

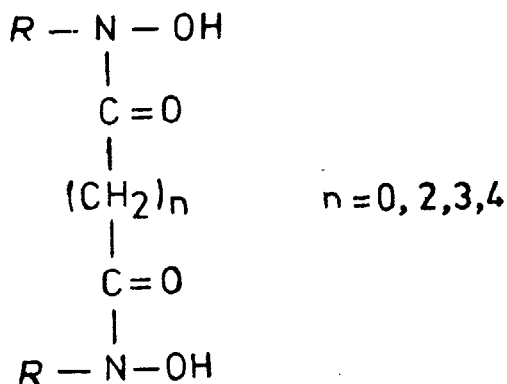
## ORGANOTIN DERIVATIVES OF HYDROXAMIC ACIDS

AMIYA KANTI GHOSH

Chemistry Department, North Bengal University, District Darjeeling,  
734 430, India

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Hydroxamic acids belong to the most versatile class of ligands for metallic cations. The organotin derivatives of these hydroxamic acids have been investigated since 1970s. So far, a number of different types of organotin derivatives of hydroxamic acids of the type  $R.N.(OH).CO.R'$  ( $R'$ -alkyl or aryl groups) have been investigated. More recently, it has been possible to prepare organotin derivatives of the following types of hydroxamic acids:—



The hydroxamic acids of the above type can act as a potential tetradentate ligand for organotin moieties. Though oxalyl hydroxamic acids act as 2X bidentate ligands, possibly due to steric reasons, the succinyl analogues act as tetradentate ligands for a number of organotin moieties. These have been characterised by physico-chemical data. It has not been possible to isolate organotin derivatives of glutaryl or adipyl hydroxamic acids except dimethyl and possibly a tricyclohexyl tin derivatives.

The tricyclohexyltin derivatives have been found to be commercially successful acaricides. Tricyclohexyl tin hydroxamate, prepared and characterised in this laboratory have been found to possess excellent acaricidal properties. Moreover, triorganotin hydroxamates exhibit remarkable fungicidal properties.

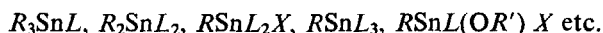
**Key Words :** Organotin Hydroxamates; Tetradentate Ligands; Pesticidal Properties

### INTRODUCTION

HYDROXAMIC acids form part of the most versatile class of organic ligands for a large variety of metal cations.<sup>1</sup> The first report of organotin derivatives of

hydroxamic acid was made by Harrison<sup>2</sup> in 1972, who isolated  $(C_6H_5)_3-Sn(ON.C_6H_5.CO.C_6H_5)$  and a few more triorganotin derivatives. The triphenyl tin compound was found to be monomeric both in crystalline and solution phases, while the corresponding trimethyl tin derivative was found to be associated in solid state. In an attempt to prepare  $Ph_3Sn(ONH.CO.C_6H_5)_3$ , they obtained tetraphenyl tin in high yield, presumably due to disproportion reactions and obtained some evidence of diphenyl tin hydroxamate, which they could not characterise properly.

Shortly, thereafter, a number of diorganotins, along with mono organotin derivatives were reported.<sup>3</sup> Later, more organotin derivatives have been published.<sup>4-9</sup> These hydroxamates are as follows :—



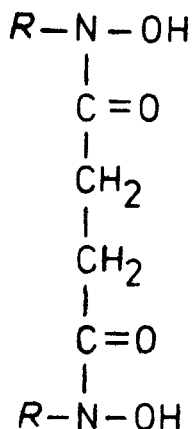
(where  $L$  = hydroxamic acids;  $X$  = halogen)

All these organotin hydroxamates were prepared from hydroxamic acids obtained from monobasic carboxylic acid chlorides. The organotin derivatives of hydroxamic acids obtained from dibasic carboxylic acid chlorides (e.g. oxalyl chloride) have been reported in 1984.<sup>10</sup> These hydroxamic acids were oxalyl-bis-N-phenyl and oxalyl *bis-N-p*-tolyl hydroxamic acids. We now report some new organotin derivatives of the following hydroxamic acids :—

