Some Complexes of Stannic Chloride with Aliphatic Aldehydes

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The complexes SnCl$_4$·2L, where L = acetaldehyde, propanal and 2-methylpropanal were prepared and examined. Some physical and spectroscopic data are given. A cis *configuration was found in all the complexes, which are more unstable and reactive than the corresponding complexes of aromatic aldehydes. The Sn–O bonding interaction increases in the sequence acetaldehyde < propanal < 2-methylpropanal.*

Introduction

Studies of addition complexes of stannic chloride with aldehydes have been concentrated on those of aromatic aldehydes [1, 2]. No work on corresponding complexes of aliphatic aldehydes is known, with the exception of the acetaldehyde complex, but few data are given in this case [3]. On the other hand, aliphatic ketone complexes of stannic chloride have been studied to some extent [3, 4]. The reason for this is probably the great reactivity of the aliphatic aldehydes and their complexes.

In the present paper systematic examinations of addition complexes of stannic chloride with acetaldehyde, propanal and 2-methylpropanal are reported.

Experimental

All operations were carried out in inert atmosphere. Stannic chloride was dried over phosphorus pentoxide and distilled. Pentane was refluxed for one h over sodium dispersed in paraffin, and then distilled. The aldehydes represent a special problem due to their reactivity (polymerizations *etc.*) and the formation of azeotropes with water. They were repeatedly dried over calcium sulphate (drierite) and fractionated in long columns in argon atmosphere [5]. 2-Methylpropanal could only be used in solution, due to trimerization.

The complexes were most conveniently prepared by adding the aldehyde dropwise with good stirring to a solution, 1:40 by volume, of stannic chloride in pentane at −78 °C (dry ice–acetone bath). A molar ratio 1:2 of stannic chloride–aldehyde was used. Volatile components were removed on a vacuum line. The best results were obtained without further purifi-

cation. The complexes could be sublimed *in vacuo*, but the most important impurity, moisture, is difficult to remove in this way.

The white acetaldehyde complex often contained small, yellow-green particles. No changes however were observable in the infrared spectra. A possible explanation may be local concentration differences in the reaction mixture.

The tin contents were determined both gravimetrically and by atomic absorption spectroscopy using an air–acetylene flame. The high chlorine contents made the gravimetric method less suitable. The chlorine contents were determined both by potentiometric titration with 0.1 *M* sodium hydroxide solution, and by the Mohr method. The first method gave slightly better results than did the second.

Infrared spectra in the range 4000–650 cm^{-1} were obtained on Perkin Elmer 225 and Jasco IRA-1 grating spectrophotometers. Solid compounds were examined as nujol mulls between sodium chloride plates. Pure liquids were pressed between sodium chloride plates and solutions were kept in 0.1 mm sodium chloride cavity cells. The spectra were obtained at room temperature. Attempts at −60 °C gave very similar spectra, but of lower resolution.

In the far infrared region a Bruker IFS 114C - Fast Scan evacuable Fourier transform spectrometer was used. Solid compounds were examined as nujol mulls between polyethylene plates. Solutions were examined in 0.1 mm polyethylene cells. All runs were carried out at room temperature.

Proton NMR spectra were obtained with a Varian EM 360 A NMR spectrometer, cw mode. The runs were carried out at room temperature with TMS as a reference. The concentrations used were mostly around 0.1 *M*.

Results

SnCl$_4$·2L, L = acetaldehyde, propanal and 2-methylpropanal, respectively, were isolated as the only products from mixtures of stannic chloride and aldehyde. The molar ratios, the way of mixing, the temperature and the use of solvent had no influence on the composition of the products. The products were obtained as white solids, which could be sub-

TABLE I. Some Infrared Absorptions of $SnCl_4 \cdot 2L$ Observed in the Region 600–150 cm^{-1}.

L = acetaldehyde		L = propanal		L = 2-methylpropanal		Assignments[a]
Nujol mulls	Benzene sol.	Nujol mulls	Benzene sol.	Nujol mulls	Benzene sol.	
568(s)		561(m)		566(w)		C–C=O in pl. def.
405(m)	390(m)	405(w)	404, 395(m)	405(m)	402, 392(m)	Sn–O str.
368(s)	356(s)	353(s)	356(s)	358(s)	358(s)	Sn–Cl str. ν_7
335(m)	345(s)	339(s)	345(s, sh)	333(s)	346(s)	Sn–Cl str. ν_8
328(m)		325(w, sh)		325(s)		Sn–Cl str. ν_1
303(s)	308(m)	296(m, sh)	303(w, sh)	299(m, sh)	302(w)	Sn–Cl str. ν_2
~150(s)	150(s)	~150(s)	150(s)	150(s)	150(s)	Cl–Sn–Cl def.

[a]References: [2, 8, 9, 11, 12].

TABLE III. PMR Shifts of $SnCl_4 \cdot 2L$ in Deuterated Chloroform and Benzene Solutions, Given in ppm Units. Shifts relative to free ligands are given as $\Delta\delta$.

