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STRUCTURE AND PROPERTIES OF A TRIMETHYLLEAD CHLORIDE COMPLEX WITH METHYLALUMINIUM DICHLORIDE

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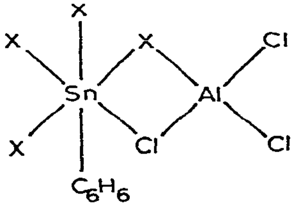
Summary

The structure of a trimethyllead chloride complex with methylaluminium dichloride $(CH_3)_3PbCl \cdot CH_3AlCl_2$ has been investigated by NMR, IR and Raman spectroscopy and by molecular weight and electrolytic conductance measurements.

Introduction

A number of papers on complexes of the periodic table's fourth group elements with aluminium compounds have already been published. For most of the investigated compounds containing chlorine the presence of a chlorine bridge between the Group IV metal atom and aluminium was ascertained [1—4].

Complexes formed by tin derivatives R_nSnCl_{4-n} ($n \leqslant 4$) with aluminium chloride [5, 6] are especially interesting because they are the intermediate products in the alkylation of tin. In the proposed structure the tin atom is six-coordinated, a molecule of the aromatic solvent is the sixth ligand. The following structure for the complexes with the formula $X_4Sn \cdot AlCl_3$ (where X = R or Cl) has been proposed.



A complex $[Ar \cdot SnCl \cdot (AlCl_4)]$ [3] (where Ar = C_6H_6, $C_6H_5CH_3$) was also isolated and the stucture determined by X-ray crystallography. An ionic structure of the complex has been proposed in which the dicentered $Sn_2Cl_2^{2+}$ ion is joined with the tetrahedral $AlCl_4^-$ anions. In the determined structure, tin is six-coordinated and the free coordination position is occupied by an aromatic hydrocarbon molecule.

During our studies on the synthesis of tetramethyllead and the reactions of organoaluminium compounds with lead salts we isolated complexes of dimethyllead dichloride and lead chloride with methylaluminium dichloride [7]. The formation of a complex between trimethyllead chloride and methylaluminium dichloride [8] was also noticed. Particular studies on the properties and structure of this last complex is the object of the present paper.

Results and discussion

Trimethyllead chloride is slightly soluble in hydrocarbon solvents and dissolves at room temperature in benzene and toluene solutions of methylaluminium dichloride. This is conditioned by the forming of a complex with the organoaluminium compound [8].

$$(CH_3)_3PbCl + CH_3AlCl_2 \rightarrow (CH_3)_3PbCl \cdot CH_3AlCl_2 \qquad (1)$$

The complexation reaction is slightly exothermic. The pale crystals of the complex decompose at 52—58° and also in the presence of oxygen, moisture and ultraviolet radiation. The results of analysis of the complex are shown in Table 1. The amount of hydrolyzable methyl groups is 3.14 in comparison with the theoretical value 3.78%. During the hydrolysis, formation of tetramethyllead is observed which explains the lower percentage share of the Al—C bonds. The presence of benzene in the studied complex has not been ascertained, as is suggested in the literature for tin complexes [3, 4].

The complex between trimethyllead chloride and methylaluminium dichloride is soluble in benzene only immediately after isolation from the solution. After desiccation or longer storage it loses its solubility probably due to association. This conclusion is confirmed by the molecular weight studies shown in Table 2. The obtained results show that molecules associate in solution.

$$2(CH_3)_3PbCl \cdot CH_3AlCl_2 \rightleftharpoons [(CH_3)_3PbCl \cdot CH_3AlCl_2]_2 \qquad (2)$$

The degree of association increases with increased concentration of the complex and time of storage.

Further studies of the complex in solution were carried out by NMR. The analysis of changes in the chemical shifts of the protons from the methyl groups bonded with aluminium and lead in NMR spectra as a function of the molar

TABLE 1

ANALYSIS OF THE COMPLEX $(CH_3)_3PbCl \cdot CH_3AlCl_2$

	Found (%)	calcd. (%)
Al	6.78	6.73
Pb	49.05	51.71
Cl	26.89	26.60
C	11.22	11.99
H	3.12	3.02
Hydrolyzable CH_3 groups	3.14	3.78

TABLE 2

THE DEGREE OF ASSOCIATION OF THE COMPLEX $(CH_3)_3PbCl \cdot CH_3AlCl_2$ (MOL. WT. 400.6) AS A FUNCTION OF CONCENTRATION AND TIME OF STORAGE

Concentration (wt. %)	Time	Molecular mass	Degree of association
4.8	Immediately after preparation of the solution	507	1.27
9.57	Immediately after preparation of the solution	695	1.74
9.57	After 24 hours	785	1.96
7.1	After a week	913	2.28

ratio of reactants (Fig. 1) also leads to the conclusion that trimethyllead chloride with methylaluminium dichloride forms a complex with the Pb/Al molar ratio 1/1.

