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THE ^1H NMR SPECTRA OF METHYLMETHOXYALUMINIUM CHLORIDE AND METHYLMETHOXYALUMINIUM IODIDE

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Summary

It has been shown by means of ^1H NMR, IR and cryometrical measurements that, with oxygen bridges, Me(OMe)AlCl and Me(OMe)AlI are trimers in solutions.

Two isomers, *cis* and *trans*, are present, which are responsible for the multiple ^1H NMR spectra. The proton signals of Me—Al and O—Me groups are assigned in each isomer.

Introduction

The degree of association of alkoxyaluminium compounds depends mainly on the bulk of the O—R substituent. The majority of methoxyaluminium compounds are trimers, while ethoxy compounds are dimers after synthesis and change their degree of association to $n = 3$ on storage [1]. Dimethylmethoxyaluminium is the best known and most thoroughly investigated of the methoxy compounds. It has been determined that the compound both in solution and in the gas phase, is a trimer with oxygen bridges [2,3]. It has also been shown, by means of gas phase electron diffraction, that the six-membered Al_3O_3 ring is nonplanar, but that the three oxygen bonds lie in one plane [2]. The purpose of this study was to determine the structure of methylmethoxyaluminium chloride and methylmethoxyaluminium iodide.

Results and discussion

We have determined by means of cryometrical measurements that both methylmethoxyaluminium chloride and methylmethoxyaluminium iodide are trimers in benzene solution (degree of association $n = 3$).

The IR spectra show characteristic bands at a frequency of ν 960 cm^{-1} (Me(OMe)AlCl, Table 1) and ν 935 cm^{-1} (Me(OMe)AlI, Table 1). These bands

TABLE 1

IR SPECTRA OF Me_2AlCl, $Me(OMe)AlCl$, Me_2AlI, $Me(OMe)AlI$ IN BENZENE

Me_2AlCl $\nu(cm^{-1})$	$Me(OMe)AlCl$ $\nu(cm^{-1})$	Me_2AlI $\nu(cm^{-1})$	$Me(OMe)AlI$ $\nu(cm^{-1})$
1210s	1212m		1206s
		1191s	
	998m(sh)		
	960—970st		975m(sh)
			935s
718vst	718vst		
		695vs	
	635s		
585m	585w		
		570s	
	560w		
	502m		
440st	440w		470m
			420w
			399w
	365vw		
360w(sh)			
			345s
339m			
		330vw	
307s			
		300w	
		250s	
	213w	213s	

are attributed to the vibrations of the C—O bond in the bridging MeO group. We observed two strong bands at 213 and 250 cm^{-1} in the IR spectra of Me_2AlI, which are probably connected with the Al—I bridge vibrations. They are not present in the case of Me(OMe)AlI. In the spectrum of the methoxy compound we observed a new strong band at 345 cm^{-1} which may be due to the vibrations of the Al—I terminal group.

The ^1H NMR spectra of both compounds are surprisingly alike (Fig. 1, 2). The spectrum of Me(OMe)AlI at room temperature shows 3 signals of O—Me protons and 2 signals of Al—Me protons (Fig. 2a). At lower temperatures we observe six signals, as for Me(OMe)AlCl. Two of the Al—Me proton signals of Me(OMe)AlI (B′, C′) overlap at room temperature and are observable only when shifted after cooling (Fig. 2b, c). In the case of both the compounds the medium signals (C, C′) show a tendency to shift to higher fields at lower temperatures, with respect to the highest ones (B,B′).

The multitude of signals cannot be due to different conformational isomers of the non-planar ring, since the intensity and amount of the signals did not vary with temperature, when cooled. The chemical shifts of the signals, however, are distinctly solvent-, concentration-, and temperature-dependent (Table 2).

