*, 2005) PVC stabilizers (Thoonen *et al.*, 2004) and anti-tumour drugs (Tabassum and Pettinari, 2006) as well a polymer catalysts (Angiolini *et al.*, 2006).

Vast studies have been focused on organotin carboxylates and many of them have been characterized recently either by single crystal structure determination or by spectroscopy (Katsoulakou *et al.*, 2008 and Baul *et al.*, 2007) This paper describe the preparation and characterization of organotin(IV) complexes of benzamidoacetic acid.

MATERIALS AND METHODS

Synthesis of Benzamidoacetic Acid:

A one gram of glycine was dissolved in (25ml) of 5% NaOH solution in a conical flask. To this mixture benzoyl chloride (2.25ml) was added in a five portions in (0.49 ml increments) and shaken vigorously until all the chloride has reacted, and the odor of benzoyl chloride has disappeared. Acidified with diluted hydrochloric acid and the crude product was washed with cold ether to remove any benzoic acid which may be present. Finally, the desired product was recrystallized from Ethanol.

Preparation of Complexes:

Complexes were synthesized by dissolving the free ligand (2 mmol) in hot toluene and adding the diorganotin salts (1 mmol) to the solution. The solution was refluxed for 6 hours with magnetic stirrer and then cooled and filtered. The filtrate was reduced under vacuum to a small volume and solid was precipitated by the added of petroleum ether, dried at 60 °C and recrystallized from Ethanol.

Instrumentation:

Elemental C, H and N analysis were carried out on a Fison EA 1108 analyzer, the FTIR spectra in the range (4000-200) cm^{-1} cut were recorded as CsI disc on FTIR.8300 Shimadzu Spectrophotometer, atomic absorption measurements of the prepared complexes were obtained using Shimadzu 680cc-flame.

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The ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a jeol 400 MHz spectrometer in deuterated DMSO, relative to the internal standard tetramethylsilane (TMS). Melting points were recorded on a hot stage Gallen Kamp melting point apparatus.

RESULTS AND DISCUSSION

The ligand was prepared by the reaction of benzoyl chloride with glycine in presence of sodium hydroxide. Table (1) shows the physical data for the ligand and the prepared complexes. The data of CHN and Tin analysis were obtained using flame atomic absorption technique. The calculated values were in a good agreement with the experimental values.

Infra-Red Spectroscopy:

The FTIR spectrum of the ligand, shows a characteristic stretching absorption bands at 3779 cm^{-1} , 3341 cm^{-1} , 1759 cm^{-1} , 1029 cm^{-1} and 849 cm^{-1} assigned to hydroxyl, N-H, carbonyl, C-O and C-H of the aliphatic group respectively

The reaction between this ligand with Diorganotin (IV) gave different types of complexes. In the free ligand, the bands at 1759 cm^{-1} and 1029 cm^{-1} were assigned to the stretching of C=O and C-O of the hydroxyl in the carboxylate group. On complexation these bands were shifted to a lower frequency region (Masood *et al.*, 2004).

This shift is probably due to the complexation of the metal to the ligand through oxygen of the carbonyl group, the disappearance of the hydrogen from hydroxyl group on complexation indicate the complexation is through the oxygen atom.

The bands for $\nu(\text{Sn-C})$ and $\nu(\text{Sn-O})$ are assigned in the range of (545-547) and (446-465) cm^{-1} respectively (Shahid *et al.*, 2002).

The IR data of the complexes are shown in Table (2). The Table lists the stretching frequency ν for some of the characteristics groups exhibited by the ligand and complexes.

Table 1: Physical data for preparation ligand and the complexes prepared.

compound	Color	%Yield	M.P, °C	Found (Calcd.)%			
				C	H	N	Sn
L _H	White	83	188-189	60.31(60.33)	4.87(5.06)	6.86(7.82)	-
Ph ₂ SnL ₂	White	77	140-141	57.84(57.26)	4.33(4.16)	4.23(4.45)	18.98(18.78)
Bu ₂ SnL ₂	White	85	110-112	51.85(52.99)	5.81(5.82)	4.86(4.75)	20.42(20.15)
Me ₂ SnL ₂	White	87	101-103	47.44(47.56)	4.45(4.39)	5.29(5.55)	24.11(23.50)

Table 2: Characteristic absorption bands of benzamidoacetic acid and its complexes

compound	O-H	N-H	C=O	C-O	C-H aliphatic	C-H aromatic	Sn-C	Sn-O
L _H	3779	3341	1759	1029	849	3072	-	-
Ph ₂ SnL ₂	-	3340	1759	1029	850	3071	545	446
Bu ₂ SnL ₂	-	3340	1760	1028	847	3069	547	483
Me ₂ SnL ₂	-	3343	1742	1027	848	3071	546	465

