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Spectroscopic Studies of the Structures of the Dimer of Diethylaluminum 2-Aminoethoxide $(AlEt_2OCH_2CH_2NH_2)_2$ and Related Compounds*[1]

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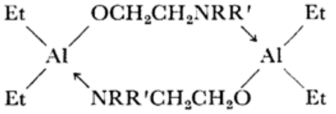
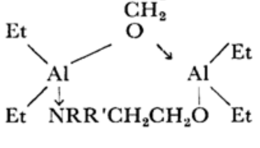
The infrared and proton nuclear magnetic resonance spectra of the solutions of diethylaluminum 2-aminoethoxide $(AlEt_2OCH_2CH_2NH_2)_2$ and related compounds were measured. The infrared frequencies and intensities of the NH_2 stretching, scissors, and rocking vibration bands, and the NMR internal chemical shifts of the ethyl groups attached to the aluminum atom were compared with the corresponding data of suitable model compounds. It was concluded by taking the results of these experiments into consideration that $(AlEt_2OCH_2CH_2NH_2)_2$ was represented by the structural formula I with two $Al \leftarrow NH_2$ coordination bonds. Similarly, most of the related compounds studied were reasonably represented by the formulas with two $Al \leftarrow NRR'$ coordination bonds, while $(AlEt_2OCH_2CH_2N(C_6H_{11})_2)_2$ was assumed to be represented by formula III with two $Al \leftarrow O$ coordination bonds, exceptionally.

It has been reported by one of the authors and by Hurley and his coworkers that the reactions of triethylaluminum $(AlEt_3)_2$ with several aminoethanols ($HOCH_2CH_2NRR'$; $R,R'=H$, alkyl, cycloalkyl, and/or aryl groups) in the 1 : 1 molar ratio give the crystals of the dimers of diethylaluminum 2-aminoethoxides formulated as $(AlEt_2OCH_2CH_2NRR')_2$ quantitatively.[1-3] There are three possible structural formulas, I, II, and III, for these dimeric substances, $(AlEt_2OCH_2CH_2NRR')_2$:


[I]


[II]

[*1] Presented at the Symposium on Organometallic Compounds, Tokyo, October, 1968.

[1] H. Higashi and S. Namikawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 93, 368 (1967).

[2] H. Higashi and K. Watabe, *ibid.*, **70**, 1800 (1967).

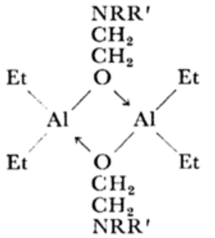
[3] T. J. Hurley, M. A. Robinson, J. A. Scruggs and S. I. Trotz, *Chem. Abstr.*, **67**, 7582h (1967).

TABLE 1. DIETHYLALUMINUM 2-AMINOALKOXIDES (NEW COMPOUNDS)

Compound	Yield (%)	Al(%)		Mol wt		Mp, °C*1
		Found	Calcd	Found*2	Calcd	
$(AlEt_2OCH_2C(CH_3)_2NH_2)_2$	75.7	15.57	15.57	340.1	346.5	119—121.5
$(AlEt_2OCH_2CH(CH_3)NH_2)_2$	47.7	16.80	16.95	311.6	318.4	110.5—112.5
$(AlEt_2OCH_2CH(C_2H_5)NH_2)_2$	82.2	15.58	15.57	343.7	346.5	90—92.5

*1 Uncorrected.

*2 Determined by measuring the freezing point depression of benzene solution.



[III]

Formula I with a 10-membered ring has two Al← NRR′ coordination bonds, formula II with a 7-membered ring has one Al←NRR′ and one Al←O bond, and formula III with a 4-membered ring has two Al←O bonds. Several attempts were made by Higashi and by Hurley to assign the most probable formula on the basis of several experimental facts but no decisive evidence was obtained.[2,3)] In this paper this problem will be investigated by the infrared (IR) and proton nuclear magnetic resonance (NMR) spectra of the solution of diethylaluminum 2-aminoethoxide $(AlEt_2OCH_2CH_2NH_2)_2$. At first, the IR and NMR spectra of ethylaluminum chloride-*n*-propyl amine coordination compounds—$AlEt_{3-m}Cl_m \cdot n\text{-}PrNH_2$ (m=0, 1, 2, 3)—will be studied and the results will be used to discuss the problem mentioned above.

