

## STUDY OF Al-H STRETCHING VIBRATIONS OF SODIUM HYDRIDO-2-METHOXYETHOXOALUMINATES

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Temperature and concentration dependences of intensities of Al-H stretching vibration bands ( $1900-1600\text{ cm}^{-1}$ ) revealed that the common ways of preparation of the substance  $\text{NaAlH}_2 \cdot (\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$  do not lead to a single compound, but to an equilibrium mixture whose additional components are  $\text{NaAlH}_4$ ,  $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ , and possibly also  $\text{NaAl} \cdot (\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$ . The fractions of the individual components vary with the concentration of the initial substance in the solution. Based on analogous studies, two equilibrium structures of  $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ , with five- and six-coordinated aluminium, were suggested. The structure of  $\text{Al}_2\text{H}_3(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$  suggested previously was confirmed.

In the series of sodium hydrido-2-methoxyethoxoaluminates, the structure of  $\text{Al}_2\text{H}_3(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$  (*I*) has been suggested<sup>1</sup>. In the case of  $\text{NaAlH}_2(\text{OCH}_2 \cdot \text{CH}_2\text{OCH}_3)_2$  (*II*), data concerning some fundamental physicochemical properties, solubilities, heats of dissolution, conductivities and viscosities of solutions in aromatic solvents<sup>2</sup>, molecular weights, and association degrees<sup>3,4</sup> have been published. Infra-red spectral studies are so far lacking; still this method could yield valuable information, as the wavenumbers of stretching vibrations of the terminal Al-H bonds are very sensitive to a change of the coordination number of aluminium<sup>5-7</sup>.

The absence of the band of stretching vibration of bridge Al-H-Al bond (below  $1500\text{ cm}^{-1}$ ) (ref.<sup>8</sup>) rules out oligomerization of *I*, *II*, and  $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$  (*III*) via this type of bond. If oligomers of the hydrides were formed through Al-O-Al bridges, then the fraction of aluminium atoms possessing a higher coordination number would increase with increasing association degree. Kinetic energy of the molecule is depressed on lowering temperature, which favours the stability of the donor-acceptor bond; this manifests itself in the spectrum by increased intensity of the band of the Al-H stretching vibrations involving aluminium possessing the higher coordination number. Analogous spectral changes are to be expected, if the coordination number increases due to solvation, or if the equilibrium is shifted towards higher association degrees as a result of a change of the concentration of the solution. It is the aim of this work to complete the study in order to facilitate the elucidation of the structure of the hydrides in question.

## EXPERIMENTAL

Variations of the positions and intensities of bands of the Al-H stretching vibrations in dependence on concentration were investigated for benzene, tetrahydrofuran, and ether solutions of *I*, *II*, and *III*; the corresponding temperature dependences were examined for desolvated *I*, *II*, and *III* in the range of +30 to -180°C (ref.<sup>9</sup>).

All operations with the hydrides were carried out in a dry nitrogen or argon atmosphere in a dry box, from the glass equipment the occluded moisture was removed by heating up to 160°C and allowing to cool down in vacuum. The infrared spectra (1900-1600 cm<sup>-1</sup>) were run on a Beckman 20A spectrophotometer, the wavenumber scale was expanded 4 times for a more accurate reading. As the bands overlap considerably in the spectral range studied, the experimental spectra were subjected to numerical separation of the individual bands. The concentration dependences were measured using the flow-through arrangement<sup>10</sup> with the cell connected through teflon capillaries with a micropump and a mixing flask equipped with a magnetic stirrer and a burette with the dry solvent. The mixing flask was filled with the solution of the highest concentration measured, and lower concentrations were obtained by successive dilution. The temperature dependences of the IR spectra of desolvated, viscous *I*, *II*, and *III* in the range of +30 to -180°C were measured between KBr cell windows in a low-temperature cell VLT-2 (RIIC - Beckman). The solvents used were predried with a molecular sieve, the drying was completed immediately before use by distilling from LiAlH<sub>4</sub> or *II*. 2-Methoxyethanol was dried by boiling with CaH<sub>2</sub> and redistilled before use.

*Bialuminium sesqui-tris(methoxyethoxy)hydride* (*I*) was prepared<sup>11</sup> from LiAlH<sub>4</sub>, 2-methoxyethanol, and AlCl<sub>3</sub>. For benzene solution found 7.10% Al, 0.359% H<sup>-</sup>, hence the ratio Al : H<sup>-</sup> = 1 : 1.37.

