

DISCUSSION

In course of the present investigation, the β -carboalkoxy ethyl tin complex compounds of the types R_2SnL_2 , R_2SnLX , $RSnL_2X$, $RSnL_3$, R_2SnL' and $RSnCLL'$ [where $R = CH_3CO_2CH_2CH_2-$, $C_4H_9CO_2CH_2CH_2-$, $CH_3CO_2CH(CH_3)CH_2-$; $X = Cl, SCN$ etc; $LH = 8$ -hydroxy quinoline (Oxine), 5,7-dichloro oxine, 5,7-dibromo oxine, phenyl-5-azo-oxine, 5-(2'-carboxy phenyl) azo oxine, Dithizone, 1,5-diphenyl carbazone, Alizarin, 1-nitroso-2-naphthol and $L'H_2 =$ Alizarin etc] were isolated. The complex $RSnCLL_2$ (where $R = CH_3COCH_2C(CH_3)_2-$ and $LH =$ Oxine) and β -carboalkoxy ethyl tin derivatives of the types R_2SnX_2 and $RSnXCl_2$ (where $R = CH_3CO_2CH_2CH_2-$ and $X = SCN$ etc.) were also obtained.

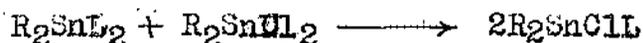
The complexes R_2SnL' , $RSnCLL'$, R_2SnL_2 , $RSnCLL_2$ and $RSnL_3$ were prepared by the reaction of one mole of β -carboalkoxy ethyl tin halide with one, two or three moles of the ligand in an appropriate solvent. The liberated hydrochloric acid was neutralised with concentrated ammonia solution (17N) and the precipitated ammonium chloride was removed by filtration.



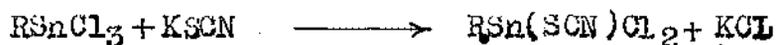
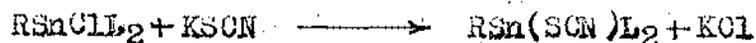
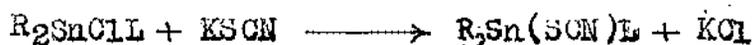


The compound $RSnClL_2$, where $R = CH_3CO \cdot CH_2C(CH_3)_2 -$ was also prepared by the same method.

R_2SnClL type of complexes were prepared by reacting R_2SnL_2 and R_2SnCl_2 in 1:1 mole ratio in an appropriate solvent.



The compounds like $R_2Sn(SCN)L$, $RSn(SCN)L_2$, $R_2Sn(SCN)_2$ and $RSn(SCN)Cl_2$ were prepared by the following reactions and potassium chloride was removed by filtration.

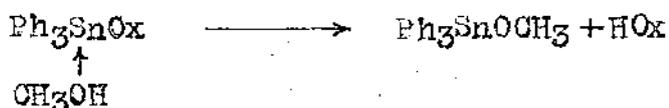


A number of workers have studied the electronic spectra of different metal chelate compounds (217,511-323) and have shown that the ligand absorption band is shifted to longer wave length due to chelate formation and the

extent of this shift parallels the stability of chelate complex. Kawakami and Okawara (213) have shown that the organotin oxinates are chelated compounds in solution since the band of oxine in UV region shifts to longer wave length in complexes. The sequence of stability constants of those oxinates was associated with the band shifts in non-polar solvents. Noltes et al (316) reported that the shift to longer wave length of the 320 nm absorption of oxine in an organometallic complex is generally considered to be a reliable indication for the presence of a chelating oxine ligand.

The electronic spectra of β -carboalkoxy alkyl tin oxinates (Table III) correspond to those of other chelated metal oxinates (236, 217, 312-316, 318-321). Oxine in methanol (Fig. 96) exhibits two major bands in the UV region at 235 nm and at 310 nm. The 235 nm band is of high intensity and the 310 nm band has been assigned by earlier workers as the ligand band, which suffers considerable red shift due to chelate formation. The electronic spectra of all β -carboalkoxy ethyl tin oxinates (Table III) show two or more bands in UV/Visible region. All these spectra are characterised mainly by an intense absorption in the region \sim 255 nm, an inflexion in the

region 310-315 nm and a strong band in the region 370-375 nm. The band at 235 nm of free oxine undergoes small red shift in all cases as generally observed for complex formation. The 310 nm band of oxine suffers displacement to 370-375 nm in all β -carboalkoxy ethyl tin oxinates reported here. The considerable shift observed in these cases and near constancy of the oxinate absorption at ~ 375 nm indicate strongly that the chelate formation of similar stability has taken place (313, 316, 322). The band at ~ 375 nm is most probably a $\pi-\pi^*$ absorption of the oxine ligand (324). In the spectra of some β -carboalkoxy ethyl tin oxinates certain additional bands (fine structures) appear along with the main bands. Such bands are also observed in other chelated metal oxinates (312). The inflexion observed in the region 310-315 nm in most oxinate complexes may be due to the presence of some free ligand obtained from the rupture of Sn-N bond in methanol (322, 325). It may be pointed out here that Ph_3SnOx (Triphenyl tin oxinate) suffers solvolysis in methanol (231).



(where Ph = C₆H₅ and HOx = Oxine)

The electronic spectra of 5,7-dichloro oxine (Fig. 98) and 5,7-dibromo oxine (Fig. 99) also reveal two bands one at 245 nm and the other at 324 nm. In case of β -carboalkoxy ethyl tin complexes of these ligands, we observe three major bands (Table IV). The 245 nm band suffers small red shift to \sim 260-265 nm due to complex formation. In few instances additional bands appear in this region. Similar fine structure has also been observed in the spectra of other metal oxinates. Apart from these, two well separated bands are observed in case of β -carboalkoxy ethyl tin (substituted oxine) complexes. These bands appear at \sim 333-340 and at \sim 385-390 nm. From the position and intensity, the band at \sim 385-390 nm is supposed to be the ligand band (originally at 324 nm) strongly shifted from its original position. The ligand band at 324 nm is possibly $\pi - \pi^*$ transition in origin, comparable to similar band of oxine. The shift to longer wave length of 324 nm absorption band suggests that, in solution these organotin compounds contain a chelated (substituted oxinato) ligand (236, 312-314, 316, 317). The near constancy of the band position at \sim 385-390 in these complexes indicate strong chelation

of similar stabilities.

The other band at $\sim 338-340$ observed with β -carboalkoxy ethyl tin substituted oxinates is possibly due to unchelated ligand bands or its some modified forms(312, 313, 315, 316).

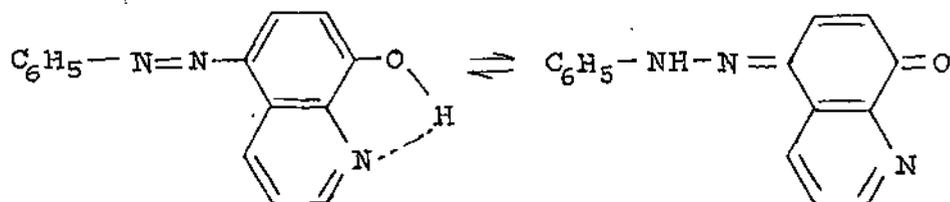
The electronic spectra of azobenzene and related compounds have been studied extensively by several workers (326-341). Three to four absorption bands in the UV/Visible region generally observed for these compounds may be divided into two types. In azobenzene and related compounds the weak to moderate intensity band ($\epsilon_{\max} \approx 10^2 - 10^3$) at longest wave length is ascribed to the $n-\pi^*$ transition and the other more intense absorption bands ($\epsilon_{\max} \approx 10^4$) are ascribed to $\pi-\pi^*$ transitions. The position of the first $\pi-\pi^*$ band varies considerably from compound to compound and the position of the $n-\pi^*$ band remains almost unaffected by the aryl groups and occurs at about 440-460 nm. Substitutents like $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$, $-\text{NMe}_2$ etc. which are capable of producing large bathochromic shift of the $\pi-\pi^*$ transitions by extending the conjugation, may often shift the first $\pi-\pi^*$ band in the azo compound to such an extent that the characteristic $n-\pi^*$ absorption is masked by the strong absorption (331).

One of the ligands, 5(2'-carboxy phenyl) azo oxine used in the present investigation belongs to this category and no separate band due to $n-\pi^*$ transition could be observed.

The azo-hydrazone tautomerism in hydroxy azo derivatives has been studied in great detail by several workers (328, 332, 334, 335, 342, 343). For example, 4-phenyl azo-1-naphthol is known to exist in absolute alcohol as an equilibrium mixture of the azo and phenyl hydrazone tautomer, the absorption curve consisting of two broad bands at 408 nm (azo form) and 462 nm (hydrazone form) (344). It has been well established that the hydrazone form always absorbs at longer wave-lengths compared to the azo form (343, 345). Again, it has been reported that the existence of intramolecular hydrogen bonding influences the azo-hydrazone tautomeric equilibria. For example, phenyl-5-azo oxine in absolute alcohol shows two regions of absorption at 387 nm ($\epsilon = 21.1 \times 10^3$) and 462 nm ($\epsilon = 5.5 \times 10^3$) but the longest wave length absorption appears only as an inflexion (346).

In the present investigation, the electronic spectrum of free ligand, phenyl-5-azo oxine (Fig. 100) shows absorption bands at 245 nm and 380 nm and an

inflexion at 450 nm which indicates the azo-hydrazone tautomerism, well known in such systems (347, 348) and also the existence of intramolecular hydrogen bonding in the azo form.



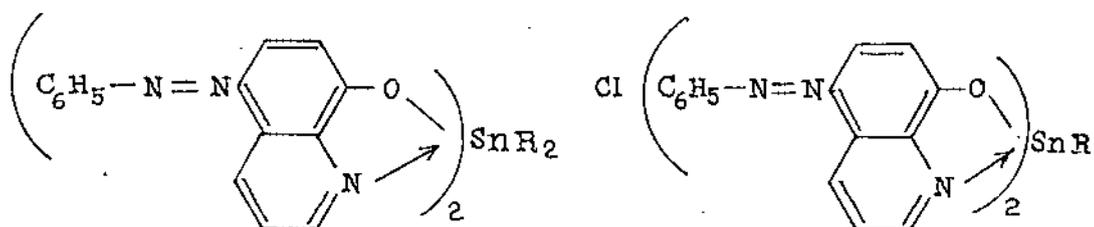
(Azo-form)

(Hydrazone form)

In phenyl-5-azo oxine the band at 380 nm is due to the $\pi-\pi^*$ transition of the azo form and the inflexion at 450 nm is due to the hydrazone form.

In the electronic spectra of all the (β -carboalkoxy ethyl tin phenyl-5-azo oxinates (Table - V) we observe three bands at ~ 260 nm (~ 240 nm for bis chelates), in the region 320-340 nm and in the region 400-430 nm. In the complexes the 450 nm band of the free ligand is completely absent since the hydrazone form is

not relevant for chelate formation. The 380 nm band of the free ligand suffers red shift to 400-430 nm in the complexes and may be assigned to the $\pi-\pi^*$ transition of the azo form. Therefore, all the phenyl-5-azo oxine complexes exist only in the azo form. In the organotin compounds where the oxygen atom is expected to have large negative charge because of the high polarity of tin-oxygen bond ($\overset{\delta+}{\text{Sn}} - \overset{\delta-}{\text{O}}$), the $\pi-\pi^*$ transition energy is expected further lowered (202, 349). Therefore, the organotin oxinate derivatives are expected to show a bathochromic shift. The bathochromic shift of 380 nm free ligand band to 400-430 nm in all the compounds therefore results due to the chelation of the ligand. Such bathochromic shifts have been observed in all previous cases. The β -carboalkoxy ethyl tin phenyl-5-azo oxinates are thus structurally quite similar to the organotin oxinates (80, 213, 217, 350, 351) and may be formulated as

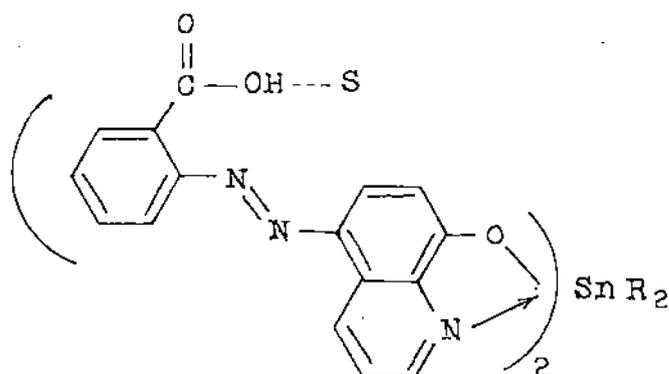


(R = CH₃CO₂CH₂CH₂⁻ , C₄H₉CO₂CH₂CH₂⁻ , CH₃CO₂CH(CH₃)CH₂⁻
and X = Cl).

It may be assumed that the band observed at 240 nm/260 nm in the complexes are somewhat modified band of 245 nm of the free ligand whereas the band at 320-340 nm is possibly associated with ligand band as also observed in other metal chelates discussed earlier.

