



SYNTHESIS AND CHARACTERIZATION OF SOME Diorganotin(IV) COMPLEXES OF *N*-Tolyl- *m*-Nitrobenzohydroxamic 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 *N*-tolyl *m*-Nitrobenzohydroxamic acid. Ligand formed by condensation reaction of 3-Nitrobenzoyl chloride with *N*-tolyl hydroxylamine in presence of sodium hydrogen carbonate as a catalyst. The prepared complexes were characterized by FTIR Spectroscopy, electronic spectroscopy, ^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.

Keywords: characterization, diorganotin(IV) complexes, hydroxamic acid.

INTRODUCTION

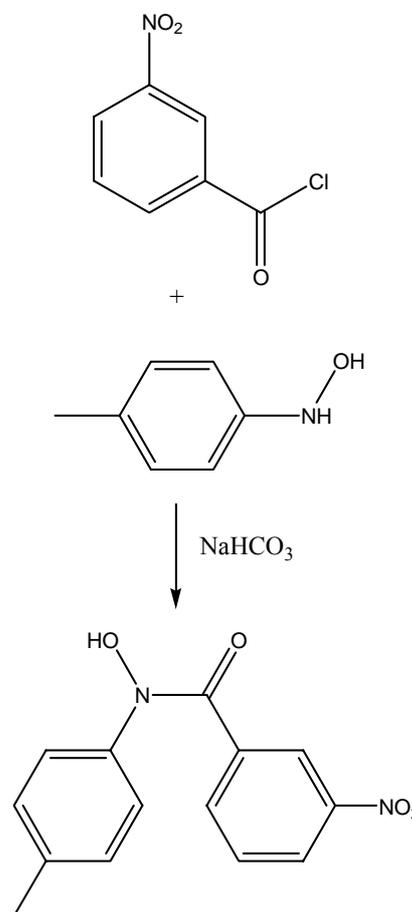
Hydroxamic acids constitute a very important class of chelating agents with versatile biological activity [1,2]. The research on their coordination properties is mostly oriented towards modeling the biological function such as microbial transportation products [2] and inhibition of urease activity [3], although they also have been extensively used as detectors for many metal ions in analytical chemistry [4]. In particular, arylhydroxamic acids are nucleoside reductase inhibitors and thus exhibit some antitumor activity [5].

Organotin(IV) compounds have attracted much attention owing to their potential biocidal activities[6,7] as well as industrial and agricultural applications [8]. In general, the biochemical activity of organotin compounds is influenced greatly by the structure of the molecule and the coordination number of the tin atoms [9,10].

As part of our on-going interest in the synthesis of organotin(IV) compounds, we prepared a new ligand *N*-tolyl *m*-Nitrobenzohydroxamic acid (L_H) and its organotin(IV) compounds-Diphenyltin(IV) Bis (*N*-tolyl *m*-Nitro benzohydroxamate) (Ph_2SnL_2), Dibutyltin (IV) Bis (*N*-tolyl *m*-Nitro benzohydroxamate) (Bu_2SnL_2) and Dimethyltin(IV) Bis (*N*-tolyl *m*-Nitro benzohydroxamate) (Me_2SnL_2).

MATERIALS AND METHODS

Synthesis of *N*-tolyl *m*-Nitrobenzohydroxamic acid 3- Nitro benzoyl chloride (0.01 mole) dissolved in ether was added to *N*-tolyl hydroxylamine (0.01 mole) dissolved in ether in the presence of sodium hydrogen carbonate (0.01 mole). The reaction was carried out in an ice-bath. The solid that formed on removal of the solvent was extracted with ethyl acetate (10 ml). The solution yield formed after being set aside and cooled. The steps of the synthesis of *N*-tolyl *m*-Nitrobenzohydroxamic acid can be shown as follows:



Preparation of complexes

Complexes were synthesized by dissolving the free ligand (5 mmol) in hot toluene and adding the tin (2.5 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 (60-80°C).



Instrumentation

The percentage composition of the elements (CHN) for the compounds was determined using an elemental analyzer CHNS Model Fison EA 1108 by using sulphoylamide as a standard. The infrared spectra were recorded as potassium bromide discs using a Perkin-Elmer spectrophotometer GX. The ^1H and ^{13}C nuclear magnetic resonance spectra were recorded using the JEOL JNM-ECP 400 spectrometer.

RESULTS AND DISCUSSIONS

The ligand was prepared by the reaction of 3-Nitrobenzoyl chloride with one mole *N*-tolyl hydroxylamine in the presence of sodium hydrogen carbonate as a catalyst. The purity of the ligand and its complexes were checked by TLC using silica gel-G as adsorbent. Their physical properties and analytical data are recorded in Table-1. The calculated values were in a good agreement with the experimental values.