*Sodium dihydrido-bis(2-methoxyethoxy)aluminate* (*II*) was prepared from 3.3207 g (61 mmol) of NaAlH<sub>4</sub> in 100 ml of dry tetrahydrofuran by adding dropwise 10.05 ml (122 mmol) of 2-methoxyethanol at -20°C. The solution was filtered over a layer of granulated aluminium powder and desolvated at 60°C and 10<sup>-3</sup> Pa. For C<sub>6</sub>H<sub>16</sub>O<sub>4</sub>AlNa (202.16) calculated (%): Na 11.4, Al 13.35, H<sup>-</sup> 0.99; found (%): Na 11.0, Al 12.70, H<sup>-</sup> 0.88.

*Sodium hydrido-tris(2-methoxyethoxy)aluminate* (*III*) was prepared by applying the same procedure from 3.1270 g (58 mmol) of NaAlH<sub>4</sub> and 14.20 ml (174 mmol) of 2-methoxyethanol. For C<sub>9</sub>H<sub>22</sub>O<sub>6</sub>AlNa (276.24) calculated (%): Al 9.76, H<sup>-</sup> 0.364; found (%): Al 9.84, H<sup>-</sup> 0.318.

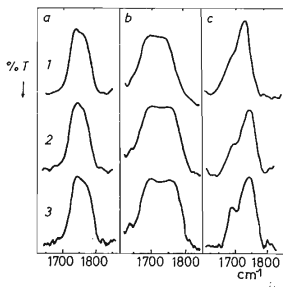


FIG. 1

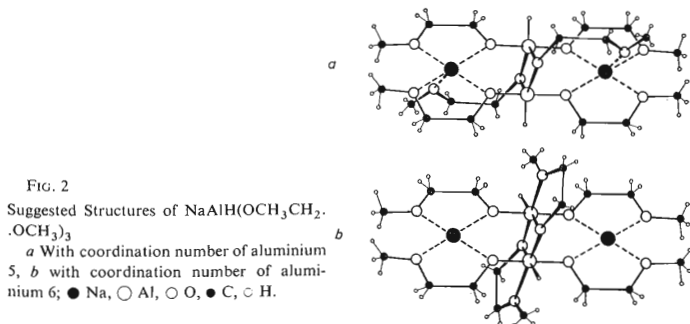
Temperature Dependences of Intensities of Al-H Stretching Vibration Bands

*a* Al<sub>2</sub>H<sub>3</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>3</sub>, *b* NaAlH<sub>2</sub>·(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>, *c* NaAlH(OCH<sub>2</sub>CH<sub>2</sub>·OCH<sub>3</sub>)<sub>3</sub>; 1 +30°C, 2 -100°C, 3 -180°C.

## RESULTS AND DISCUSSION

*Temperature dependences.* From the molecular weight measurements it follows that the sesquihydride *I* is present as dimer and that the association degree is invariant over the whole concentration region<sup>1</sup>. In the infrared spectrum of *I*, two bands are found in the range of stretching vibrations of terminal Al-H bonds, at 1759 and 1785  $\text{cm}^{-1}$  (Fig. 1a). The intensity ratio of the two bands remains constant over the temperature interval from +60 to  $-180^\circ\text{C}$ , which proves that no changes in the structure or oligomerization degree occurs. Contrary to expectations, however, no intensity change in the temperature range from +30 to  $-180^\circ\text{C}$  appears for the dihydride *II* either (Al-H stretching vibrations at 1670, 1698, and 1775  $\text{cm}^{-1}$ ) (Fig. 1b). It can be thus inferred that no oligomerization takes place in the case of that dihydride either, since otherwise the coordination number of aluminium would have to change, which would manifest itself by variations of the intensities and/or positions of the Al-H stretching vibration bands. A temperature dependence appeared, however, in the case of the monohydride *III*. Since – according to the molecular weight measurements<sup>3,4</sup> – the compound *III* is a dimer and the association degree does not change with concentration, the temperature dependence cannot be accounted for by oligomerization equilibrium. Evidently, then, two equilibrium dimer structures exist, *viz.* the structures *IIIa* and *IIIb* shown in Fig. 2, with the minor fraction of the structure *IIIb*, with the coordination number of aluminium 6, increasing with decreasing temperature.