Similar to phenyl-5-azo oxinates, the complex Bis(β-carbomethoxy ethyl) tin bis-5(2'-carboxy phenyl)-azo oxinate (Fig. 101) in which the carboxyl group is expected to be free, absorbs predominantly at 420 nm in donor solvent such as methanol. Since, only donor solvents capable of forming strong hydrogen bond give rise to a blue shift, for this complex the following structure (Fig. IV) may be suggested which is expected to exist in donor solvents (S) due to intramolecular hydrogen bonding involving the carboxylic proton and the donor atom of the solvent. Moreover, any interaction with the azo-nitrogen-atoms, through intramolecular hydrogen bond as in 5(2'-carboxy phenyl)azo-oxine is expected to lead to a bathochromic shift relative to that in the non-interacting systems such as the phenyl-5-azo oxine complexes. In the structure IV, since the hydrogen atom is not directly involved in the π-system, such interaction

will have little influence on the $\pi-\pi^*$ transition and consequently the absorption spectra closely resemble those of the corresponding phenyl-5-azo-oxinates.



(s = donor solvent, R = $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2^-$)

The visible absorption spectrum of dithizone in an organic solvent exhibits two well defined bands at 440-450 nm and 590-640 nm (352) that have been assumed to be originated from the thione and thiol tautomer (208) (Fig. V).

infrared and NMR spectroscopy suggested that solution of dithizone contained a thione dimer (Fig. VII) and a thiol form (Fig. VIII).

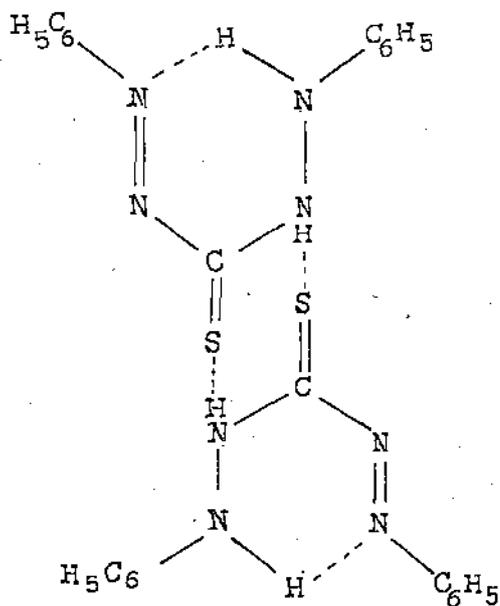


Fig. VII

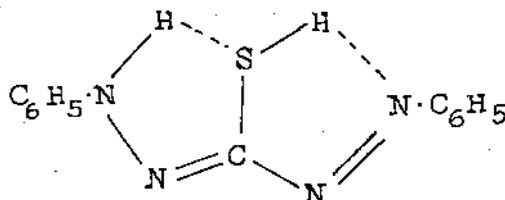


Fig. VIII

Although there is no evidence of dimerisation in solution or in the solid state, it should be noted that the long wave length band is now ascribed to the thiol form whereas the short wavelength band is ascribed to thione dimer (353). But from the recent measurements (354) which have included studies of several homologues of dithizone and both isomeric forms of the corresponding S-methyl derivatives, the conclusion is that the thiol form (comprising about 25% of the total in CDCl_3) has the (resonating) structure (Fig. IX) or less likely (Fig. X) whereas the thione form could be (Fig. XI) or (Fig. XII).

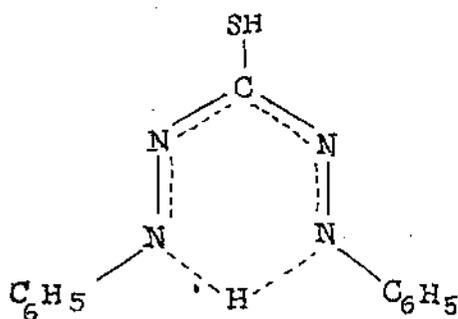


Fig. IX.

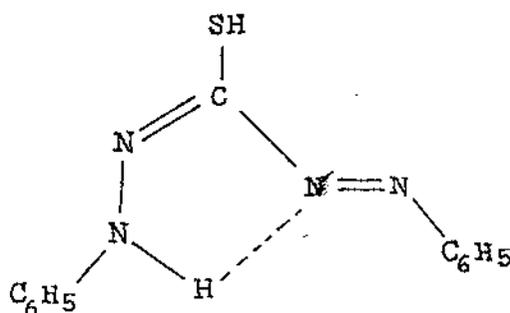
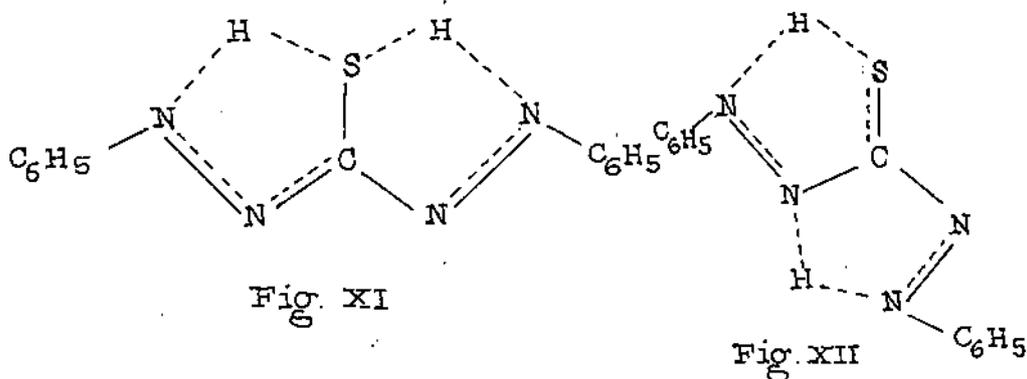


Fig. X.



However, according to the current view, the allocation of band and tautomeric equilibrium of dithizone in an organic solvent may be represented as follows:

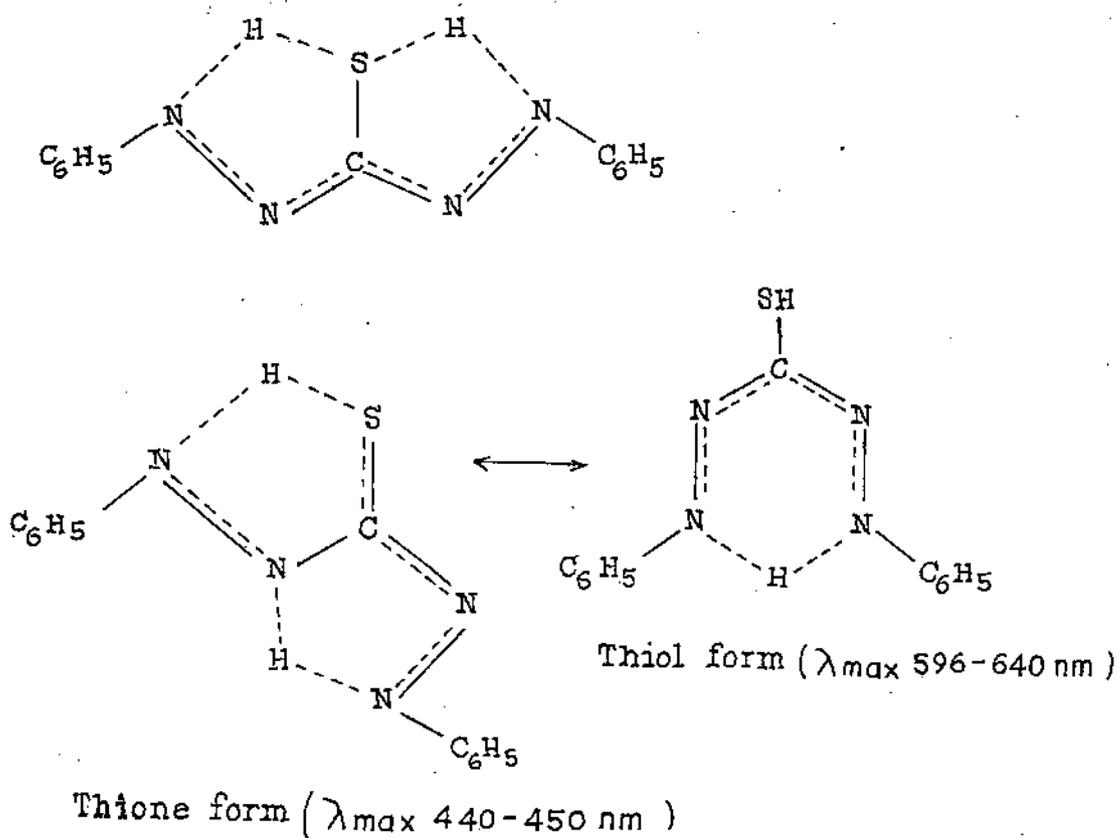


Fig. XIII

Ghosh et al (209, 210) also reported two absorption bands of dithizone in chloroform viz. at 620 nm and 450 nm. But in all organotin dithizonates reported by Ghosh there was only a single visible absorption band at 470-500 nm (in chloroform) which was explained by the disappearance of thiol band at ~ 600 nm and a bathochromic shift of the thione form at ~ 450 nm. Since there was a bathochromic shift of the absorption band at 450 nm in free dithizone to 450-510 nm in organotin dithizonates, all those organotin dithizonates were supposed to be chelated complexes. Thus, the thiol form interacted with the organotin chlorides or oxides in the following way to form organotin dithizonates and attained the structure (Fig. XIV) or (Fig. XV) (210).

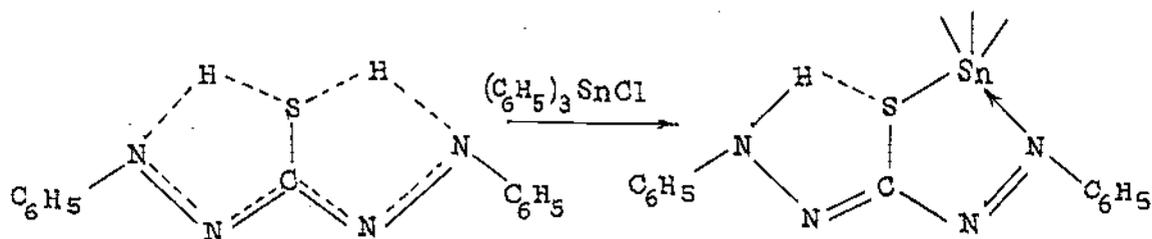


Fig. XIV

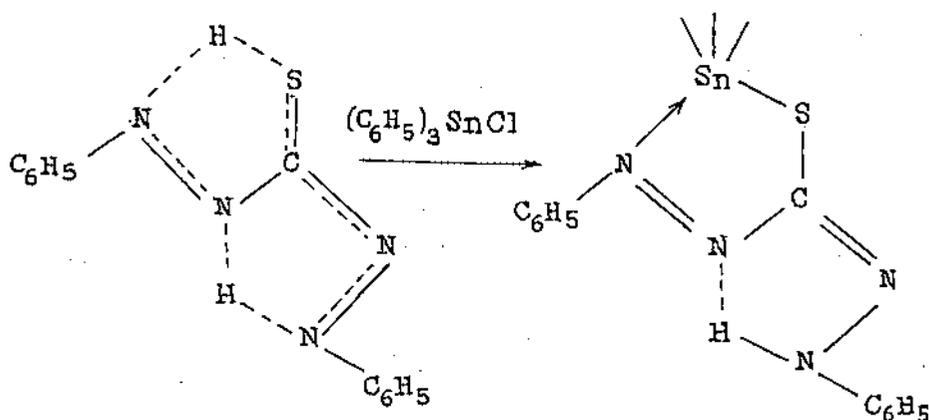


Fig. XV

Ghosh (loc. cit) also reported that while free dithizone in methanol absorbs strongly in the visible region at ~ 470 nm and in the UV region at 272 nm, organotin dithizonates absorb in methanol in the region 255-285 nm and 430-500 nm.

In the present investigation we also observe that while dithizone (Fig. 102) in methanol absorbs strongly in the visible region at ~ 470 nm, all the β -carboalkoxy alkyl tin dithizonates (Table VI) show absorption bands in the region 430-503 nm which indicate a bathochromic shift of the ligand band on complexation. Therefore, the structure of all these β -carboalkoxy ethyl tin dithizonates may be similar to the structures as described in Fig. XIV or Fig. XV. From the shifting of the bands

to higher wavelength in these complexes observed (Table VI) it can be suggested that the bis-chelates are more stable than the chloro or thiocyanato derivatives.

The visible absorption spectrum of 1,5-diphenyl carbazone in a polar solvent gave two absorption maxima (355). The more intense one at about 455 nm and the other with much lower intensity at 565 nm. Willems and Zeeger-Huyskens (356) attributed 565 nm band to the thiol form present in low concentration. The 455 nm absorption band is generally attributed to the free keto form as shown below (Fig. XVI).

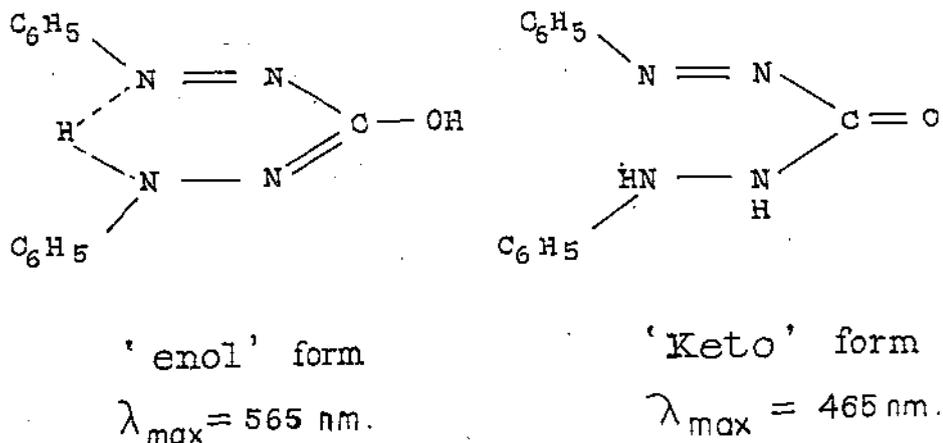


Fig. XVI

As discussed earlier dithizone also exhibits two well defined bands at 450 nm and 620 nm respectively for thione-thiol tautomerism.