According to the integration the intensity ratios of the O—Me/Al—Me proton signals are: A/A′ = B/B′ = C/C′ = 1/1. The intensity ratio of the O—Me signals is B/C = 2/1, and of the Al—Me proton signals B′/C′ = 2/1. This would be con-

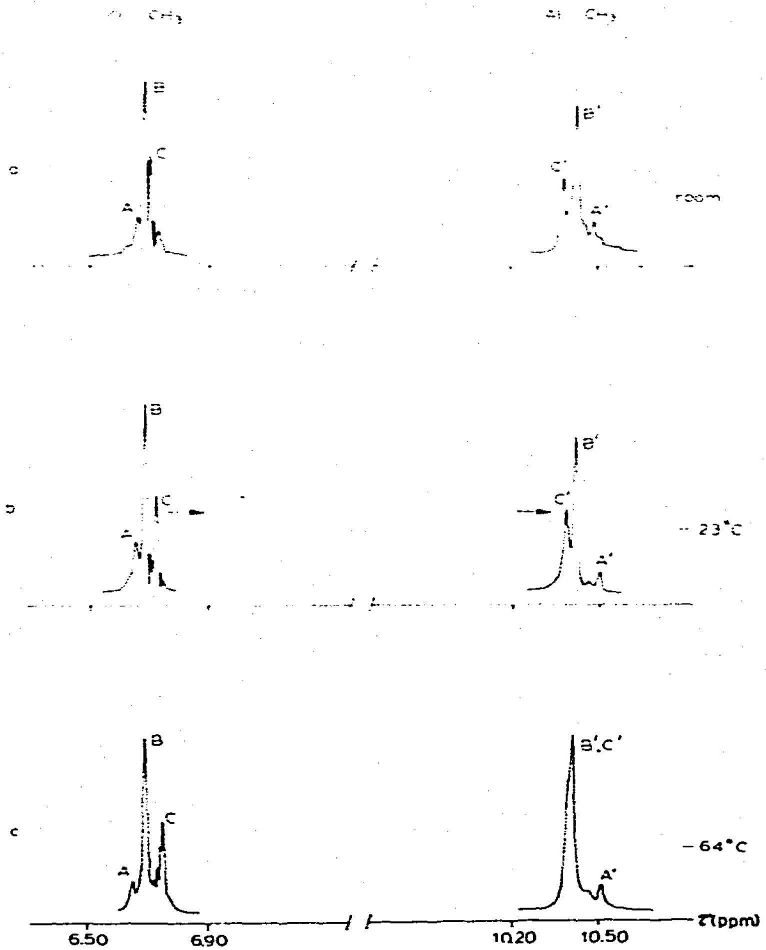
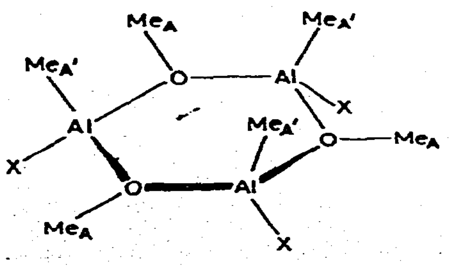
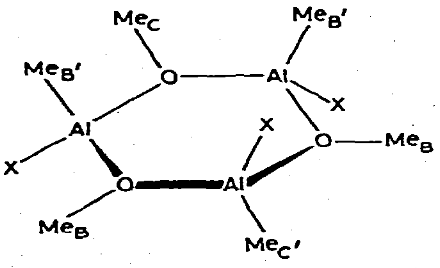


Fig. 1. The 100 MHz ^{1}H NMR spectra of Me(OMe)AlCl in toluene. 270 Hz. (a) A, 6.66; B, 6.68; C, 6.71; A', 10.51, B', 10.42, C', 10.38 (τ-values (ppm), toluene as a standard (7.66 ppm)). → direction of the shift of the C signals compared with the position of B.

sistent with the presence of two geometrical isomers, a *cis* (I) and a *trans* (II) form.