1. Succinyl bis-N-phenyl hydroxamic acid (SPHA)
2. Succinyl bis-N-*p*-tolyl hydroxamic acid (STHA)
3. Glutaryl bis-N-phenyl hydroxamic acid (GPHA)
4. Adipyl bis-N-phenyl hydroxamic acid (APHA)
5. Adipyl bis-N-*p*-tolyl hydroxamic acid (ATHA)

#### EXPERIMENTAL

All hydroxamic acids were prepared in this laboratory by the reaction of appropriate acid chlorides and corresponding hydroxylamine derivatives. The hydroxamic acids were characterised by elemental analyses and IR spectral data. The organotin derivatives were obtained by the reaction of organotin oxide/hydroxides and the corresponding hydroxamic acid under refluxing condition in benzene. The water separated was removed azeotropically with help of a separator. On concentration of the reaction products, organotin hydroxamates separated in crystalline forms, which were purified by repeated crystallisation. Alternately, the organotin hydroxamates can also be prepared from organotin chlorides with hydroxamic acids. The HCl liberated was neutralised by ammonia. The products obtained by different methods are not similar. The following compounds have been isolated and characterised so far by elemental analyses, IR and NMR spectral data and in some cases by molecular weight determinations :—



(L)

*R* = PhenylMe<sub>2</sub>SnLBu<sub>2</sub>SnLPh<sub>2</sub>SnLBz<sub>2</sub>SnL(Cy<sub>3</sub>Sn)<sub>2</sub>L(Me<sub>2</sub>SnCl)<sub>2</sub>L

PhSnClL

*R* = *p*-tolylMe<sub>2</sub>SnLBu<sub>2</sub>SnLPh<sub>2</sub>SnLBz<sub>2</sub>SnL

PhSnClL

With corresponding Adipyl-bis-N-phenyl and Adipyl-bis-*p*-tolyl hydroxamic acids and also with glutaryl bis-N-phenyl hydroxamic acids, the Me<sub>2</sub>SnL type of compounds have been isolated and characterised. Glutaryl hydroxamic acid also give a tricyclohexyl tin derivative. Few more compounds are in the process of characterisation.

## DISCUSSION

### IR Spectra

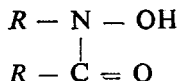
Hydroxamic acids give characteristic OH, C = O and NO bands at 3140–3170, 1620–1630 and 910–930cm<sup>-1</sup> region respectively. In organotin hydroxamates, there is complete absence of OH band and the C = O shifts to 1560–1580cm<sup>-1</sup> region and NO appeared in the region of 910–960cm<sup>-1</sup>. The Sn - C was found in the region of 500–560cm<sup>-1</sup>. The IR spectra clearly indicate the formation of organotin hydroxamates.

### NMR Spectra

The <sup>1</sup>H and <sup>119</sup>Sn (in selected cases) were recorded. The position of the peaks and proton counts are in good agreement with formulae assigned to these organotin hydroxamates. For want of facilities the <sup>119</sup>Sn NMR spectra could not be recorded so far for all compounds.

*Structural Aspects*

Organotin hydroxamates obtained from the hydroxamic acids of the type



are either penta or hexa coordinated around tin atom, where the hydroxamic acids behave as a bidentate ligand. But the hydroxamic acids obtained from dibasic acid chlorides (e.g. oxalyl, succinyl, glutaryl, adipyl etc) have the potentialities to behave as a tetradentate ligand. In case of oxalyl hydroxamic acids, the hydroxamic acid residues are possibly in *trans* orientation and hence cannot as tetradentate ligands. In our earlier investigations with oxalyl hydroxamic acids, we have found that these hydroxamic acids behave as 2X bidentate ligands, resulting in dimeric, trimeric or polymeric compounds (Figs 1-2.) For example,  $(Ph_2SnL)_3$  is trimeric in nature.