In the present investigation we also observe that 1,5-diphenyl carbazone absorbs at 230 nm, 290 nm, 460 nm and 565 nm respectively (Table VII). The complex $\text{Bis}(\beta\text{-carbomethoxy ethyl})$ chloro tin diphenyl-carbazonate exhibits a peak at 530 nm (Table VII) in methanol. By an analogy with β -carboalkoxy ethyl tin dithizonates and other organotin dithizonates it may be concluded that the 460 nm band of diphenyl carbazone suffers a bathochromic shift to 530 nm due to chelate formation. Similar shift has been noticed for six alkyl and aryl diphenyl carbazonates in chloroform, where the absorption took place in the region of 530-550 nm (211).

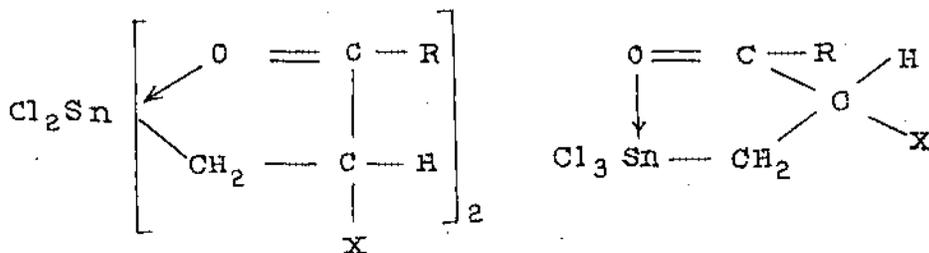
The UV/Visible spectrum of alizarin in methanol shows a number of absorption bands at 250 nm, 275 nm, 325 nm, 430 nm and 530 nm respectively (Fig. 104). In all the β -carboalkoxy ethyl tin alizarinates (Table VII) the presence of the band in the region 460-480 nm is possibly due to the bathochromic shift of the ligand band (430 nm) suggesting the complex formation of alizarin in these compounds. From the extent of shifts of the bands it may

also be suggested that Bis(β -carboalkoxy ethyl) tin alizarinates are possibly more stable in solution than the chloro derivatives.

The UV/Visible spectrum of Bis (β -carbomethoxy ethyl) chloro tin 1-nitroso-2-naphtholate (Table VII) shows a band at 580 nm possibly due to bathochromic shift of the 370 nm band observed in case of free ligand, (Table VII) indicating strong chelation.

In their IR spectra, the carbonyl stretching frequencies $\nu(\text{C}=\text{O})$ in all the (β -carbomethoxy ethyl tin halides (estertin chlorides) used in the present investigation lie between 1640 to 1680 cm^{-1} , at a lower frequency than the saturated analogues of the parent α,β -unsaturated carbonyl compounds. In methyl acrylate, methyl propionate and butane-2-one the carbonyl stretching frequency is seen at 1720, 1728 and 1723 cm^{-1} respectively (260, 300). Moreover in PMR spectra the ester methyl in $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ is situated down field from the corresponding signal in $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$ and a similar effect is observed for the methyl signals in $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{COCH}_3$ and $\text{CH}_3\text{CH}_2\text{COCH}_3$ (260). On the basis of IR and PMR data Hutton *et al* (260) suggested that these spectroscopic effects are consistent with carbonyl coordination to tin, since the phenomenon reduces the $\text{C}=\text{O}$

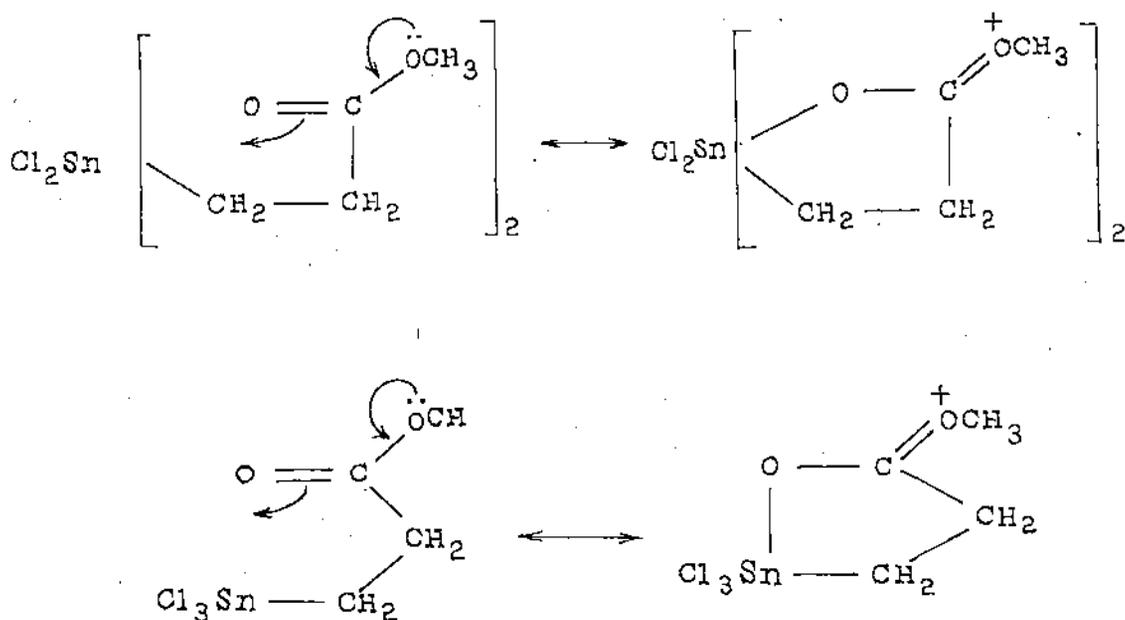
bond order (270) and hence the carbonyl stretching frequency and also the perturbation of the electron distribution causes a shielding effect on the relevant protons. Moreover, since the carbonyl stretching frequency for these compounds remains unaffected by dilution in toluene or ethereal solvents, the carbonyl co-ordination to tin is almost certainly intramolecular in origin. Therefore, the structure of β -carboalkoxy ethyl tin chlorides has been suggested as follows by Hutton et al (loc. cit).



($\text{R} = \text{OCH}_3, \text{OC}_4\text{H}_9, \text{CH}_3$; $\text{X} = \text{H}$ or CH_3)

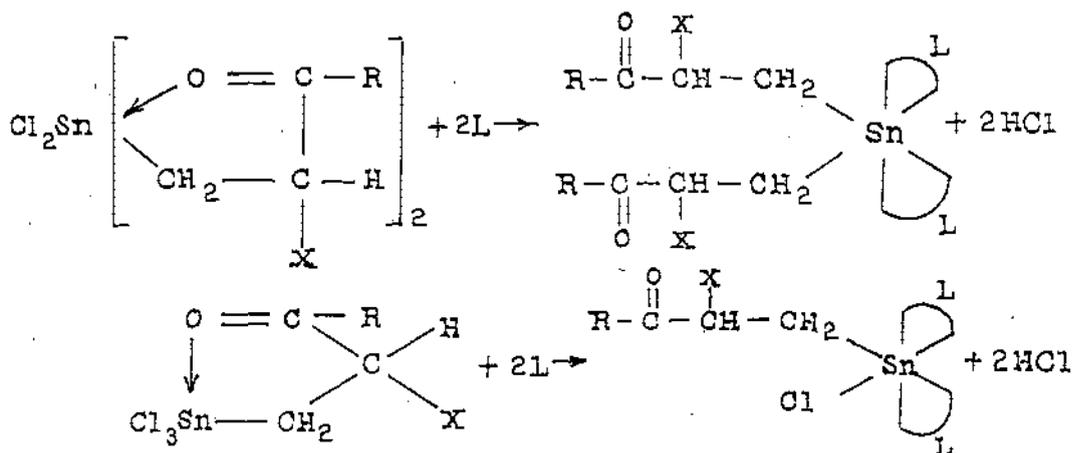
The $\nu(\text{C}-\text{O})$ phenolic also suffers a shift to the higher frequency region due to proton replacement by tin metal. Hutton et al also reported that a closer examination of

the IR spectra of $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$ shows that $\nu(\text{C}-\text{O})$ for the ester group in $\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ lies some 63 cm^{-1} to higher frequency than the same vibration in $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$ (1270 cm^{-1} vs 1207 cm^{-1}). Possibly the methoxy oxygen lone-pair electrons are also involved in the delocalisation of the ester carbonyl electron density on to tin. The intramolecular coordination has, therefore, been represented as



In Bis(β -carbomethoxy ethyl) tin dichlorides the metal is hexa coordinated having two five membered rings (260, 262). Intramolecular carbonyl coordination of the type described above is significantly stronger in the esters and ketones than that in the corresponding dialkyl tin compounds described in a review by Omas (262).

The IR spectra of all the β -carboalkoxy ethyl tin coordination compounds prepared during the present investigation show that the carbonyl stretching frequency in the parent lewis acids i.e. in β -carboalkoxy ethyl tin chlorides is significantly displaced to higher wave number. This indicates the non-chelating nature of the ester carbonyl group. The intramolecular carbonyl coordination of the β -carboalkoxy ethyl tin chlorides is cleaved, which is indicated by the shifting of $\nu(\text{C}=\text{O})$ frequency in the region $1720\text{--}1730\text{ cm}^{-1}$ (position for non-coordinated $\text{C}=\text{O}$ group) in all cases.



much value in the understanding of the structures and bonding in the complexes. Valuable information can, however, be obtained from the frequencies of C = O stretch, Sn-O stretch, C(aryl)-O \angle C₈-O stretch of the quinoline ring), Sn ← N vibration, Sn-C stretch and Sn-Cl vibrations (in case of chloro complexes). Unfortunately, even these modes can not be identified with certainty in all the cases because either of the presence of ligand vibrations or alkyl tin chloride vibrations or the experimental inadequacy. In all the β -substituted alkyl tin oxinates the carbonyl stretching frequency is assigned at $\sim 1720-1730 \text{ cm}^{-1}$.

The existence of intramolecular hydrogen bonding in oxine is shown by its high melting point, steam volatility and IR spectrum etc. (344). In the IR spectrum of oxine the broad band at $\sim 3200 \text{ cm}^{-1}$ may be assigned to the phenolic -OH stretch which is known to form intramolecular hydrogen bond with the quinoline nitrogen atom. As expected, the OH stretching mode disappears in the β -carboalkoxy ethyl tin oxinates confirming bonding through the oxygen atom of the ligand.

Both $\nu(\text{Sn-C})$ and $\nu(\text{Sn-O})$ are expected to occur in $400-600 \text{ cm}^{-1}$ (302, 357-361). $\nu(\text{Sn-C})$ is probably rather weak in these complexes. All the spectra of oxine complexes

show in addition to the Sn-O stretching modes, one other strong absorption band in $\sim 520-540 \text{ cm}^{-1}$. This band which is absent in the spectrum of uncomplexed ligand may reasonably be assigned to Sn-O vibration (oxygen of the 8-OH group) (302). The presence of a number of ligand bands in the region expected for Sn-O stretching, has created some confusion in assigning the Sn-O band in a conclusive manner.

As the spectra were recorded by using KBr windows, the region below 400 cm^{-1} , where Sn \leftarrow N stretching frequency is expected (213, 217, 302, 357), could not be explored.

In the chloro complexes, the far infrared spectra could provide better picture for the assignment of Sn-Cl frequency, but the lack of proper facilities in this respect have restricted us to investigate further in this area.

In the complexes the assignment for $\nu_{\text{asym}}(\text{OSnO})$ [at $\sim 640-65 \text{ cm}^{-1}$] (216) was not possible due to the presence of ligand bands in this region.

The C = N stretching frequency somewhat coupled with pyridine ring vibration appears as a strong band in oxine at 1580 cm^{-1} . In all the oxine complexes this band,

however, shifts to $\sim 1560-1570 \text{ cm}^{-1}$ (362).

In the complexes the presence of quinoline ring can be easily identified from the appearance of characteristic bands such as (i) a number of bands (more than six) due to ring breathing vibrations between $1360-1625 \text{ cm}^{-1}$ (ii) a sharp band due to characteristic C-O stretching frequency at $\geq \text{C-O-Sn}$ site at $\sim 1100 \text{ cm}^{-1}$ (363) and (iii) a number of sharp strong bands due to the CH deformation modes in the region between 900 cm^{-1} and 700 cm^{-1} (364). As all the spectra were recorded in nujol mull, no assignment for ν_{OH} frequency has been attempted.

The spectra of thiocyanate complexes are nearly identical to those of the corresponding halide complexes except that a very intense absorption band at $\sim 2000-2050 \text{ cm}^{-1}$. The ambident ligand $-\text{SCN}-$ can coordinate to metal either through S or through N or it can act as a bridge. Sabatini and Bertini (365) have suggested the following criteria to distinguish between these two types of coordinations:

$\nu(\text{C}\equiv\text{N})$	$\text{M-N}\equiv\text{C-S}$ below 2100 cm^{-1} (broad)	$\text{M-S-C}\equiv\text{N}$ 2100 cm^{-1} (sharp)
$\nu(\text{C-S})$	$360-780 \text{ cm}^{-1}$	$690-720 \text{ cm}^{-1}$
$\nu(\text{NCS})$	$490-450 \text{ cm}^{-1}$	$440-400 \text{ cm}^{-1}$

Though the C-S stretching frequency is more useful in distinguishing these two isomers (365-367) the oxine has many absorptions in this region that they may obscure the C-S stretching band. Hence on the basis of the $C\equiv N$ stretching frequency alone, the thiocyanate group may be thought to be linked to tin atom through the nitrogen of the group as all the spectra show absorption band at $\sim 2000-2050\text{ cm}^{-1}$.

