

## Synthesis and Structure of Some Diorganotin(IV) with *N*-methyl-*m*-nitrobenzohydroxamic Acid

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**Abstract:** Complexes of the type  $R_2SnL_2$ , where R = phenyl, butyl and methyl and  $L_H = N$ -methyl-*m*-nitrobenzohydroxamic acid, have been synthesized and characterized by physico-chemical (elemental analysis, and electrolytic conductance) and spectral (UV-Visible, IR and  $^1H$  and  $^{13}C$  and  $^{119}Sn$  NMR) techniques. Monomer structures for the complexes, bidentate and Octahedral geometry was proposed for the complexes prepared.

**Key words:** *N*- methyl *m*-nitrobenzohydroxamic acid, Diorganotin(IV) Complexes, spectral studies.

### INTRODUCTION

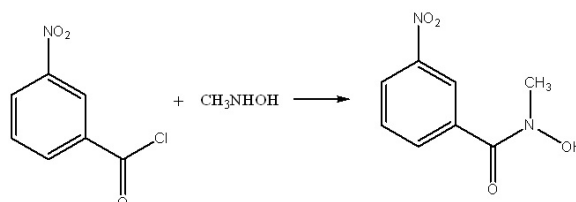
Tin(IV) and organotin(IV) compounds, a deceptively simple area of inorganic and metal-organic chemistry, have been receiving more attention due to the important industrial (Tammy and Georges, 2005) and environmental applications. Nitrogen, oxygen, and sulfur donor ligands have been used to enhance the biological activity of organotin derivatives (Mohammad *et al.*, 2004; Jason *et al.*, 2000). Also organotin compounds with such ligands have widely been tested for their possible use in cancer chemotherapy (Shang *et al.* 2008; Zhou *et al.* 2005). The coordination chemistry of tin is extensive with various geometries and coordination numbers known for both inorganic and organometallic complexes (Katsoulakou *et al.* 2008; Baul *et al.*, 2007). Hydroxamic acids constitute a very important class of chelating agents with versatile biological activity (Farkas *et al.* 2002; Wang *et al.* 2003).

In view of the diverse fields of applications of organotin complexes, we have synthesized new ligand *N*-methyl - *m*-nitrobenzohydroxamate( $L_H$ ) and its organotin (IV) complexes Diphenyltin(IV) Bis( *N*- methyl *m*-nitrobenzohydroxamate) ( $Ph_2SnL_2$ ), Dibutyltin (IV) Bis( *N*- methyl *m*- nitrobenzohydroxamate) ( $Bu_2SnL_2$ ) and Dimethyltin (IV) Bis( *N*- methyl *m*-nitrobenzohydroxamate) ( $Me_2SnL_2$ ).

### MATERIALS AND METHODS

#### *Synthesis of N-methyl M-nitrobenzohydroxamic Acid:*

3- nitrobenzoyl chloride (0.01 mole) dissolved in ether was added to *N*- methyl hydroxylamine (0.01 mole) dissolved in ether in 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*- methyl *m*-nitrobenzohydroxamic acid can be shown in below.



#### *Preparation of Complexes:*

Complexes were synthesized by dissolving the free ligand (5 mmol) in hot toluene and adding the organotin(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).

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**Instrumentation:**

The percentage compositions of the elements (CHN) for the compounds were determined using an elemental analyzer CHNS Model Fison EA 1108. Molar conductance measurements were made in anhydrous DMF at 25 °C using Inolop-Cond Level 1 WTW, The infrared spectra were recorded as potassium bromide discs using a Perkin-Elmer spectrophotometer GX. The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectra were recorded using the JEOL JNM-ECP 400 spectrometer. And for ultraviolet using Shimadzu-UV-Vis spectrophotometer UV -2450, DMSO used as solvent.

**RESULTS AND DISCUSSION**

The ligand was prepared by the reaction of 3-nitrobenzoyl chloride with one mole *N*-methyl *m*-hydroxylamine in 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. The conductance of these complexes has been recorded in DMF at room temperature in the range 11-18 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, suggesting their non-electrolytic nature. 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 <sub>H</sub>	Yellow	77	165-166	49.25 (48.98 )	4.12 (4.11)	14.32 14.28	-
Ph <sub>2</sub> SnL <sub>2</sub>	Yellow	88	173-174	50.44 (50.71)	3.77 (3.65)	8.39 (8.45)	18.11 (17.90)
Bu <sub>2</sub> SnL <sub>2</sub>	Yellow pale	79	156-157	46.23 (46.25)	5.22 (5.18)	8.78 (8.99)	20.11 (19.05)
Me <sub>2</sub> SnL <sub>2</sub>	Yellow	89	182-183	49.11 (49.10)	3.55 (3.74)	10.33 (10.39)	22.09 (22.02)

**Infra-Red Spectroscopy:**

Solid state infrared spectra of the *N*-methyl *m*-nitrobenzohydroxamic acid are recorded in the range 4000-370 cm<sup>-1</sup> 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 -OH, 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 1638cm<sup>-1</sup> significantly, below the typical ketonic (C=O) of 1600 cm<sup>-1</sup>. The (O-H) band is located at 3163 cm<sup>-1</sup> 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 1431, 934cm<sup>-1</sup> respectively (Shahid *et al.*2002).