The triorganotin derivatives are expected to be monomeric with the following penta coordinated tin atom structure (Fig 3).

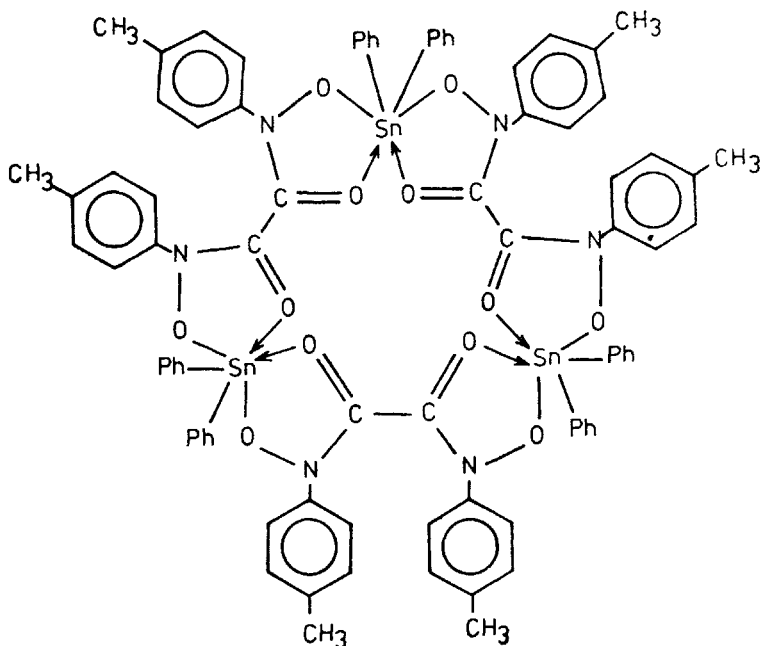


FIG 1

The molecular weights of the compounds support such structures.

With introduction of  $-CH_2-$  groups in such hydroxamic acids, the succinyl or higher homologues are expected to have the hydroxamic acid residues oriented in such way so that all the  $-OH$  and  $-CO$  groups to come in close proximities resulting in tetradentate behaviour of hydroxamic acid for organotin moieties.

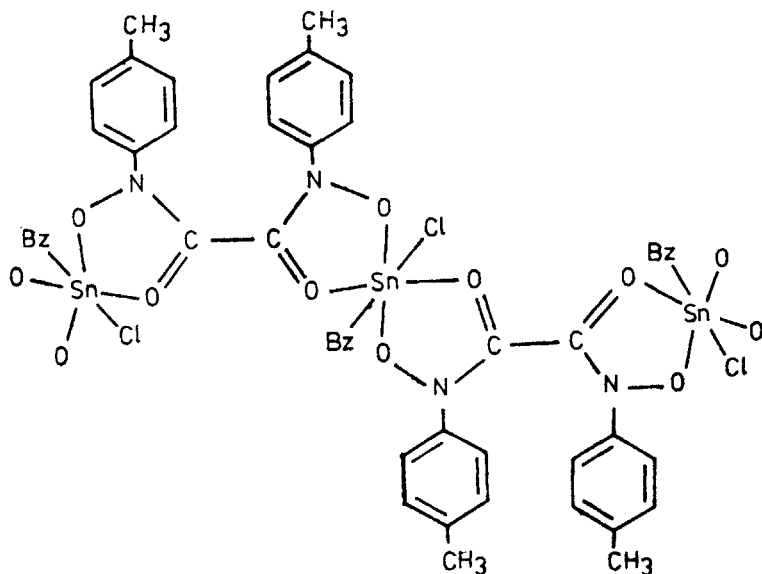
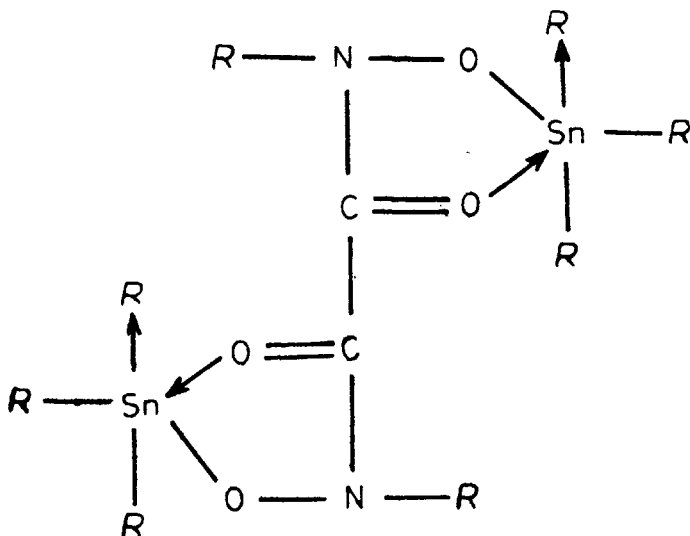


