

Organotin complexes of succinyl bis-N-phenylhydroxamic acid

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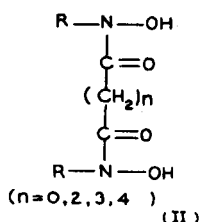
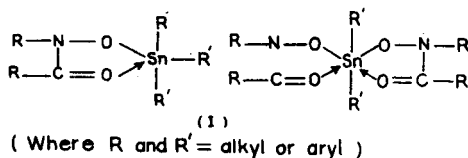
Succinyl bis-N-phenylhydroxamic acid (L) produces new organotin complexes of the types $[\text{Ph}_2\text{SnL}]$, $[(\text{Cyclohexyl})_3\text{Sn}]_2\text{L}$ and $[\text{Me}_2\text{ClSn}]_2\text{L}$ which have been characterised on the basis of elemental analyses, IR and NMR (^1H , ^{13}C and ^{119}Sn) spectral data. The spectral and analytical data indicate that in $[\text{Ph}_2\text{SnL}]$, the ligand is tetradentate, whereas in $[(\text{Cyclohexyl})_3\text{Sn}]_2\text{L}$ and $[\text{Me}_2\text{ClSn}]_2\text{L}$, the ligand is bidentate in nature.

Hydroxamic acid obtained from monobasic acid chloride and substituted hydroxylamine has proved to be an excellent bidentate ligand for organotin moieties (Structure I).

A number of such complexes have been reported during the last decades¹⁻⁸. But hydroxamic acid obtained from dibasic acid chlorides, viz., oxalyl chloride and succinyl chloride may potentially behave as a tetradentate ligand (Structure II).

Recently two hydroxamic acids viz. oxalyl bis-N-phenyl and oxalyl bis-N-p-tolyl hydroxamic acids have been prepared and their organotin derivatives have been reported by us⁹.

Succinyl bis-N-phenylhydroxamic acid has been reported to act as a tetradentate ligand for certain metal ions possibly due to lengthening of the chain between hydroxamic acid residues. A few reports¹¹ have appeared for the preparation of some new organotin compounds of this ligand to show the tetradentate nature of succinyl bis-N-phenylhydroxamic acid. In this note, we report the



preparation and characterization of a few organotin hydroxamates where both bidentate and tetradentate nature of the ligand has been discussed.

Experimental

Succinyl bis-N-phenylhydroxamic acid (LH_2) was prepared by the literature method¹⁰. All solvents were purified and dried.

Tin was estimated gravimetrically by following the method of van der Kerk and Luijten¹². The elemental analyses was carried out at RSIC, CDRI, Lucknow.

The UV spectra were recorded in spectral grade methanol using Shimadzu UV 240 Spectrophotometer. The infrared spectra was measured in the range $4000\text{--}5000\text{ cm}^{-1}$ using Beckman IR 20 and Pye Unicam SP 300S infrared spectrophotometer in nujol.

The ^1H and ^{13}C NMR spectra of succinyl bis N-phenylhydroxamic acid were recorded in d_6 DMSO through the courtesy of Dr. D J Greenslade with Bruker WP 80 SY multinuclear 80 MHz FT NMR and JEOL PMX SI CW ^1H Spectrophotometers at the University of Essex, Colchester, UK. The NMR spectra were recorded in CDCl_3 against TMS while ^{119}Sn shifts were recorded against tetramethyl tin.

Preparation of complexes

The complexes were prepared by refluxing the organotin oxides/chlorides and the hydroxamic acid in benzene. Water liberated was removed azeotropically. In case of chlorides, the HCl liberated was neutralised by NH_3 . Two typical preparations are described as follows:

Dibutyl tin succinyl bis-N-phenylhydroxamate

Dibutyl tin oxide (850 mg) and succinyl bis-N-phenylhydroxamic acid (500 mg) were taken in 100 ml benzene and refluxed for 6 h using a Dean and Stark Water Separator. The solution was filtered and concentrated on a steam bath to 10 ml and methanol (5 ml) was added. On cooling the solution overnight, shining white crystals appeared from the benzene-methanol mixture. The compound was purified by repeated crystallisation from the same solvent (m.p. 174°C ; yield $\sim 60\%$).

bis(Dimethyl chlorotin) succinyl bis-N-phenylhydroxamate

Dimethyl tin chloride (750 mg) and succinyl

bis-N-phenylhydroxamic acid (500 mg) were taken in 100 ml benzene and 4-5 drops of conc. NH_4OH were added and the resulting NH_4Cl was filtered. The filtrate was refluxed for 6 h. The refluxed solution after filtration was concentrated over a steam bath to about 10 ml and petroleum ether (60-80°) added to precipitate the compound and purified from chloroform-methanol mixture (m.p. 202°; yield ~40%).