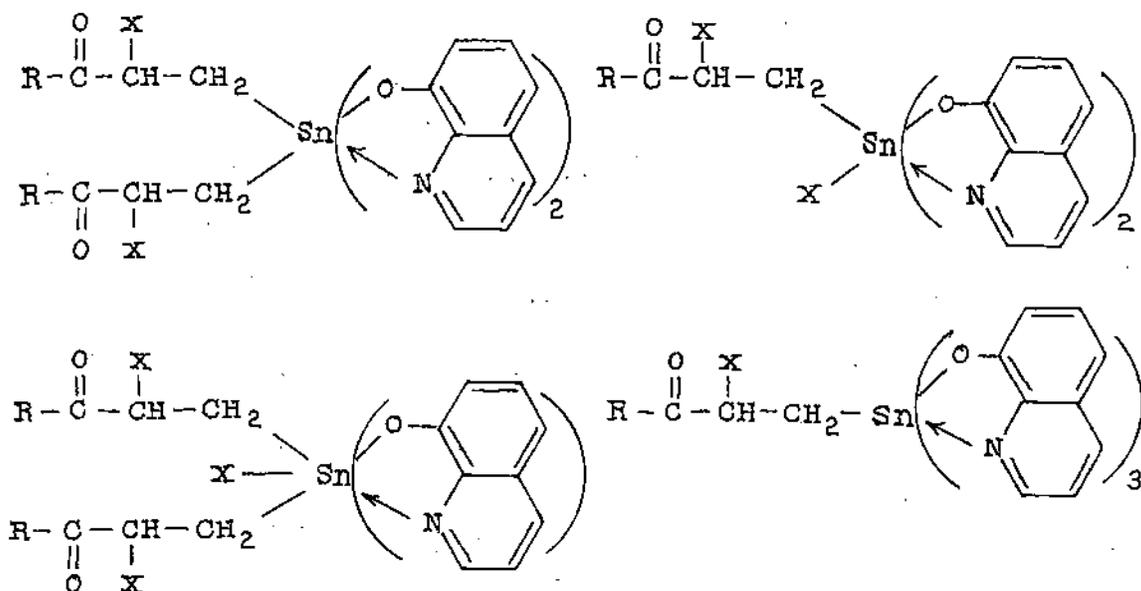
Mullins and Curran (223) have shown that $\text{Ph}_2\text{Sn}(\text{SCN})(\text{Ox})$ [$\text{Ph} = \text{C}_6\text{H}_5$ and $\text{Ox} = 8\text{-hydroxy quinoline}$] does not contain any -NCS- bridging in the solid state since absorption by this compound is at 2025 cm^{-1} in KBr compared to 2035 cm^{-1} in benzene solution and they have suggested a penta-coordinated tin in $\text{Ph}_2\text{Sn}(\text{SCN})(\text{Ox})$. They have also suggested from dipolemoment measurement a cis arrangement of hydrocarbon groups for this compound. From Mossbauer spectra $\text{Ph}_2\text{SnX}(\text{Ox})$ ($X = \text{SCN}, \text{Cl}$) have been shown (216) to have a preferable penta-coordinated structure. Kumar Das et al (302) have reported trigonal bipyramidal geometry with equatorial disposition of R groups for $\text{R}_2\text{SnCl}(\text{Ox})$ [$\text{R} = \text{CH}_3\text{COO}_2\text{CH}_2\text{CH}_2$ -] from Mossbauer spectral data. By an analogy from these data a penta-coordinated trigonal bipyramidal structure may be suggested for $(\text{CH}_3\text{COO}_2\text{CH}_2\text{CH}_2)_2\text{SnX}(\text{Ox})$ [$\text{Ox} = 8\text{-hydroxy quinoline}$ and $X = \text{Cl}, \text{SCN}$] types

of compounds.

A number of diorganotin bis-chelates have been isolated (80, 117, 214, 215, 217, 368-370) and found to contain hexa-coordinated tin atom. McGrady and Tobias (368) suggested a trans-octahedral configuration for the diorganotin bis-oxinate from their I.R., Raman and NMR studies. A trans- configuration has been suggested for $\text{Ph}_2\text{Sn}(\text{Ox})_2$ on the basis of IR, NMR, dipole moment and optical resolution studies (215) and a cis configuration for $\text{Sn}(\text{Ox})_2\text{Cl}_2$ from IR studies (371). A cis- R_2Sn octahedral geometry was suggested for $(\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2)_2\text{Sn}(\text{Ox})_2$ from Mössbauer spectral study (302). From three dimensional X-ray studies of dimethyl tin bis-oxinate, Schlemper (220) showed a highly distorted octahedral structure. The bond angle in the octahedron range from 73.4° to 110.7° . Though the tin atom in dimethyl tin bis-oxinate is six coordinated, $\text{O} - \widehat{\text{Sn}} - \text{O}$ angle is nearly tetrahedral. Diphenyl tin bis-(N-N'-diethyl dithiocarbamate) possesses a distorted octahedral geometry (372). The angle subtended at the tin atom by the group is $101.4(6)^\circ$, with the two Sn-C bond distances equal. Harrison et al (189) have determined the crystal structure of $\text{Me}_2\text{Sn}(\text{Me.CO.NOMe})_2$ by X-ray method. The compound has also been shown to be distorted octahedral, the two N-acyl hydroxyl amine residue function as a bidentate ligand where $\text{Me} - \text{Sn} - \text{Me}$ group is not linear, the $\text{C} - \widehat{\text{Sn}} - \text{C}$ angle being 145.8° . Thus a distorted

octahedral structure may be a general feature of six-coordinated organotin chelate compounds. So, in the light of the above discussion, it seems probable that $R\text{CO}\cdot\text{CH}(\text{X})\text{CH}_2\text{SnCl}(\text{Ox})_2$ (where $R = \text{OCH}_3, \text{OC}_4\text{H}_9, \text{CH}_3$ etc; $\text{X} = \text{H}, \text{CH}_3$ and $\text{Ox} = 8\text{-hydroxy quinoline}$) compounds may also be six coordinated complexes with a distorted octahedral geometry where the cis- or trans- configuration is of less significance.

From the above discussions the nature of bonding in β -carboalkoxy ethyl tin oxinates may be represented as follows



(where $R = \text{OCH}_3, \text{OC}_4\text{H}_9, \text{CH}_3$; $\text{X} = \text{Cl}, \text{SOH}$)

In the IR spectra of 5,7-dichloro oxine and 5,7-dibromo oxine a broad, medium to weak intensity band at 3200 cm^{-1} , which may be associated with an inter/intramolecularly bonded OH vibration, is observed. In the solution spectra of several 5,7-substituted-oxine, Badger and Moritz (371) observed such band at $3400\text{-}3350\text{ cm}^{-1}$. The medium intensity band present in the ligands at $\sim 1400\text{ cm}^{-1}$ can be ascribed to the phenolic OH in plane deformation vibration coupled with C-O stretching mode. The second coupled mode expected at $\sim 1200\text{ cm}^{-1}$ could be located in both the 5,7-substituted oxines. The band at $\sim 860\text{ cm}^{-1}$ in both the ligands may be due to the OH out of plane deformation vibration. In the spectra of all the 5,7-substituted oxine complexes the complete absence of any ν_{OH} frequency at the region around 3200 cm^{-1} , the shifting of the carbonyl stretching frequencies to higher wave numbers between $1720\text{-}1735\text{ cm}^{-1}$ and also the presence of some other characteristic bands show the chelation of the 5,7-substituted oxines in these complexes. In both the 5,7-substituted oxines the C = N stretching frequency somewhat coupled with pyridine ring vibration appears as a strong band at 1580 cm^{-1} . In the substituted oxinate complexes this band occurs at $\sim 1550\text{-}1560\text{ cm}^{-1}$. The bands observed at around $1280, 1190, 1150\text{ cm}^{-1}$ in

most of the substituted oxinate complexes may be attributed to in the substituted pyridine ring vibrations (372). Although the C-Cl absorption in 5,7- dichloro oxine and C-Br absorption in 5,7- dibromo oxine are reported to occur at $750-700\text{ cm}^{-1}$ and $700-650\text{ cm}^{-1}$ respectively (364), these could not be assigned in the complexes due to the presence of β -carboalkoxy ethyl tin chloride bands in this region. The presence of quinoline ring in all the substituted oxine complexes complexes can also easily be identified by the presence of characteristic bands such as (i) a number of bands between $1360-1625\text{ cm}^{-1}$ due to ring breathing vibration (ii) a sharp band of C-O stretching frequency at $\geq\text{C-O-M}$ site is observed at $\sim 1100\text{ cm}^{-1}$ (iii) a number of strong bands between $900-700\text{ cm}^{-1}$ due to CH deformation modes. Of course, the complexes exhibit lesser number of absorptions compared to the oxinate complexes due to lesser number of free ring hydrogen atoms.

In the spectra of organotin substituted oxinates the strong band at 450 cm^{-1} was assigned to Sn-O stretching vibration on the basis of corresponding assignment in organotin-8-quinolinolates by Sen *et al* (236). They also assigned the band at $\sim 370\text{ cm}^{-1}$ to $\nu(\text{Sn-N})$ modes (74) and at $\sim 560-580\text{ cm}^{-1}$ to Sn-O stretching frequency.

The ligands and the ~~and the~~ β -carboalkoxy ethyl tin chlorides have a large number of bands in the region 500-800 cm^{-1} . In the complexes also, the presence of many bands in the region 500-800 cm^{-1} and the unreliability of the data below 500 cm^{-1} due to certain experimental inadequacy make the assignment of Sn-C, Sn-O and Sn-N absorptions rather difficult. Due to the lack of far infrared spectra, the assignment for Sn-Cl absorption in the β -carboalkoxy ethyl chloro tin substituted oxinates could not ^{be} made. The strong band observed in the region 640-650 cm^{-1} in the substituted oxinate complexes may tentatively be assigned to $\nu_{\text{asym}}(\text{OSnO})$.

The IR spectra of the products of reaction No. 17, 25 and 30 (Fig. 21 and 37) respectively are similar to the other β -carboalkoxy ethyl tin oxinates and therefore indicate possibly the chelation of the ligands with β -carboalkoxy ethyl tin chlorides. The IR spectrum of the product of reaction No. 13 shows a band at 2070 cm^{-1} , (in addition to the similar bands like other oxinates) which may be assigned to $\text{N} = \text{N} = \text{N}$ frequency (364) and this possibly indicates the replacement of chlorine by the azide group. Purification and characterisation of these products will be taken up in near future.

The reaction between α, α' -dimethyl β -acetyl ethyl

tin trichloride and oxine in 1:2 molar proportion in chloroform gave interesting products. Towards the end of refluxing period very light crystals (yellow in colour) separated. These crystals had a melting point of 310°C and was virtually insoluble in most of the organic solvents. The IR spectrum of the compound (Fig. 31) probably indicated that it is a tin oxinate-chloride derivative as it showed the characteristic bands of oxine and also a sharp band at 1100 cm^{-1} which may be due to Sn - O - C group. But surprisingly, it did not show any band above 1600 cm^{-1} nor around $3200\text{-}3400\text{ cm}^{-1}$ region. Hence, it may be assumed that due to some unknown reasons the β - carboalkoxy ethyl tin part is cleaved possibly. The elemental analysis of this product showed the following results:

Found: C = 36.95, H = 1.73 and N = 4.64 percent

The calculated values for empirical composition like $\text{C}_9\text{H}_6\text{ON} \cdot \text{SnCl}_2$ are as follows

C = 32.34, H = 1.79 and N = 4.19 percent.

The percentage of carbon as found in the sample is rather high in comparison to the calculated value for the empirical formula, $\text{C}_9\text{H}_6\text{ON} \cdot \text{SnCl}_2$. The compound could

not be purified to the desired level and the anomaly may be due to impurity. However, the above suggestion is somewhat speculative in nature.

The other solid isolated from this reaction showed a melting point of 220°C and was found soluble in chloroform, methanol etc. The analytical results correspond quite well to a molecular formula $\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{SnCl}(\text{C}_9\text{H}_6\text{ON})_2$. But the IR spectrum (Fig. 30) of this compound is quite different from all other β -carboalkoxy ethyl tin oxinates isolated so far and somewhat puzzling in nature. The compound showed a strong absorption at 3320 cm^{-1} and the total absence of the $\nu(\text{C}=\text{O})$ band at $\sim 1720\text{ cm}^{-1}$ (as found in all β -carboalkoxy ethyl tin oxinates). It showed a new peak at 1620 cm^{-1} (probably due to $>\text{C}=\text{CH}$ group). The presence of 3320 cm^{-1} and 1620 cm^{-1} bands and absence of $\sim 1720\text{ cm}^{-1}$ band may point to an unusual structure of this compound, which can be as follows.

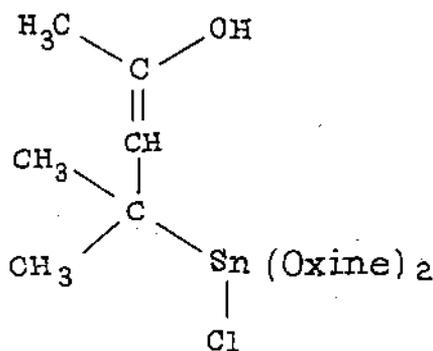


Fig. XVII

The above structure may be proposed on the basis of a mechanism given by Hutton et al (305).