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 1618-1604 cm<sup>-1</sup> in there respective diorganotin (IV) complexes. The bands for  $\nu$ (Sn-C) and  $\nu$ (Sn-O) are assigned in the range of (519-522) and (411-446) cm<sup>-1</sup> respectively (Saad *et al.* 2003). The IR data of the complexes are shown in Table (2). The Table lists the stretching frequency ( $\nu$ ) for some of the characteristics groups exhibited by the ligand and complexes. Major bands in the electronic spectra of the ligand and their tin(IV) complexes also are given in Table (2). The spectrum of the ligand exhibit a band at 264 nm attributable to the intra-ligand  $\pi$ - $\pi^*$ . This band shift to shorter wavelengths in the spectra of tin complexes.

**Table 2:** Infrared Spectral Data for the ligand and its complexes

Compound	$\nu$ (O-H) cm <sup>-1</sup>	$\nu$ (C=O) cm <sup>-1</sup>	$\nu$ (C-N) cm <sup>-1</sup>	$\nu$ (N-O) cm <sup>-1</sup>	$\nu$ (Sn-C) cm <sup>-1</sup>	$\nu$ (Sn-O) cm <sup>-1</sup>	UV ( $\lambda$ )
LH	3163	1728	1431	920	-	-	264
Ph <sub>2</sub> SnL <sub>2</sub>	-	1709	1393	920	519	420	265
Bu <sub>2</sub> SnL <sub>2</sub>	-	1726	1427	910	519	411	265
Me <sub>2</sub> SnL <sub>2</sub>	-	1720	1418	921	522	446	263

**Nuclear Magnetic Spectroscopy:**

The  $^1\text{H}$ 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  $^1\text{H}$ NMR studies of a few compounds lend further support to suggested formation of *N*-methyl-*m*-nitrobenzohydroxamic acid. Ligand ( $\text{L}_\text{H}$ ) give a singlet -OH resonance near  $\delta$  11.39 ppm. The hydroxy resonance 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. The complexes  $\text{Ph}_2\text{SnL}_2$ ,  $\text{Bu}_2\text{SnL}_2$  and  $\text{Me}_2\text{SnL}_2$  Show additional signals. The methyltin ( $\text{Sn-CH}_3$ ) occurs at 1.36, 1.34 and 1.32 ppm as on the sharp singlet at integrates for the protons accompanied by satellites due to the  $^1\text{H}$ - $^{119}\text{Sn}$  coupling that corresponds to the hydrogen atom of the methyl protons of the  $\text{Me-Sn}$  for the  $\text{Me}_2\text{SnL}_2$ . In dibutyltin(IV) complex the butyl protons appear as a multiple and a triplet in the range 1.53-0.70 ppm due to  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  group. The aromatic protons in  $\text{Ph-Sn}$  appear in the 7.19-7.97 ppm (Shahid *et al.* 2002).

**Table 3:**  $^1\text{H}$ NMR spectral data ( $\delta$ ,ppm) of the ligand and complexes

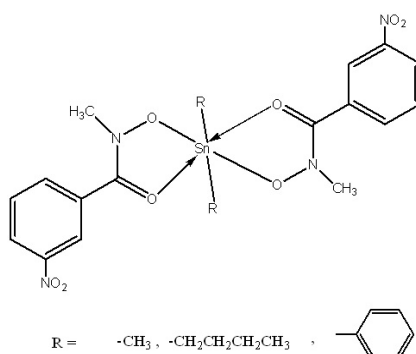
compound	-O(1)H	Aromatic	N-CH3(S)
$\text{L}_\text{H}$	11.39	7.78-7.60	1.27
$\text{Ph}_2\text{SnL}_2$	-	7.54-8.75	0.82
$\text{Bu}_2\text{SnL}_2$	-	7.75-8.62	0.79
$\text{Me}_2\text{SnL}_2$	-	7.77-8.60	0.96

The  $^{13}\text{C}$ NMR of the ligand and its complexes are presented in Table (6). The C=O resonance group of the complexes at (159.27-165.65) ppm where shifted downfield compared with the position in the free ligand which appeared at 171.17 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 (Saad *et al.* 2003).