Experimental

Preparation of the Samples. $(AlEt_2OCH_2CH_2NH_2)_2$, $(AlEt_2OCH_2CH_2NMeH)_2$, $(AlEt_2OCH_2CH_2NMe_2)_2$, $(AlEt_2OCH_2CH_2NEtH)_2$, $(AlEt_2OCH_2CH_2NEt_2)_2$, $(AlEt_2OCH_2CH_2NPhH)_2$, $(AlEt_2OCH_2CH_2NPh_2)_2$, $(AlEt_2OCH_2CH_2N_2(C_6H_{11})_2)_2$, $(AlEt_2OCH_2CH_2CH_2NH_2)_2$, and $(AlEt_2OCH(CH_3)CH_2NH_2)_2$ were prepared by the reactions of $(AlEt_3)_2$ with the corresponding alkanolamine, following the synthetic methods described in Refs. 1 and 2. $(Al\textit{i}\text{-}Bu_2OCH_2CH_2NH_2)_2$ was prepared by the reaction of $Al\textit{i}\text{-}Bu_3$ with monoethanolamine, following the method given in Ref. 3. $(AlEt_2OCH_2C(CH_3)_2NH_2)_2$, $(AlEt_2OCH_2CH(CH_3)NH_2)_2$, and $(AlEt_2OCH_2CH(C_2H_5)NH_2)_2$ were obtained by the reaction of $(AlEt_3)_2$ with the corresponding alkanolamine as transparent prismatic crystals. Since the last three substances are new compounds, their yields in syntheses, aluminum contents, measured molecular weights and melting points are summarized in Table 1.

Measurements of IR and NMR Spectra. The IR spectra of the dilute solutions of the samples (in general, the concentrations of the solutions were fixed to either 5.26 g/100 m*l* soln for the measurements using the cell of thickness of 0.1 mm or 1.10 g/100 m*l* soln for the measurements using the cell of thickness of 0.5 mm) were measured in the 4000—420 cm^{-1} region by using KRS-5 liquid fixed cell (thickness: 0.1 mm and/or 0.5 mm). Another cell of the same thickness filled with the solvent was put in the reference optical path to compensate the absorption of the solvent. A Japan Spectroscopic Co. Model DS-402G infrared spectrophotometer was used. In general, benzene was used as solvent except for the measurement in the 720—620 cm^{-1} region, in which the absorption of benzene was very intense. In the 720—620 cm^{-1} region, *p*-xylene was used because it was transparent in this region.

The NMR spectra were measured by Varian A-60 A high resolution NMR spectrometer at 60 Mc, 14092 gauss, and at room temperature. About 0.5 m*l* of the benzene solution of the sample (5% weight/volume solution) was injected into the sample tube by a hypodermic syringe under nitroegen atmosphere and sealed. The values of chemical shifts were represented by ppm units (standard: benzene, the field higher than benzene signal was taken as positive).

Results and Discussion

The Spectra of $AlEt_{3-m}Cl_m \cdot n\text{-}PrNH_2$ (m= 0, 1, 2, 3). The NMR spectra of the equimolar mixtures of $(AlEt_{3-m}Cl_m)_2$ (m=0, 1, 2) and $n\text{-}PrNH_2$ in benzene were measured. The internal

TABLE 2. NMR SPECTRA OF $AlEt_{3-m}Cl_m \cdot n\text{-}PrNH_2$ (m=0, 1, 2); THE INTERNAL CHEMICAL SHIFTS (δ) OF al-Et GROUPS

	δ (ppm)
$AlEt_3 \cdot n\text{-}PrNH_2$	−1.30
$AlEt_2Cl \cdot n\text{-}PrNH_2$	−1.16
$AlEtCl_2 \cdot n\text{-}PrNH_2$	−1.04

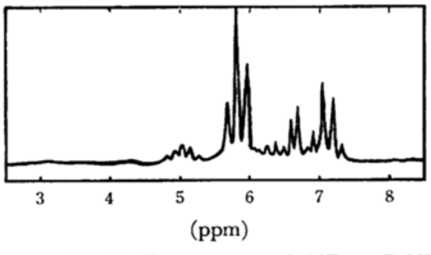


Fig. 1. The NMR spectrum of $AlEt_3 \cdot n\text{-}PrNH_2$.

TABLE 3. OBSERVED IR FREQUENCIES OF $AlEt_{3-m}Cl_m \cdot n\text{-}PrNH_2$ (m=0, 1, 2, 3)*1,*2