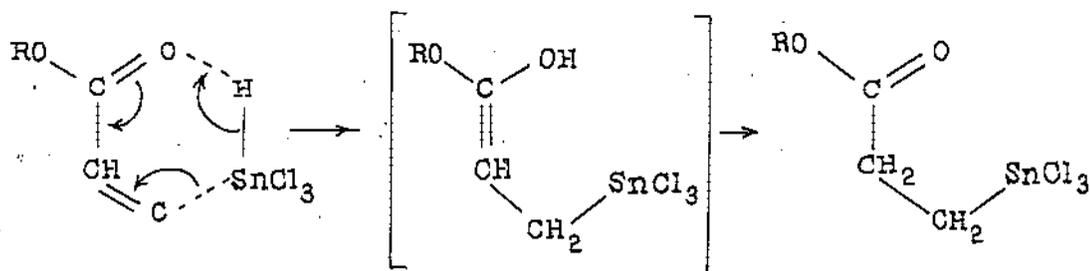


Fig. XVIII

In case of α, α' -dimethyl β -acetyl ethyl tin trichloride the ^{Fig.}XVIII type of structure may produce the α, α' -dimethyl β -acetyl ^{ethyl}chloro tin bis-oxinate complex (Fig. XVII). The enol form of β -substituted alkyl tins ^{has} not yet been reported. Without the assumption of such an enol form it is rather difficult to explain the IR spectrum of this compound (m.p. 220°C), because the spectrum strongly suggests the formation of a oxinate complex in all other aspects. Due to certain difficulties, the PMR spectrum of the compound having m.p. 220°C, could not be recorded so far. Hence the above suggestions are only tentative in nature.

The ligands phenyl-5-azo oxine and 5(2'-carboxy phenyl)azo oxine form similar β -carboalkoxy ethyl in complexes like oxine and substituted oxines as discussed earlier. The OH stretching frequency in phenyl-5-azo oxine occurs at $\sim 3380 \text{ cm}^{-1}$ as a broad band and at $\sim 3480 \text{ cm}^{-1}$ (very broad) and 3360 cm^{-1} (shoulder) in 5(2'-carboxy phenyl)azo oxine indicating the presence of hydrogen bonding interactions involving the OH group. The two frequencies in the 5(2'-carboxy phenyl) azo oxine are presumably due to the carboxylic -OH and phenolic -OH groups respectively. The phenolic -OH groups in both the ligands are known to form intramolecular hydrogen bond with the quinoline nitrogen atom (344). The carboxylate stretching $\nu_{\text{as}}(\text{OCO})$ occurs at $\sim 1630 \text{ cm}^{-1}$ in the free ligand, 5(2'-carboxy phenyl)azo oxine. The lower value of $\nu_{\text{as}}(\text{OCO})$ may be due to the hydrogen bonding involving the hydrogen atom of the COOH group.

In the IR spectra of β -carboalkoxy ethyl tin phenyl-5-azo oxinates the absence of any ν_{OH} frequency, the shifting of the carbonyl stretching frequencies to higher wave number at $\sim 1715\text{-}1725 \text{ cm}^{-1}$ and the presence of C = N stretching frequency somewhat coupled with pyridine ring vibration at 1580 cm^{-1} , the Sn-O stretch at

$\sim 510-520 \text{ cm}^{-1}$, characteristic C-O stretching at $\rightarrow \text{C}-\text{O}-\text{Sn}$ site at $\sim 1100 \text{ cm}^{-1}$ and some characteristic bands for quinoline ring absorptions clearly indicate the chelating nature of the ligand. A strong band at 1245 cm^{-1} in phenyl-5-azo oxine moves to $\sim 1250 \text{ cm}^{-1}$ in the complexes can be assigned to the C(aryl)-O (C₈-O stretch of the quinoline ring) stretch. An upward shift of this shifting is expected in the organotin compounds because of the large polarity of $-\text{O}-\text{Sn} \leftarrow$ bond (361) increases the conjugative interaction of the oxygen atom with the Π -ring resulting in an increase of the C-O bond order. The N = N stretching mode is of little use though the vibration $\delta(\text{N} = \text{N})$ in the complexes is expected to provide valuable clue to the participation or otherwise the azo group in the organotin complexes. This is because the substitution on the azo group in dyes are fairly symmetrical (as far as the local symmetry is concerned, the group in azo-dyes always being $\rightarrow \text{C}-\text{N} = \text{N} - \text{C} \leftarrow$) and is, therefore, likely be weak in IR spectrum. Although the vibration has been reported by some authors to occur at 1400-1450 cm^{-1} region (373), Miller (374) has emphasised that no diagnostically useful band can be found in this region in azo dyes. The latter studies involving complexes of aryl azo benzoic acids (201, 375-377) also confirm this.

The compound Bis(β -carbomethoxy ethyl) tin bis-5(2'-carboxy phenyl)azo oxinate shows similar nature in its IR spectrum. The bands at 1570 cm^{-1} , 508 cm^{-1} and 1100 cm^{-1} may be assigned to the C = N stretching frequency of the pyridine ring, Sn-O stretch and C-O stretching at >C-O-Sn site respectively. The broad band at $\sim 3460\text{ cm}^{-1}$ may be due to the hydrogen bonded carboxy OH stretch and the band at 1650 cm^{-1} may be due to the $\nu_{\text{as}}(\text{OCO})$ stretch of the carboxyl group. The bands at 1725 cm^{-1} and 1690 cm^{-1} may possibly indicate that the intramolecular coordination of one of the two carbonyl groups of the alkyl proton is cleaved whereas other is still dominating to some extent. In that case the complex may be suggested to be penta coordinated around tin.

Dithizone is a dibasic acid, it contains two labile hydrogen per molecule, one of which attacks the chlorine of the organotin chloride in equilibrium reaction to give hydrochloric acid along with the formation of the organotin derivatives of dithizone. Solid dithizone exists mainly in the thioketone form (Fig. V) but in solution it undergoes rapid tautomeric equilibrium with the thiol form (Fig. V) (208).

There is no evidence of dithizone losing a second proton to form Dz^{-2} (H_2Dz = Dithizone) in aqueous solution. However, Fischer (378) realized that two types of metal dithizone complexes could be obtained and he obtained these complexes as keto (Fig. XIX and XX) and enol form (Fig. XXI and XXII).

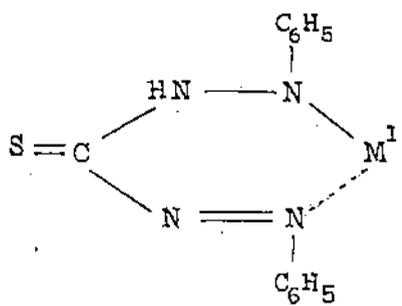


Fig. XIX

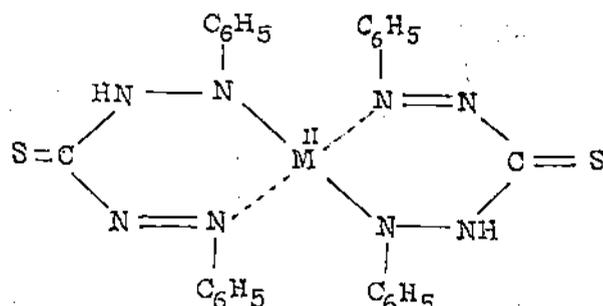


Fig. XX

Keto form.

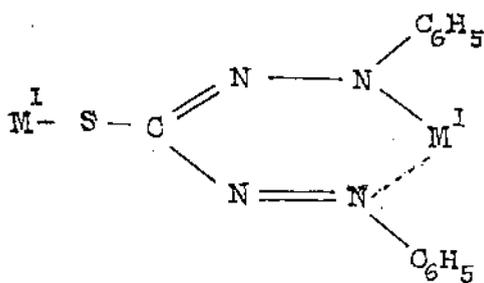


Fig. XXI

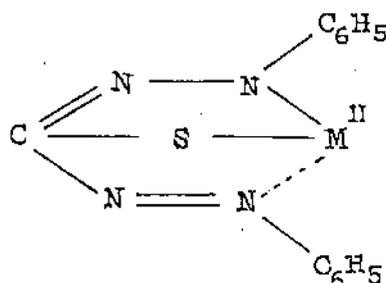


Fig. XXII

Enol form

(379)

Instead of keto and enol dithizonates, Sandell referred to these compounds as primary and secondary dithizonates respectively.

Later on, X-ray crystallographic studies of metal dithizonates showed a common pattern for the structure of solid primary dithizonates of positive cation like Fig. XXIII (379).

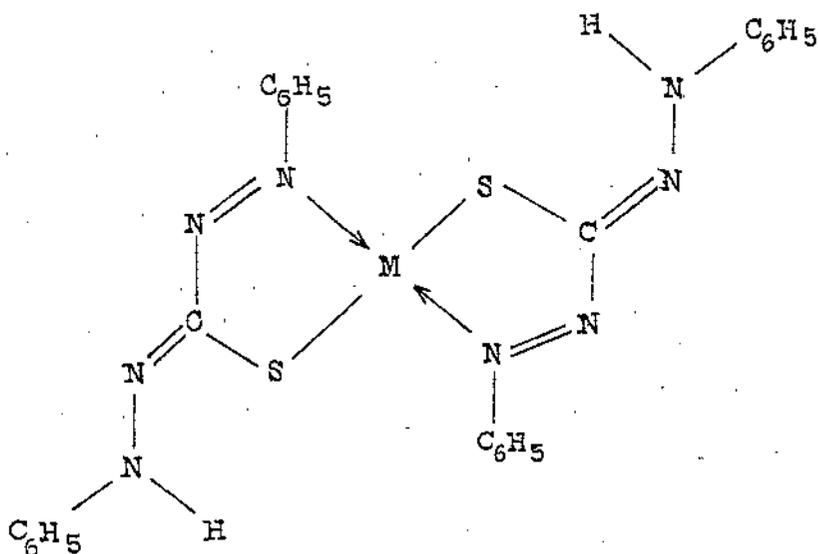


Fig. XXIII

Kemula and Ganko (380, 381) from the molecular weight, magnetic property and X-ray analysis of the secondary

dithizonates of bivalent cation proposed the structure (Fig. XXIV) and for monovalent cation they proposed the

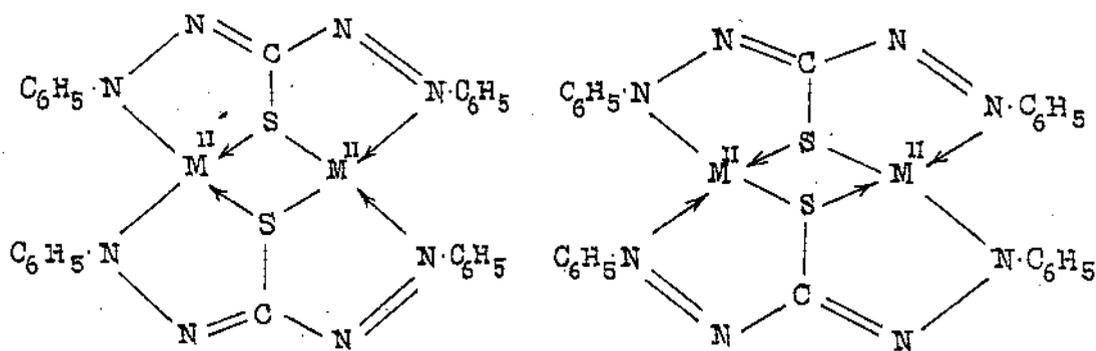


Fig. XXIV

structure of secondary dithizonate as Fig. XXV.

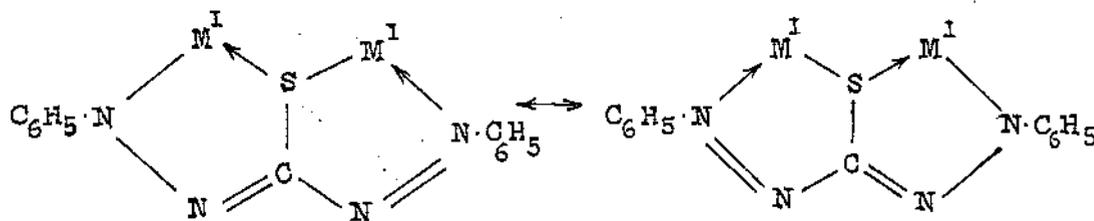


Fig. XXV

Thus from the above discussions it may be expected that two types of organotin dithizonates could be obtained like the metallic dithizonates. The β -carboalkoxy ethyl tin dithizonates so far have been synthesized in the present investigation, all show absorption band due to stretching of N-H bond in the IR spectrum in the region of $\sim 3160-3220 \text{ cm}^{-1}$ and PMR spectra of these complexes also show -NH signal corresponding to a single proton. Thus the possibility of β -carboalkoxy ethyl tin dithizonates, prepared in the present investigation, to have a bonding like secondary dithizonates in which both the hydrogen of dithizone are replaced by metal ion is ruled out. So, the β -carboalkoxy ethyl tin dithizonates so far prepared are suggested to be primary dithizonates, in which only one hydrogen atom of dithizone has been used in bonding with organotin moiety.