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	Yellow	85	137-139	61.76 (60.89)	4.44 (4.69)	10.29 (10.24)	-
Ph_2SnL_2	White	77	142-144	52.32 (52.12)	4.56 (4.30)	9.74 (9.03)	14.01 (15.11)
Bu_2SnL_2	White	91	189-191	55.76 (55.59)	5.20 (6.13)	7.23 (7.09)	15.31 (15.27)
Me_2SnL_2	White	79	122-124	52.12 (53.09)	4.08 (4.77)	8.10 (7.82)	17.17 (17.95)

Infra-red spectroscopy

Solid state infrared spectra of the *N*-tolyl *m*-Nitrobenzohydroxamic acid are recorded in the range 4000-370 cm^{-1} and the most important bands are presented in the below table studied here. In agreement for diagnostic purpose, the principal infrared absorption bands are those due to O-H, C=O, C-N and N-O stretching vibrations of the hydroxamate group free hydroxamic acids have been shown to exist principally in the keto form. In compound (C=O) group is positioned at 1688 cm^{-1} significantly, below the typical ketonic (C=O) of 1613 cm^{-1} . The (O-H) band is located at 3435 cm^{-1} as broad band. The presence of the carbonyl band at lower frequency where together with the broad OH band. In general, the (C-N) and (N-O) bands occur as a sharp peak in the ranges 1448, 913 cm^{-1} respectively [11].

On complexation, there are clear differences between the infrared spectra of the free ligand and the diorganotin(IV) complexes. In all cases, the most important features of the infrared spectra are the absence of the (OH) bands due to the complexation of the metal to the ligand through oxygen of the carbonyl group. This suggests the deprotonation of the hydroxamate group on complex formation, and (C=O) group are shifted to lower frequencies in the range 1688-1613 cm^{-1} in there respective diorganotin (IV) complexes.

The bands for $\nu(\text{Sn-C})$ and $\nu(\text{Sn-O})$ are assigned in the range of (509-512) and (420-446), respectively[12].

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-2. Infrared spectral data for the ligand and its complexes.

Compound	$\nu(\text{O-H}) \text{ cm}^{-1}$	$\nu(\text{C=O}) \text{ cm}^{-1}$	$\nu(\text{C-N}) \text{ cm}^{-2}$	$\nu(\text{N-O}) \text{ cm}^{-3}$	$\nu(\text{Sn-C}) \text{ cm}^{-3}$	$\nu(\text{Sn-O}) \text{ cm}^{-1}$
L_H	3435	1688	1448	913	-	-
Ph_2SnL_2	-	1633	1527	909	509	446
Bu_2SnL_2	-	1613	1531	906	512	420
Me_2SnL_2	-					

NMR spectroscopy

The ^1H NMR spectra for all compounds were recorded in [$^2\text{H}_6$] DMSO using tetramethylsilane as the internal standard. The data is compiled in Table-3. The conclusion drawn from ^1H NMR studies of a few compounds lend further support to suggested formation of *N*-Tolyl-*m*-Nitrobenzohydroxamic Acid. Ligand (L_H) gives a single resonance near δ 8.89 ppm attributable to the CH_3 proton. The spectra also exhibit a singlet -OH

peaks at 9.02 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 [14]. 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 (3.74) due to protons of alkyl, butyl and phenyl groups, respectively[11].

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

Compound	-O(1)H	Aromatic	-O-C(3)H	Ph-C(3)H
L_H	9.02	7.26-8.51	2.34	0.86
Ph_2SnL_2	-	7.20-8.61	2.30	0.77
Bu_2SnL_2	-	6.67-8.75	2.23	.83
Me_2SnL_2	-	6.65-8.59	2.49	0.84

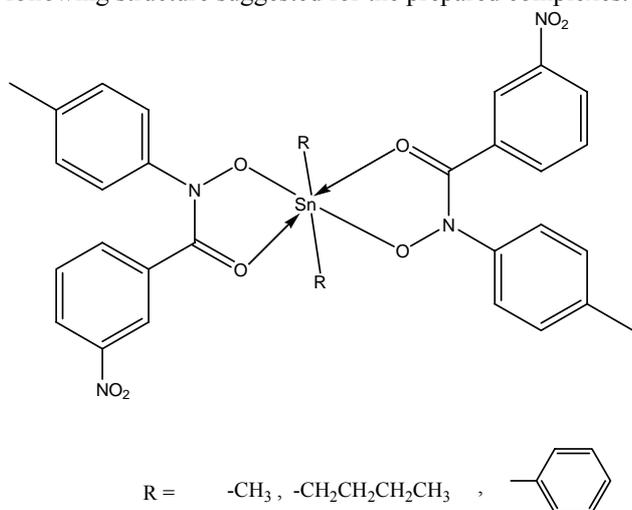
The ^{13}C NMR of the ligand and its complexes are presented in Table-4. The C=O resonance group of the complexes at (158.46-159.64) ppm where shifted downfield compared with the position in the free ligand

which appeared at 196.51 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 [12].

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

Compound	C=O	Aromatic	Aliphatic
L_H	159.21		76.24-55.32
Ph_2SnL_2	165.63	123.10-147.95	20.63
Bu_2SnL_2	130.44	126.40-130.44	20.74
Me_2SnL_2			

On the basis of the observed spectral evidence, the following structure suggested for the prepared complexes.



CONCLUSIONS

The ligand N-tolyl m-Nitrobenzohydroxamic 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 oxygen to the Tin atom leading to the formation of five membered ring chelate. Octahedral geometry was proposed for the prepared complexes.

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