Results and discussion

The analytical data of the organotin complexes are presented in Table 1.

The IR spectrum of succinyl bis-N-phenylhydroxamic acid showed a strong absorption $\sim 3130 \text{ cm}^{-1}$ due to the presence of hydrogen bonded hydroxyl group. The intense band at 1618 cm^{-1} is due to carbonyl stretching frequency. The N-O stretching frequency appeared at 915 cm^{-1} . In addition, the usual bands for other constituent parts of the ligand were obtained at expected wavenumber.

In organotin hydroxamates, the νOH frequency of hydroxamic acid was absent indicating the replacement of the hydrogen by organotin moieties. Moreover, the $\nu\text{C}=\text{O}$ frequencies are further lowered due to coordination of the carbonyl group to tin atom. The carbonyl frequencies are observed in the range $1555-1590 \text{ cm}^{-1}$. The $\nu\text{N}-\text{O}$ frequency in organotin derivatives were indicated at $920-960 \text{ cm}^{-1}$. In all organotin derivatives, a medium to strong band appeared at $1000-1040 \text{ cm}^{-1}$, which may be attributed to $\text{Sn}-\text{O}-\text{C}$ frequencies. There were two new bands in the range $490-600 \text{ cm}^{-1}$ for all

organotin compounds as compared to the ligand. The $\nu\text{Sn}-\text{C}$ bands usually appeared at $490-530 \text{ cm}^{-1}$ and the other band $540-600 \text{ cm}^{-1}$ is due to $\nu\text{Sn}-\text{O}$ frequencies.

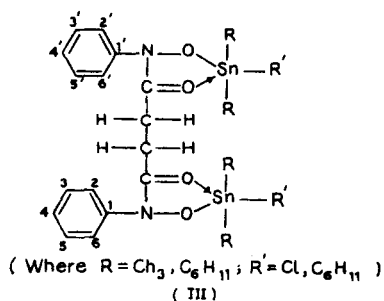
The ^1H NMR spectrum of succinyl bis-N-phenylhydroxamic acid in d_6 DMSO gave methylene protons at δ 2.90 (singlet), aromatic protons in between δ 6.95-7.70 (multiplet) and hydroxyl protons at δ 10.6 (singlet). In all organotin derivatives, the hydroxyl protons were found to be absent. In some organotin derivatives, the ligand methylene protons appeared as two distinct doublets as in dibutyl tin derivatives (δ 2.24 and 2.64), diphenyl tin derivative (δ 2.25 and 3.00) and dibenzyl tin derivatives (δ 1.83 and 2.62). In all these cases, $J_{\text{H}_A-\text{H}_A}$ and $J_{\text{H}_B-\text{H}_B}$ were found to be 14 Hz. The splitting of methylene protons compared to ligand is due to chelation with organotin moieties, which resulted in a somewhat rigid structure. The H_A protons are closer to tin atom while the H_B protons are away from tin atom. Both methylene peaks in these derivatives were highly symmetrical, though associated with smaller peaks due to long range couplings. In dibenzyl tin derivatives, the benzyl methylene protons gave two peaks at δ 2.42 ($J=11$ Hz) and δ 2.52 ($J=11$ Hz). In dibutyl tin derivative, the methyl protons appeared at δ 0.84 (triplet) and the methylene protons attached to tin appeared at δ 0.96-1.14, 1.26-1.36 and 1.45-1.60. Compared to dibutyl tin dichloride, all aliphatic protons were found shielded in nature¹³.