From the IR spectral data of all the β -carboalkoxy ethyl tin dithizonates, we have noticed that all these compounds show N-H stretching frequency in the region $\sim 3150-3220 \text{ cm}^{-1}$. Duncan and Thomas (382) reported that -NH bond not involved in hydrogen bonding has stretching frequency at 3326 cm^{-1} in diazo amino benzene, $\text{C}_6\text{H}_5\text{N} = \text{N-NH.C}_6\text{H}_5$, which is somewhat analogous with the dithizone

structure. Thus, the presence of N-H stretching frequency at $\sim 3160-3220 \text{ cm}^{-1}$ indicates intramolecular hydrogen bonding in β -carboalkoxy ethyl tin dithizonates. Ghosh (210) also reported the intramolecular hydrogen bonding in organotin dithizonates.

Meriwether et al (383), Ashizawa (384), Dyferman (385), Ramkrishna (386) and Kemula and Ganko (380) have suggested for metallic dithizonates the band at $3180-3350 \text{ cm}^{-1}$ for $\ddot{\text{N}}\text{H}$ stretch, band at $1515-1545 \text{ cm}^{-1}$ for $\text{N}\ddot{\text{H}}$ bend, the band at $1257-1375 \text{ cm}^{-1}$ for N-phenyl and a group of bands in the region of $1130-1238 \text{ cm}^{-1}$ for coupled N-C-S bond vibrations. All the organotin dithizonates reported by Ghosh (loc. cit.) show the following absorptions. Chelated nature of organotin dithizonates was also

<u>Compound</u>	<u>NH-stretching vibration</u>	<u>NH-bending vibration</u>	<u>N-phenyl vibration</u>	<u>Coupled N-C-S bond vibration</u>
Triorgano-tindithizonates	3210-3246 cm^{-1}	1508-1512 cm^{-1}	1342-1360 cm^{-1}	1150-1182 cm^{-1}
Diorganotin-dithizonates	3210-3242 cm^{-1}	1510-1520 cm^{-1}	1345-1370 cm^{-1}	1130-1195 cm^{-1}

supported by their PMR spectra e.g. ⁱⁿ dibutyl tin bis dithizonate the alkyl group attached to tin in chelate

exhibited shielding which is due to the increased electron density on the tin via ligand donation (210) τ for complexed dibutyl tin dichloride $\tau_{\text{CH}_3} = 9.04$ (triplet), $\tau_{\text{CH}_2} = 8.19$ (complex pattern) (387); for dibutyl tin bis-dithizonate $\tau_{\text{CH}_3} = 9.34$ (triplet) and $\tau_{\text{CH}_2} = 8.38$ (complex pattern) 7.

In the IR spectra of all the β -carboalkoxy ethyl tin dithizonates prepared in the present investigation the band in the region $\sim 1705-1732 \text{ cm}^{-1}$ is assigned to the free carbonyl stretching frequency of the ester group which is originally present as intramolecularly coordinated carbonyl group in the region $\sim 1640-1680 \text{ cm}^{-1}$ in the parent β -carboalkoxy ethyl tin chlorides. This shifting of carbonyl frequency to higher wave number is due to the cleavage of the intramolecular coordination on complex formation with dithizone. Moreover, in these complexes the presence of bands in the region $\sim 3160-3220 \text{ cm}^{-1}$, $\sim 1500-1530 \text{ cm}^{-1}$ and $\sim 1110-1200 \text{ cm}^{-1}$ are assigned to -NH stretching, -NH bending and N-C-S coupled vibrations respectively. The chelation of the ligand in these complexes are also supported by UV/ Visible spectral data (discussed earlier) and PMR spectral data (discussed later) also.

The ligand dithizone has a large number of absorption bands particularly in the region of 490-800 cm^{-1} . The presence of so many bands in this region has made the assignment for Sn-C, Sn-N rather difficult in β -carboalkoxy ethyl tin dithizonates. Moreover, the unreliability of assignment below 400 cm^{-1} due to experimental inadequacy made the assignment of Sn-Cl bond not feasible. The far infrared measurement could provide a better picture for such assignments but the lack of proper facilities have restricted us to investigate further in this area for the time being.

The IR spectrum of $(\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2)_2\text{Sn}(\text{HDz})(\text{SCN})$ [$\text{H}_2\text{Dz} = \text{Dithizone}$] is exactly identical to that of corresponding halide complexes except a very strong intense absorption band at 2020-2040 cm^{-1} (broad) like Bis(β -carbomethoxy ethyl) thiocyanato tin oxinate. On the basis of suggestions by Sabatini and Bartini (365) it may be mentioned that the thiocyanato group in Bis(β -carbomethoxy ethyl) thiocyanato tin dithizonate is linked to tin atom through the nitrogen. Like other diorganotin halo oxinates, a penta-coordinated trigonal bipyramidal structure may be suggested for this thiocyanato dithizonate complex.

On the basis of existence of intramolecular hydrogen bonding and chelated nature of the β -carboalkoxy ethyl tin dithizonates the nature of bonding of the organotin moieties with dithizone may be one of the following possibilities.

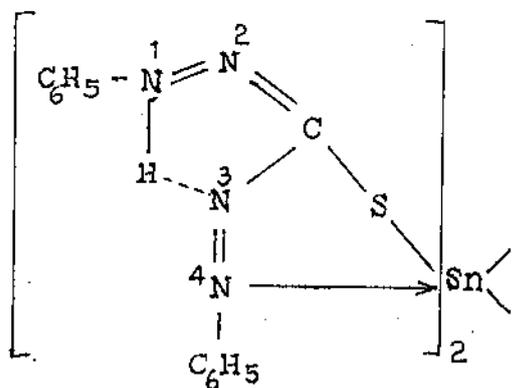


Fig. XXVI

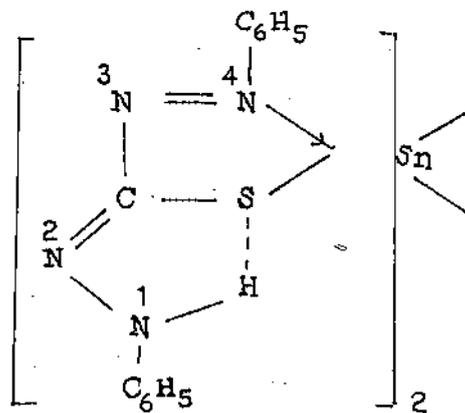


Fig. XXVII

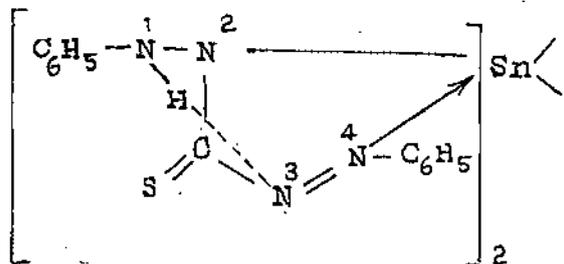


Fig. XXVIII.

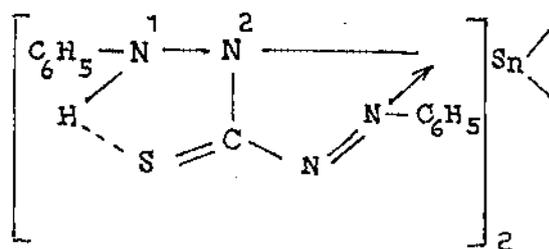


Fig. XXIX.

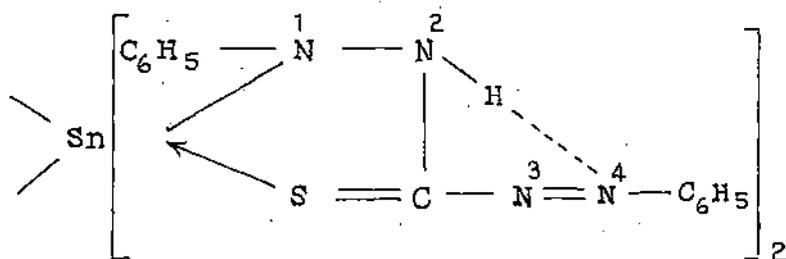


Fig. xxx

Of these structures, Fig. XXVI and XXVII would appear to be more likely for the following reasons.

X-ray analysis of primary metallic dithizonates (388) show the existence of metal-sulphur bond and as the IR spectra of these complexes are very similar to those of metallic dithizonates, the possibility of structures Fig. XXVIII and XXIX are rather unlikely. Structure in Fig. XXX is also rather unlikely on the ground that the hydrogen atom attached to 2-N atom in dithizone would be expected to be more acidic than that attached to the 1-N

atom due to the proximity of the sulphur atom.

Laing (389) determined the crystal structure of dithizone by X-ray method and found ^{that} the molecule (Fig. XXXI) is nearly planar, with the C-S bond lying on the intersection of two mirror planes, although phenyl groups are twisted slightly out of the mean plane in opposite sense. It is evident from the measured bond length that the π -electrons in the N-N-C-N-N chains are delocalised in all cases, and that there are no localised single or double bonds. The two imino hydrogen atoms are located as shown in Fig. XXXI which is equivalent.

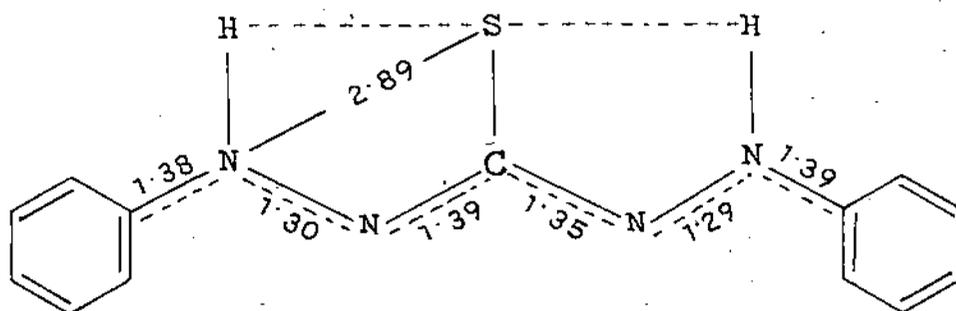


Fig. XXXI

Crystal structure studies of dithizone may rule out the possibility of the structure proposed in Fig. XXX.

Since all the β -carboalkoxy ethyl tin dithizonates studied here show absorption bands between ~ 1110 - 1200 cm^{-1} indicating the presence of N-C-S group, these compounds can be suggested to have bonding like Fig. XXVI and XXVII. The tin atom in R_2SnL_2 and $RSnL_2X$ ($R = \beta$ -carboalkoxy ethyl tin moiety and $L =$ Dithizone) type of complexes is possibly hexa coordinated. A large number of diorganotin bis-chelates have been found to be hexa coordinated. So, by an analogy with those (189, 220, 372), it seems highly probable that R_2SnL_2 and $RSnL_2X$ ($X = Cl, SCN$) type of β -carboalkoxy ethyl tin dithizonates may also be six-coordinated complex with a distorted octahedral geometry where the term cis- and trans- configuration is of less significance. Like other organotin chelates, in R_2SnLX ($X = Cl, SCN$) type of dithizonate complexes the arrangement of the groups around tin atom, may possibly be a trigonal bipyramidal one.

From the IR measurements on 1,5-diphenyl (carbazone powder (KBr pellets), Blaton et al (355) concluded that solid diphenyl carbazone is present only as the keto form (Fig. XVI) as the ν_{OH} stretching band was absent and the $\nu_{C=O}$ stretching band is strong (1707 cm^{-1}). The bands observed in the region 3000 - 4000 cm^{-1} due to intramolecular and intermolecular bonded N-H vibrations, were

also attributed by them. From X-ray crystal structure determination also, they concluded that in the solid state, the diphenyl carbazone exists only in the keto form and that no intramolecular but only intermolecular N-H-----O bonds are present.

The spectra of diphenyl carbazone taken in nujol mull using KBr windows (Fig. 77) showed absorptions at $\sim 3300-3400\text{ cm}^{-1}$, 1707 cm^{-1} and 1652 cm^{-1} . The band at $\sim 3300-3400\text{ cm}^{-1}$ is probably due to N-H stretching vibrations, the band at 1707 cm^{-1} is due to $\Delta\text{C} = \text{O}$ stretching mode and the band at 1652 cm^{-1} is possibly due to N-H bending vibration or it may be an additional band for carbonyl group at the vicinity of NH group.

In the IR spectrum of the complex Bis(β -carbomethoxy ethyl) chloro tin diphenyl carbazonate (Fig. 78), a new band at 1542 cm^{-1} appears. This is most probably due to chelated carbonyl group of diphenyl carbazone. Thus considerable shift of the carbonyl stretching frequency is observed in the complex, indicating the chelated nature of the ligand. The spectrum also shows a very characteristic nature in the ^{region} $1100-1220\text{ cm}^{-1}$. The broad band in this region is probably due to coupled N-C-O vibrations. The bands at $\sim 1550\text{ cm}^{-1}$ and $\sim 1100-1220\text{ cm}^{-1}$ were also observed in other organotin diphenyl carbazonates (211). The $\Delta\text{C} = \text{O}$

frequency of the ester grouping appeared at 1720 cm^{-1} and 1670 cm^{-1} in the complex which indicates that one of the two internally coordinated carbonyl group of the ester part is cleaved while the other is still dominating. Due to presence of ligand bands the assignment for Sn-O stretch in the complex could not be done with certainty.

The IR spectrum of the product of reaction No. 101, is similar to that of Bis(β -carboalkoxy ethyl) chloro tin diphenyl carbazonate, which also indicates the chelating nature of diphenyl carbazone.