(I)



(II)

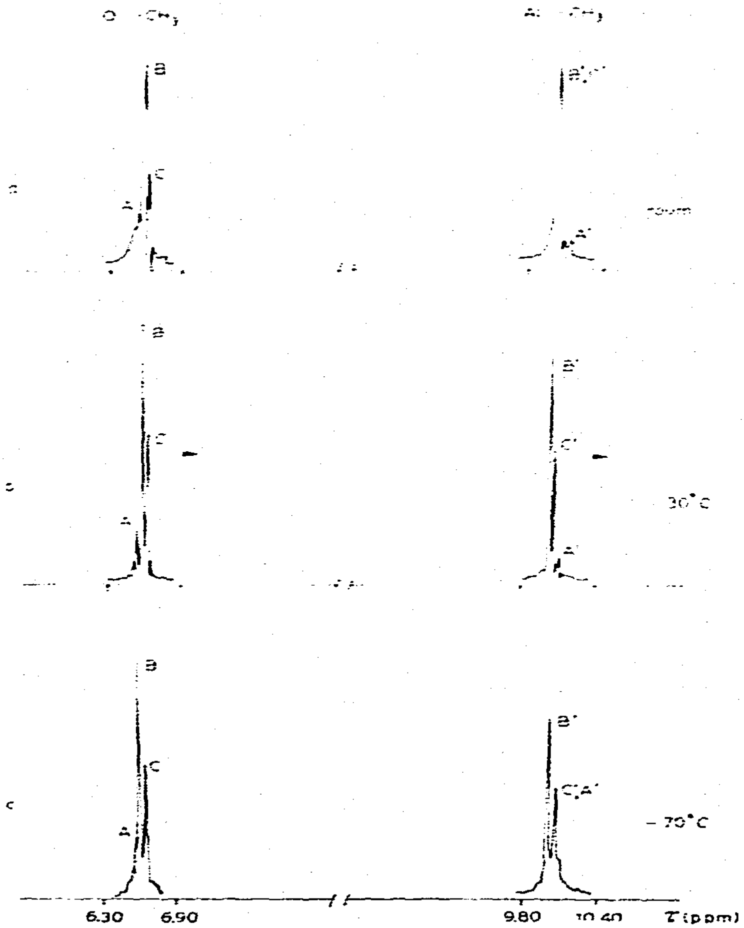


Fig. 2. The 100 MHz ^{1}H NMR spectra of Me(OMe)AlI in toluene. 1080 Hz. (a) A, 6.53; B, 6.56; C, 6.65; A', 10.20; B', C', 10.04, (τ-values (ppm), toluene as a standard (7.66 ppm)). → direction of the shift of C signals compared with the position of B.

TABLE 2

^{1}H NMR SPECTRA OF Me(OMe)AlCl AND Me(OMe)AlI [a]

Compound	Temperature	O—Me			Al—Me		
		A	B	C	A'	B'	C'
Me(OMe)AlCl	room temperature	6.68(7)	6.69(22)	6.71(10)	10.52(6)	10.41(23)	10.38(11)
Me(OMe)AlI	—30°C	6.68(10)	6.73(56)	6.84(28)	10.20(10)	9.98(56)	10.07(28)

[a] τ-values in ppm downfield and upfield from toluene at 7.66 ppm ca. 10% solutions in toluene, intensities of the signals upon integration in parentheses.

