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Some Solid Hydrogen-bonded Complexes of Stannic Chloride whith Diisopropyl Ether and Carboxylic Acids

M. M. MOSTAFA

Department of Chemistry, Mansoura University, Mansoura, Egypt

K. TAUGBØL and T. K. LØVENG

*Department of Chemistry, University of Oslo, Blindern, Norway**

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A solid hydrogen-bonded complex with formic acid has been reported in a previous paper [1]. In the present work corresponding complexes of acetic-, propionic-, butyric-, isobutyric- and trimethylacetic acid are described.

Experimental

All chemicals used were of analytical quality and were carefully dried before use. Tin tetrachloride and diisopropyl ether and propionic-, butyric- and isobutyric acids were dried over phosphorus pentoxide and finally obtained by fractional distillation at the appropriate temperatures. Acetic acid was heated with its anhydride and isolated by fractional distillation. Trimethylacetic acid was distilled at reduced pressure and recrystallized.

All solid complexes for examinations and analysis were prepared by slowly adding diisopropyl ether to tin tetrachloride with stirring of the solutions for 2 h. The acid was then added dropwise with stirring. Trimethylacetic acid was added as a nearly saturated solution in pentane.

Samples for analysis were hydrolyzed and dissolved in excess of 0.1 *M* sodium hydroxide solution. The sum of carboxylic acid and hydrochloric acid formed was determined by potentiometric titration with 0.1 *M* hydrochloric acid solution to pH ~8. The solutions were then reflexed for 1/2 h, cooled, and pH adjusted with acid to a colour change to yellow with thymol blue as an indicator. Precipitates of stannic acid were usually observed. By this method the titration of stannic acid was avoided. The chlorine contents were determined by the Mohr method. The ether contents were found indirectly by difference.

Results and Discussion

The solid complexes were formed as white precipitates immediately upon addition of acid to the mixtures of stannic chloride and diisopropyl ether. The optimal conditions for the formation of solid complexes were nearly the same for all acids in question. The volume ratios $(iPr)_2O/SnCl_4$ used were 3.5–5 (molar ratios 3–4). In volumes containing 1 ml of stannic chloride the detection limits of precipitation corresponded to the addition of ~0.02 ml of acid at 20 °C and ~0.01 ml at 0 °C. The precipitates were rinsed with diisopropyl ether and then dried on a fritted glass filter in a slow stream of argon gas. A constant weight cannot be obtained in this way at room temperature. The most volatile component, ether, is gradually evaporating and finally the samples deliquesce. The ether contents of the solids at the formation can thus only be obtained as an approximation.

In an attempt to standardize the analyses they were carried out a 'dry conditions', *i.e.* after drying the samples until the fine powder did not stick to a spatula and after additional drying for 3 min.

All the complexes are very reactive towards moisture. They dissolve easily in chloroform, carbon tetrachloride, benzene and pentane and also by further addition of the corresponding acid. The melting points in a closed tube for samples of nearly A type (see discussion below) were found in terms of complexing acids: acetic acid: 58 °C, propionic acid: 59 °C, butyric acid: 48 °C, isobutyric acid: 51 °C and trimethylacetic acid: 45 °C.

All the complexes decompose noticeably at room temperature after a few days.

Some analytical results are given in Table I. The Table shows that molar ratios acid/$SnCl_4$ (x) are within the range $0.5 \leqslant x < 1$. The ratios remain nearly constant on drying, but vary somewhat for different preparations. The values are consistent with an open chain structure of the type: E|EHE|E··· HE|E (E = ether, | = planar $SnCl_4$-group, H = acid proton), which is described earlier for the formic acid complex and shown in Fig. 1. The x values for this structure, which can be called the A type, will be given by $x = n - 1/n$, where n is the chain length. The chain length can thus be calculated from the x values. The y values in Table I, which for the A type of structure should be 2, show that these complexes only have a small stability.

Some infrared absorption bands associated with carboxyl groups are given in Table II. Bands in the region below 1500 cm^{-1} are not included, since the absorptions are fairly complex due to super-impositions with absorptions of the aliphatic groups in acids and ether. Although the contents of ether are some-

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*All correspondence should be sent to this address.

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TABLE I. Analytical Data, Given as Molar Ratios.

Complexing acid	Preparation number	Acid/$SnCl_4$ = x	$(iPr)_2O/SnCl_4$ = y	Calculated chain length[b]
Acetic	1a	0.62	3.96	2.6
	1b[a]	0.61	3.44	2.6
	2a	0.66	2.87	3.0
	2b	0.67	1.59	3.0
Propionic	1a	0.69	2.60	3.2
	1b	0.69	1.45	3.2
	2a	0.53	1.48	2.1
	2b	0.52	1.35	2.1
Butyric	1a	0.63	1.65	2.6
	1b	0.61	1.36	2.6
	2a	0.70	1.45	3.3
	2b	0.70	1.34	3.3
Isobutyric	1a	0.66	1.43	3.0
	1b	0.67	1.17	3.0
	2a	0.69	2.28	3.3
	2b	0.70	1.45	3.3
Trimethylacetic	1a	0.62	1.65	2.6
	1b	0.62	1.41	2.6
	2a	0.59	2.11	2.4
	2b	0.58	1.44	2.4

