

Preliminary communication

A VOLATILE DERIVATIVE OF ALUMINOXANES: TETRAMETHYLALUMINOXANE-*N,N,N',N'*-TETRAMETHYLETHYLENE- DIAMINE

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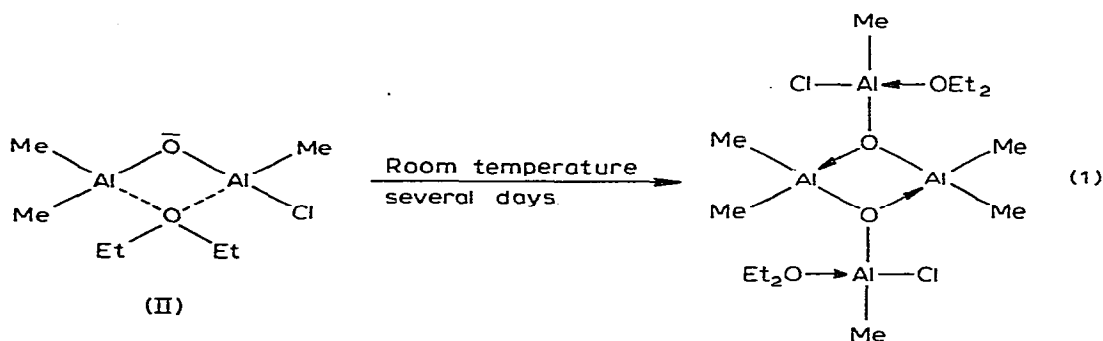
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Summary

The Lewis acidity and complexing ability of tetramethylaluminum-*N,N,N',N'*-tetramethylenediamine are discussed. The complex is proven to be monomeric in the gaseous state but the residue is polymeric.

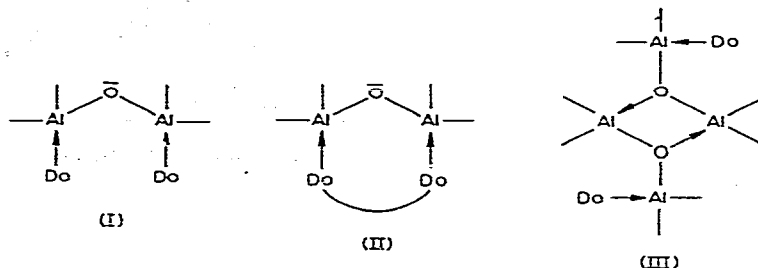
Aluminoxanes of the general formula $R_2AlOAlR_2$ ($R = \text{alkyl or halogen}$) are the subject of our interest since they were shown to be excellent catalysts for polymerization reactions of polar monomers [1]. Their Lewis acidity and complexing ability, the important factors from the viewpoint of catalysis, are being investigated. Aluminoxanes and their complexes with organic electron donors tend to form oxygen-bridged associates as could be distinctly observed for $Me_3ClAl_2O \cdot OEt_2$ [2], eq. 1:



We have already discussed this tendency in terms of the donicity competition between the oxygen atom in the methylaluminoxane molecule and an external electron donor [3]. However, we had still to find an electron donor

strong enough to break the oxygen bridging of methylaluminoxanes and thus obtain a monomeric complex (I or II).

Furthermore, we expected the monomeric complex to be volatile in contrast to the dimeric species (III) which easily underwent polycondensation reactions when distilled or sublimed. The vaporization of the aluminoxane complexes would be of great practical importance: it would provide easier methods for their purification and would make it possible to study aluminoxanes with the spectral methods which require a gaseous state sample, e.g. mass spectrometry or electron diffraction.



Bidentate electron donors were considered promising counterparts for binuclear Lewis acids, as are aluminoxanes. Some thermodynamic advantage and therefore an increased stability might have been expected for the cyclic structures (II).

A complex of tetramethylaluminoxane and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was obtained in a routine way, i.e. by the partial hydrolysis of trimethylaluminium (eq. 2):



After the reaction had been completed and the solvent removed in vacuo the product was subjected to sublimation (room temp 1×10^{-3} mmHg). Pale crystals (m.p.) $78-82^\circ \text{ C}$ in 5-10% yield were obtained.

Spectral data of the sublimate (Figs. 1 and 2) differ from those of $(\text{Me}_3 \text{ Al})_2 \cdot \text{ TMEDA}$ (which could be an unreacted substrate) and correspond to the aluminoxane complex $\text{Me}_4 \text{ Al}_2 \text{ O} \cdot \text{ TMEDA}$.

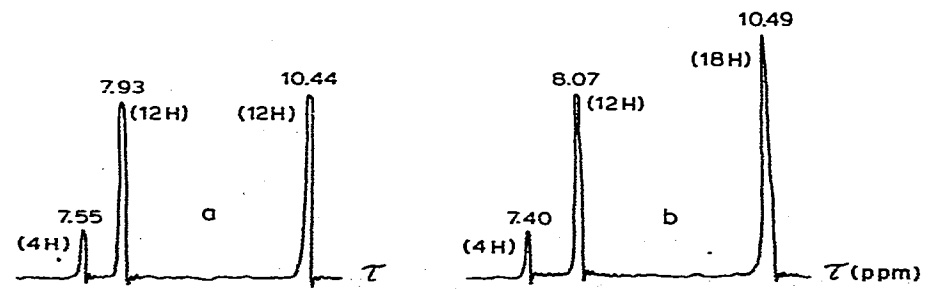


Fig. 1. $^1 \text{ H NMR}$ (100 MHz) spectra: (a) the sublimate $\text{Me}_4 \text{ Al}_2 \text{ O} \cdot \text{ TMEDA}$ (b) $(\text{Me}_3 \text{ Al})_2 \cdot \text{ TMEDA}$. Solvent $\text{C}_6 \text{ H}_6$.

