

THE PROPOSED STRUCTURE OF SESQUI(2-DIMETHYLAMINOETHOXY)ALANE IN SOLUTION

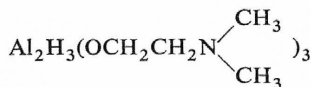
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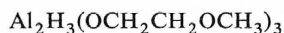
Received November 24th, 1977

A structure was proposed for sesqui(2-dimethylaminoethoxy)alane, prepared in our laboratory, on the basis of measured molecular weights and infrared and $^1\text{H-NMR}$ spectra. At laboratory temperature the hydride is a dimer in the measured concentration range and its structure consists of one aluminium atom with a coordination number of 6 connected through oxygen bridges with three aluminium atoms with coordination numbers of 4. Each of the terminal aluminium atoms is bonded to two hydride hydrogens. The chemical shifts of the individual elements in the $^1\text{H-NMR}$ spectrum practically do not change in the temperature region -50°C to $+100^\circ\text{C}$.

Sesqui(2-dimethylaminoethoxy)alane (*I*) was prepared as an analogue of sesqui(2-methoxyethoxy)alane (*II*) (refs^{1,2}) by the reaction of sodium tetrahydridoaluminate and aluminium 2-dimethylaminoethoxide (*III*) with aluminium chloride in benzene solution.

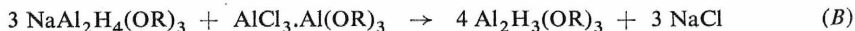
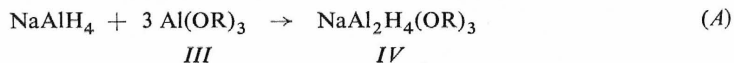


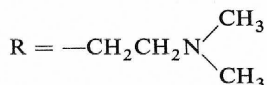
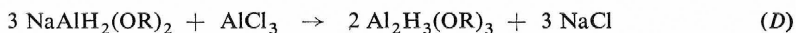
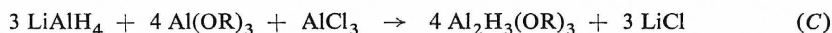
I



II

The first phase of the reaction for the preparation of *I* (equation (A)) produces sodium tetrahydrido-tris(2-dimethylaminoethoxy)dialuminate (*IV*) which was isolated from the reaction mixture³. Substance *IV* yielded final product *I* according to equation (B). Substance *I* can also be prepared from lithium tetrahydridoaluminate — overall equation C — or from sodium dihydrido-bis(2-dimethylaminoethoxy)aluminate³ — equation (D).





Hydride *I* is a white crystalline substance, readily soluble in ether and aromatic hydrocarbons. Its molecular weight in benzene changes very little with concentration and corresponds to the dimer in cryoscopic determinations; the degree of association found from ebulliometric measurements is somewhat lower ($n = 1.7$).

It can be assumed that the structure of hydride *I* is similar to that of its oxygen analogue *II*, whose structure in solution was found in our laboratory⁴ and later verified on the basis of its reactivity⁵. Both hydrides are formed from sodium tetrahydridoaluminate and the corresponding aluminium alkoxide by reaction with aluminium chloride and are dimers in benzene solution. Table I contains the wavenumbers of the bands in the Al—H bond stretching vibration region in the infrared spectra of hydrides *I* and *II*. This spectral region is similar for both hydrides and the bands have similar intensities. Dichloromethane is an exception; here *I* probably reacts with the solvent, although hydrogen was not evolved and the solution did not become cloudy. The different structure of *I* in dichloromethane or reaction with the solvent is confirmed by the marked decrease in the band intensity at 810–830 cm^{-1} , corresponding to the deformation vibration of the Al—O—Al bridge in this solvent.

TABLE I

The Position (cm^{-1}) of the Bands of the Stretching Vibrations of the Al—H Bonds in Sesqui-(2-dimethylaminoethoxy)alane (*I*) and in Sesqui(2-methoxyethoxy)alane (*II*) in the Solid Phase and in Solution

Solvent	<i>I</i>		<i>II</i> ^a	
None	1 711	1 748	1 759	1 785
Benzene	1 739	1 757	1 758	1 786
Dichloromethane	1 805		—	—
Diethylether	—	—	1 758	1 788
Tetrahydrofuran	1 731	1 753	1 756	1 788
1,2-Dimethoxyethane	1 727	1 754	—	—

^a From the literature⁹.

