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# Hydrolysis of organoaluminium compounds

So far hydrolysis of organoaluminium compounds with water did not lead to crystalline product [1—3]. An attempt was made to hydrolyze organoaluminium compounds with water at a 3 : 2 molar ratio to obtain crystalline aluminoxane derivative containing an >Al-O-Al-O-Al< moiety and to study its structural properties. Such compounds will be called oligoaluminoxanes.

The hydrolysis of various alkylaluminium halides was carried out by a continuous method according to the equation [3]:

$$3R_3Al + 2H_2O \longrightarrow R_5Al_3O_2 + \text{side products} \qquad (1)$$

$$R = Et,\ i\text{-}Bu,\ Cl,\ Br,\ I$$

From the reaction:

$$3(i\text{-}Bu)_2AlCl + 2H_2O \xrightarrow[\text{toluene}]{195\,K\,(-78^\circ C)} (i\text{-}Bu)_3Cl_2Al_3O_2 + \text{side products} \qquad (2)$$

the crystalline oligoaluminoxane was obtained with ca. 20% yield. The results of elemental analysis are in good agreement with the composition of triisobutyldichlorooligoaluminoxane.

$(i\text{-}Bu)_3Cl_2Al_3O_2$ (355.2) calculated: Al — 22.7%,
Cl — 20.1%
i-Bu — 47.6%,

found: Al — 22.8%,
Cl — 20.0%,
i-Bu — 48.2%.

From cryoscopic measurements of molecular weight M = 1108 the association degree n = 3.12 was calculated. The hypothetic molecular structure of the crystalline oligoaluminoxane trimer is shown in Fig. 1.

As can be seen, in a trimeric molecule three rings of monomers form together a new central ring consisting of aluminium and oxygen atoms.

Results of spectroscopic measurements confirm the proposed structure. In the IR spectrum (Fig. 2) two very strong bands at 753 $cm^{-1}$ and at 790 $cm^{-1}$ appear. Usually in the region of 800 $cm^{-1}$ a very strong and broad band characteristic for the Al-O-Al moiety vibrations in aluminoxanes is observed. The presence of these two bands may be due to the existence of bigonally and trigonally coordinated oxygen atoms in the trimetric molecule. Moreover, a strong band at 412 $cm^{-1}$ appears, which is connected with the Al-Cl bridge vibrations [4].

In the PMR spectrum the following signals are observed (Fig. 3): multiplet at 7.78 ppm and three dublets: at 8.81 ppm, at 8.84 ppm and at 9.32 ppm (in $\tau$ scale).

The ratio of the signal intensities is as 1 : 2.3 : 4.2 : 2.1, respectively. Chemical shifts and ratio of the intensities allow us to conclude that the signal at 7.78 ppm corresponds to the methylidyne $(\equiv CH)$ the signals at 8.81 ppm and at 8.84 ppm correspond to the protons of methyl groups and the signal at 9.32 ppm corresponds to the methylene protons ($-CH_2-$).

As you can see two kinds of isobutyl groups in the proposed structure are present: the first kind of three isobutyl groups which are inside the trimeric molecule and the second kind of six isobutyl groups which are outside it (Fig. 1, 3).

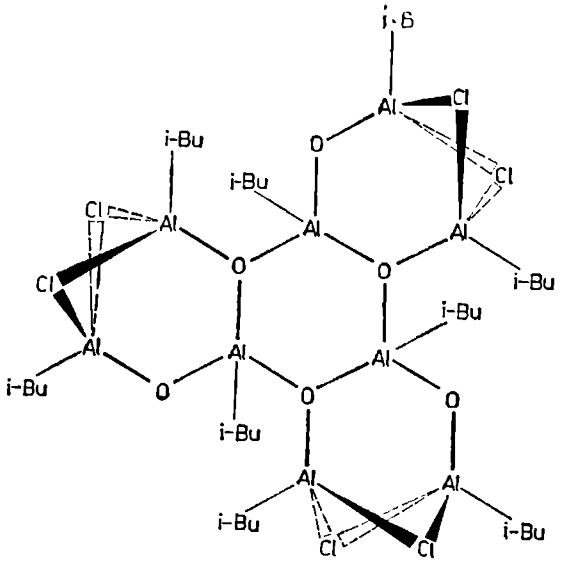

*Fig. 1. The hypothetic molecular structure of the crystalline triisobutyldichlorooligoaluminoxane trimer*

