

THE STRUCTURE OF ALUMINIUM
SESQUI(2-METHOXYETHOXY)HYDRIDE AND
ALUMINIUM 2-METHOXYETHOXIDE*

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The structure of aluminium sesqui(2-methoxyethoxy)hydride has been determined from its molecular weight and ¹H NMR spectra. The hydride was dimeric throughout the concentration range measured. The centre of the skeleton is an aluminium atom, free of hydride hydrogens, attached *via* oxygen bonds to three aluminium atoms, each of which is bound to two hydride hydrogens. All the aluminium atoms are six-coordinated. Up to a temperature of 103°C in toluene no evidence of decomposition or a changed structure of the dimer was observed. An analogous structure is assigned to aluminium 2-methoxyethoxide.

Our studies on the syntheses and properties of sodium alkoxyhydridoaluminates¹⁻⁴ and aluminium alkoxyhydrides^{5,6} with a donor oxygen or nitrogen on the β-carbon include an attempt at the determination of the structure of aluminium sesqui(2-methoxyethoxy)hydride (*I*). The measured molecular weights in benzene, the IR spectra of the pure substance and its solutions in benzene, tetrahydrofuran and ether⁷, and finally even the ¹H NMR spectra⁸ demonstrate that the compound *I* is a chemical individual, dimeric in the concentration range investigated. On the basis of these facts it was possible to proceed to a deeper NMR study of the compound.



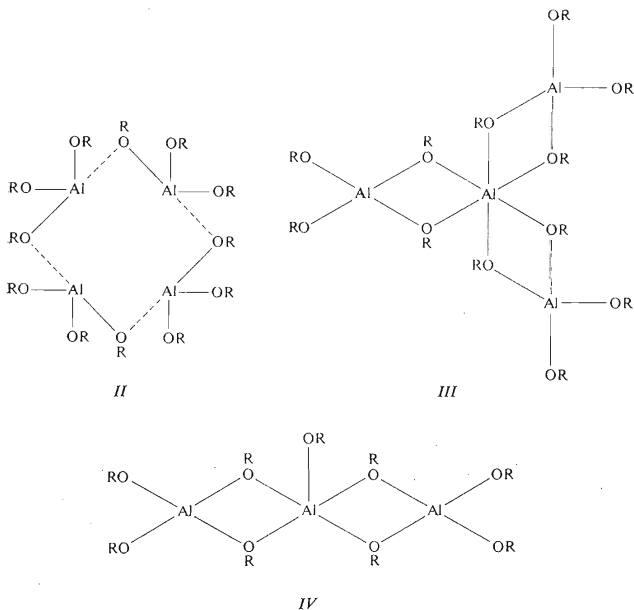
I

With compounds containing four aluminium atoms in a molecule, *i.e.* in the case of analogues of the hydride *I*, the following structures have been considered: *a*) Ulich and Nespital⁹, on the basis of molecular weights and dipole moments, assign tetrameric alkoxides of aluminium structure *II*. Ayres and coworkers¹⁰ have drawn

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a similar conclusion from the ^1H NMR spectra of aluminium benzyl oxide. *b*) Bradley¹¹ assumes that metallic alkoxides have structures in which the lowest polymerization degree is consistent with the attainment of the maximum covalency of the metal. This means that tetrameric alkoxides of aluminium with a simple alkoxy should have a six-coordinated central aluminium atoms and three four-coordinated aluminium atoms. In accordance with this idea and the ^1H NMR spectra, Shiner and coworkers¹² assign the tetrameric aluminium 2-propoxide structure *III*, and Oliver and Worrall¹³ propound the same structure even for aluminium benzyloxyde and 4-chlorobenzyloxyde. *c*) It is also necessary to consider linear polymers, assumed with aluminium dimethoxyhydride¹⁴⁻¹⁶ and trimeric aluminium 2-propoxide (*IV*) on the basis of their IR and Raman spectra¹⁷.