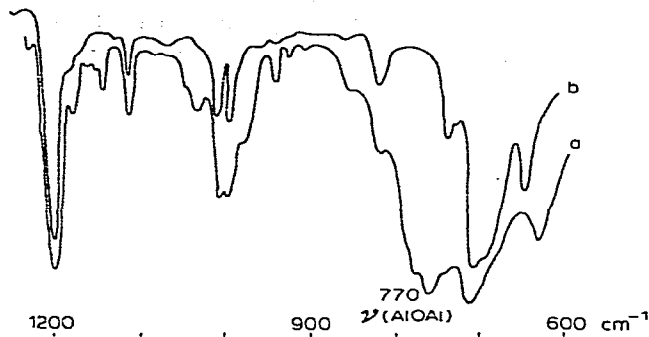
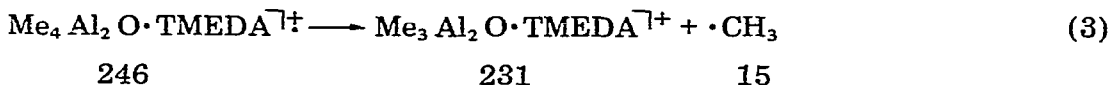


Fig. 2. IR spectra: (a) the sublimate $\text{Me}_4\text{Al}_2\text{O}\cdot\text{TMEDA}$, (b) $(\text{Me}_3\text{Al})_2\cdot\text{TMEDA}$. Solvent C_6H_6 .

The molecular weight of the sublimate determined by the cryoscopic method in benzene (concn. 1.09%) was 240 which suggests the complex to be monomeric (mol. wt. of $\text{Me}_4\text{Al}_2\text{O}\cdot\text{TMEDA}$ 246).

The mass spectra of the $\text{Me}_4\text{Al}_2\text{O}\cdot\text{TMEDA}$ complex were recorded. The heaviest ion detected was that of m/e 231 which corresponds to the loss of a methyl group from the molecular ion (eq. 3):



It is known that the most abundant ions in the mass spectra of alkylaluminium compounds are formed by loss of one radical moiety from the molecular ion [4].

The correctness of the assignment of the m/e 231 peak to the $\text{Me}_3\text{Al}_2\text{O}\cdot\text{TMEDA}^{\bar{1}\dagger}$ ion was confirmed by mass spectra analysis of the ^{18}O labelled $\text{Me}_4\text{Al}_2\text{O}\cdot\text{TMEDA}$ complex (Table 1).

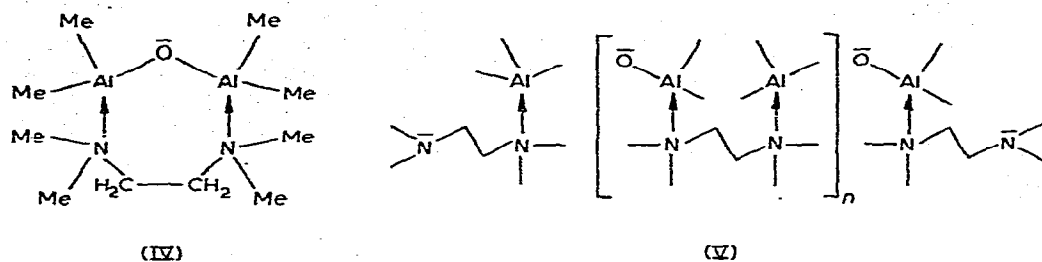
TABLE 1

THE ISOTOPIC CONTRIBUTIONS OF THE m/e 231 PEAK (M) IN THE MASS SPECTRA^a OF TETRAMETHYLALUMINOXANE- N,N,N',N' -TETRAMETHYLETHYLENEDIAMINE COMPLEXES

$\text{Me}_4\text{Al}_2\text{O}\cdot\text{TMEDA}$		$\text{Me}_4\text{Al}_2\text{ }^{18}\text{O}\cdot\text{TMEDA}^b$	
m/e	% M	m/e	% M
231 (M)	100.0	231 (M)	100.0
232 ($M+1$)	15.1	232 ($M+1$)	14.7
233 ($M+2$)	3.5	233 ($M+2$)	39.6

^aRecorded with the JEOL SG01 apparatus, using an ionizing voltage of 75V, ion source temperature 90°C. ^b43.6 mol per cent enriched $\text{H}_2\text{}^{18}\text{O}$ was used in the synthesis according to eq. 2.

The data presented prove the existence of the monomeric tetramethylaluminumoxane-*N,N,N',N'*-tetramethylethylenediamine complex of structure IV.



The highly viscous residue of sublimation which is also insoluble in hydrocarbons seems to be of the donor-acceptor type polymers like V.

Acknowledgement

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References

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