The β -carboalkoxy ethyl tin chlorides form deep coloured compounds with hydroxy anthraquinone derivatives like Alizarin, Quinalizarin, Sodium Alizarin Sulphonate (Alizarin - S). Though it has not been possible to isolate crystalline compounds in all cases, four alizarin complexes in crystalline and pure state were obtained. Alizarin (Fig. 79) exhibits $\nu_{\text{C}=\text{O}}$ frequency at 1630 cm^{-1} with a shoulder at 1655 cm^{-1} and a very strong ν_{OH} frequency at 3400 cm^{-1} apart from other characteristic frequencies. The IR spectra of all the β -carboalkoxy ethyl tin alizarinates show some interesting features. All these spectra show the absence of any ν_{OH} absorption which signifies that the two hydroxyl groups of alizarin have been utilised in the complex formation (200) i.e. in the complexes both the hydrogen atoms

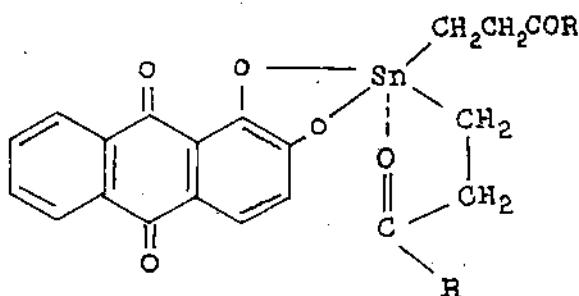
of the hydroxyl groups in alizarin have been removed by two chlorine atoms of β -carboalkoxy ethyl tin chlorides. The PMR spectra (0-10 δ ppm) also showed the absence of any hydroxyl proton in the complexes.

In the spectrum of Bis(β -carbomethoxy ethyl) tin alizarinate four (Fig. 80) bands appear in the region 1620-1730 cm^{-1} . The bands at 1630 cm^{-1} and 1620 cm^{-1} may be assigned to the carbonyl stretching frequencies of frequencies of alizarin. The two additional bands at 1730 cm^{-1} and 1675 cm^{-1} are probably due to carbonyl stretching frequencies of Bis(β -carbomethoxy ethyl) tin moiety. These two bands viz, at 1730 cm^{-1} and 1675 cm^{-1} possibly indicate that one of two internally coordinated carbonyl frequencies of Bis(β -carbomethoxy ethyl) tin dichloride (originally at 1677 cm^{-1}) is cleaved and shift to longer wave length in the complex while the other is still dominating.

In Bis(β -carbobutoxy ethyl) tin alizarinate (Fig. 83) four such bands also appear at 1725 cm^{-1} , 1670 cm^{-1} , 1635 cm^{-1} and 1620 cm^{-1} . The former two bands are probably due to the carbonyl frequencies of ester grouping while the latter two bands are due to carbonyl frequencies of alizarin.

In case of two β -carboalkoxy ethyl chloro tin alizarinates (Fig. 82 and 85) we observed a single band at $\sim 1710-1705$ due to $\nu_{C=O}$ frequency of ester carbonyl and two bands in the region $\sim 1625-1640$ cm^{-1} due to $\nu_{C=O}$ of alizarin.

All four β -carboalkoxy ethyl tin alizarinates show close similarity in their spectra and on comparing these with the spectrum of alizarin, it seems that carbonyl groups of alizarin are not markedly involved in complex formation. In absence of more detailed studies like Mossbauer spectra, X-ray analysis etc, which we could not get due to lack of facilities, it would not be judicious to suggest any definite structure for such complexes. However, on the evidence of IR and PMR studies, so far carried out, we may tentatively suggest structure in Fig. XXXII for Bis-complexes and structure in Fig. XXXIII for Bis chloro complexes.



(R = OCH_3 , OC_4H)

Fig. XXXII

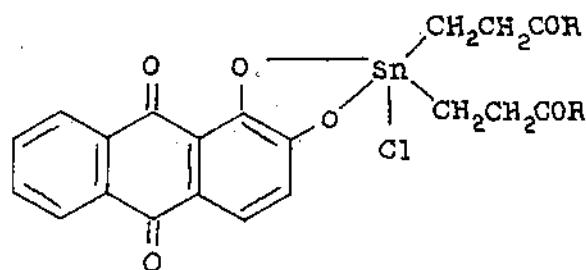


Fig. XXXIII

So far we have not yet been successful to isolate β -carboalkoxy alkyl tin derivatives of Quinalizarin or Sodium Alizarin sulphate in pure state. The IR spectra of the product of reaction No. 53 and 54 (Fig. 87 and 89), are somewhat similar to those of alizarin complexes and also indicate the chelating nature of the ligands.

The IR spectra of the ligand, 1-nitroso-2-naphthol (Fig. 90) does not show normal ν_{OH} vibration due to strong intramolecular hydrogen bonding and this has been attributed to chelation (364). The very strong broad band at $\sim 3400 \text{ cm}^{-1}$ may be due to this type of OH frequency. The band at 1610 cm^{-1} in the spectra of the ligand may be assigned to the $N = O$ group frequency. In the complex Bis(β -carbomethoxy ethyl) chloro tin 1-nitroso-2-naphtholate (Fig. 91) this $N = O$ group frequency at 1610 cm^{-1} may shift to lower wave number on coordination to tin and possibly appears in the region $\sim 1510-1565 \text{ cm}^{-1}$ somewhat coupled with ring breathing mode. The shifting of the carbonyl frequency of ester grouping to higher wave number in the complex and the absence of any OH frequency may suggest that it is a chelated complex.

During the attempts to replace the chlorine atoms of β -carboalkoxy ethyl tin chlorides by thiocyanate, azide and acetate groups, it has been possible to isolate solid thiocyanato derivatives. The infrared spectra of Bis (β -carbomethoxy ethyl) tin dithiocyanate (Fig. 92) shows the appearance of new bands at 2060 cm^{-1} and 860 cm^{-1} . The band at 2060 cm^{-1} may be assigned to $\nu_{\text{C}\equiv\text{N}}$ vibration of thiocyanato group whereas the band 860 cm^{-1} is due $\nu_{\text{C-S}}$ absorption. The position of these two bands, on the suggestion of Sabatini and Bertini (loc. cit), strongly suggests that the thiocyanato group is linked to tin atom through nitrogen. As Bis(β -carbomethoxy ethyl) tin dichloride has a band at $\sim 490\text{ cm}^{-1}$, it is not possible to assign $\nu_{\text{(NCS)}}$ frequency in this region. It may also be noted that the $\nu_{\text{C=O}}$ frequency in the thiocyanato derivative appears at 1650 cm^{-1} whereas in chloro derivative it is at 1677 cm^{-1} . The shifting of $\nu_{\text{C=O}}$ from 1677 cm^{-1} to 1650 cm^{-1} in the thiocyanato derivative is rather likely due to more electropositive character of SCN group in comparison to chloride. The IR spectra of β -carbomethoxy ethyl thiocyanato tin dichloride is almost similar to the dithiocyanato derivative described above.

The IR spectrum of the product of reaction No. 59 shows a band at 2070 cm^{-1} which may be due $\overset{\text{to}}{\underset{\wedge}{\text{N}} = \text{N} = \text{N}}$

frequency and a band at 1660 cm^{-1} due to $\nu\text{C}=\text{O}$ frequency. The appearance of the band at 2035 cm^{-1} possibly suggests the replacement of chlorine by azide group although the product could not be isolated in pure state.

The IR spectrum of the very hygroscopic product having m.p. 110°C , of reaction No. 59 (Fig. 94) shows the $\nu\text{C}=\text{O}$ frequency of ester grouping at $\sim 1720\text{ cm}^{-1}$ and $\nu\text{C}=\text{O}$ absorption of acetate group at $\sim 1580\text{ cm}^{-1}$ which indicates that chelating acetate group may possibly be present. Further work is necessary to discuss this compound in more detail.

In most of the PMR spectra recorded the presence of a signal for $-\text{CH}$ proton of solvent CHCl_3 at ~ 7.2 ppm was found to be present and was given due consideration while interpreting the spectra. From the integration of the curves, the ratio of different protons have been found to be consistent with the composition of the complexes.

In their PMR spectra, all the β -carboalkoxy ethyl tin chlorides exhibit three signals for α - CH_2 [H_α], β - CH_2 [H_β] and $-\text{OCH}_3$ or $-\text{OCH}_2$ [H_γ] protons respectively. In addition to these, the β -carboboxy ethyl tin chlorides exhibit two more signals of the butyl group, one for four methylene protons (complex pattern) and the other for methyl

protons while β -carbomethoxy β' -methyl ethyl tin trichloride exhibits an additional signal for the methyl protons (along with the signal for methine proton [β -CH] instead of β -CH₂ protons). In general, on complex formation all types of protons of the β -carboalkoxy ethyl groups should exhibit shielding and thereby resonate at higher magnetic field which is in agreement with an increased electron density on the tin via ligand donation. In addition, the normal inductive effect of the coordinating ligand and the magnetic influence of the tin atom also combine to govern the alkyl resonance positions. Depending upon the basicity of the donor, the α -methylene protons should be shielded most. The PMR spectrum of methyl propionate in CDCl₃ furnished methoxy signal at 3.66 (δ ppm) (300). In β -carboalkoxy alkyl tin chlorides this signal is shifted to downfield due to deshielding of the methyl protons by the lone pair of electrons of methoxy oxygen delocalised because of coordination to tin.

In the PMR spectra of all β -carboalkoxy ethyl tin oxinates, it is seen that the alkyl protons (H_α , H_β , H_γ) attached to tin are shielded compared to the parent β -carboalkoxy ethyl tin chlorides, which is quite expected due to complex formation. Again in the β -carboalkoxy ethyl

thiocyanato oxinates the amount of deshielding is less than the corresponding β -carboalkoxy ethyl chloro tin oxinates due to the less electronegative character of the thiocyanate group. Of the alkyl protons the α -methylene protons are mostly shielded in all the β -carboalkoxy ethyl tin oxinates except in case β -carbomethoxy β' -methyl ethyl chloro tin bis-oxinate, where the methoxy proton is most shielded, which may be due to some steric reasons. When the chlorine atoms are replaced by bidentate ligands, the ester coordination is broken off, as seen from the IR spectra. Further evidence for the non-chelating nature of the ester carbonyl group in these complexes is obtained from the values of chemical shifts of β -methylene and methyl protons. Both the β -methylene and methyl protons in the β -carboalkoxy ethyl tin chelates also suffer shielding and revert to positions, characteristic of free ester group.

From the data given in table VIII, it appears that some complexes isolated contain probably mixture of isomers. Attempts would be made in future to isolate these isomers in pure state. Due to probable presence of isomeric forms, difficulties were encountered to correctly assign the signals. Moreover, the quality of the PMR spectra and resolution of the signals unfortunately were not satisfactory

in certain cases. Hence, some of the assignments of the signals given here may be tentative in nature. Attempts will be made to obtain further spectral data in future. Moreover in absence of detailed structural data for the complexes, the interpretation of PMR spectral data may not be unambiguous in all cases. In spite of these difficulties, we would like to attempt to rationalize the data, so far obtained.

The chemical shifts observed for the ring protons in β -carboalkoxy ethyl tin oxinates (Table VIII) show that the proton at the 2-position (2-H) of quinoline ring is most affected. A shielding or deshielding is observed for 2-H protons while the other protons remain unaltered or slightly altered. Electron donation to tin on coordination has produced a deshielding of the 2-H proton of oxine in Bis(β -carbomethoxy ethyl) thiocyanato tin oxinate (Fig. 14), β -carbomethoxy ethyl tin tris-oxinate (Fig. 20) and β -carbobutoxy ethyl tin tris-oxinate (Fig. 27) and is observed at lower magnetic field compared to the resonance positions in the free ligand. In all other oxine complexes, shielding of the 2-H proton is observed which indicates that Bis (β -carbomethoxy ethyl) thiocyanato tin oxinate, β -carbomethoxy ethyl tin tris-oxinate and β -carbobutoxy ethyl tin tris-oxinate possibly appear to

involve a greater extent of chelation in solution compared to other oxinate complexes. Kumar Das et al (302) also observed a shielding effect (~ 0.31 ppm) for 2-H proton of oxine in Bis(β -carbomethoxy ethyl) tin bis-oxinate, but did not offer any explanation for such shielding. On the other hand they concluded that the chelating nature of oxine in Bis(β -carbomethoxy ethyl) tin bis-oxinate is not so strong as in case of Bis(β -carbomethoxy ethyl) chloro tin oxinate where 2-H proton of oxine ring suffered a deshielding of ~ 0.39 ppm and appeared at 9.12 ppm. They anticipated a considerable downfield shift for 2-H (oxine) and 4-H (oxine) resonances in such complexes. In general, it is expected that the proton at 2-position of oxine ring will be appreciably affected due to the donation of electrons from the neighbouring nitrogen atom and consequently this proton would suffer considerable downfield shift. But the actual position of such proton may also be influenced by other factors (390, 391). In certain cases, it may be possible that ring current effects and other factors can compensate such downfield shifts and as a result such proton may resonate at higher magnetic field also. In a number of cases, after complexation shielding of aromatic protons have been known (185). Moreover, in Bis(β -carbomethoxy ethyl) chloro tin oxinate, the presence

of Sn-Cl bond may influence the position of aromatic protons markedly. Hence, it may not be possible to conclude in a definite manner about the extent of chelation, from such downfield shift of the 2-H (Oxine) proton only.