FIG 2



(bis-Tri organotin derivatives of oxalyl hydroxamic acids)

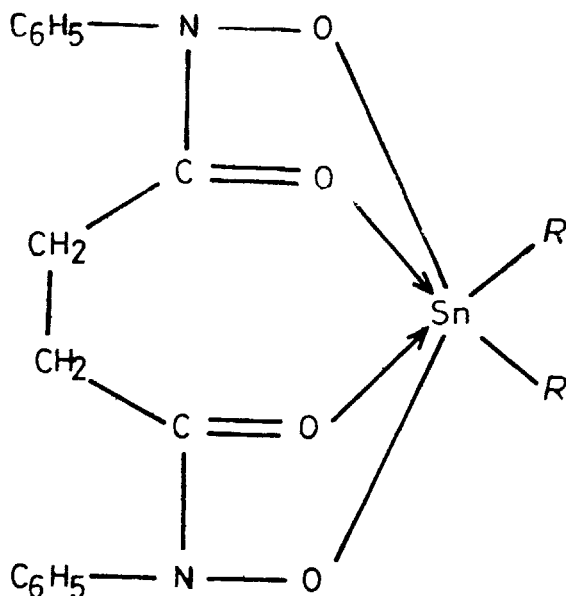
FIG 3

Substituted succinyl and adipyl hydroxamic acids have been reported to act as a tetradentate ligand for some metal cations.<sup>11</sup> We have been able to isolate some organotin hydroxamates, where hydroxamic acids behave as tetradentate ligands. The molecular weights and <sup>119</sup>Sn peaks in NMR spectra of some of these compounds are as follows:—

TABLE I

Compound	Molecular weight Found (Calc)	$^{119}\text{Sn}$ (ppm)
$(\text{C}_6\text{H}_5)_2 \text{SnSPHA}$	554(531)	-225.9
$(\text{C}_6\text{H}_5)_2 \text{SnSPHA}$	540(571)	-359.6
$(\text{C}_6\text{H}_5\text{CH}_2)_2 \text{SnSPHA}$	540(599)	-311.6

Above values strongly support the tetradentate nature of hydroxamic acid ligand which may be represented as follows:—



(Diorganotin derivatives of Succinyl N-phenyl hydroxamic acid)

FIG 4

Other derivatives having the formulae of  $R_2\text{SnL}$  and  $R\text{SnCIL}$  are most probably have structures, where  $L$  behaves as tetradentate ligand. The *bis*-tricyclohexyltin derivative  $(\text{Cy}_3\text{Sn})_2L$ , the ligand behave as  $2X$  bidentate one with penta coordinated tin. The  $^{119}\text{Sn}$  NMR spectra along with molecular weight determinations which will be undertaken in near future is expected to prove these contentions.