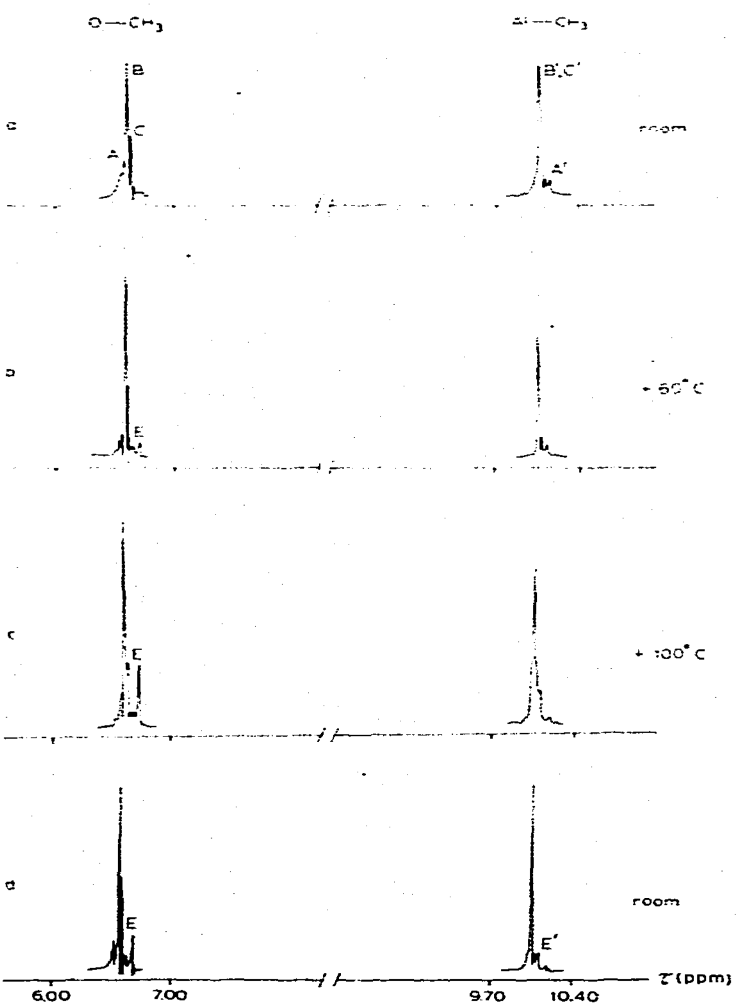


Fig. 3. The 100 MHz ^{1}H NMR spectra of Me(OMe)AlI in toluene. 1080 Hz. (d) After cooling back to room temperature A, 6.46; B, 6.51; C, 6.58; E, 6.79; A', 10.21; B', C', 10.06; E', 10.11 (τ-values (ppm), toluene as a standard (7.66 ppm)).

The A and A' signals are assigned to the *cis* isomer. The B,B', C,C' are assigned to the *trans* form where two Al—Me groups are above the plane of the ring (B') and one beneath it (C'). Two O—Me groups are equivalent (B) and the third is nonequivalent (C). We have calculated upon integration that there is ~20% of the *cis* isomer of Me(OMe)AlCl and ~10% of *cis*-Me(OMe)AlI.

The ^{1}H NMR spectrum of Me(OMe)AlCl did not change after heating to +130°C and cooling immediately to room temperature. This means that the compound's degree of association does not change, and it has the same bridging atoms. However, the spectrum of Me(OMe)AlI changed during heating (Fig. 3b). A new signal (E) appeared and increased at higher temperatures. It was still present in the spectrum after cooling to room temperature (Fig. 3d). We also observed changes in the Al—Me region but as the main signal is broad we cannot say anything definite about the intensities. It is quite possible that the compound changed its association upon heating.

Experimental

Methylmethoxyaluminium chloride was obtained by the reaction of dimethylaluminium chloride with methyl alcohol. The synthesis was carried out at 0°C in n-heptane. The precipitate obtained, after evaporation of the solvent, was sublimated under vacuum and analysed. Anal. Found: Al, 24.87; Me, 13.10; Cl, 31.93. Me(OMe)AlCl calcd.: Al, 24.85; Me, 13.83; Cl, 32.68%.

Methylmethoxyaluminium iodide was similarly obtained. Methyl alcohol was distilled from magnesium, and the organoaluminium compounds purified by distillation.

NMR spectra were recorded on a JNM-100-H (JEOL, Tokyo) spectrometer using 10% solutions in toluene. IR spectra were recorded on a Perkin—Elmer Model 577 spectrometer using benzene solutions. The solutions were prepared and tested in a purified nitrogen atmosphere.

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