In solving the structure of the hydride *I* we proceeded from the spectra of the proton magnetic resonance (Table I) and from the cryoscopically determined degree of association in a 15% solution in benzene⁵. The effects of a modification in the alkoxy and of the hydride hydrogen on structure *I* have been assessed by comparison



with other compounds: aluminium 2-methoxyethoxide (V) and aluminium bis(2-methoxyethoxy)hydride (VI) – complete or partial replacement of the hydride hydrogens in I by 2-methoxyethoxy; aluminium sesqui(2-isopropoxyethoxy)hydride (VII) – replacement of β -methoxyl in the alkoxy by the bulkier isopropoxyl; aluminium sesqui(3-methoxybutoxy)hydride (VIII) and aluminium sesqui(1-

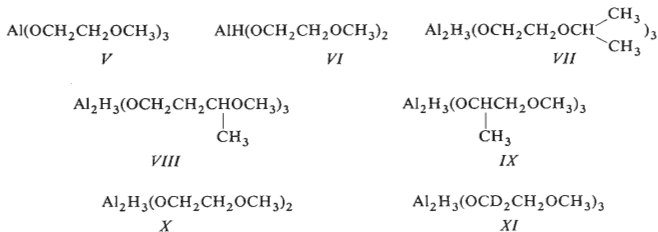
TABLE I

Proton NMR Spectra of Aluminium Alkoxyhydrides, Aluminium 2-Methoxyethylate and the Starting Alcohol in Benzene (chemical shifts in δ , coupling constants in Hz)

Compound	α -CH ₂ or CH ^a	β -CH ₂ or CH ^a	CH ₃ O ^a	The others ^a
I	3.65–4.15 (m)	3.2–3.5 (m)	3.14 (s)	—
V	3.70–4.29 (m)	3.3–3.7 (m)	3.20 (s)	—
	4.05 (t; $J = 6$)	3.46 (t; $J = 6$)	3.24 (s)	—
VI	3.7–4.3 (m)	3.25–3.6 (m)	3.13 (s)	—
			3.14 (s)	
			3.20 (s)	
XV ^b	3.58 (q; $J = 6$)	3.28 (t; $J = 6$)	3.16 (s)	OH: 4.1 (t; $J = 6$)
X	3.70–4.20 (m)	—	3.12 (s)	—
XVI ^c	3.53 (s)	—	3.08 (s)	OH: 3.4 (s)
XI	—	3.2–3.5 (m)	3.12 (s)	—
XVII ^d	—	3.23 (s)	3.13 (s)	OH: 3.6 (s)
VII	broad multiplet	3.30–4.30 ^{i,j}	—	CH ₃ : 0.97 (d; $J = 4.8$) ^h 1.03 (d; $J = 4.8$) 1.06 (d; $J = 6$) CH: 3.64 (m) ^h
XVIII ^e	3.75–4.10 (m)	3.10–3.50 (m) ^j	—	CH ₃ : 1.14 (d; $J = 6.5$) CHO: 3.10–3.50 (m) ^j OH: 3.40 (s)
VIII	3.7–4.3 (m) ⁱ	1.6–2.1 (m) ⁱ	3.10 (s) 3.18 (s) 3.21 (s)	CH ₃ : 1.02 (d; $J = 5$) CHO: 3.1–3.5 (m)
XIX ^f	3.16–3.70 (m) ^j	1.30–1.80 (m)	3.05 (s)	CH ₃ : 0.95 (d; $J = 6.5$) CHO: 3.16–3.70 (m) ^j
IX	3.8–4.4 (m) ⁱ	2.8–3.3 (m) ⁱ	3.15 (s)	CH ₃ : 1.05–1.4 (m) ^{i,j}
XX ^g	3.60–3.90 (m)	3.06 (d)	3.12 (d)	CH ₃ : 1.02 (d; $J = 6.5$) OH: 3.70 (s)

^a s singlet, d doublet, t triplet, q quadruplet, m multiplet. Chemical shifts in p.p.m. (σ scale) in respect to tetramethylsilane. ^b XV is 2-methoxyethanol. ^c XVI is 2-methoxy-2,2-[²H₂]-ethanol. ^d XVII is 2-methoxy-1,1-[²H₂]-ethanol. ^e XVIII is 2-isopropoxyethanol. ^f XIX is 3-methoxy-1-butanol. ^g XX is 1-methoxy-2-propanol. ^h By decoupling. ⁱ Wide undistinguished bands. ^j Overlapping signals.

methoxy-2-propoxy)hydride (*IX*) – prolongation of the carbon chain between the two oxygen atoms in the alkoxy and/or replacement of a hydrogen atom in the alkoxy by a methyl group. The determined degrees of association⁵ reveal that the alkoxide *V* and especially the hydride *I* exist in solutions as particles with four



aluminium atoms. It appears that neither the degree of association nor the structure is changed in benzene solutions in the concentration range below 15%. The hydride *IX*, with a substitution at the α -position in the alkoxy, must evidently be different in structure since its degree of association in a 15% solution

