

S U M M A R Y

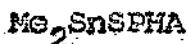
The present investigation concerns about the organotin derivatives of hydroxamic acids obtained from succinyl, glutaryl and adipyl chlorides. Organotin hydroxamates obtained from chlorides of monobasic acids have been studied during last decade or so. These hydroxamic acids behave as bidentate chelating agents. Organotin derivatives of oxalyl bis-N-substituted hydroxamic acids behave as double bidentate chelating agents and these derivatives are mainly polymeric in nature.

The present thesis is divided into three parts. In the introduction, a brief review of applications and environmental aspects of organotin compounds have given, which has been followed by a concise account of organotin adducts and coordination compounds. Attempts have been made to give an account of organotin hydroxamates, so far carried out.

The current investigations primarily carried out to isolate organotin hydroxamates, where hydroxamic acids can behave as tetradentate ligands. As pointed out earlier, the oxalyl bis-N-substituted hydroxamic acids act as double bidentate groups, though these have four sites in the molecules which could be potentially a tetradentate ligand, but the failure to behave as a tetradentate ligand, possibly lies in their structural disposition where these sites may in trans disposition.

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In order to make hydroxamic acids to behave as a tetradentate chelating agent, some higher homologues such as succinyl bis-N-substituted hydroxamic acids were taken. In the higher homologues of oxalyl hydroxamic acid, there ^{are} two methylene groups in succinyl analogues, three methylene groups in glutaryl and four methylene groups in adipyl hydroxamic acids. The presence of methylene groups in between carbonyl groups will very likely to orient these hydroxamic acids into a tetradentate ligand by bringing all carbonyl and hydroxyl groups in close proximity. Organotin derivatives of these higher hydroxamic acids isolated under present investigation proved this contention. The following organotin compounds have been isolated, where the corresponding hydroxamic acids behave as tetradentate ligands.



SPHA = succinyl bis-N-phenyl hydroxamic acid

STHA = succinyl bis-N-p-tolyl hydroxamic acid

GPHA = glutaryl bis-N-phenyl hydroxamic acid

APHA = adipyl bis-N-phenyl hydroxamic acid

ATHA = adipyl bis-N-p-tolyl hydroxamic acid.

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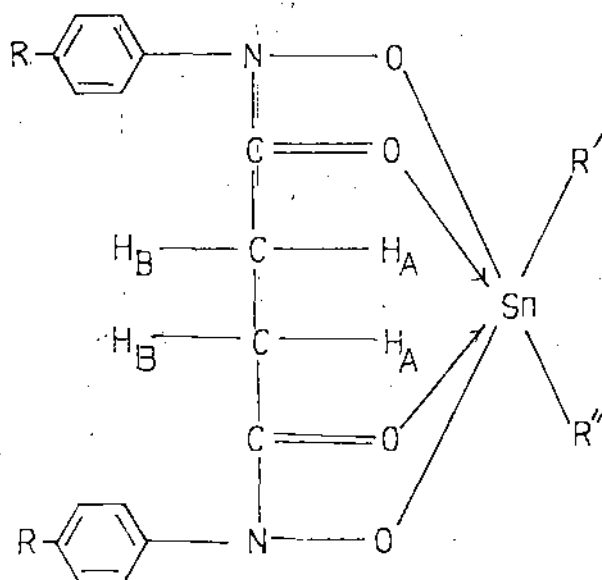
The i.r. spectra of hydroxamic acids, studied under the present investigation gave ν_{OH} band at 3100-3160 cm^{-1} and the $\nu_{\text{C=O}}$ band is appeared $\sim 1615 \text{ cm}^{-1}$ along with other bands for the constituent groups at usual positions. The organotin derivatives showed the complete absence of ν_{OH} in all cases. The ν_{CO} bands is shifted to 1555-1590 cm^{-1} indicating the coordination of the carbonyl group to the tin atom. In all organotin derivatives, three new bands appeared for $\nu_{\text{Sn-C}}$, $\nu_{\text{Sn-O}}$ and $\nu_{\text{Sn-O-C}}$ bands appeared in the ranges of 490-530 cm^{-1} , 540-600 cm^{-1} and 1000-1040 cm^{-1} respectively.

In $\text{Et}_2\text{SnCl}_2 \cdot \text{SPHA}$ the Sn-Cl band gave $\nu_{\text{s}} \sim 300$ and ν_{as} 320 cm^{-1} respectively.

The tetradentate nature of the above hydroxamic acid is supported by elemental analyses and NMR spectra. Molecular weight support the monomeric nature of some of these compounds. Moreover from the some available ^{119}Sn NMR data, it was found that the tin atoms are most probably hexa coordinated in nature. The ^{13}C NMR data also support the structures assigned to these types of complexes.

On the basis of available data, the structures of diorganotin succinyl bis-N-substituted hydroxamates can be suggested as follows.

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R = H, CH₃ ; R' = alkyl, aryl

R'' = alkyl, aryl, Cl

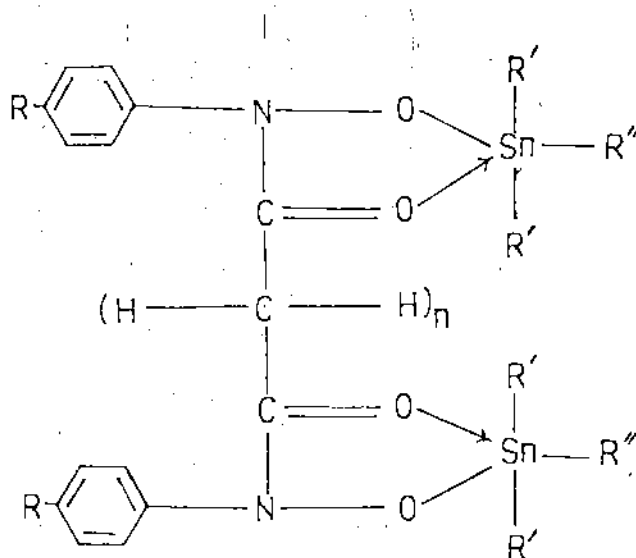
In all these complexes the ¹H NMR spectra gave two types of methylene protons, corresponding to H_A and H_B protons. The H_A protons are more shielded than H_B protons and the H_A protons are possibly in the field of influence of tin atom. The ¹³C NMR spectra gave one single peak for two carbonyl carbon atoms and compared to the ligands are shielded in character due to coordination of carbonyl groups to the tin atom.

Some penta coordinated tin complexes of organotin hydroxamates have been isolated with the above mentioned

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hydroxamic acids. These are $(\text{Cy}_3\text{Sn})_2\text{SPHA}$, $(\text{Me}_2\text{SnCl})_2\text{SPHA}$,
 $(\text{Cy}_3\text{Sn})_2\text{GPHA}$.

The structures of these compounds can be indicated



The penta coordinate nature of tin in $(\text{Me}_2\text{SnCl})_2\text{SPHA}$ is supported by ^{119}Sn peak at $\delta-52.5$. One interesting feature is observed in the above type of compounds is that the methylene protons are equivalent and exhibit one single peak, showing a symmetrical structure.