$AlEt_3 \cdot n\text{-}PrNH_2$	$AlEt_2Cl \cdot n\text{-}PrNH_2$	$AlEtCl_2 \cdot n\text{-}PrNH_2$	$AlCl_3 \cdot n\text{-}PrNH_2$	$n\text{-}PrNH_2$	Assignment
			3319 w		
3320 m	3298 m	3274 m	3262 m	3390 w	NH_2 antisym. str.
3268 m	3252 m	3234 m	3224 m	3330 vw	NH_2 sym. str.
	3133 vw	3126 vw			
2959 sh	2966 w	2967 m	2966 m	2959 vs	CH str.
2936 vs	2938 s	2941 m	2935 w	2928 s	
2895 s	2899 s	2902 m	2895 vw	2872 m	
2855 vs	2861 vs	2867 m	2876 w	2859 sh	
2789 w	2791 w	2791 vw		2752 vw	
2718 vw					
1578 m	1576 m	1571 m	1571 m	1626 w	NH_2 scissors
1449 w	1457 m	1455 m	1448 w	1451 m	
1411 m	1410 w	1407 w			
	1387 w	1388 w			
1374 w	1376 w	1377 vw	1383 vw	1381 w	
1314 vw	1317 w	1319 w	1318 w	1295 vw	
1275 vw	1274 vw	1276 vw	1275 w	1260 vw	
	1221 vw		1206 sh		
1184 m	1192 m	1201 m	1186 m		
1160 m					
1074 s	1084 m	1091 m	1080 m	1094 vw	
	1046 w	1040 w		1071 m	
982 s	988 s	986 m	990 w		
			974 w	975 w	
946 m	952 m	946 w	956 w		
			941 vw		
916 w	918 w	920 vw			
	888 w	887 w	888 w	897 s	
	877 vw	878 vw	879 sh		
	847 vw	845 vw	849 vw		
				810 s	NH_2 wag
663 vs	673 s	673 s	673 m		NH_2 rock, AlC str. CH_2 rock (AlC_2H_5)
651 vs	668 s		662 m		
	636 sb	626 s	601 w		
		575 w			
	541 w	537 w	532 s		
		525 m	526 s		
492 vw	483 vw	491 s	499 w		
			467 s		

*1 m, medium; s, strong; w, weak; v, very; b, broad.
*2 4000—720 cm^{-1} and 620—420 cm^{-1}; benzene solution.
720—620 cm^{-1}; p-xylene solution.

chemical shifts (δ) of the ethyl group attached to the Al atom (hereafter abbreviated as the al-Et group) are shown in Table 2. The NMR spectrum of $AlEt_3 \cdot n\text{-}PrNH_2$ is shown in Fig. 1. Although in benzene solution the solvent effect on the chemical shift values of the NMR signals of the solute is very large, such an effect can be neglected so far as the internal chemical shift value ($\delta = \delta_{CH_3} - \delta_{CH_2}$) of the compounds of CH_3CH_2X type is concerned.⁴⁾ It has been known that in ethylaluminum compounds the magnetic anisotropy of the atom in the β-position relative to the methylene group affects the δ value of the al-Et group.⁵⁾ The δ value of the al-Et group of $AlEt_3 \cdot n\text{-}PrNH_2$ is -1.30 ppm, which is almost equal to the δ value of the al-Et group in $AlEt_3 \cdot NEt_3$ (-1.29 ppm).

The IR spectra of the equimolar mixtures of $(AlEt_{3-m}Cl_m)_2$ (m=0, 1, 2, 3) and n-$PrNH_2$ in benzene and in p-xylene were measured. The spectra in the 4000—2700 cm^{-1} region are shown in Fig. 2. The frequencies and the intensities (qualitative) are shown in Table 3, and these data for the NH_2 stretchings and NH_2 scissors are summarized in Table 4. The bands at 3390 and 3330 cm^{-1} of n-$PrNH_2$ correspond to the bands at 3389 and 3323 cm^{-1} found by Wolff and Schmidt in carbon tetrachloride solution and assigned to the NH_2 antisymmetric and symmetric stretching vibrations, respectively, by them.⁶⁾ The band at 1626 cm^{-1} is assigned to the NH_2 scissors. All of these three bands—the NH_2 antisymmetric and symmetric stretchings and the NH_2 scissors—shift to lower frequencies and their intensities increase when n-$PrNH_2$ forms coordination compounds with $AlEt_{3-m}Cl_m$. As regards the magnitudes of the shifts and the intensities of these three bands caused by the coordination bond formation with

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4) P. T. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82**, 34 (1960).

5) O. Yamamoto, This Bulletin, **36**, 1463 (1963).

6) H. Wolff and U. Schmidt, *Ber. Bunsenges. Physik. Chem.*, **68**, 579 (1964).

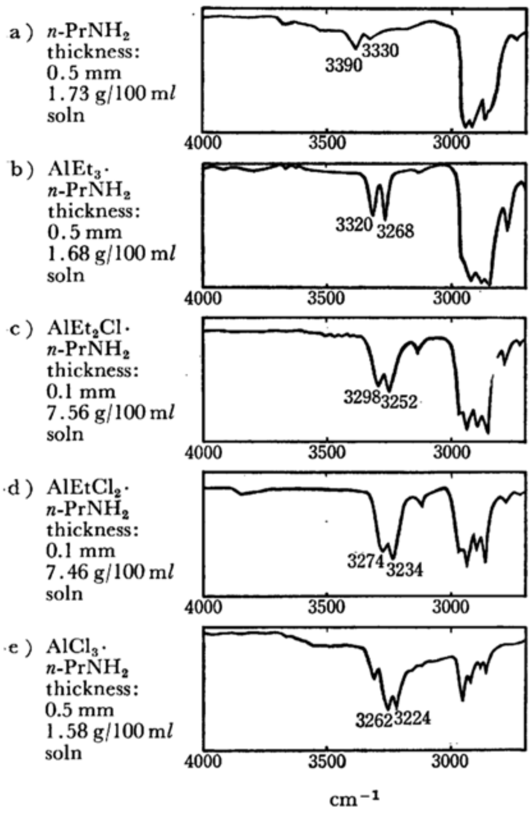

Fig. 2. The IR spectra of $AlEt_{3-m}Cl_m \cdot n\text{-}PrNH_2$ ($m=0, 1, 2, 3$).