[a] All a-samples were dried to 'dry conditions' (see discussion), all b-samples for additional 3 min. [b] A structure of the formic acid type (A) is assumed, (see discussion) The standard deviations for the analytical values for chlorine and acid are less than 0.5

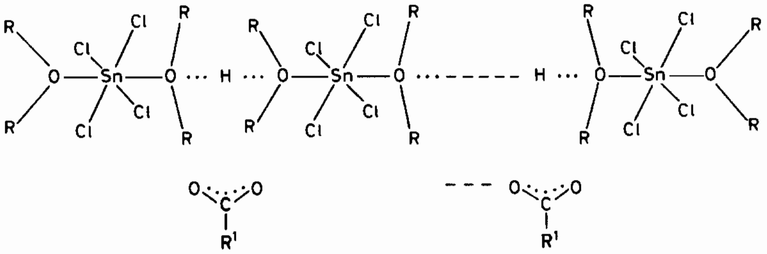

Fig. 1. Proposed structure of the complexes.

what arbitrary, the complexes at 'dry conditions' represent the most intact structures and they have all typical D-band spectra as reported for the formic acid complex [2–4]. By prolonged drying the D-band absorptions gradually dissappear and bands due to 'free' acid appear near 1700 cm^{-1} [5]. At the same time a band in the region 1650–1630 cm^{-1} increases in intensity and the absorptions in the 1550–1500 cm^{-1} region decrease. By dissolution of the complexes in a few drops of the corresponding acid these changes are still more marked. In complexes where carboxylic acids are coordinated to stannic chloride by the carbonyl groups, the $\nu C{=}O$ bands can be found in the region 1650–1630 cm^{-1} [6, 7]. Different species with this type of coordination may, however, be possible in more or less decomposed chain molecules. According to the x values in Table I, acid molecules cannot have been regular terminating groups in the original structure. A substitution is not likely under the present conditions. The absorptions in the region 1550–1500 cm^{-1} indicate the presence of some form of carboxylate ions. These bands are not present in spectra of corresponding solid complexes with hydrochloric acid [8]. The frequencies are, however, somewhat lower than those found for the corresponding sodium salts [9]. The shifts may perhaps be explained by deformations of the carboxylate groups for steric reasons. Absorptions in the far infrared region show a D_{4h}-symmetry or planar stannic chloride moieties as found by us for

TABLE II. Some Infrared Absorption Bands Associated with Carboxyl Groups (in wave numbers).

Complexing acid	Solid complex, 'dry conditions' [a,b]	Solid complex, 3 min. extra drying	Complex dissolved in a slight excess of acid[c]
Acetic	1650(w), 1610(w), 1550–1500(sh,m) Weak or no absorptions above 3000 D-band spectra	1710(sh,w), 1650(m), 1610(sh,w), 1550–1500(sh,m), 35–3000(m) D-band absorption less pronounced	1757(w), 1710(s), 1650(s), 1600(sh,w), 1520(sh,m) 35–3000(m)
Propionic	1645(m–w), 1500(s) Weak or no absorptions above 3000 D-band spectra	1710(sh,w), 1645(m), 1500(sh,m), 35–3000(m–w) D-band absorptions uncertain	1710(s), 1644(s), 1505–1500(sh,w), 35-3000(m)
Butyric	1645(m–w), 1535(sh,w), 1500(m–s) Weak or no absorptions above 3000 D-band spectra	1645(m), 1535(sh,w), 1500(sh,m), 35–3000(m) D-band absorptions uncertain	1710(s), 1645(s), 1500(w), 35–3000(m)
Isobutyric	1640(m–w), 1500(s) Weak or no absorptions above 3000 D-band spectra	1715(sh,w), 1640(m), 1535(sh), 1500(sh), 35–3000(m) D-band absorptions uncertain	1730(sh), 1705(m–w), 1640(s), 1500(m), 35–3000(m)
Trimethylacetic	1635(m), 1540–1500(sh) Weak or no absorptions above 3000 D-band spectra	1700(w), 1635(m), 1565(w), 1525(sh), 35–3000(m) D-band absorptions uncertain	1730(sh), 1697(s), 1640(sh,w), 1540(w), 35–3000(m)

[a] 'Dry conditions' – see explanation in the text. [b] Solid samples examined as nujol or fluorolube mulls between sodium chloride plates. [c] Dissolved samples pressed between sodium chloride plates.

the formic acid complex [1]. This is also in accordance with the structures found for $SnCl_4 \cdot 2(iPr)_2O$ and $SnCl_4 \cdot 2Et_2O$ [10–12].

PMR spectra of deuterated chloroform solutions give no evidence of different ether species. The chemical shifts for methyl- and methin protons were found near 1.20 ppm and 3.80 ppm, respectively, *i.e.* downfields to those found for free ether (1.07 and 3.56 ppm). The shifts for the acid hydroxyl protons were found in the region 9.50–12.60 ppm.

The examinations so far seem to confirm the assumption of an open chain structure for all the complexes of the same type as proposed earlier for the formic acid complex (see figure).

The rapid formation of solid complexes may possibly be of analytical interest, although the scope is not yet clarified.

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