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coordinated tin (IV) complex of ethylpropylⁿ tin dichloride with benzyl amine (bzam) have been prepared. The reactions of these complexes with benzoyl chloride in nitrobenzene have been studied conductometrically. In case of hexa-coordinated complexes, formation of $(RR'SnCl_4)^{2-}$ and $(C_6H_5COL)^+$ [where RR' = methylethyl (MeEt), ethylpropylⁿ (EtPrⁿ); and L = pip, prⁿam, buⁿam and an] species takes place while in case of penta-coordinated complex, $(EtPr^nSnCl_3)^-$ and $(C_6H_5COBzam)_2^+$ ions are formed in the solution. Compound $(EtPr^nSnCl_4)^{2-} (C_6H_5COAn)_2^+$ has also been isolated and analysed.

127. β -Substituted Alkyl Tin Co-ordination Compounds

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Though β -substituted alkyltin compounds have been known for some time, no co-ordination compounds of these has been reported so far. Some complexes of β -substituted mono- and dialkyltin compounds with ligands like 8-hydroxy quinoline, diphenyl thiocarbazon (dithizone), diphenyl carbazon, N-phenyl benzo hydroxamic acids etc. are reported here. Method of preparation and spectral data (e. g. I.R. and PMR) have been discussed. The spectral data clearly indicate the chelating nature of these compounds.

128. Dithiol derivatives of Tin(IV)

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Reactions of tin tetrachloride with dithiols (ethane-1, 2-, propane-1, 3-butane-1,4- and hexane-1,6-dithiols) in benzene or toluene at low or refluxing temperature yielded different types of products. Transthiolysis reactions between tin tetra-alkanethiolates and dithiols have also been carried out in 1:1 and 1:2 stoichiometric ratios. These complexes have been characterized on the basis of elemental analysis, conductance measurements and I.r. spectra.

β -Substituted alkyltin Co-ordination Compounds

by

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Introduction:

The industrial importance of Organotin Compounds is reflected from the increasing amount of consumption of such compounds in the last decade or so. In 1965, the world consumption was 5,000 tons whereas in 1975 more than 25,000 tons were consumed. It is expected to grow further at a high rate. A major proportion of this tonnage is used to produce organotin stabilizers for thermal stabilization of PVC. Though β -substituted alkyltin compounds have been known for some time, no co-ordination compounds of these types of organotin compounds has been reported. We like to report here some coordination compounds of β -substituted mono- and di-alkyl tin compounds.

Experimental:

Materials: Representative β -substituted alkyltin halides e.g. Bis (β -carbomethoxy ethyl) tin dichloride was prepared by reacting methyl acrylate with metallic tin and anhydrous hydrogen chloride and $\left[(\beta\text{-acetyl}, \alpha, \alpha'\text{-dimethyl}) \text{ ethyl} \right]$ tin trichloride was prepared by the reaction of mesityl oxide with Tin (II) chloride and anhydrous hydrogen chloride. All solvents were purified and dried. All melting points are uncorrected.

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Method of preparation: The organotin co-ordination compounds were prepared by reacting β -substituted alkyl tin halides with ligands like 8-hydroxy quinoline, diphenyl thio carbazone (dithizone), diphenyl carbazone, N-phenyl benzo hydroxamic acids etc. Representative methods are as follows:

Bis (β -Carbomethoxy ethyl)tin bis-oxinate:

To the solution of 1.160 gms of 8-hydroxy quinoline in chloroform, 1.450 gms of Bis (β -carbomethoxy ethyl) tin dichloride solution in chloroform was added with shaking. To the mixture calculated amount of ammonia solution was added and filtered. It was then refluxed for an hour. Then the mixture was concentrated on a water bath to a very small volume and treated with methanol. Yellow crystals were obtained when kept in a refrigerator for few hours. It was recrystallized twice from chloroform-methanol solution. The final yellow crystal had a melting point 152°C . (Found: C-53.80; H-4.28; N-4.80; $\text{C}_{26}\text{H}_{26}\text{O}_6\text{SnN}_2$ Calculated: C-53.70; H-4.48; N-4.82 %).

Bis (β -carbomethoxy ethyl) tin bis dithizonate:

1.536 gms of dithizone was dissolved in chloroform and to it a solution of 1.092 gms of Bis (β -carbomethoxy ethyl) tin dichloride was added with shaking. After adding calculated amount of ammonia solution to it, the mixture was filtered. It was then refluxed for two hours. The mixture was then concentrated on a water bath and methanol was added to it. The mixture was then kept undisturbed for several

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hours. A bright greenish-black crystal separated out. It was then recrystallised from chloroform-methanol solution. The final crystal gave a m.p. 187°C. (Found: C-50.72; H-4.47; N-13.72; $C_{34}H_{36}O_4N_8SnS_2$ Calculated: C-50.81; H-4.48; N-13.95).