*Solvent effect.* In order to establish the possibility of solvation, the infrared spectra of *I*, *II*, and *III* were measured in the desolvated state and in solutions in benzene, diethyl ether, and tetrahydrofuran (Table I). Increase of the coordination number



of aluminium appears in a decrease<sup>5-7</sup> of the wavenumbers of the band of Al-H stretching vibration, which has been proved also in the case of lithium hydridoalkoxo-aluminates<sup>8</sup>. As is clear from Table I, in the case of the hydrides *I*, *II*, and *III* no such shift occurs — the positions of the bands are roughly the same *in substantia* and in the solutions. It can be thus stated that solvation with even so strong a Lewis base as tetrahydrofuran does not increase the coordination number of aluminium. This can be explained in terms of the steric conditions within the molecule resisting the solvation. The favourable position of the two oxygen atoms of the methoxyethoxy ligand enables the formation of energy-favoured five-membered rings with an O-Al donor-acceptor bond (Fig. 3). The energy deficit at the aluminium can be levelled off either intramolecularly, or, during oligomerization, through the ligands of the neighbouring monomer molecule.

*Concentration dependences of infrared spectra (range 1900–1600 cm<sup>-1</sup>).* The dependences of the molar integrated intensities *B* (mol<sup>-1</sup> l cm<sup>-2</sup>) of the separated bands of stretching vibrations of the terminal Al-H bonds on the concentrations of *I*, *II*, and *III*, respectively, were measured in benzene (Fig. 4), diethyl ether, and tetrahydrofuran solutions. For *I* and *III* the values of the molar integrated intensities of all the bands followed were found to remain approximately constant.

TABLE I

Positions (cm<sup>-1</sup>) of Bands of Stretching Vibrations of Al-H Bonds in Al<sub>2</sub>H<sub>3</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>3</sub> (*I*), NaAlH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>, (*II*), and NaAlH(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>3</sub> (*III*) in the Desolvated State and in Solutions

Solvent	<i>I</i>	<i>II</i>	<i>III</i>
Desolvated	1 759 1 785	1 670 1 698 1 775	1 698 1 772
Benzene	1 758 1 786	1 665 1 712 1 773	1 708 1 773
Ether	1 758 1 788	1 662 1 710 1 772	1 712 1 774
THF	1 756 1 788	1 664 1 703 1 772	1 710 1 773

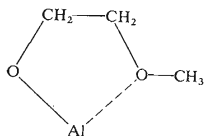


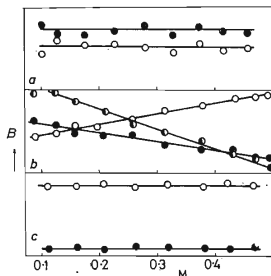
FIG. 3  
Possibility of Five-Membered Ring Closure Through a Coordination Bond O-Al

This indicates that no change in structure takes place for *I* and *III* in solutions. The dependences are identical for all the three solvents. In the spectrum of *II*, three bands of the terminal Al-H bond stretchings appear at 1665, 1712, and 1773  $\text{cm}^{-1}$ . The molar integrated intensities of the bands at 1665 and 1773  $\text{cm}^{-1}$  decrease with increasing concentration, hence they behave as if the content of the substance in the solution increased more slowly than the actual concentration. On the other hand, the *B* value of the band at 1712  $\text{cm}^{-1}$  increases with increasing concentrations (Fig. 4b). The variations of *B* of the individual bands of *II* display the same trend in all the solvents used, which rules out the result being due to random experimental error. Solvation does not account for it either, as is evident from the identity of the band wavenumbers of *II* in solutions and *in substantia* (Table I); in addition, the solvation degree drops with increasing concentrations, so that the highest-wavenumber band (at 1773  $\text{cm}^{-1}$ ) would have to gain intensity. This band would be attributed to Al-H stretching for aluminium possessing the coordination number 4, which in fact can be considered only in the nonsolvated monomer. The concentration of the monomer would have to be high, with regard to the high *B* value of the band at 1773  $\text{cm}^{-1}$ , which is inconsistent with the results of molecular weight measurements<sup>3</sup>. The decreasing intensity of the band at 1773  $\text{cm}^{-1}$  can, really, be explained in terms of association equilibria, this concept fails, however, in explaining the intensity decrease of the band at 1665  $\text{cm}^{-1}$ . From all this it can be concluded that the change of the association degree does not show up in a change of the coordination number of aluminium. The association equilibrium in the concentration region examined does not affect appreciably the Al-H stretching vibration and obviously no change of the coordination number of aluminium, accounted for by the formation of a coordination bonding of the oxygen atom to the sodium atom, occurs.