The comparison of chemical shifts and of coupling constant values of the protons with lead nucleus $J(^{207}Pb—CH_3)$ in the spectra of methylaluminium dichloride, trimethyllead chloride, and complex are shown in Fig. 2. In the complex spectrum two signals of protons of $Al—CH_3$ and $Pb—CH_3$ with the ratio 1/3 were observed. The signals of protons of methyl groups bonded with aluminium $Al—CH_3$ undergo a shift from τ 10.14 ppm in pure methylaluminium dichloride to 9.96 ppm in the complex (δ 0.18 ppm). The respective value of δ, e.g. for $MeAlCl_2 \cdot PhCN$ complex is 0.28 ppm [8]. The signals of protons of methyl groups bonded with lead undergo a considerable shift from τ 8.94 ppm in free trimethyllead chloride to 8.13 ppm in the analyzed complex. Such a large change of chemical shift of protons of methyl groups $Pb—CH_3$ (δ 0.81 ppm) to a lower field may testify to the occurrence of $(CH_3)_3Pb^+$ cations in the solution. For example the signal of protons of t-butyl cations $(CH_3)_3C^+$ occurs at τ 5.65 ppm in comparison with 8.70 ppm for methyl group protons in $(CH_3)_3CF$ [9].

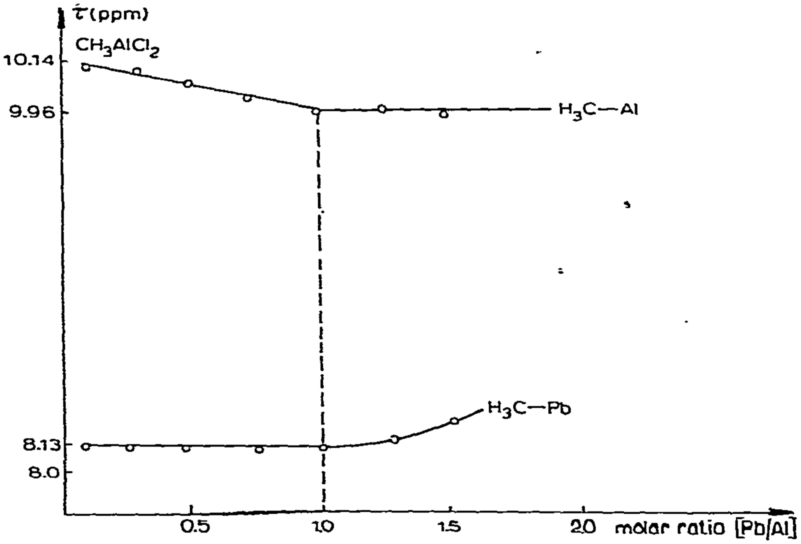


Fig. 1. Change of chemical shifts of protons of the $Al—CH_3$ and $Pb—CH_3$ groups as a function of the molar ratio of Pb/Al in the NMR spectra.

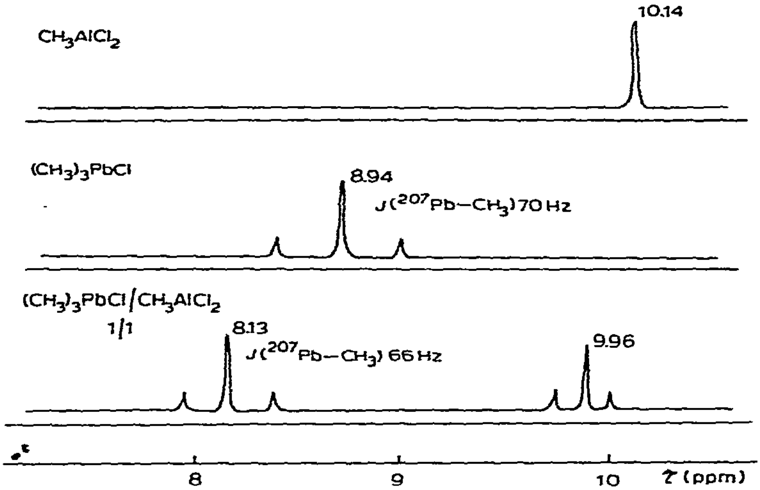
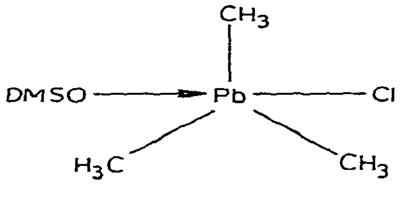