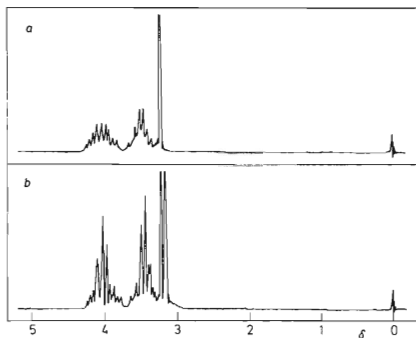


FIG. 1

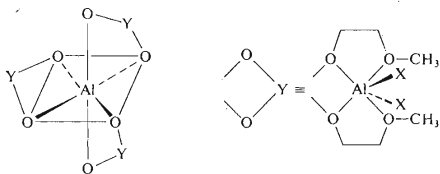
¹H NMR Spectra of Benzene 15% Solutions of *a* Aluminium Sesqui(2-methoxyethoxy)hydride, *b* Aluminium 2-Methoxyethoxide

in benzene is 1:2. Association of the hydrides *VI*, *VII* and *VIII* is also lower and is similar to that observed with compounds having four aluminium atoms in a molecule in more dilute solutions.

The proton NMR spectrum of the hydride *I* (Fig. 1a) exhibits a sharp singlet of the methoxyl hydrogens and two multiplets of the methylene groups. To assign signals to the α - and the β -methylene groups of the alkoxy the spectrum was compared with the NMR spectra of the alkoxy-deuterated hydrides *X* and *XI*, prepared by alcoholysis of bis-trimethylamine of aluminium hydride⁵ (Table I). The spectra of the hydride *I* in benzene and in toluene were identical. Since an exchange of oxygen ligands between aluminium atoms seemed possible we investigated the spectrum of the hydride *I* in toluene in a temperature range from -60°C to $+103^{\circ}\text{C}$. Apart from an extension of the lines at -60°C , due to a strong increase in viscosity of the solution, there was no visible change of the spectrum, not even a tendency of splitting of the methoxyl singlet. This fact and the pattern of the spectrum in the region of the methylene proton signals (the spectra ABCD to ABXY with markedly greater differences of the chemical shift in lower-field signals) demonstrate that the compound *I* has a rigid, definable structure with equivalent methoxy groups and with evidently non-equivalent protons of the α -methylene group, and that the alkoxy ligands do not migrate within the molecule. The strength of the bonds and the high coordination number of aluminium atoms in the hydride *I* can be inferred not only from IR spectroscopy⁷, but also from the fact that not even very strong solvation agents such as triethylamine or pyridine bring about solvation⁶ (difference in behaviour from aluminium 2-propoxide¹⁸ and benzyloxide¹⁰). In this connexion it is of interest to compare the hydride *I* with aluminium 2-propoxide; either its trimer contains only four-coordinated aluminium¹², or, what now seems more likely, one of the three aluminium atoms is five-coordinated^{17,19}. It was only at temperatures below -13°C that the NMR spectrum of the trimer revealed a clear difference between the signals of methyls on the bridge group and on the terminal isopropoxy group. No migration occurred in the tetramer of the same compound, containing one central aluminium atom of coordination number 6 (*III*, $i = \text{C}_3\text{H}_7$); interchange of the bridge group and the terminal isopropoxy group would require participation of the unfavoured seven-coordinated aluminium¹⁸. A new peak appeared only when the temperature exceeded 49°C and a complete rearrangement into the trimer occurred at 110°C ¹².