In the chloro oxinate complexes (Table VIII) the H_{α} , H_{β} and H_{γ} protons are less shielded compared to the bis-oxinate or tris-oxinate complexes. The presence of Sn-Cl bond and other steric factors may possibly deshield somewhat the H_{α} , H_{β} and H_{γ} protons compared to the bis- and tris - oxinate complexes. The PMR spectra of β -carbomethoxy ethyl thiocyanato tin bis-oxinate (Fig. 25), β -carbomethoxy ethyl tin tris-oxinate and β -carbobutoxy ethyl tin tris-oxinate indicate the possible presence of mixture of geometrical isomers.

In the PMR spectrum of oxine (Fig. 10), the protons at 2- and 4- positions are clearly separated by two signals at 8.73 (doublet) and 8.11 (doublet) ppm respectively at the downfield region, while the other four protons (at 3-, 5-, 6- and 7- positions) formed a complex pattern signal in the region 7.11-7.58 ppm. But β -carboalkoxy ethyl tin oxinates exhibit four types of signals which may be due to 2-H, 4-H, 7-H and (3-, 5- & 6-) H (complex pattern) protons respectively at the downfield region. This trend can not be clearly identified for all protons where the

complexes are possibly formed as a mixture of geometrical isomers. Moreover, in case ^{of} Bis(β -carbomethoxy ethyl) thiocyanato tin oxinate these four signals are possibly due to 2-H, 4-H (5- & 7-)H and (3- & 6-)-H protons respectively.

In the PMR spectrum of Bis (β -carbomethoxy ethyl) tin bis-5, 7-dichloro oxinate (Fig. 35) shielding of the H_{α} , H_{β} and H_C protons is observed. The amount of shielding of α -methylene proton is maximum in this case also. Of course the amount of shielding of these protons is less compared to oxine and dibromo-oxine complexes. The spectrum of 5,7-dichloro oxine (Fig. 33) reveal that the protons at 2- and 4- positions appear at downfield region as two well separated doublets but the protons at 3- and 6-positions unlike dibromo oxine (discussed later) are not well separated but form a complex pattern in 7.44-7.68 ppm region. But in the case of Bis(β -carbomethoxy ethyl) tin bis-5,7-dichloro oxinate the protons at 3- and 6- positions appear as two separate signals at 7.52 and 7.70 ppm respectively and the proton at 2- and 4- positions are deshielded to 9.10 ppm and 8.54 ppm as is expected. In this spectrum the protons at 2- and 4- position appear as two doublets at the downfield region and the proton at 6-position appears as a sharp singlet due to the

presence of two chlorine atoms at 5- & 7-positions of quinoline ring. The proton at 3-position shows a four lined multiplet.

In the β -carboalkoxy ethyl tin 5, 7-dibromo oxinates (Table VIII) H_{α} , H_{β} and H_{γ} protons are also shielded compared to the parent β -carboalkoxy ethyl tin chlorides. Like oxine complexes, here also the α -methylene proton is shielded most except in β -carbomethoxy β' -methyl ethyl chloro tin bis-5,7-dibromo oxinate (Table VIII), where the methoxy proton is most shielded. The amount of shielding of the alkyl protons in dibromo oxine complexes is either equal ^{to} or more than that of the oxine complexes. In β -carbomethoxy ethyl chloro tin bis-5, 7-dibromo oxinate (Fig. 45) and β -carbomethoxy β' -methyl ethyl chloro tin bis-5, 7-dibromo oxinate the increased amount of shielding of the H_{α} , H_{β} and H_{γ} protons than that of the similar oxine complexes may possibly be due to higher donor capacity of the dibromo oxine compared to oxine. The spectra of β -carbomethoxy ethyl chloro tin bis-5, 7-dibromo oxinate (Fig. 45), β -carbomethoxy β' -methyl ethyl chloro tin ^{bis} 5,7-dibromo oxinate (Table VIII) and β -carbobutoxy ethyl tin tris 5,7-dibromo oxinate (Fig. 47) indicate the possible presence of geometrical isomers.

Like the ligand protons, the aromatic protons of β -carboalkoxy ethyl tin 5,7-dibromo oxinates are clearly resolved and separated. The proton at 2- and 4-positions appeared separately as doublets at downfield region and the proton at 6-position appeared as a sharp singlet due to the presence of two bromine atoms at 5- and 7- positions of quinoline ring. The proton at 3-position shows a four line multiplet as is expected. The signals for aromatic protons of β -carbomethoxy ethyl chloro tin bis-5,7-dibromo oxinate, β -carbomethoxy β' -methyl ethyl chloro tin bis-5,7-dibromo oxinate and β -carbobutoxy ethyl tin tris-5,7-dibromo oxinate are of complex pattern due to the possible presence of mixture of geometrical isomers. In case of all 5,7-dibromo oxinate complexes (Table VIII) the proton at 2-position suffers deshielding, the protons at 4- and 6- positions either suffer slight deshielding or remain practically unaffected (except in β -carbomethoxy β' -methyl ethyl chloro tin bis-5,7-dibromo oxinate where the 4-H proton is shielded slightly) while the proton at 3-position undergoes slight shielding.

The chemical shifts observed for the aromatic ring protons in the substituted oxine complexes are consistent with the shifts reported earlier (235, 391-394). The electron donation to the tin on coordination has

produced a deshielding of the ligand protons at 2-position and in some cases at 4-position also, the magnitude of which appears to be influenced by the inductive effect of the alkyl group. The downfield shift of the protons may be attributed to strong interaction between Sn and N. The behaviour of 2-H can be explained by paramagnetic anisotropic effect of Sn-N bond of the substituted oxine ligand and to an intramolecular electric field and that of the 4-H by latter effect (395). The deshielding of the proton at 6-position of the substituted oxine complexes possibly indicates depressed electron density at C-6. This can arise from electron movement towards the metal through a $d\pi-p\pi$ overlap between the metals and the oxygen atoms (396). The 4-H signal in β -carbomethoxy β' -methyl^{ethyl} chloro tin bis-5,7-dibromo oxinate shifts upfield.

Like the β -substituted ethyl tin oxinates and 5,7-substituted oxinates, all types of alkyl protons (H_α , H_β and H_γ) in β -carboalkoxy ethyl tin phenyl-5-azo oxinates and 5(2'-carboxy phenyl)-azo-oxinate exhibit shielding as expected. In all these types of complexes also, the α -methyleneic proton is shielded most except in β -carbomethoxy β' -methyl ethyl chloro tin^{bis} phenyl-5-azo oxinate where the methyl proton is shielded most like its similar oxinate and dibromo oxinate complexes. The

shielding effect in Bis(β -carbobutoxy ethyl) tin bis-phenyl-5-azo oxinate (Fig. 55) is different from the other phenyl-5-azo oxine complexes which may possibly be due to its steric nature. For all the phenyl⁵-azo oxine complexes and 5(2'-carboxy phenyl) azo oxine complex, in addition to four types of signals of aromatic protons like oxine and substituted oxine complexes, one more signal of complex pattern appears due to the phenyl rings of the ligands. Similar to the oxine and substituted oxine complexes, the protons at 2- and 4-position of phenyl-5-azo oxine ligand are most affected in its complexes and appear at the downfield region. The spectrum of Bis (β -carbomethoxy ethyl) tin bis-5(2'-carboxy phenyl)-azo oxinate possibly indicates the presence of mixture of isomers and its eighteen aromatic protons are distributed in the ratio of 2:1:1:2:2:10 from the extreme downfield region.

From the PMR spectra of β -carboalkoxy ethyl tin dithizonates (Table VIII) it appears ^{that} the H _{β} and H_C protons of the alkyl groups are shielded in all cases while the H _{α} and other protons (due to presence of butyl or methyl group) are marginally shielded or remain practically unaffected in some cases. However, in certain cases appreciable shielding is also observed. It is also interesting

to note that the amount of shielding of H_{α} protons is less than that of H_{β} , H_{γ} and other protons which may possibly be due to steric nature of the dithizone complexes or other reasons. Compared to oxinate and substituted oxinate complexes the H_{α} , H_{β} and H_{γ} protons are less shielded. In the complexes, Bis (β -carbomethoxy ethyl) tin bis-dithizonate (Fig. 64), Bis (β -carbomethoxy ethyl) chloro tin dithizonate (Fig. 66) and Bis(β -carbomethoxy ethyl) thiocyanato tin dithizonate the signals at 9.45 ppm, 9.15 ppm and 9.45 ppm respectively are due to the imino proton (-NH) of dithizone. Again signal for imino proton (-NH) in other dithizonate complexes appear in the region 4.10-6.66 ppm. The absorption position of this -NH group is concentration dependent and varies due to the change in the extent and nature of hydrogen bonding.

Coleman et al (397) were unable to obtain the PMR spectrum of dithizone itself owing to its low solubility, but by using, 1,5(o-diethyl phenyl) thiocarbazono in $CDCl_3$ they observed $\tau = -2.03$ (1.6 protons), 1.90 and 2.67 (8-aromatic protons), 7.00 (4 methylene protons) and 8.60 (6 methyl protons). It should be noted that they only observed 1.6 non-aromatic protons at $\tau = -2.03$ in place of the total 2.0 protons to 8.0 aromatic protons. In all β -carboalkoxy ethyl tin dithizonates the signals in the region

6.71-8.15 ppm are due to the aromatic protons of dithizone and in most cases show that two protons of the phenyl rings of dithizone are shielded most than the other eight protons. The aromatic protons in all these complexes probably appear to be deshielded markedly.

On the basis of lesser amount of shielding of H_{α} , H_{β} and H_{γ} alkyl protons of dithizone complexes than the oxine and substituted oxine complexes it will not be proper to conclude that dithizone form a weaker complex with organotin moieties. Even deshielding of alkyl protons have been observed in case of Dimethyl tin bis-dithizonate where the methyl protons gave signal at 1.27 ppm compared to methyl protons of Dimethyl tin dichloride (1.22 δ ppm) (210). The methyl signals of Dimethyl tin bis-oxinate was found around 0.44 ppm. It may be suggested that $(CH_3)_2SnCl_2$ has formed a stronger complex with oxine compared to dithizone. But recently in our laboratory it has been observed that when dithizone is reacted with Dimethyl tin bis-oxinate, it can also quantitatively displace oxine and form Dimethyl tin bis-dithizonate. Therefore, in our opinion the extent of chelation can not be always predicted from the relative amount of shielding, because the shielding of protons is possibly very closely related with the structure of the compounds and other related factors.

The β -carboalkoxy ethyl tin alizarinates are different from other complexes discussed so far. In Bis(β -carbomethoxy ethyl) tin alizarinate and Bis(β -carbo-butoxy ethyl) tin alizarinate complexes both the hydrogen atoms of the hydroxyl groups are removed by two chlorine atoms of the Bis(β -carboalkoxy ethyl) tin dichlorides. The composition of the complexes are possibly supported by their PMR spectra also. In these complexes also (Fig. 81 and 84) the H_α , H_β and H_γ protons of the alkyl groups are all shielded like other complexes discussed above. In both the complexes the H_α proton is shielded most. The aromatic protons of these complexes show four types of signals separated in the ratio 1:2:2:1 from the downfield region.

In Bis(β -carbomethoxy ethyl) tin dithiocyanate, possible existence of mixture of isomers is indicated by its PMR spectrum. However, in this compound the H_α , H_β and H_γ protons appear at upfield compared to that of Bis(β -carboalkoxy ethyl) tin dichloride. This effect is quite expected due to less electronegative character of the thiocyanate group.

The spectra of the complex Bis(β -carbomethoxy ethyl) chloro tin diphenyl carbazonate is not well resolved (Table VIII) which indicates possibly the presence of

mixture of isomers. However, the complex formation is indicated from the shielding of all the alkyl protons and also the H_{α} proton is shielded most like other complexes. The imino proton ($-NH$) of diphenyl carbazone complex appears at 5.85 δ ppm and its absorption position may change on dilution because of the change in nature and amount of hydrogen bonding. The aromatic protons show two types of signals distributed in the ratio 2:8 at downfield region.

The resolution of the spectrum of Bis(β -carbomethoxy ethyl) chloro tin 1-nitroso-2-naphtholate is not satisfactory. However, tentatively the complex formation is indicated by the appearance of the alkyl protons upfield compared to the corresponding Bis(β -carbomethoxy ethyl) tin dichloride. Here also H_{α} proton is shielded most. The aromatic protons appear in the region 6.58-8.34 ppm.

The PMR spectra of some apparently hepta-coordinated complexes of the type $RSnL_3$ (R = carboalkoxy ethyl moiety; L = Oxine, 5,7-dibromo oxine and Dithizone) are not well resolved in all cases. Moreover, the possible presence of mixture of isomers makes interpretation somewhat difficult. In order to get better idea about the compounds, further detailed investigation on PMR spectral data will be taken up in near future.

From the preceding discussion on UV-Visible, IR and PMR spectral data it is obvious that the β -carboalkoxy ethyl tin chlorides and related compounds can form stable coordination compounds with a variety of ligands. Majority of these complexes are well defined crystalline compounds. Hence, the Lewis acidity of β -carboalkoxy ethyl tin chlorides can be considered to be well established and comparable to simple alkyl and aryl tin derivatives. The spectral properties of these derivatives have been investigated upto a reasonable extent, which possibly provide sufficient evidences about their chelating nature. But presently it has not been possible to investigate the stereo chemistry of these complexes due to the lack of more sophisticated instrumental techniques in our laboratory. Attempts have been made to indicate tentatively the geometry of these complexes on the basis of IR and PMR data, in some cases. Among the complexes studied, the alizarin complexes are somewhat different from other complexes due to possible non-participation of carbonyl groups of alizarin in complex formation, which in turn yield different type of stoichiometry compared to the complexes of other ligands. Detailed structural studies of these β -carboalkoxy ethyl tin derivatives are expected to be of considerable interest.