TABLE 4. THE FREQUENCIES AND INTENSITIES (MOLAR EXTINCTION COEFFICIENTS: l/cm·mol— SHOWN IN PARENTHESES) OF THE NH_2 VIBRATION BANDS OF $AlEt_{3-m}Cl_m \cdot n\text{-}PrNH_2$ ($m=0, 1, 2, 3$)

	$\gamma_{as}(NH_2)$ cm^{-1}	$\gamma_s(NH_2)$ cm^{-1}	$\delta(NH_2)$ cm^{-1}
n-PrNH$_2$	3390 (8.7)	3330 (4.9)	1626 (10)
AlEt$_3$·n-PrNH$_2$	3320 (44)	3268 (50)	1578 (68)
AlEt$_2$Cl·n-PrNH$_2$	3298 (70)	3252 (80)	1576 (100)
AlEtCl$_2$·n-PrNH$_2$	3274 (94)	3234 (113)	1571 (93)
AlCl$_3$·n-PrNH$_2$	3262 (121)	3224 (113)	1571 (98)

$(AlEt_3)_2$, $(AlEt_2Cl)_2$, $(AlEtCl_2)_2$, and $(AlCl_3)_2$, the shifts and the intensities (molar extinction coefficients) increase in this order. This observation can be explained by the well-known fact that the electron-accepting tendency of $AlEt_{3-m}Cl_m$ becomes larger in the order of $m=0, 1, 2, 3$, and corresponds with the fact that the lower frequency shifts of the COC stretching absorption bands of diethyl ether (Et_2O) in the coordination compound $AlEt_{3-m}Cl_m \cdot Et_2O$ become larger in the order of $m=0, 1, 2, 3$.[7]

The IR Spectrum of $(AlEt_2OCH_2CH_2NH_2)_2$. The IR spectrum of the solution of $(AlEt_2OCH_2CH_2NH_2)_2$ is shown in Figs. 3a and 3b, together with the spectrum of the solution of $(AlEt_2OCH_2CH_2NMe_2)_2$ in Fig. 3c. The tentative assignments of the principal absorption bands given in Table 5 are made by taking the assignments of $(AlEt_2OEt)_2$,[8] ethanol,[9] ethylamine,[10] and n-PrNH$_2$,[6] into consideration.

Two sharp bands at 3375 and 3309 cm^{-1} are assigned to the NH_2 antisymmetric and symmetric

TABLE 5. OBSERVED IR FREQUENCIES OF $(AlEt_2OCH_2CH_2NH_2)_2$—BENZENE SOLUTION— AND ASSIGNMENT[*1]

	Assignment
3375 w	NH_2 antisymmetric str.
3309 vw	NH_2 symmetric str.
2935 s	CH_3 degenerate str. (AlC_2H_5), overtone of CH_3 deform. (AlC_2H_5)
2892 s	CH_2 antisymmetric str. (AlC_2H_5, $OC_2H_4NH_2$)
2858 vs	CH_3 symmetric str. (AlC_2H_5),
2793 w	CH_2 symmetric str. (AlC_2H_5, $OC_2H_4NH_2$)
2718 vw	
1590 m	NH_2 scissors
1454 w	CH_3 degenerate deform., CH_3 symmetric deform. (AlC_2H_5), CH_2 scissors (OCH_2)
1414 w	CH_2 scissors (AlC_2H_5), CH_2 scissors (CH_2NH_2)
1368 w	CH_2 wag (CH_2NH_2)
1281 w	CH_2 wag (OCH_2), CH_2 twist ($OC_2H_4NH_2$)
1256 w	
1228 vw	
1190 m	CH_2 wag, CH_2 twist (AlC_2H_5)
1108 s	CH_3 rock (AlC_2H_5), NH_2 twist
1051 vw	CCN anti-phase str.
1016 s	CCO anti-phase str.
974 s	CC str.
950 w	
902 m	CCO in-phase str.
868 w	CCN in-phase str., NH_2 wag
664 vs[*2]	AlC_2 antisymmetric str. B_{1u}, NH_2 rock
639 vs[*2]	CH_2 rock (AlC_2H_5)
565 vw	
478 w	AlC_2 symmetric str. B_{3u}

[*1] m, medium; s, strong; w, weak; v, very.
[*2] p-xylene solution.