Fig. 2. Comparison of chemical shifts and coupling constant $J(^{207}Pb—CH_3)$ in the NMR spectra of the $(CH_3)_3PbCl \cdot CH_3AlCl_2$ complex.

The lead atom in the solution of trimethyllead chloride with methylaluminium chloride has a geometry approximated to the geometry of lead in trimethyllead chloride. The coupling constant $J(^{207}Pb—CH_3)$ confirms this. It equals 66 Hz in the complex compared with the value for $J(^{207}Pb—CH_3)$ of 62 Hz in tetramethyllead and 70 Hz in trimethyllead chloride.

As Puddephatt and Thistlethwaite ascertained [10], the coupling constant $J(^{207}Pb—CH_3)$ in methyllead compounds is determined not only be the electronegative value of all the groups bonded with lead but also by the stereochemistry of lead. For example for trimethyllead chloride in a methyl sulphoxide solution, in which lead probably has a trigonal bipyramid geometry, the coupling constant $J(^{207}Pb—CH_3)$ is 83 Hz [10].



Measurements of conductance of electrolytes were carried out, but for trimethyllead chloride and methylaluminium dichloride it was not possible to determine the specific conductivity values because they were below the range of the apparatus used. The determined conductivity value of $(CH_3)_3PbCl \cdot CH_3AlCl_2$ complex at a temperature of 20° was $1.2 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$. It may be ascertained that the complex has a high degree of ionic character and may be represented by the following equilibrium scheme:

$$(CH_3)_3PbCl \rightarrow Al(CH_3)Cl_2 \rightleftharpoons (CH_3)_3Pb^+ \cdots Cl^-Al(CH_3)Cl_2 \rightleftharpoons (CH_3)_3Pb^+ + {}^-Al(CH_3)Cl_3$$

The structure of the complex in the solid phase has been studied by IR and Raman spectroscopy. The results of studies are shown in Tables 3 and 4.

TABLE 3

ABSORPTION BANDS IN THE INFRARED 400—2000 cm^{-1} REGION (NUJOL)

Compound	Absorption bands (cm^{-1})
CH_3AlCl_2	482 s, 585 m, 602 m, 680 m, 701 s, 745 m, 808 m, 940 w (br), 1020 w, 1211 m, 1310 m, 1370 m (br), 1465 m (br), 1630 w (br)
$(CH_3)_3PbCl$	490 s (br), 790 s (br), 1148 m, 1390 s
$(CH_3)_3PbCl \cdot CH_3AlCl_2$	440—460 w (br), 475—502 m (br), 536 m, 675—695 s (br), 735 s, 820 s (br), 872 s, 965 m, 1040 m, 1167 s, 1200 s, 1275 m, 1393 s, 1480 m (br), 1625 m

The IR spectrum of the complex in the 400—2000 cm^{-1} range shows characteristic absorption bands for pure components vanish and new bands appear. Especially important is the non-occurrence in the complex spectrum of bands at frequencies of ν 701 s and 482 cm^{-1} s attributed to aluminium—chlorine bridge oscillations of the methylaluminium chloride dimer. Due to the addition of a big mass to the aluminium atom the vibrational frequency of the aluminium outer chlorine band probably undergoes a shift from the value of ν(Al—Cl) 585 in methylaluminium dichloride to ν(Al—Cl) 536 cm^{-1} in the complex. In the IR spectrum of the complex the appearance of a wide band in the 475—502 cm^{-1} range was observed. This band may be attributed to the $[RAlCl_3]^-$ ions that occur in the complex structure. As has been previously observed by one of the authors, the occurrence of a wide absorption band in the 470—500 cm^{-1} range testifies to the presence of $[AlCl_4]^-$ anions [13].