Type of proton	L = acetaldehyde				L = propanal				L = 2-methylpropanal			
	Chloroform		Benzene		Chloroform		Benzene		Chloroform		Benzene	
	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$
Aldehyde	9.88	+0.18	9.21	−0.09	9.81	+0.13	9.36	+0.06	9.79	+0.23	9.47	+0.17
α alkyl	2.49	+0.33	1.37	−0.28	2.75	+0.31	1.65	−0.25	2.79	+0.32	1.81	−0.16
β alkyl					1.17	+0.10	0.52	−0.25	1.25	+0.14	0.61	−0.26

limed *in vacuo* at room temperature to give colourless crystals. Yields with pentane as a solvent were above 90%. The analytical results for tin and chlorine deviated less than 1% from the theoretical values for $SnCl_4 \cdot 2L$.

The complexes are unstable at room temperature and are very sensitive with respect to moisture. They change to viscous, yellow or red liquids, but can be kept at low temperature (−78 °C) for some time without decomposition. Attempts at determination of melting points (in argon atmosphere) showed that visible decomposition had already started at 40–50 °C, varying with even very low contents of moisture.

The same trend in solubility with decreasing polarity of the solvents was observed for all three complexes:

Water and ethanol: Soluble with decomposition.
Methylene chloride and chloroform: Soluble with partial decomposition.
Benzene: Soluble without decomposition.
Carbon tetrachloride and pentane: Very little and insoluble, respectively. No decomposition [2, 6, 7].

The dissociation was examined by infrared spectra.

Molecular weights were determined by the Beckmann method with benzene as a solvent. The measured values in g mol^{-1} were for L = acetaldehyde, propanal and 2-methylpropanal, respectively: 373 (348.6), 378(376.7) and 394(405.9). Theoretical values for $SnCl_4 \cdot 2L$ are given in parentheses. Relative

standard deviations in per cent, s_r, were 4.81, 2.77 and 4.05 in the same order.

Dipole moments were measured in benzene solutions at 25 °C. In the same sequence as above the values found were: 6.1 D, 6.5 D and 6.5 D.

Infrared spectra of the complexes were taken in the region 4000–150 cm^{-1}. Some absorptions in the far infrared region are given in Table I. Carbonyl absorptions of the complexes and the free aldehydes are given in Table II.

NMR data are given in Table III.

Discussion

The analytical results show that acetaldehyde, propanal and 2-methylpropanal form complexes of

TABLE II. Infrared Carbonyl Absorptions of $SnCl_4 \cdot 2L$ and the Free Ligands[a].

Ligand	ν(C=O) ligand	ν(C=O) complex	$\Delta\nu$(C=O)
Acetaldehyde	1723	1664	59
Propanal	1729	1654	75
2-Methylpropanal	1738	1653	85

[a]All frequencies refer to benzene solutions and are given in wave numbers.

the stoichiometry $SnCl_4 \cdot 2L$. They are found to be monomeric in benzene solution. However, the solutions are unstable and the molecular weights increase gradually, indicating that polymerizations take place.

For octahedral complexes, $SnCl_4 \cdot 2L$, the *trans* configurations are expected to give dipole moments close to zero. The high values found for the present complexes are of the same order as those found earlier for *cis* complexes of aromatic aldehydes with stannic chloride [2]. The absorptions observed in the far infrared region support the assumption of *cis* configuration for all three complexes. The $SnCl_4$ moiety gives rise to four bands (see Table I), as expected for *cis* structures [8, 9]. Table I also shows that the Sn–O bands in the propanal- and 2-methylpropanal complexes are split in benzene solution, which may be indicative of coupling in *cis* structures [10].

Table II shows that the $\nu(C=O)$ frequencies are shifted to lower values by complex formation. The shifts increase with the number of carbon atoms in the aldehydes, showing increasing Sn–O bonding interaction. For ketone complexes the opposite trend has been observed [4, 13]. This may be due to steric effects. Aromatic aldehydes give considerably larger shifts for $\nu(C=O)$ by complex formation with stannic chloride than do aliphatic aldehydes. For benzaldehyde it is thus found that $\Delta\nu = -130$ cm^{-1}, as compared with $\Delta\nu = -59$ cm^{-1} for acetaldehyde [2]. The band due to the Sn–O interaction is less influenced and is actually found at 405 cm^{-1} for both complexes. The increased bond strength in aromatic aldehyde complexes seems reasonable because the positive charge formed by the donor interaction can be distributed in the aromatic systems by resonance. However, the low stabilities of the aliphatic aldehyde complexes compared with those of aliphatic ketones can not be explained in terms of the donor–acceptor interaction, since the bond strength is found to be nearly the same [4]. A steric protection in the ketone complexes may play a part here.

Table III shows that proton NMR signals for the aldehyde protons in the complexes are shifted about 0.2 ppm towards higher frequency in chloroform solutions relative to those for the free aldehydes. These observations are in agreement with those for aliphatic aldehyde complexes of antimony pentachloride [14]. Complex formation also causes a deshielding for alkyl protons due to the inductive effect, which is most pronounced for α protons. The values in benzene solutions are influenced by the anisotropy effect from π-electrons.

No difference between the two aldehyde ligands could be observed in any of the complexes.

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