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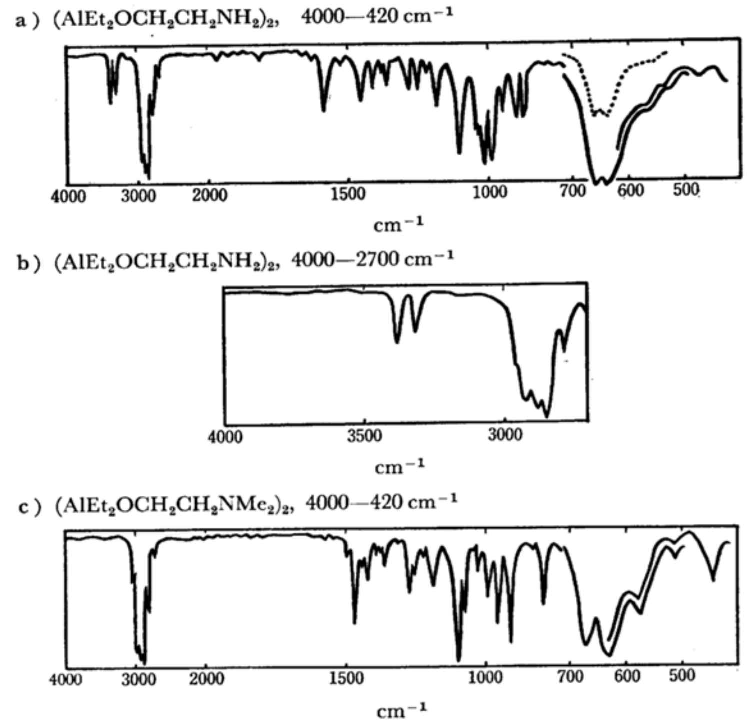
[7] S. Takeda and R. Tarao, This Bulletin, **33**, 1567 (1965).

[8] R. Tarao, *ibid.*, **39**, 2126 (1966).

[9] C. Tanaka, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **81**, 1042 (1960); **83**, 398, 521, 657, 661, 792 (1962).

[10] C. Matsuoka, A. Hirakawa, K. Tamagake and M. Tsuboi, Preprints for the 19th Annual Meeting of the Chemical Society of Japan (April, 1966), 1C 204.



a) $(AlEt_2OCH_2CH_2NH_2)_2$, 4000—420 cm^{-1}

b) $(AlEt_2OCH_2CH_2NH_2)_2$, 4000—2700 cm^{-1}

c) $(AlEt_2OCH_2CH_2NMe_2)_2$, 4000—420 cm^{-1}

Fig. 3. The IR spectra of $(AlEt_2OCH_2CH_2NH_2)_2$ and $(AlEt_2OCH_2CH_2NMe_2)_2$.
Cell thickness: 0.1 mm
Concentration: a) Real Line: 5.26 g/100 m*l* soln.
Dotted Line: 1.10 g/100 m*l* soln.
b) 5.26 g/100 m*l* soln.
c) 6.22 g/100 m*l* soln.

stretching vibrations respectively. These assignments are consistent with the fact that these two bands disappear in the spectrum of $(AlEt_2OCH_2CH_2NMe_2)_2$.

A sharp band at 1590 cm^{-1} is assigned to the NH_2 scissors. $(HgNH_2)^+$ has a sharp band due to the NH_2 scissors at 1543 cm^{-1}.[11] This band disappears in the spectra of $(AlEt_2OCH_2CH_2NMeH)_2$ and $(AlEt_2OCH_2CH_2NMe_2)_2$.

The broad and strong band at 664 cm^{-1} is assigned to the NH_2 rocking band overlapped by the AlC_2 antisymmetric stretching band. As shown in Fig. 4, this band (AlC_2 antisymmetric stretching) is much narrower in $(AlEt_2OEt)_2$, $(AlEt_2OCH_2CH_2NMeH)_2$, and $(AlEt_2OCH_2CH_2NMe_2)_2$, in which no NH_2 group exists. In each spectrum of $AlEt_{3-m}Cl_m \cdot n\text{-}PrNH_2$ ($m=0$, 1, 2, 3), there is a band of considerable intensity at about 670—660 cm^{-1}, which can be assigned to the NH_2 rocking, as shown in Table 3. In $(HgNH_2)^+$, the NH_2 rocking band appears at 668 cm^{-1}. These facts support this assignment.

Next, the problem to assign the most probable formula from among I, II, and III as the structural formula of the dimer $(AlEt_2OCH_2CH_2NH_2)_2$ will be discussed by taking the IR spectroscopic observations described above into consideration. The frequencies and intensities of the NH_2 stretchings, scissors, and rocking of $(AlEt_2OCH_2CH_2NH_2)_2$ will be compared with the frequencies and intensities of these bands of $AlEt_3 \cdot n\text{-}PrNH_2$, in which the NH_2 group coordinates with Al atom, and of $n\text{-}PrNH_2$ in dilute solution, in which the NH_2 group does not coordinate with any atom. The detailed discussion will be given below.