Table 3: ^1H NMR spectral data (δ ,ppm) of the ligand and complexes

compound	O-H	N-H	C-H aromatic	C-H ₂ aliphatic
L _H	9.54	8.89	7.47-7.89	3.95
Ph ₂ SnL ₂	-	8.69	7.46-7.88	3.85
Bu ₂ SnL ₂	-	8.67	7.45-7.87	3.83
Me ₂ SnL ₂	-	8.85	7.39-7.85	8.84

Table 4: ^{13}C NMR spectral data (δ ,ppm) of the ligand and complexes

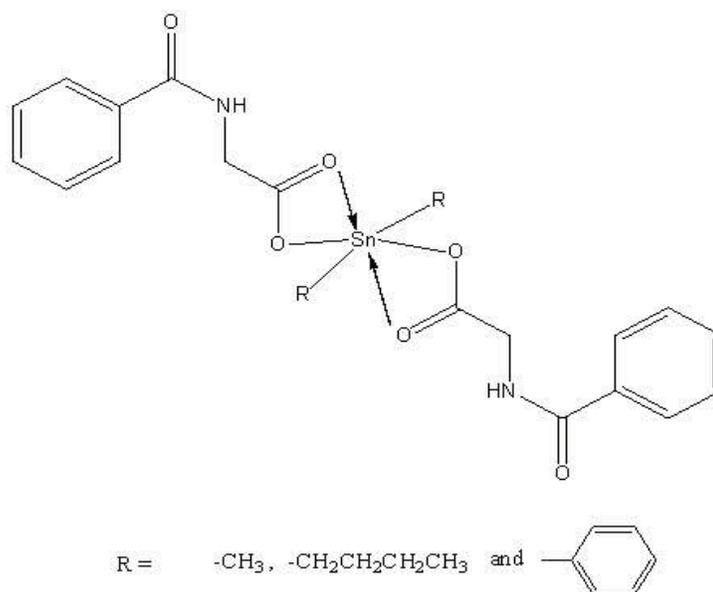
compound	C=O amide	C=O acid	C-H aromatic	C-H ₂ aliphatic
L _H	167.58	171.58	121.41-131.63	41.44
Ph ₂ SnL ₂	167.55	158.46	127.15-134.24	42.07
Bu ₂ SnL ₂	167.57	158.53	127.43-132.32	42.11
Me ₂ SnL ₂	167.57	159.64	126.99-133.65	42.34

NMR Spectroscopy:

The ^1H NMR spectra for all compounds were recorded in $[\text{D}_2\text{O}]^6$ DMSO using tetramethylsilane as the internal standard. The data are compiled in Table 3. The conclusion drawn from ^1H NMR studies of a few compounds lend further support to suggested formation of benzamidoacetic acid chelate. Ligand (L_H) give a single resonance near δ 8.89 ppm attributable to the N-H proton. The spectra also exhibit a singlet -OH peaks at 8.88 ppm due to hydroxy group. The hydroxy resonances is absent in the spectra of the complexes indicating deprotonation and coordination of Tin to the oxygen. There is a small upfield shift of the aromatic protons resonances of the ligand upon chelation with the diorganotin (IV) moiety (Shahid *et al.*, 2002). The complexes Ph_2SnL_2 , Bu_2SnL_2 and Me_2SnL_2 Show additional signals at δ (1.02), (1.18 and 1.20) and (4.43) due to protons of alkyl, butyl and phenyl groups, respectively.

Table 4 shows the most relevant ^{13}C NMR data. Due to scant solubility of the ligand and its complexes in the CDCl_3 , their spectra were recorded in $[\text{D}_2\text{O}]^6$ DMSO. The C=O resonance group of the complexes at (158.46-159.64) ppm were shifted downfield compared with the position in the free ligand which appeared at 171.58 ppm. It is most likely that shift is due to the decrease of electron density at carbon atoms when oxygen is bonded to metal ion (Masood *et al.*, 2004). This observation lends further evidence that the complexation occurred through the oxygen atoms of the carboxylate group.

On the basis of the preceding discussion, the structure of the complexes suggested as follows:

**Conclusion:**

The ligand benzamidoacetic acid was successfully synthesized. The ligand was treated to different diorganotin (IV) oxide metal salts to afford the corresponding complexes. It may be concluded that the ligand coordinated through carboxylate to the Tin atom leading to the formation of four member ring chelate. Tetrahedral geometry was proposed for the prepared complexes.

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