An increase in the coordination number of aluminium appears generally as a decrease in the wavenumber of the band of the Al—H stretching vibration⁶⁻⁸. It can be seen from Table I that the wavenumbers of both bands of hydride *I* are always lower than for hydride *II*. However, as the aluminium atom bound to hydrogen atoms in *II* is generally hexadentate⁴, the lower wavenumber $\nu(\text{Al—H})$ must be attributed to factors other than an increase in the coordination number alone (the presence of a nitrogen atom in the alkoxy, solvation of another type of aluminium atom). On the other hand, the wavenumber of both bands decreases slightly from solutions of *I* in benzene to 1,2-dimethoxyethane, which can readily be explained by an increase in the co-

TABLE II

The ¹H-NMR Spectra of Alkoxyalanes (*I*, *II*, *V*), Aluminium 2-Dimethylaminoethoxide (*III*) and 2-Dimethylaminoethanol (*IX*)

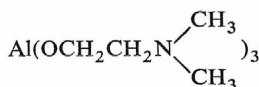
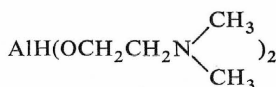
Chemical Shifts in δ , coupling constants in Hz.

Compound	Solvent	$\alpha\text{-CH}_2^a$	$\beta\text{-CH}_2^a$	CH_3^a
<i>I</i>	benzene	3.7 — 4.0 (m)	2.61 (t; $J = 6.5$)	2.22 (s)
		4.1 — 4.35 (m)		
	toluene	3.65—3.95 (m)	2.55 (t; $J = 6.5$)	2.20 (s) ^b
		4.0 — 4.3 (m)		
	n-hexane	3.55—3.85 (m)	2.52 (t; $J = 6.5$)	2.21 (s)
		3.9 — 4.2 (m)		
	dichloromethane	3.55 (a) ^c	2.53 (t; $J = 7$) ^c	2.22 (s) ^c
		3.71 (s) ^c		
tetrahydrofuran	^d	2.56 (t; $J = 6.5$)	2.23 (s)	
1,2-dimethoxyethane	^d	2.55 (t; $J = 6.5$)	2.22 (s)	
pyridine	3.7 — 4.5 (m)	2.79 (t; $J = 6.5$)	2.33 (s)	
<i>V</i>	benzene	3.62—3.94 (m) ^e	2.56 (t; $J = 6.5$)	2.29 (s)
		3.96—4.34 (m) ^e	2.53 (t; $J = 6.5$)	2.22 (s)
<i>III</i> ^f	1,2-dichlorobenzene	4.08 (t)	2.47 (t)	2.24 (s)
				2.35 (s)
<i>IX</i> ^{g,h}	cyclopentane	3.50 (t)	2.35 (t)	2.17 (s)
<i>II</i> ⁱ	benzene	3.65—4.15 (m)	3.2—3.5 (m)	3.14 (s)

^a s Singlet, t triplet, m multiplet, chemical shifts in ppm (δ scale) referred to tetramethylsilane; ^b approximate value, signal partially overlaps with the solvent signal, ^c broad peak; ^d signal completely obscured by the solvent signal; ^e unsymmetrical, overlapping peaks, ratio of the integral intensities of the two multiplets is 1/2; ^f from the literature¹⁰; ^g *IX* is 2-dimethylaminoethanol; ^h from the literature¹¹; ⁱ from the literature⁴.

ordination number of the aluminium atom as a result of coordination with the solvent. Desolvated *I* apparently does not fall in this order because it is always crystalline in the solid state. In the noncrystalline oxygen analogue *II*, $\nu(\text{Al}-\text{H})$ does not depend on the solvent; even Lewis bases as strong as tetrahydrofuran do not produce an increase in the aluminium coordination number⁹.

