Inorganica Chimica Acta, 44 (1980) L201–L202
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

A Solid Complex of Stannic Chloride with Diisopropyl Ether and Formic Acid

T. K. LØVENG and K. TAUGBØL

Department of Chemistry, University of Oslo, Blindern, Norway

Received November 27, 1979

Octahedral complexes of stannic chloride with ethers and their structures have been extensively studied. The complex $SnCl_4 \cdot 2(iPr)_2O$ has been studied by Brune and Zeil and found to have a *trans* configuration [1]. To some extent complexes with carboxylic acids have been examined [2, 3]. The three-component complex $SnCl_4 \cdot 2AcOH \cdot Et_2O$ has also been reported [4].

In the present paper we report the formation of a solid complex, formed by the addition of a few drops of formic acid to a solution of stannic chloride in diisopropyl ether at room temperature. The molar ratios of ether, stannic chloride and acid were: 50:10:1. A high ratio ether:acid is essential. With larger amounts of acid the solid precipitate disappears.

The melting point is 55–56 °C in a closed tube as well as the mother liquid. Only in the mother liquid the same solid can be obtained by cooling. After a few days at room temperature noticeable decomposition of the compound is observed. It is very reactive towards moisture. Prolonged refluxing of the reaction mixture results in substitution of the stannic chloride. The compound is soluble in benzene, chloroform and methylene chloride, and practically insoluble in nonpolar solvents such as carbon tetrachloride and cyclohexane.

Analytical data: Molar ratios, Sn:Cl:HCOOH:$(iPr)_2O$ = 1.00:4.07:0.82:2.18. The figures are mean values of six different samples. Standard deviations for Sn, Cl and HCOOH are 0.34, 0.24 and 0.42 respectively.

Tin was determined gravimetrically as dioxide. The chlorine content was found by titration with silver nitrate, as well as by potentiometric titration as hydrogen chloride after hydrolysis of the sample. The formic acid was determined by the same titration. The ether content was found indirectly by difference. Occlusion of ether by precipitation may contribute to the high content found.

PMR data for deuterated chloroform solutions are given below in ppm units. Integrated values are in parentheses. Values for formic acid protons are variable with concentration.

Assignments	$(iPr)_2O$	$SnCl_4 \cdot 2(iPr)_2O$	Complex
Methyl protons in ether	1.07	1.20	1.20 (15.0)
Methin protons in ether	3.56	3.78	3.83 (2.4)
H–(C) protons in acid			~8.5 (0.6)
H–(O) protons in acid			~13.0 (0.6)

IR spectra were taken of nujol and fluorolube mulls with potassium bromide discs. In the far infrared region polyethylene pellets were used.

In the region 4000–1200 cm^{-1} the following absorptions were found: 3500–3000(w), 3000–2800(s), 1565(s), 1470(s), 1458(w), 1382(s), 1372(m), 1325 (m) and 1210(m). Between 1200 and 600 cm^{-1} the spectra were rather complex with bands superimposed on a broad, general absorption in the whole region below 1800 cm^{-1}.

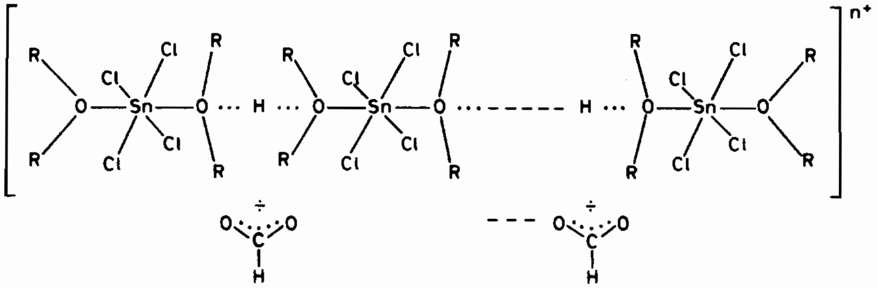
In the region 600–100 cm^{-1} the following absorptions were observed: 340(s) and 160–145(m). In Raman spectra bands were observed at: 415(w), 330 (s), 283(w), 265(w), 154(w), 135–130(w). IR-spectra of the complex in benzene solution showed the following bands in the region 4000–1200 cm^{-1}: 3600–3400(m), 3100–2900(s), 1748(m), 1723(m), 1480(m), 1378(s), 1367(m) and 1325(m). A 0.1 mm sodium chloride cavity cell was used in this case.