In the Raman spectrum (Table 4) of the complex, an absorption band at a frequency of 132 cm^{-1} s occurs which can be attributed to the skeleton vibrations. This band is slightly shifted by 8 cm^{-1} in comparison to the analogous band in trimethyllead chloride and hence confirms the preservation of the trimethyllead chloride structure in the complex. The above conclusion is confirmed by the occurrence in the complex spectrum of absorption bands for the (PbC_3) arrangement, symmetrical 464 s and asymmetrical 493 cm^{-1} m, completely unchanged in ratio to trimethyllead chloride. The presence of 225 w and 355 cm^{-1} w bands can be attributed to the ν(Pb—Cl) and ν(Al—Cl) vibrations in the complex.

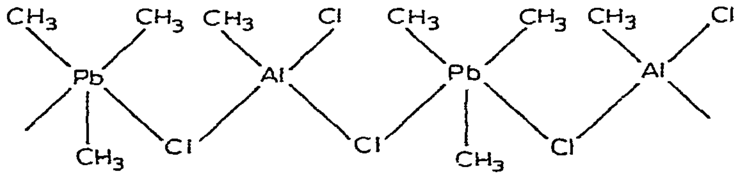
TABLE 4

RAMAN SPECTRUM IN THE 50—600 cm^{-1} REGION

Assignment [a]	$(CH_3)_3PbCl$	CH_3AlCl_2	$(CH_3)_3PbCl \cdot CH_3AlCl_2$
			503 m
$\nu_{as}(PbC_3)$	496 m		493 m
$\nu_s(PbC_3)$	464 vs		464 vs
ν(Al—X) bridge		345	355 w
ν(Pb—X)	149 w		225 w
Skeleton vibrations	124 s		132 s

[a] Assignment of bands in trimethyllead chloride [14] and methylaluminium dichloride [15].

On the basis of experimental data the following structure of the complex between trimethyllead chloride and methylaluminium dichloride in the solid phase may be proposed (see over):



The structure of the complex is to a large degree similar to the structure of pure trimethyllead chloride. The complex preserves the initial trimethyllead chloride structure in which every second lead atom is substituted by an aluminium atom. The lead and aluminium atoms are joined with each other by chlorine bridges, forming long chains of a linear polymer.

In the proposed structure, lead atoms have a coordination number 5 which is consistent with data published by Clark and coworkers for trimethyllead chloride [14]. The aluminium atoms with coordination number 4, have a methyl group and three chlorine atoms surrounding them. This allows them to form $[RAlCl_3]^-$ ions, (475—502 cm^{-1} band in IR). It should be presumed that the complex between trimethyllead chloride and methylaluminium dichloride has to a large degree an ionic structure. The $[RAlCl_3]^-$ and $[R_3Pb]^+$ ions are set alternately in the polymer chain. Also, the conductance of electrolytes of the complex solutions confirms such a structure.

Experimental

Substrates

Methylaluminium dichloride and trimethyllead chloride were obtained by known methods. Immediately before use methylaluminium dichloride was distilled, trimethyllead chloride was sublimed at 130—150°C under pressure of $\simeq$ 0.1 mmHg and benzene and toluene were distilled in a pure nitrogen atmosphere from sodium and then from lithium aluminium hydride.

Reaction of trimethyllead chloride complex with methylaluminium dichloride

Into a nitrogen-flushed three necked flask equipped with a stirrer and cold trap methylaluminium dichloride was placed and dissolved in benzene. Trimethyllead chloride was added so that the $CH_3AlCl_2/(CH_3)_3PbCl$ molar ratio was 1/1. After a few minutes a clear solution with a slightly higher temperature was obtained. After evaporation of the solvent, a solid was obtained which was crystallized from benzene.

Analysis

Aluminium, chlorine, lead, and methyl groups were determined by methods described in the literature [8]. Hydrogen and carbon were determined by burning the sample.

Spectroscopic studies

NMR spectra were recorded on a J.N.M. 60-H spectrometer using benzene as an internal standard. The solutions were prepared and sampled in a purified nitrogen atmosphere. IR spectra were recorded on a Zeiss UR-10 spectrometer as nujol mulls. Raman spectra were recorded on a Coderg He—Ne laser spectrometer at 74 mW.

Molecular weight studies

Molecular weight was determined in benzene by the cryoscopic method using vessels adapted for work with organoaluminium compounds.

Conductivity studies

Conductivity measurements were carried out on about 0.09 *M* solution of the complex and methylaluminium dichloride in chlorobenzene, at room temperature in a pure nitrogen atmosphere using a Hungarian OK-102/1 Conductivity meter.

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