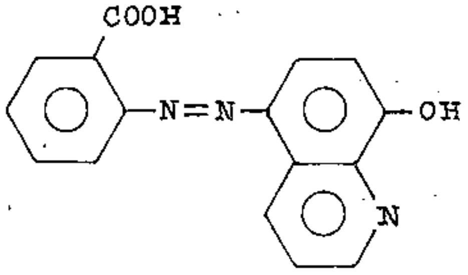
P R E F A C E

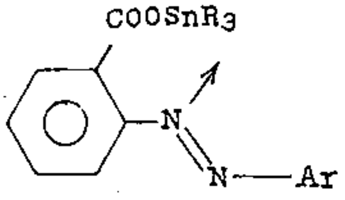
Although a great variety of organotin complexes have been reported during the last two decades, the extent literature contains no reference to mixed complexes of the type $(R_nSnL)_xM$ where the polyfunctional ligand L coordinates simultaneously to an organotin group as well as a metal, particularly a transition metal, M. Such complexes may be looked upon as the counterpart of the mixed complexes of the type $R_2SnL.L'$ (L and L' are different ligands) which are now quite well known. The present work was therefore undertaken as a part of a general programme aimed at the synthesis and study of such mixed complexes. The main difficulty in preparing transition metal-organotin mixed complexes arises from the usually much greater stability of the transition metal complex of a ligand compared to its organotin complex. This generally results in a facile replacement of the organotin group by the transition metal ion whenever an attempt is made to prepare the mixed complexes.

It was soon realised that such mixed complexes can only be obtained through the use of heterofunctional ligands having two coordinating sites which can be discriminated by the metal ions by means of widely different coordinating abilities of the two sites. A study of different factors, e.g., ease of synthesis, stabilities of the resulting complexes, easily accessible spectral features which may be utilised to study the structural characteristics etc., led to the choice of 5-(2'-carboxy phenyl) azo-8-quinolinol (I) as a model ligand for the present study.



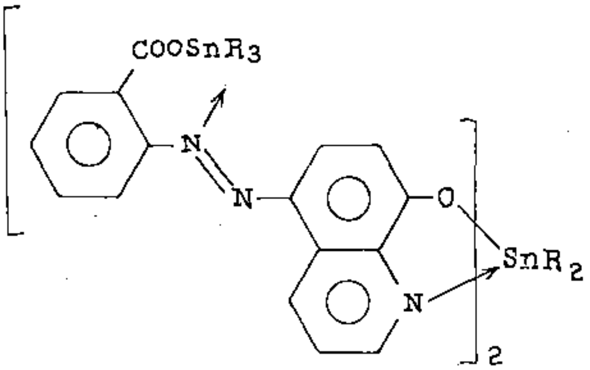
(I)

This ligand contains the 8-quinolinol moiety which is expected to form quite strong complexes with the transition metal ions, while the carboxylate group which has much lower coordinating power towards the transition metal compared to that of the quinolinol moiety, can be readily used to coordinate the organotin group since organotin arylazo benzoates (II) are quite well known.

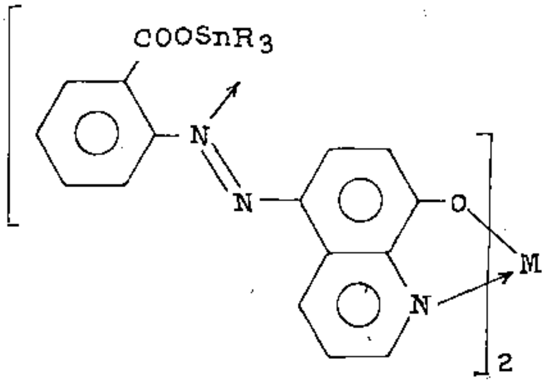


(II)

In the present work more emphasis was laid on the preparation and study of the properties of the polynuclear organotin complexes of the type (III) because a study of such complexes would lead a better understanding of the transition metal-organotin mixed complexes (IV).



(III)



(IV)

The thesis is divided into four chapters. A survey of the azoderivatives of 8-quinolinols and their chemistry with emphasis on their metal complexes are reviewed in Chapter - I.

The synthesis of the ligands, 5-(phenyl) azo-8-quinolinol and 5-(2'-carboxy phenyl) azo-8-quinolinol and their organotin derivatives constitute the subject matter of Chapter - II. The structure of organotin derivatives has been discussed using IR absorption frequencies.

The asymmetric carboxylate stretch in the free ligand occurs at ~ 1650 cm^{-1} due to intramolecular H-bonding. Methylation of the -COOH group shifts the $\nu_{as}(COO)$ to normal position while stannylation leading to the derivatives of the type R_3SnL lowers it to the region $\sim 1630-35$ cm^{-1} which is same as that found in triorganotin aryl-azobenzoates. On the other hand, $\nu_{as}(COO)$ occurs at $\sim 1700-1730$ cm^{-1} in the diorganotin 5-(2'-carboxy phenyl) azo-8-quinolinolates.

The electronic absorption spectra and the effect of solvents have been discussed in Chapter - III. A CNDO/2 type calculation shows that the longest wave length transition is indeed a $\pi - \pi^*$ transition which involves mostly a transfer of electron density from the quinoline N and O_8 atoms to the azo group, the β-N atom getting greater share of the electron transfer during transition. The absorption spectral data supports the presence of $N \rightarrow Sn$ coordinate link in the organotin derivatives.

Preparation and properties of transition metal-organotin mixed complexes (IV) have been discussed in Chapter - IV using IR, electronic absorption spectra and magnetic moment data. These complexes are structurally quite similar to the binuclear organotin derivatives (III). The larger bathochromic shift of these complexes as compared to the corresponding organotin derivatives can be interpreted in terms of $d_{\pi} - p_{\pi}$ interaction involving the metal 'd' and ligand π-MO's. On the basis of the physicochemical studies, particularly, the magnetic moment data, the transition metal-organotin mixed complexes are expected to have tetrahedral stereochemistry about the transition metal atom.