Table II contains the ¹H-NMR spectra of hydride *I* and of bis(2-dimethylaminoethoxy)alane (*V*), compared with the literature data¹⁰ for aluminium 2-dimethylaminoethoxide (*III*) and hydride⁴ *II*.

*III**V*

The spectrum of hydride *I* consists of a singlet corresponding to the methyl protons bound to nitrogen, the simple triplet of the β -methylene group of the alkoxy and two symmetric multiplets of the α -methylene group (Fig. 1). It follows from Table II that the chemical shift of the signals of the protons of the β -methylene group change most and the signals of the methyl protons change least in dependence on the solvent used. The fact that the α -methylene group is primarily affected by the solvation of aluminium atom *I* indicates that either aluminium-nitrogen coordination of the dimethylaminoethoxy does not exist or that it is present to a far smaller degree than aluminium-oxygen coordination. The positions of the individual alkoxy signals and their multiplicity in the NMR spectrum practically do not change at low temperatures. Only at -60°C in toluene solution do the triplet and both multiplets combine to give broad singlets, probably as a result of the high viscosity of the solution; with a further decrease in the temperature these singlets broaden. No indication of splitting of the methylene group singlet was observed.

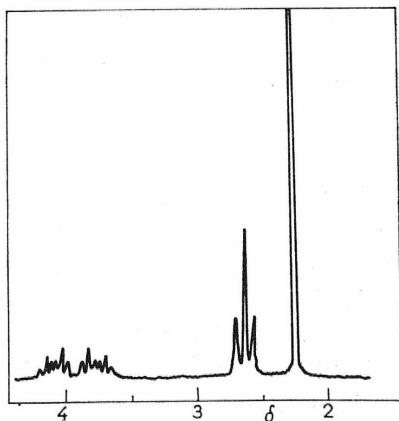
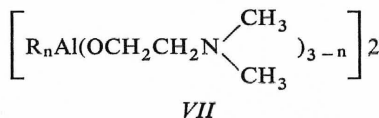
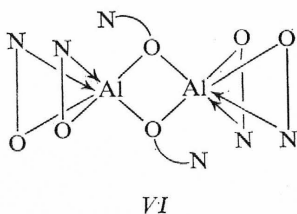


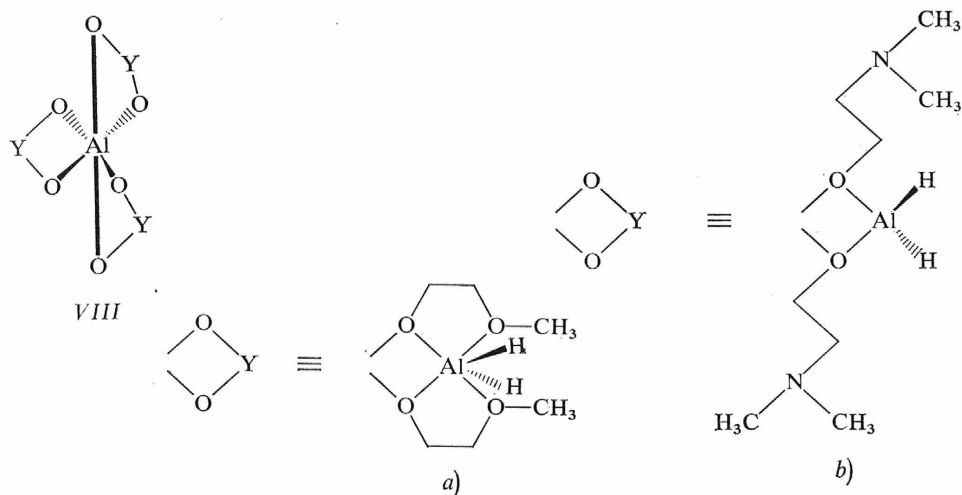
FIG. 1
The ¹H-NMR Spectrum of a 5% Benzene Solution of Sesqui(2-dimethylaminoethoxy)alane (*I*)