The reactions between Bis(β -carbomethoxy ethyl) tin dichloride and ligands like diphenyl carbazone, N-phenyl benzo hydroxamic acids etc. were also being investigated. We have already isolated few compounds out of these reactions. Characterization of these compounds are in the final stages. We hope to present these data during the presentation of the paper.

We have also isolated a number of co-ordination complexes of $[\beta\text{-acetyl, } \alpha,\alpha\text{-dimethyl) ethyl}]$ tin trichloride with ligands like 8-hydroxy quinoline, diphenyl thio carbazone, diphenyl carbazone, N-phenyl hydroxamic acids etc. These are also in the process of complete characterization. We like to report these complexes during the presentation of the paper.

Spectroscopy:

Infrared spectra were recorded to nujol mulls using Beckmann IR-20, Spectrophotometer and N.M.R. spectra were recorded in Varian EM-390 90 MHz NMR Spectrometer.

Results and discussion:

The spectra of Bis(β -carbomethoxy ethyl) tin bis oxinate is very similar to other oxinate complexes [1].

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In the I.R. spectra of this complex the strong band at 525 cm^{-1} has been assigned to the Sn-O frequency as no strong band is present in this region in the spectra of Bis (β -carbomethoxy ethyl) tin dichloride or of oxine. The same bands have been assigned to Sn-O stretching modes by Okawara *et al* [2]. The characteristic -OH frequency of free oxine is also absent in the spectra of the oxinate complex as expected. A very strong band at 1677 cm^{-1} in Bis(β -carbomethoxy ethyl) tin dichloride is being shifted to 1729 cm^{-1} in Bis (β -carbomethoxy ethyl) tin bis oxinate, which indicates that the chelating nature of the carbonyl group has been changed to ester type carbonyl group [3].

I.R. spectra of Bis(β -carbomethoxy ethyl) tin bis-dithizonate showed a large number of bands. By comparing the spectra of Bis(β -carbomethoxy ethyl) tin dichloride and free dithizone with Bis (β -carbomethoxy ethyl) tin bis dithizonate, it is found that the characteristic bands have been shifted as also observed with other organotin dithizonates [4]. The dithizone complex has characteristic bands at 3220 cm^{-1} (indicating -NH stretching frequency involving intramolecular hydrogen bonding), at 1515 cm^{-1} (for -NH bending) and a group of bands in the region $1130-1190\text{ cm}^{-1}$ (N-C-S bond vibration) respectively. The group of bands in the region $1220-1140\text{ cm}^{-1}$ in free dithizone has been assigned for coupled N-C-S bond vibration and the shifting of these bands to lower frequencies in between

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1130-1190 cm^{-1} indicates the complexation of organotin moieties with dithizone. Like the oxinate complex, the shifting of the very strong band at 1677 cm^{-1} of the alkyl tin dichloride to 1735 cm^{-1} in alkyl tin bis dithizonate indicates that the chelating nature of carbonyl group has been changed to ester type carbonyl group. This seems quite reasonable since diphenyl thio carbazone or 8-hydroxy quinoline is much stronger chelating ligand and with the advent of these ligands in the complexes, the carbonyl group in alkyl tin dichloride are likely to be converted as ester type instead of chelating one.

PMR spectra of Bis (β -carbomethoxy ethyl) tin bis oxinate and bis(β -carbomethoxy ethyl) tin bis dithizonate were recorded in CDCl_3 . These spectra were compared with the PMR spectra of Bis(β -carbomethoxy ethyl) tin dichloride and several organotin dithizonates and organotin oxinates which support the strong co-ordination with ligands and also their composition.

Spectral data:

<u>Compound</u>	<u>IR(cm^{-1})data</u> $\nu(\text{C}=\text{O})$	<u>Chemical shifts(τ)</u>			Others
		<u>CH(α)</u>	<u>CH(β)</u>	<u>Aromatic Protons</u>	
Bis(β -carbomethoxy ethyl)tin dichloride	1677	8.07	7.07	-	6.18(OMe)
Bis(β -carbomethoxy ethyl) tin bis Oxinate	1725	8.64	7.56	1.46 1.85 2.42 2.84	6.45 (OMe)
Bis(β -carbomethoxy ethyl) tin bis dithizonate	1735	8.07	7.38	2 to 2.90	6.48 (OMe) 0.55(NH)

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References:

1. D. Dutta Ph.D. Thesis, North Bengal University (1970)
2. Y. Kawasaki, T. Tanaka and R. Okawara J. Organometallic Chem., 6 (1966)95.
3. I. Omae, Rev. on Silicon, Germanium, Tin and lead compounds, 1 (1972)59.
4. Goutam C. Ghosh Ph.D. Thesis, North Bengal University (1978)

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