As described previously the NH_2 antisymmetric and symmetric stretching bands of $(AlEt_2OCH_2CH_2NH_2)_2$ exist at 3375 cm^{-1} (molar extinction coefficient, $\kappa=58$ *l*/cm·mol) and 3309 cm^{-1} ($\kappa=42$), respectively. In $n\text{-}PrNH_2$, these appear at 3390 cm^{-1} ($\kappa=8.7$) and 3330 cm^{-1} ($\kappa=4.9$) respectively. On the other hand, in $AlEt_3 \cdot n\text{-}PrNH_2$, these appear at 3320 cm^{-1} ($\kappa=44$) and 3268 cm^{-1} ($\kappa=50$) respectively. The data of frequencies do not make clear the problem whether the NH_2 group coordinates to the Al atom or not. The values of molar extinction coefficients of $(AlEt_2OCH_2CH_2NH_2)_2$, however, are almost equal to the values of $AlEt_3 \cdot n\text{-}PrNH_2$, and too large for the NH_2 group not to be coordinated with the Al atom. The lower frequency shift and the increase of

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[11] S. Mizushima, I. Nakagawa and D. M. Sweeny, *J. Chem. Phys.*, **25**, 1006 (1956).

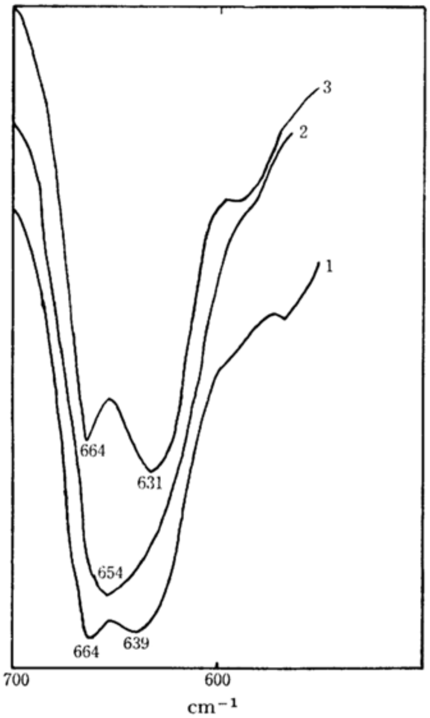

Fig. 4. The IR bands containing the NH_2 rocking band (superposed by the AlC_2 antisymmetric stretching and the CH_2 rocking band of al-Et group). Cell thickness: 0.1 mm, *p*-xylene solution.
1. $(AlEt_2OCH_2CH_2NH_2)_2$ 5.26 g/100 m*l* soln.
2. $(AlEt_2OEt)_2$ 5.26 g/100 m*l* soln.
3. $(AlEt_2OCH_2CH_2NMeH)_2$ 5.75 g/100 m*l* soln.

the intensity of the NH_2 antisymmetric and symmetric stretching vibration bands caused by the coordination of the NH_2 group are generally interpreted by the increase of the polar character of the N-H bond owing to the coordination bond formation.[12]

The NH_2 scissors band of $(AlEt_2OCH_2CH_2NH_2)_2$ exists at 1590 cm^{-1} ($\kappa=69$). The frequency and the intensity of this band are almost equal to the values of the corresponding bands of $AlEt_3 \cdot n\text{-}PrNH_2$ (1578 cm^{-1}, $\kappa=68$), and different from the values of the corresponding bands of $n\text{-}PrNH_2$ (1626 cm^{-1}, $\kappa=10$).

The NH_2 rocking band of $(AlEt_2OCH_2CH_2NH_2)_2$ exists at 664 cm^{-1}; this frequency coincides with the frequencies of the NH_2 rocking bands of $AlEt_{3-m}Cl_m \cdot n\text{-}PrNH_2$ ($m=0$, 1, 2, 3), though the intensity is uncertain owing to the superposition of the band with the AlC_2 antisymmetric stretching band.

These observations apparently support formula I; they cannot be interpreted reasonably by assuming either formula II or III.

The relative intensities and frequencies of all bands (including the NH_2 stretching and the NH_2 scissors) remained unchanged when the concentration of $(AlEt_2OCH_2CH_2NH_2)_2$ in the solution was changed from 1.10 g/100 m*l* to 10.0 g/100 m*l*; this implies that intermolecular hydrogen bondings are not present. The relation between the concentrations and the molar extinction coefficients are shown in Table 6.

In Table 7, the frequencies and the molar extinction coefficients of the NH_2 stretching and scissors bands are shown for $(AlEt_2OCH_2CH_2NH_2)_2$ and six related compounds. It is apparent from these data that the dimers of these six related compounds also take the structures with two $Al \leftarrow NH_2$ coordination bonds, in other words the structures corresponding to formula I.