Smith¹⁰ proposed a structure for dimer *III* in which two aluminium atoms and two alkoxy oxygen atoms from a four-membered ring and four of the six nitrogen atoms are coordinated to the aluminium atom by a chelate bond (structure *VI*). The ¹H-NMR spectrum of substance *III* (Table II) exhibits two peaks of the methyl group; the signal at 2.24 ppm corresponds to the protons of the free dimethylamine group; the signal at 2.35 ppm corresponds to the dimethylamino group coordinated through the nitrogen atom to the aluminium atom. Both peaks are replaced by a new peak at 2.28 ppm (the rate of ligand exchange is greater than the NMR time constant) at 135°C. The α and β methylene groups appear in the spectrum as a simple triplets. In dimeric compounds of type *VII* (R = alkyl) for $n = 1$ and 2, 2-dimethylaminoethoxyl also appears in the ¹H-NMR spectrum as two triplets of the α and β methylenes and a singlet of the apparently uncoordinated dimethylamino group at 2.21 ppm^{10,11}. The fact that chelate bonds of type *VI* are formed in compound *VII* can be explained by suggesting that the possibility of octahedral arrangement around the aluminium atom in the first type does not involve steric hindrance in formation of a five-membered chelate ring containing the chelate atom, while in the tetrahedral arrangement (*VII*, $n = 2$) steric hindrance must be considerable¹².



It follows from the ¹H-NMR spectrum of hydride (*V*) (Table II) and from the dependence of the molecular weight of this substance on the concentration that a greater number of structural entities are involved and are in equilibrium under the experimental conditions.

Hydride *I* is very similar to its oxygen analogue *II* in the infrared spectrum in the Al—H stretching region and in the dependence of the molecular weight on the concentration of the solution. The remaining compounds studied (*III*, *V*) contain less than four aluminium atoms in the molecule in solution. In the ¹H-NMR spectrum of *II*, the protons of both the α and β methylene groups appear as a sharp singlet as for compound *I*. Except for band broadening, the spectrum of *II* practically doesn't change in the temperature interval -50°C to $+100^\circ\text{C}$. The results given indicate the probability of a certain analogy between structures *I* and *II*. The already elucidated structure⁴ of hydride *II* is depicted in formula *VIIIa*. Structure *VIIIb*, involving one central hexacoordinated and three tetraordinated aluminium atoms, is proposed on the basis of the following considerations: 1) The two clearly separated



multiplets of the protons of the α -CH₂ group correspond to two magnetically non-equivalent protons in a rigid arrangement maintained by hexacoordination by the central aluminium atom. Similarly as in the spectrum of hydride *I*, non-equivalence of the protons of the methyl groups of the 2-propoxyl and methylene groups of the benzyl forming a bridge between hexa-coordinated and tetracoordinated aluminium atoms appears in tetrameric 2-propoxide¹³ or aluminium benzyl oxide¹⁴ with analogous skeletons. The protons of the terminal alkoxy of these compounds¹⁴ or the protons of the α -methylene group of dimeric¹⁰ *III* with a defined skeleton¹⁰ (Table II) appear as a simple singlet, doublet or triplet. Similarly, the presence of a terminal 2-dimethylaminoethoxyl bound to a skeleton with four aluminium atoms in dialkoxyhydride *V* appears in the α -methylene protons as a new signal only in the multiplet region at lower field strengths. 2) The sharp triplet of the α -methylene group corresponds to protons in a non-rigid arrangement allowed by free rotation around the C—C axis of the alkoxy. For the same reason the protons of the dimethylamine group appear as a sharp singlet even at low temperatures. In oxygen analogue *II*, the α -methylene group also appears as a multiplet⁴. If the dimethylamino group of the 2-dimethylaminoethoxyl enters into the chelate bonding on the aluminium atom, then at laboratory temperature there are also two peaks for the protons of the dimethylamino group¹⁰; if all the nitrogen atoms enter into chelate formation, the signal of the dimethylamino group is shifted compared with the free ligand by about 0.3 ppm to lower field strengths¹¹.