FIG. 4

Dependences of Molar Integrated Intensities  $B$  ( $\text{mol}^{-1} \text{ l cm}^{-2}$ ) of  $^1\text{Al-H}$  Stretching Vibration Bands on Concentration in Benzene Solutions

*a*  $\text{Al}_2\text{H}_3(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ ,  $\circ$  1758  $\text{cm}^{-1}$ ,  $\bullet$  1786  $\text{cm}^{-1}$ ; *b*  $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ ,  $\bullet$  1665  $\text{cm}^{-1}$ ,  $\circ$  1712  $\text{cm}^{-1}$ ,  $\bullet$  1773  $\text{cm}^{-1}$ ; *c*  $\text{NaAlH}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ ,  $\circ$  1708  $\text{cm}^{-1}$ ,  $\bullet$  1773  $\text{cm}^{-1}$ .



*Chemical equilibrium.* Ruling out the effect of solvation and association, we are able to explain the concentration dependence of the band intensities of the Al—H stretching vibrations only in terms of chemical equilibria. The substance *II* can disproportionate in solution to stable products, e.g. *III*, solvated  $\text{NaAlH}_4$  (*IV*), or sodium tetrakis(2-methoxyethoxy)aluminate (*V*). These substances occur probably in the solution together with *II* and are interrelated through an equilibrium. The complex of the infrared spectra of *II* do suggest the possibility of a simultaneous occurrence of *II*, *III*, and *IV* in an equilibrium. The wavenumbers of the bands at 1773 and 1665  $\text{cm}^{-1}$  in the spectrum of *II* are in a good accordance with the positions of the Al—H stretching bands of *III* or *IV*. The presence of the band at 1712  $\text{cm}^{-1}$  indicates that the disproportionation is not complete and irreversible and that *II* is present in the solution in a high fraction. If a simple disproportionation equilibrium of the  $\text{A} \xrightleftharpoons[v_2]{v_1} \text{B} + \text{C}$  type is assumed, then the disproportionation rate,  $v_1$ , depends only on the concentration of the component A and the rate of the reverse reaction,  $v_2$ , on the concentration of the two components B and C. In more concentrated solution the rate  $v_2$  should then prevail and the equilibrium should be shifted in favour of the component A. This model fits exactly the experimental dependences (Fig. 4b). The concept of chemical equilibrium in solutions of *II* is also supported by the ability of the substance to alter its composition and association degree in relation to the amount of components added. Following the infrared spectra on gradual additions of 2-methoxyethanol to a solution of *IV* in tetrahydrofuran we obtained a similar dependence as with solutions of lithium hydridoethoxyaluminates, where the equilibrium is evident<sup>8</sup>. The intensities of the corresponding bands in the spectra of mixtures of *II* with *IV* or with *V*, too, vary in conformity with the model proposed (Table II). The equilibrium on addition of *II* establishes very

TABLE II

Dependence of Molar Integrated Intensities, *B*, of Al—H Stretching Vibration Bands of  $\text{NaAlH}_2 \cdot (\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$  in Benzene Solution on the Substance Added

The intensities are given in relative units.

Substance added	Association degree	<i>B</i>		
		1 665 $\text{cm}^{-1}$	1 712 $\text{cm}^{-1}$	1 773 $\text{cm}^{-1}$
—	6.0	100	100	100
$\text{NaAlH}_4$	8.1	125	132	108
$\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$	2.4	0	21	180
$\text{H}_2\text{O}$	5.0	29	57	90

slowly. *II* enters the solution, takes part in the equilibrium, and is separated again from the solution through the disproportionation reaction, which shows itself by the recrystallization of the originally large crystals of *IV* to a microcrystalline turbidity, identified by X-ray diffraction as *IV*.

With this state of art it is not possible to propose a structure of *II*. Attempts to set up the structure by employing spatial models led to very flexible skeletons with low symmetries, suggesting the possibility of planar or spatial association. The principal obstacle for the elucidation of the structure of *II* is the impossibility to prepare pure substance, as it disproportionates readily.

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