The NMR Spectrum of $(AlEt_2OCH_2CH_2NH_2)_2$. The NMR spectrum of the solution of $(AlEt_2OCH_2CH_2NH_2)_2$ is shown in Fig. 5. For the sake of comparison, the spectrum of $(AlEt_2OCH_2CH_2NMe_2)_2$ is shown in Fig. 6. The broad signal at 6.3 ppm present in Fig. 5 is assigned to the NH_2 protons because it disappears in Fig. 6. The quintet at 5.17 ppm present in Fig. 5 turns to a triplet in Fig. 6. This quintet can be assigned to the NCH_2 protons because this change (quintet→triplet) is interpreted as due to the presence or the absence of the spin-spin coupling with the NH_2 protons. The assignments of the rest of the signals can also be easily made as shown in these figures by considering the signal intensities and the spin-spin couplings. In Fig. 7, the chemical shifts of methyl and methylene protons of the al-Et groups of $(AlEt_2OCH_2CH_2NH_2)_2$ and twelve related compounds are shown. For the sake of comparison, the corresponding chemical shifts of $(AlEt_3)_2$ and $(AlEt_2OEt)_2$ are also shown in this figure.

TABLE 6. THE CONCENTRATION DEPENDENCE OF THE INTENSITIES (MOLAR EXTINCTION COEFFICIENTS: *l*/cm·mol) OF THE NH_2 VIBRATION BANDS OF $(AlEt_2OCH_2CH_2NH_2)_2$

Concentration		$\gamma_{as}(NH_2)$ 3375 cm^{-1}	$\gamma_s(NH_2)$ 3309 cm^{-1}	$\delta(NH_2)$ 1590 cm^{-1}
g/100 m*l*	$(mol/cm^3)\times10^3$			
1.10	0.0759	57	41	61
5.26	0.3623	58	42	69
10.0	0.6887	60	43	69

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[12] I. Nakagawa, *Kagaku no Ryoiki (J. Japanese Chem.)*, **22**, 281 (1968).

TABLE 7. THE FREQUENCIES AND INTENSITIES (MOLAR EXTINCTION COEFFICIENTS: l/cm·mol—SHOWN IN PARENTHESES) OF THE NH_2 VIBRATION BANDS OF $(AlEt_2OCH_2CH_2NH_2)_2$ AND RELATED COMPOUNDS

	$\gamma_{as}(NH_2)$ cm^{-1}	$\gamma_s(NH_2)$ cm^{-1}	$\delta(NH_2)$ cm^{-1}
$(AlEt_2OCH_2CH_2NH_2)_2$	3375 (58)	3309 (42)	1590 (69)
$(AlEt_2OCH_2CH_2CH_2NH_2)_2$	3354 (28)	3296 (19)	1586 (57)
$(AlEt_2OCH(CH_3)CH_2NH_2)_2$	3380 (47)	3319 (31)	1589 (59)
$(Al\text{-}i\text{-}Bu_2OCH_2CH_2NH_2)_2$	3374 (54)	3309 (35)	1589 (70)
$(AlEt_2OCH_2C(CH_3)_2NH_2)_2$	3359 (43)	3298 (28)	1584 (84)
$(AlEt_2OCH_2CH(CH_3)NH_2)_2$	3364 (53)	3296 (28)	1587 (73)
$(AlEt_2OCH_2CH(C_2H_5)NH_2)_2$	3369 (43)	3294 (23)	1583 (70)

As mentioned previously, in ethylaluminum compounds the magnetic anisotropy of the atom in the β-position relative to the methylene group affects the δ value of the al-Et group. For this reason, it seems quite possible to choose the most probable formula among I, II, and III as the formula of $(AlEt_2OCH_2CH_2NH_2)_2$ by considering the δ value of the al-Et group, independent of the assumption based on the IR spectroscopic observations.

The δ value of the al-Et group of $(AlEt_2OEt)_2$, which can be regarded as a model compound of the formula III, is -1.14 ppm, as shown in Fig. 7. The corresponding δ values of $(AlEt_2OCH_2CH_2NH_2)_2$ and related compounds are, except for the following three compounds, $(AlEt_2OCH_2CH_2NPhH)_2$, $(AlEt_2OCH_2CH_2NPh_2)_2$, and $(AlEt_2OCH_2CH_2N(C_6H_{11})_2)_2$, always -1.31—-1.38 ppm; these values differ from the δ value of $(AlEt_2OEt)_2$ by about 0.2 ppm.