Discussion

A molar ratio, formic acid:stannic chloride <1 seems to be significant and may indicate a chain structure.

Formic acid can displace diisopropyl ether as a ligand to tin. However, when the complex $SnCl_4 \cdot 2(iPr)_2O$ is formed in excess of diisopropyl ether, small amounts of formic acid are assumed to link the octahedral complex units together. With larger amounts of acid coordinated ether molecules are exchanged. The decomposition observed by melting can be explained in the same way.

The infrared spectra are remarkable. The usual absorptions in the region 3500–3000 cm^{-1} due to hydrogen bonds are here very weak and in some samples completely absent. On the other hand there is a broad general absorption below 1800 cm^{-1} as mentioned above. This type of spectra is observed by Hadži for some carboxylic acid adducts with hydrogen bonds (OHO) with a single minimum potential function and called D-band spectra [5, 6]. The same type of spectra is also observed for acid–salt adducts



Proposed structure of the solid complex.

of the A-type, which are found to have very strong, symmetric hydrogen bonds [7]. D-band spectra are therefore assumed by Hadži to be representative of symmetric hydrogen bonds with a single minimum potential function. The centre of the hydrogen bond is in all cases coinciding with a crystallographic symmetry centre or a two-fold axis.

Our assumption of a strong, symmetric hydrogen bond which is linking the octahedral units together is further supported by the infrared carboxyl absorptions. No band is found above 1565 cm^{-1} and the spectra show a resemblance to the spectrum of sodium formate, which has a symmetric anion [8, 9].

The discussion of *cis–trans* isomerism in octahedral complexes of stannic chloride has mainly been based on far infrared and Raman spectra [1, 10, 11]. In the far infrared region we find only one Sn–Cl stretching vibration, at 340 cm^{-1}. This observation is consistent with a D_{4h}-symmetry of the stannic chloride moiety, *i.e.* a planar structure. *Trans* configuration is further corroborated by the Raman spectra.

In solutions of the complex the symmetric hydrogen bonds disappear. The infrared spectra of benzene solutions show the presence of formic acid as well as hydrogen bonds of the usual type which give rise to absorption in the region 3600–3400 cm^{-1}.

PMR spectra of chloroform solutions of the complex show coordinated ether molecules, but only one type. The absence of end groups suggests that the chain structure is broken down in the solution.

Our conclusion is that a polymer chain cation is formed with formate anions as shown below. Based on the analytical data the average length of the cations is 5.5 units of stannic chloride.

A basic ether with diisopropyl ether is essential for the formation of the solid complex. Several carboxylic acids probably give the same type of structure.

Further investigations are in progress.

References

1 H. A. Brune and W.Zeil, *Z. physik. Chem. Neue Folge, Bd. 32,* 384 (1962).

2 O. A. Osipov, G. S. Samofalova and E. I. Glushko, *J. Gen. Chem. U.S.S.R., 27,* 1502 (1957).

3 M. I. Usanovich and E. I. Kalabanovskaya, *Zh. Obshcheĭ Khimii, 17,* 1235 (1947). *C.A., 42,* 6693 f.

4 M. I. Usanovich and E. I. Kalabanovskaya, *Izvest. Sektora Platiny i Drug Blagorod. Met., Inst. Obshcheĭ i Neorg. Khim., Akad. Nauk. S.S.S.R., 21,* 228 (1948). *C.A., 44,* 9853 a.

5 D. Hadži, *Pure Appl. Chem., 11,* 435 (1965).

6 D. Hadži, *Chimia, 26,* 7 (1972).

7 J. C. Speakman, *Struct. Bond., 12,* 141 (1972).

8 K. Itoh and H. J. Bernstein, *Can. J. Chem., 34,* 170 (1956).

9 W. H. Zachariasen, *J. Am. Chem. Soc., 62,* 1011 (1940).

10 I. R. Beattie and L. Rule, *J. Chem. Soc.,* 2995 (1965).

11 T. Tanaka, *Organometal. Chem. Rev., A5,* 1 (1970).