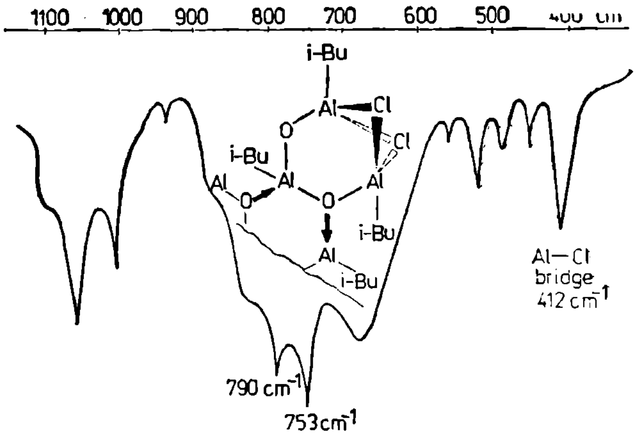

*Fig. 2. The IR spectrum of the crystalline oligoaluminoxane*

Thus the two different signals of methyl groups are probably due to steric hindrances and only one signal of the methylene protons allows us to assume that all the aluminium atoms in the trimer are of a similar electronegativity.

## REFERENCES

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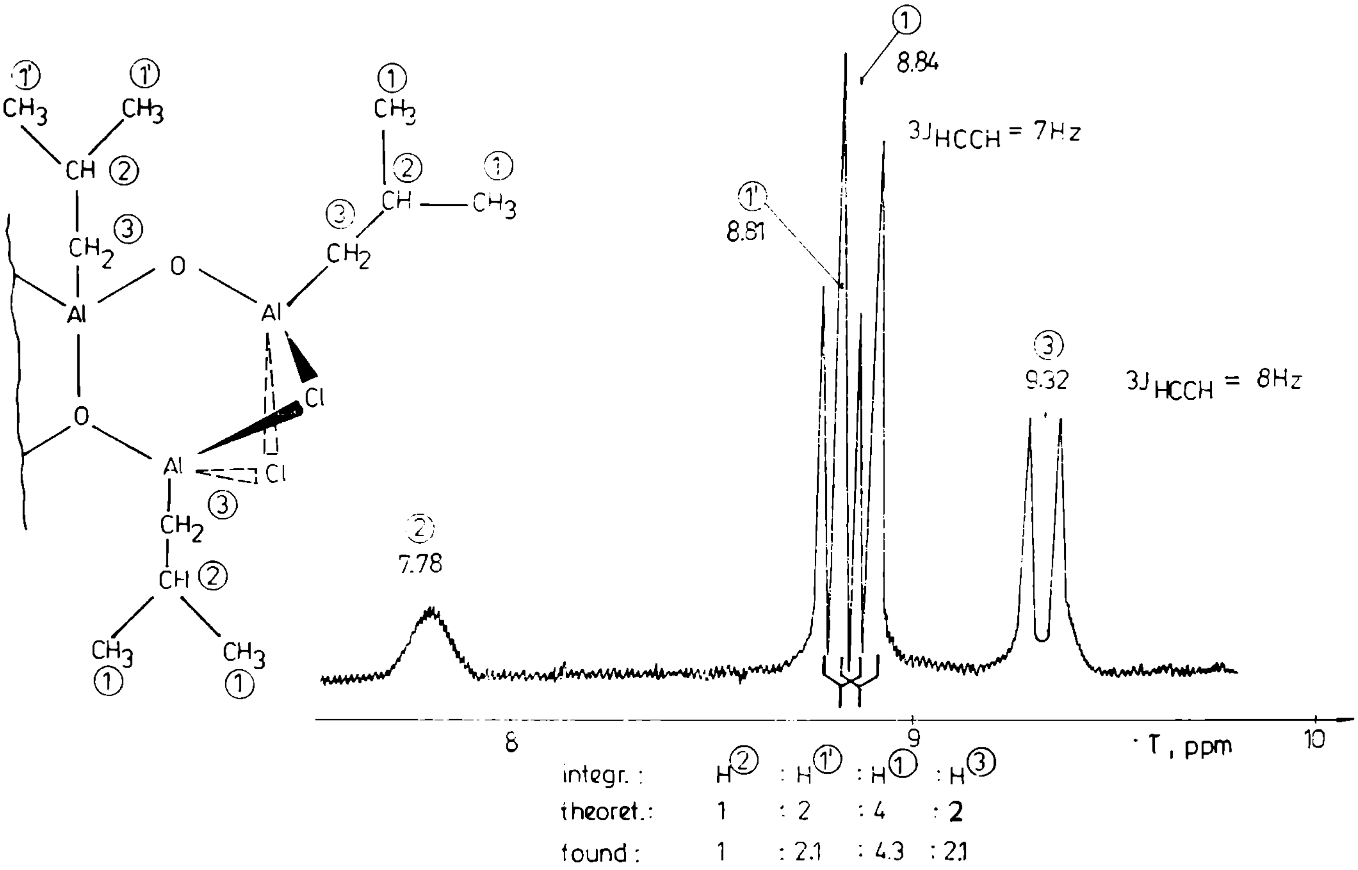

*Fig. 3. The PMR spectrum of the crystalline oligoaluminoxane*