Other structural arrangements, which could theoretically be assumed by dimeric sesquialane *I* with a skeleton containing four aluminium atoms, *i.e.* a structure involving an eight-membered ring (analogous to the structures proposed for tetra-

meric aluminium alkoxides by Ulich¹⁵ or Ayres¹⁶) or a linear arrangement with aluminium atoms joined by oxygen bridges (similar to the arrangement in trimeric aluminium 2-propoxide¹⁷) are not in agreement with our results — a rigid structure up to 100°C and non-identity of the α -methylene group protons. The presence of hydrogen bridges in the structure of hydride *I* is excluded by the absence of bands corresponding to the stretching vibration in the region below 1500 cm⁻¹ (ref.¹⁸) in the infrared spectrum.

EXPERIMENTAL

All preparations and spectral measurements were carried out in a dry nitrogen atmosphere. The pre-dried solvents used were distilled from solution or from a mixture sodium dihydrido-bis(2-methoxyethoxy)aluminate (benzene, toluene), lithium tetrahydridoaluminate (tetrahydrofuran, dimethoxyethoxyethane), 2-propyliminoalane¹⁹ (pyridine) or calcium hydride (hexane, dichloromethane) before each experiment. The infrared spectra were measured on a Beckman IR 20A instrument either in 5% solution or in a 15% suspension in perfluorokerosene. The ¹H-NMR spectra were measured on a Varian XL-100-15 instrument at 100 M Hz or on a Tesla 60 M Hz instrument in 5% solution and at low temperature in a 2% solution. Tetramethylsilane was used as an internal standard.

The molecular weights were measured cryoscopically and ebullioscopically in benzene, as described in earlier works^{20,21}. The dependence of the molecular weights of hydrides *I* and *IV* on concentration is given in Table III.

Preparation of Sesqui(2-dimethylaminoethoxy)alane (*I*) from Sodium Tetrahydridoaluminate

An amount of 37.3 g of 98.5% (0.68 mol) of sodium tetrahydridoaluminate, 200 ml of benzene and 484 ml of a 1.872M solution of *III* (ref.³) in benzene (0.907 mol) were placed in a 1 l flask fitted with an extractor with a reflux condenser. The mixture was heated until the tetrahydridoaluminate dissolved. An amount of 31 g of 97% (0.227 mol) of aluminium chloride was weighed into the extractor and the mixture was again heated to the boiling point. A small amount of diethyl ether (three times 2 ml at 1 h intervals) was added to the extractor through the reflux condenser to facilitate dissolution of aluminium chloride. The precipitated sodium chloride was

TABLE III

Dependence of the Molecular Weight of Sesqui(2-dimethylaminoethoxy)alane (*I*) and Bis(2-dimethylaminoethoxy)alane (*V*) in Benzene Solution on the Concentration

Concentration, m	0.05	0.1	0.15	0.2	0.35	0.55	0.8
<i>I</i> , cryoscopically	697	678	694	—	611	582	—
<i>I</i> , ebullioscopically	521	—	525	550	550	518	—
<i>V</i> , cryoscopically	791	—	—	740	724	690	628

centrifuged off and rinsed by decanting twice with 150 ml of benzene. The clear solutions were combined and, after evaporation and drying for three hours at 50°C and a vacuum of 50 Pa, 286.5 g of white crystalline *I* were obtained. For $\text{AlH}_3[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$ (321.4) was calculated: 16.7% Al, 0.94% H⁻, 13.7% N; found: 16.80% Al, 0.93% H⁻, 13.00% N.

Bis(2-dimethylaminoethoxy)alane (*V*)

An amount of 7.9 g (0.089 mol) of 2-dimethylaminoethanol in 15 ml benzene were added dropwise after 30 minutes with stirring to 28.5 g (0.89 mol) *I* in 50 ml benzene under a reflux condenser. The reaction was completed by heating the solution for 30 minutes at 50°C, the solution was evaporated *in vacuo* and the reaction product was dried for 3 h at a vacuum of 50 Pa and at 50°C. Compound *V* prepared in this way was used directly for the molecular weight determination and for measurement of the ¹H-NMR spectra.

The wish authors to thank Mrs K. Procházková for measuring the infrared spectra, Mr P. Pech for measuring the ¹H-NMR spectra and Mr P. Kolář for determining the molecular weights.

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Translated by M. Štulíková.