PREFACE.

Along with the tremendous growth in the industrial, agricultural and other applications of organotin carboxylates, theoretical and structural interests in this class of compounds have continued to grow during the last few decades. It has also been suggested that their practical applications are significantly connected with their structures and great interest for the study of organotin carboxylates has evinced among organotin chemists.

In almost all organotin carboxylates, unless dictated by steric factors, the solid state structure consists of carboxylate bridged polymers. However, a bonding mode alternative to carboxyl bridging, leading to either intra- or intermolecularly coordinated structure, may become possible if the carboxyl moiety contains a substituent carrying a suitably placed donor atom. This possibility has, in recent times, generated tremendous interest in the solid state structure of organotin derivatives of carboxylic acids containing an additional potential donor site. Among many such organotin carboxylates the derivatives of substituted benzoic acids, pyridine carboxylic acids and some amino acids have received much attention. But keto carboxylic acids, though apparently capable of forming intramolecularly chelated ring structure, have not received adequate attention. This has prompted us to attempt the synthesis of the organotin derivatives of α-keto carboxylic acids and to investigate their spectral properties.

The methods employed for the preparation of the organotin keto carboxylates are (i) reaction of the Na-salts of the acids with organotin halides and (ii) reaction of the free acids with organotin oxides. While the reaction (i) proceeded as expected giving organotin carboxylates, the reaction (ii) produced a unique class of addition compounds, in addition to the carboxylates, depending on the reaction condition.

The results of these investigations preceded by a comprehensive survey of organotin chemistry, are presented in this thesis.

In Chapter-I a brief review of the organotin chemistry,with special emphasis on both the donor and acceptor behaviour of the organotin compounds has been presented. The formation of addition complexes through donor-acceptor interactions has been discussed in some detail.

The Chapter-II consists of a review on organotin carboxylates, emphasis being given on the structural aspects. The various structural possibilities have been highlighted citing extensive examples from the literature.

The synthesis and characterisation of a number of new organotin α-keto carboxylates [$R_nSn(OCOCOR')_{4-n}$, n = 3, R = n-Bu, Ph, $PhCH_2$ and n = 2, R = Me, n-Bu, n-Oct; R' = CH_3, Ph, $PhCH_2$] constitute the subject matter of Chapter-III. On the basis of spectroscopic data the tin atom, in some of the organotin α-keto carboxylates, has been shown to have attained a coordination number of six through involvement of the carboxyl moiety in both inter- and intramolecular coordination. The formation of a few carboxylato diorganotin hydroxides [$R_2Sn(OCOCOR')OH$, R = Me, n-BU, n-Oct, Ph and R' = CH_3, $PhCH_2$] are also reported in this chapter.

In the last chapter, the isolation and transformation of a few carboxylic acid adducts of the general formula $R_3SnOH.R'COCOOH$ [R = n-Bu, Ph, $PhCH_2$; R' = CH_3 and R = n-Bu, R' = $PhCh_2$], formed with organostannoxanes/ triorganotin hydroxides, are reported. The isolation of these unique compounds is the most significant feature of this work, since an understanding of the formation and structure of these compounds may pave the way to design new carboxylate ligands, with which one can, possibly, isolate the intermediate complexes believed to be the first step in the reaction between the stannoxanes and carboxylic acids.