

Preparation & Nature of Complexes of Trichlorotin(IV) Ethoxide with Oxygen & Nitrogen Donors

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Complexes of trichlorotin(IV) ethoxide with monodentate and bidentate ligands, viz. dimethylformamide, dimethylacetamide, tetramethylurea, 2-, 3- and 4-picoline-N-oxides, nicotinamide, pyridine, ethylenediamine and tetramethylethylenediamine have been prepared. Infrared spectra of the complexes, formulated as $\text{SnCl}_3(\text{OEt})\cdot\text{L}$ (where L = monodentate ligand) show the presence of alkoxy bridging due to which tin acquires six-coordination number. Nature of the complexes with bidentate ligands is also discussed.

THE compound ethoxytrichlorotin(IV) monoethylate, $\text{SnCl}_3(\text{OEt})\cdot\text{EtOH}$ has been reported from X-ray diffraction studies to exist as dimer¹ where tin has six-coordination number. As tin has already its most stable coordination number in this compound, further complex formation by ligands may not occur and if the possibility of complex formation exists, it may be either by ligand replacing the alcohol molecule or by breakdown of the alkoxy bridge present in the parent compound¹ or by both. The present study reports on the preparation and nature of the complexes of $\text{SnCl}_3(\text{OEt})$ with some oxygen and nitrogen donors.

Materials and Methods

The compound $\text{SnCl}_3(\text{OEt})\cdot\text{EtOH}$ was prepared by the method of Bradley² and its purity checked, m.p. 191-93° (lit.² m.p. 192°). The complexes with ligands, viz. dimethylformamide (DMF), dimethylacetamide (DMA), tetramethylurea (TMU), 2-, 3- and 4-picoline-N-oxides, nicotinamide, pyridine(Py), ethylenediamine and tetramethylethylenediamine were prepared by mixing an ethanolic solution of $\text{SnCl}_3(\text{OEt})\cdot\text{EtOH}$ with an ethanolic or benzene solution of the ligand when solid adducts precipitated out either on keeping or by adding excess of dry ether.

Tin and chlorine were determined by the literature methods^{3,4}. Infrared spectra of the complexes were examined as Nujol mull in NaCl or CsBr plates on Perkin-Elmer 337 and 521 spectrophotometers.

Results and Discussion

Analyses of the complexes (Table 1) indicate a 1:1 composition, except for the complexes of nicotinamide and pyridine, which have 1:2 stoichiometry [$\text{SnCl}_3(\text{OEt})$: ligand] and for tetramethylethylenediamine (TME) complex which has 2:1 stoichiometry. The complexes have a very limited solubility in usual solvents which precludes molar conductance and cryoscopic measurements. Infrared spectra* of the complexes in the region

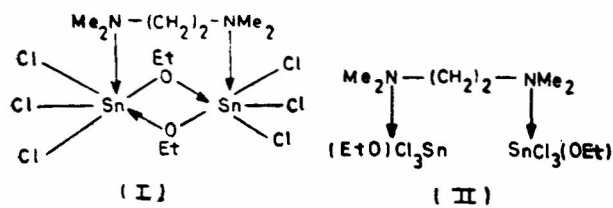
4000-250 when compared with those of the ligands and the pure alkoxide alcoholate show that the bands due to coordinated alcohol $\nu(\text{C}-\text{H})$ are absent. All the complexes show a band around 1050 assigned to $\nu\text{C}-\text{O}$ of the $\text{Sn}-\text{O}-\text{C}(\text{R})$ group⁵, indicating the presence of a coordinated alkoxy group in these complexes. The characteristic ligand vibration^{5,9} are displaced in the spectra of the complexes and direction of these shifts is comparable to that in the complexes of these ligands with tin(IV) chloride. The extent of the shifts is of course larger in the complexes of tin(IV) chloride when compared to those of trichlorotin(IV) ethoxide indicating the poor acceptor power of the latter. It can be inferred from the spectra that DMF, DMA, TMU, 2-, 3- and 4-picoline-N-oxides coordinate through their oxygen atom which becomes evident from the decrease in the $\nu(\text{C}=\text{O})$ or $\nu(\text{N}-\text{O})$ frequencies of pure amides and amine oxides respectively on complex formation. Thus the $\nu\text{C}=\text{O}$ of DMF, DMA and TMU which occur at 1680, 1670 and 1650 cm^{-1} respectively are shifted to 1650, 1580 and 1590 cm^{-1} respectively in the complexes. Similarly $\nu\text{N}-\text{O}$ of 2-, 3- and 4-picoline-N-oxide occurring around 1250 are shifted by nearly 50 cm^{-1} to lower frequency region in their complexes. The