#### *Pesticidal Properties of Organotin Hydroxamates*

Now the author would like to discuss briefly on the acaricidal and fungicidal properties of some organotin hydroxamates. The acaricidal and fungicidal properties of organotin compounds have been exploited commercially in many countries of the world. Because of ready degradation to non-toxic tin oxide, the triorganotin compounds are safe from environmental point of view. "Plictran" and "Peropal"

are currently used as commercial acaricides. Both of them are tricyclohexyltin compounds and are more active than other types of commercial acaricides. The organotin hydroxamates show equivalent activities against red spider mites, as will be evident from the following example.

TABLE II

*Acaricidal activity against red spider mite (Tetranychus neocale donicus) found in bean plants\**  
Percentage mortality on spraying after

Compound	Concentration (ppm)	1 day	4 days	7 days
1. "Plictran 50W"	0.5	43.3	56.6	60.0
Tricyclohexyl tin hydroxide (Dow Chemical)	1.0	53.3	70.0	76.6
	2.5	53.3	73.3	73.3
	5.0	56.3	83.3	83.3
	10.0	76.6	80.0	86.6
	20.0	73.3	86.6	86.6
2. bis-Tricyclohexyl tin-bis-N-phenyl succinyl hydroxamate	0.5	23.3	33.3	46.6
	1.0	30.0	60.0	60.0
	2.5	50.0	56.6	66.6
	5.0	56.6	76.6	80.0
	10.0	70.0	76.6	83.3
	20.0	70.0	83.3	93.3
Control (water)		Nil	mite population increased	mite population further increases
Control (water & acetone)		Nil	"	"

Neglecting some unusual values from the above table, we find that our hydroxamate derivative have good acaridal activities at higher concentrations particularly after 1 day. Tricyclohexyltin hydroxide ("Plictran") is a better miticide than its coordinated derivative upto 4 days but at 20ppm dose after 7 days, latter it showed better effects (93.3 per cent) compared to Plictran (86.6 per cent).

Now, the would like to point out the fungicidal properties of bis-(Triphenyl tin) oxalyl-bis-N-*p*-tolyl hydroxamate against some important plant pathogenic fungi, compared to bis-(triphenyl tin) oxide, which is the active ingredient of commercial fungicide "Duter" (Phillips Duphar).

From the above data, it can be said that organotin hydroxamates have comparable fungicidal properties in respect to parent organotin compounds. The organotin hydroxamate can control soil borne *H. oryzae* infection considerably and also can effectively protect rice seedlings against *H. oryzae* infections by spraying. Moreover, this compound has very little phytotoxicity on rice plants.

TABLE III

Concentration ( $\mu\text{g/ml}$ ) for 95% inhibition after final inoculation period (. . .h)<sup>13</sup>

## GROWTH INHIBITION

Fungus spp	<i>P. oryzae</i> (168h)	<i>A. Solani</i> (96h)	<i>V. alboatrum</i> (60h)	<i>H. Oryzae</i> (180h)
<i>Compound</i>				
Bis-(triphenyltin) oxalyl-bis-N-p-tolyl hydroxamate	0.44	0.21	1.44	0.95
Fytolan (CuOCl based commercial fungicide)	492.40	108.43	62.50 (28.0%)	102.80
<i>Conidial germination Inhibition</i>				
	<i>A. niger</i> (48h)	<i>P. jenseni</i> (48h)	<i>V. alboatrum</i> (48h)	<i>H. Oryzae</i> (48h)
Bis-(triphenyltin) oxalyl-bis-N-p-tolyl hydroxamate	7.97	2.49	3.44	6.56
bis-(Triphenyltin) oxide	4.32	2.50	3.62	5.95
Fytolan	61.38	130.92	250.00	250.00

## ACKNOWLEDGEMENTS

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