In case of bis-dimethyl chloro tin succinyl bis-N-phenylhydroxamate and bis tricyclohexyl ligand, methylene protons gave a singlet peak at δ 2.6

Table 1—Analytical data of the organotin derivatives

Reactants	Compound (Yield %)	M.Pt (°C)	Found (Calc.), %			
			C	H	N	Sn
$\text{LH}_2 + \text{Bu}_2\text{SnO}$	Bu_2SnL (60)	174	54.37	5.77	5.90	22.80
			(54.28)	(6.02)	(5.27)	(22.41)
$\text{LH}_2 + (\text{Bz}_3\text{Sn})_2\text{O}$	Bz_3SnL (50)	238	61.11	4.60	4.70	19.29
			(60.10)	(4.67)	(4.57)	(19.36)
$\text{LH}_2 + \text{Ph}_2\text{SnO}$	Ph_2SnL (60)	264	58.30	4.31	4.38	20.91
			(58.84)	(4.20)	(4.90)	(20.84)
$\text{LH}_2 + \text{Me}_2\text{SnO}$	Me_2SnL (90)	274(d)	47.39	4.33	6.00	25.91
			(48.32)	(4.47)	(6.26)	(26.62)
$\text{LH}_2 + (\text{Cy}_3\text{Sn})_2\text{O}$	$(\text{Cy}_3\text{Sn})_2\text{L}$ (50)	142	60.74	7.63	2.62	23.08
			(60.34)	(7.72)	(2.70)	(23.01)
$\text{LH}_2 + (\text{Bu}_3\text{Sn})_2\text{O}$	$(\text{Bu}_3\text{Sn})_2\text{L}$	high boiling liquid	—	—	—	16.50 (16.35)
$\text{LH}_2 + \text{Me}_2\text{SnCl}_2$	$(\text{Me}_2\text{ClSn})_2\text{L}$ (40)	202	35.39	3.78	3.80	—
			(35.98)	(3.39)	(4.19)	
$\text{LH}_2 + \text{Ph}_2\text{SnCl}_2$	$(\text{PhClSn})_2\text{L}$ (45)	239	50.05	4.02	4.98	
			(49.85)	(3.58)	(5.28)	

$\text{LH}_2 = \text{Succinyl bis-N-phenyl hydroxamic acid.}$



probably because of more symmetrical (Structure III)

The methyl group of bis (dimethyl chlorotin) derivative appeared as sharp singlet at $\delta 0.96$ ($J_{119, \text{Sn}-\text{C}-\text{H}} = 80$ Hz) compared to dimethyl tin dichloride which showed methyl peaks at $\delta 1.2^{13}$. Such shielding is due to increased electron density on the tin atom via ligand donation.

The cyclohexyl protons in tricyclohexyl tin derivatives were found as a large peak (triplet, 66 H) in the range $\delta 0.85-2.25$.

In the ligand, the aromatic protons appeared in between $\delta 6.95-7.70$, whereas these protons in organotin derivatives appeared in between $\delta 6.88-7.70$. In case of diphenyl tin derivative, the aromatic protons gave four multiplets.

A fully decoupled ^{13}C NMR spectrum of succinyl bis-N-phenylhydroxamic acid was recorded in d_6 DMSO. The methylene carbon atoms together appeared at $\delta 28.85$. The carbonyl carbon atoms gave a single peak at $\delta 172.08$. The aromatic carbon atoms gave four peaks at $\delta 121.25, 125.44, 128.87$ and 142.05 corresponding to $\text{C}_{2,2'}$, $\text{C}_{6,6'}$; $\text{C}_{4,4'}$; $\text{C}_{3,3'}$, C_5 , and $\text{C}_{1,1'}$ respectively.

The ^{13}C NMR spectrum of bis (tricyclohexyl tin) succinyl bis-N-phenylhydroxamate was recorded in CDCl_3 solution. The methylene carbon atoms appeared at $\delta 18.18$. Thirty six cyclohexyl carbon atoms indicated nine peaks in between $\delta 26.96-35.81$. The carbonyl carbon atoms were also shielded compared to ligand carbonyl atoms which appeared at $\delta 153.78$. The aromatic carbon atoms gave only

three peaks at $\delta 127.01, 128.87$ and 129.27 . The missing aromatic peak of the organotin compound may be merged with any of three peaks observed. All types of carbon atom peaks are shielded in organotin compound due to electron donation from tricyclohexyl tin moieties, if we neglect the solvent effects.

It has been possible to record ^{119}Sn NMR spectra with Me_4Sn as a standard in CDCl_3 solution for diphenyl tin ($\delta - 359.6$), dibenyl tin ($\delta - 311.6$), dibutyl tin ($\delta - 225.9$) and bis-dimethyl chlorotin ($\delta - 52.3$) derivatives. In the first three compounds, the metal is hexacoordinated while in the last compound it is probably pentacoordinated.

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