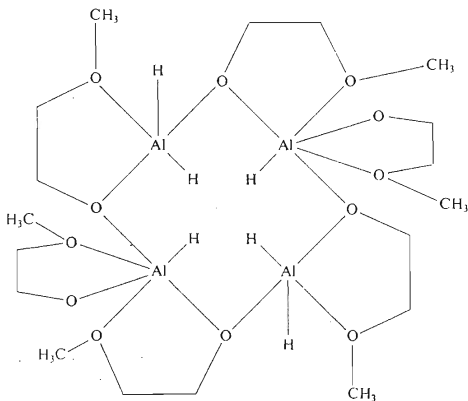
The NMR spectrum of the alkoxide *V* (Fig. 1b) is clearly a superimposition of the spectrum of the hydride *I*, one triplet in the region of the α -methylene protons, one in the region of the β -methylene protons, and one singlet of the methoxy groups. The structure of this compound can be regarded as identical with that of the hydride *I* except that the hydride hydrogens are replaced by 2-methoxyethoxy groups. These are bound to aluminium through only one oxygen atom and have two equivalent protons in the methylene groups, the spectrum in this region consequently being

of the type A_2X_2 . On the other hand, this spectrum proves indirectly the rigid constellation of alkoxy groups in the hydride *I* and the existence of aluminium atoms with coordination number 6, but rules out any role of hydrogen bonds in the structure of the hydride *I*.



XII

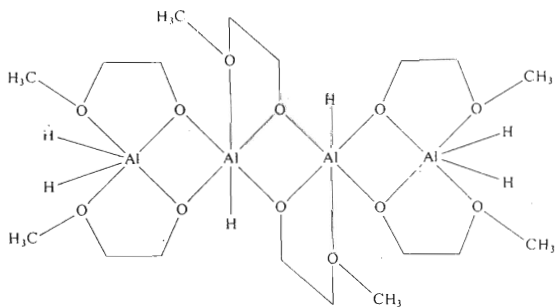
On the basis of these findings we assign the compounds *I* and *V* structure XII ($X = H$ and $OCH_2CH_2OCH_3$, respectively), which fully accords with the NMR spectra and the determined molecular weights. This structure is supported even by the NMR spectrum of aluminium bis(2-methoxyethoxy)hydride (*VI*). There are evidently alkoxy groups of two types in this compound: the free ones, bound to aluminium through only one atom of oxygen, and the alkoxy groups bound to aluminium by both oxygen atoms, whereby a rigid five-membered ring is closed. The NMR spectrum contains



XIII

two different signals of methoxy groups in an intensity ratio of 1 : 3 (Table I). The indication of splitting of the signal in the higher field might be due to a different shielding of the rigid methoxyl vicinal to the alkoxy and the hydride hydrogen, or of the two hydride hydrogens (*cf.* structure *XII*).

The spectra of the other hydrides, *VII–IX*, contain more signals and the peaks are difficult to distinguish. The determined molecular weights suggest that in the investigated ranges of concentration the compounds under study do not behave as chemical individua. This difference from the hydride *I* is probably caused by the steric demands of the substituents in the alkoxy (revealed previously² on the reduction properties of sodium alkoxyhydridoaluminates), which prevent the formation of a stable structure, analogous to the structure *XII*.



Out of the other structures regarded as possible for the dimeric hydride *I* or the alkoxide *V* none is consistent with what is known of these compounds. A cyclic, eight-membered dimer of type *II* or a linear polymer without further coordination of the methoxyl oxygen to aluminium can be ruled out on the grounds of inadequacy of the methylene groups and a high coordination number of aluminium. Structures of type *XIII*, with further solvation of aluminium atoms by methoxyl oxygens in an eight-membered ring, and of type *XIV* with the linear polymer are not possible either since the spectrum exhibited only one signal of hydrogen of the terminal methoxyls. Besides, as has already been said, the similarity of the NMR spectra of the compounds *I* and *V*, as well as the similarity of their IR spectra¹⁰, excludes the existence of hydrogen bonds.

EXPERIMENTAL

Aluminium sesquialkoxohydrides (*I*, *VII–IX*) were prepared by reaction of the corresponding sodium dialkoxodihydroaluminates with aluminium chloride in benzene. Aluminium bis(2-methoxyethoxy)hydride (*VI*) was obtained by partial alcoholysis of the hydride *I*. Aluminium 2-methoxyethoxide (*V*) was prepared by reaction of 2-methoxyethanol with metallic aluminium. The alkoxyl-deuterated aluminium sesquialkoxohydrides *X* and *XI* were obtained by alcoholysis of aluminium hydride bis(trimethylamine)⁵.

All the ¹H NMR spectra were measured at 100 MHz in an apparatus Varian XL-100-15. The samples to be measured were 15% solutions of the corresponding alcohol, alkoxide or hydride *I* in toluene. The samples were handled exclusively under dry nitrogen. The internal standard was tetramethylsilane or, at higher temperatures, hexamethyldisiloxane.

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