**Table 4:**  $^{13}\text{C}$ NMR spectral data ( $\delta$ ,ppm) of the ligand and complexes

compound	C=O	aromatic	N-CH3
$\text{L}_\text{H}$	165.65	123.56-135.44	39.50
$\text{Ph}_2\text{SnL}_2$	165.61	123.7-147.80	39.49
$\text{Bu}_2\text{SnL}_2$	147.91	123.5-135.70	39.50
$\text{Me}_2\text{SnL}_2$	147.82	123.7-135.20	39.47

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

**Conclusion:**

The ligand *N*-methyl-*m*-nitrobenzohydroxamic acid was successfully synthesized. The ligand was treated to different diorganotin(IV) oxide metal to afford the corresponding complexes. It may conclude that the ligand coordinated through oxygen to the Tin atom leading to the formation of five member ring chelate. Octahedral geometry was proposed for the prepared complexes.

**REFERENCES**

Baul, T., C. Masharing, G. Ruisi, R. Jira'sko, M. Holcapek, D. De-Vos, D. Wolstenholme and A. Linden, 2007. "Self-assembly of extended Schiff base amino acetate skeletons, 2- $\{[(2Z)$ -(3-hydroxy-1-methyl-2-butenylidene)]amino $\}$ phenylpropionate and 2- $\{[(E)$ -1-(2-hydroxyaryl) alkylidene] amino $\}$  phenylpropionate skeletons incorporating organotin(IV) moieties: Synthesis, spectroscopic characterization, crystal structures, and in vitro cytotoxic activity", *Journal of Organometallic Chemistry*, 692: 4849-4862.

Farkas, E., H. Csoka, S. Gama and M. Santos, 2002. "Dihydroxamate based siderophore model, piperazine-1,4-bis-(N-methyl-acetohydroxamic acid (PIPDMAHA), as a chelating agent of molybdenum(VI)", *Talanta*, 57: 935–943.

Katsoulakou, E., M. Tiliakos, G. Papaefstathiou, A. Terzis, C. Raptopoulou, G. Geromichalos, K. Papazisis, R. Papi, A. Pantazaki, D. Kyriakidis, P. Cordopatis and E. Zoupa, 2008. Diorganotin(IV) complexes of dipeptides containing the  $\alpha$ -aminoisobutyryl residue (Aib): Preparation, structural characterization, antibacterial and antiproliferative activities of n-Bu) $_2$ Sn(H<sub>1</sub>L)] (LH = H-Aib-L-Leu-OH, H-Aib-L-Ala-OH). *Journal of Inorganic Biochemistry*, 102: 1397–1405.

Jason, H., C. Kieran and R. Pratt, 2000. "Inhibition of Serine Amidohydrolases by Complexes of Vanadate with Hydroxamic Acids". *Biochemical and Biophysical Res. Communications*, 274: 732–735.

Mohammad, M., S. Khadija, M. Sohail, A. Saqib and B. Moazzam, 2004. "Synthesis, Spectral Characterization and Biological Applications of Tri- and Diorganotin(IV) Derivatives of 2-[N-(2,6-Dichloro-3-methylphenyl)amino]benzoic acid". *Turkish Journal of Chemistry*, 28: 17- 26.

Saad, E., Y. Farina, I. Baba and H. Othman, 2003. "Synthesis and Characterization of Some Diorganotin bis(N-methyl O-nitrobenzohydroxamate)", *Sains Malaysiana*, 32: 79-86.

Shang, X., J. Cui, J. Wub, A. Pombeiro and Q. Li, 2008. "Polynuclear diorganotin(IV) complexes with arylhydroxamates: Syntheses, structures and in vitro cytotoxic activities", *Journal of Inorganic Biochemistry*, 102: 901–909.

Shahid, S., S. Ali, M. Hussain, M. Mazhar, Mahmood S. and S., Rehman. 2002. "Synthesis, Characterization and Thermal Analysis of Organotin(IV) Derivatives of 4-(N-Maleoyl)Butanoate". *Turkish Journal of Chemistry*, 26: 589–597.

Tammy, L. and M. Georges, 2005. "New applications of LC–MS and LC–MS2 toward understanding the environmental fat of organometallics", *Trends in Analytical Chemistry*, 24: 7-12.

Wang, W., N. Ryder, B. Weidmann, D. Patel, J. Trias, R. Whitea and Z. Yuana, 2003. "Substituted Hydroxamic Acids as Novel Bacterial Deformylase Inhibitor-Based Antibacterial Agents", *Bioorganic & Medicinal Chemistry Letters*, 13: 4223–4228.

Zhou, Y.T., S. Ren, J. Yu and Z. Xia, 2005. "Synthesis, crystal structure and in vitro antitumor activity of di-n-butyltin 40-(7-oxabicyclo [2,2,1]-5-heptane-2,3-dicarboximide)benzoates", *Journal of Organometallic Chemistry*, 69: 2186–2190.