TABLE 1 — CHARACTERIZATION DATA OF THE COMPLEXES OF TRICHLOROTIN(IV) ETHOXIDE

Compound*	m.p. (°C)	Tin (%)		Cl (%)	
		Found	Calc.	Found	Calc.
$\text{SnCl}_3(\text{OEt})\cdot\text{DMF}$	240-42	34.72	34.58	30.88	31.02
$\text{SnCl}_3(\text{OEt})\cdot\text{DMA}$	235-37	33.48	33.22	29.34	29.81
$\text{SnCl}_3(\text{OEt})\cdot\text{TMU}$	208	31.06	30.72	27.30	27.56
$\text{SnCl}_3(\text{OEt})\cdot(2\text{Pic-O})$	235	31.65	31.29	28.14	28.08
$\text{SnCl}_3(\text{OEt})\cdot(3\text{Pic-O})$	203	31.70	31.29	27.70	28.08
$\text{SnCl}_3(\text{OEt})\cdot(4\text{Pic-O})$	243	31.60	31.29	27.80	28.08
$\text{SnCl}_3(\text{OEt})\cdot 2\text{Nic}$	203-5	23.87	23.07	20.38	20.07
$\text{SnCl}_3(\text{OEt})\cdot 2\text{Py}$	260	27.85	27.70	25.12	24.88
$\text{SnCl}_3(\text{OEt})\cdot\text{en}$	205-7	36.07	35.96	31.57	32.23
$2(\text{SnCl}_3(\text{OEt})\cdot\text{TME})$	260	36.74	36.20	33.08	32.46

*All the compounds, except $\text{SnCl}_3(\text{OEt})\cdot\text{en}$ which is obtained as a yellow solid, are isolated as white solids.

*Detailed IR data can be had from the authors on request. ν_{max} throughout the paper in cm^{-1} .



significant lowering ($>100\text{ cm}^{-1}$) of $\nu(\text{N-H})$ and $\nu(\text{C-N})$ of pure ethylenediamine is in keeping with the coordination of ethylenediamine through both of its nitrogen atoms to tin¹⁰. In case of tetramethylethylenediamine (TME), the $\nu\text{C-N}$ appearing at 1205 located at 1135 in the complex, suggesting that like ethylenediamine, TME also behaves as a bidentate ligand. The complex with pyridine exhibits IR bands, which are comparable to those of its complexes with some acceptors where it coordinates through its nitrogen atom¹¹. In case of nicotinamide complex, $\nu(\text{N-H})$ and $\nu(\text{C=O})$ frequencies are present at the same position as of pure nicotinamide while the $\nu(\text{C=C})$ and $\nu(\text{C=N})$ frequencies arising from the pyridine ring part of the ligand and occurring ~ 1594 are shifted to higher frequency region (1610) in the spectrum of the complex. This clearly suggests that nicotinamide coordinates through its nitrogen atom of the pyridine ring^{12,13}.

Infrared spectrum of $[\text{SnCl}_3(\text{OEt})\cdot\text{EtOH}]_2$ has a characteristic strong, broad band at 500-515 assigned to $\nu(\text{Sn-O}\rightarrow\text{Sn})$ (ref. 7). This band is retained in the spectra of the complexes formulated as $\text{SnCl}_3(\text{OEt})\cdot\text{L}$ (where L=monodentate oxygen donor). In the case of 1:2 complexes with pyridine and nicotinamide and the 1:1 complex with ethylenediamine, the spectra do not exhibit any band due to $\nu(\text{Sn-O}\rightarrow\text{Sn})$. Same is true for 2:1 complex with TMF. It has been shown that TME or even ethylenediamine¹⁴ may not function as chelating ligand. Similar to the structure proposed for the complex $2\text{Ti}(\text{OPr})_4\cdot\text{en}$ ¹⁵ it is possible that in the present

case, the complex may have either of the structures (I) or (II), but it is rather difficult to unambiguously assign a correct structure for the complex.

For the oxygen donor ligand complexes, an additional band of medium or strong intensity is observed in the region $350\text{-}425\text{ cm}^{-1}$ which may be assigned to the $\nu(\text{O}\rightarrow\text{Sn})$ vibrations^{5-7,9,16,17}. The $\nu(\text{Sn-Cl})$ in these complexes appears as one or more than one bands in the region $300\text{-}330\text{ cm}^{-1}$ region and this absorption region is close to that known for six-coordinate tin [$\nu(\text{SnCl}_6^{2-})$] absorbs at 312 cm^{-1} ^{16,17}.

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