If formula III is assumed, this difference of the δ value should be interpreted as the effect of the N atom exerted through two methylene groups. The fact that the δ value of $(AlEt_2OCH_2CH_2CH_2NH_2)_2$ is -1.37 ppm is, however, the strong evidence against this interpretation. The δ value of the ethyl group of $HOCH_2CH_2NEt_2$ is 1.47

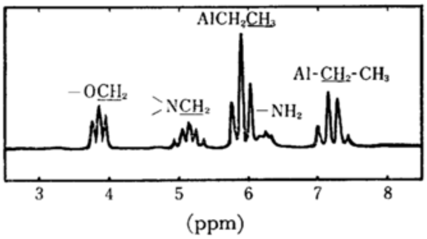

Fig. 5. The NMR Spectrum of $(AlEt_2OCH_2CH_2NH_2)_2$.

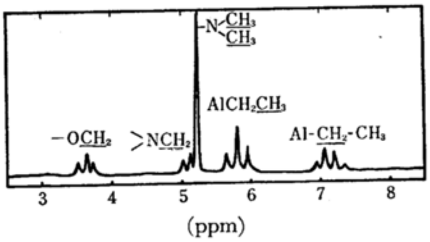

Fig. 6. The NMR spectrum of $(AlEt_2OCH_2CH_2NMe_2)_2$.

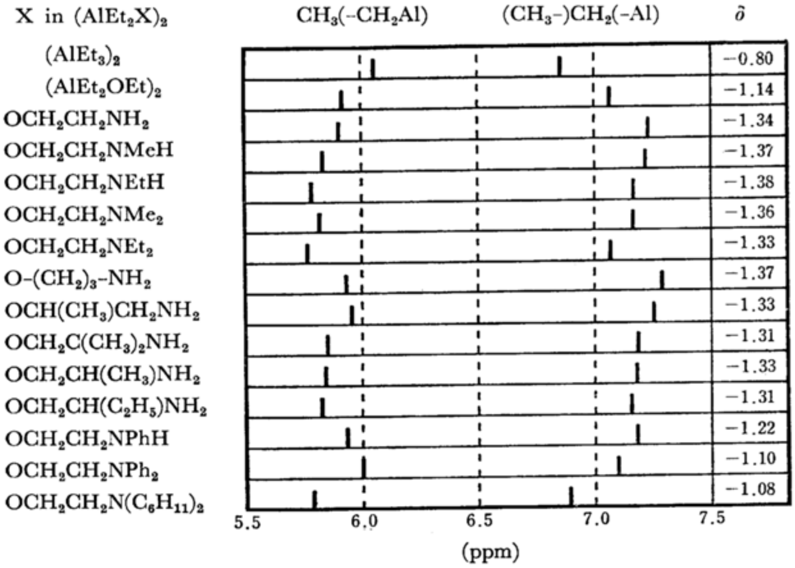

Fig. 7. The chemical shifts of al-Et groups of $(AlEt_2OCH_2CH_2NH_2)_2$ and related compounds.

ppm in benzene, and the δ value of the ethyl group of $(AlEt_2OCH_2CH_2NEt_2)_2$ attached to the N atom is 1.80 ppm. This difference of the δ value is reasonably interpreted by the decrease of the electron density of the N atom caused by the coordination of unshared electron pair of the N atom with the Al atom.

Next, if formula II is assumed, there should be two aminoethoxyl groups, one coordinating with Al atom and the other possessing an unshared electron pair. The facts that the NH_2 signal appears as a broad signal and that the NCH_2 and the OCH_2 signals do not suggest the presence of two kinds of the $-CH_2CH_2NH_2$ groups, do not support formula II.

These considerations lead to the conclusion that the dimers of $(AlEt_2OCH_2CH_2NH_2)_2$ and related compounds, whose δ values of the al-Et groups are about -1.34 ppm, are represented by the structural formula I with two Al←NRR′ coordination bonds. This conclusion is consistent with the result of considerations based on IR spectroscopic data described previously. $(AlEt_2OCH_2CH_2N(C_6H_{11})_2)_2$ has the δ value of -1.08 ppm, which is nearly equal to the δ value of the al-Et group of $(AlEt_2OEt)_2$. This anomalous value may be interpreted by the assumption that this compound exceptionally takes the structural formula III, since the unshared electron pair of the N atom could not coordinate with the Al atom owing to the steric hindrance of two cyclohexyl groups The δ values of the al-Et groups of $(AlEt_2OCH_2CH_2NPhH)_2$ and $(AlEt_2OCH_2CH_2NPh_2)_2$, -1.22 and -1.10 ppm respectively, may be due to the magnetic anisotropy of the phenyl rings, although the possibility of formula III could not be excluded.

Still another support of the formula I is obtained from the NMR spectra of the system $(AlMe_2OCH_2CH_2NMe_2)_2+(AlEt_3)_2$. In this system, the redistribution of the al-Me groups and al-Et groups take place, and the species $(AlRR'OCH_2CH_2NMe_2)_2$—R, R′ = methyl or ethyl—is produced. There are fine structures corresponding to $NMe_2 \rightarrow AlEt_2O-$, $NMe_2 \rightarrow AlEtMeO-$, and $NMe_2 \rightarrow AlMe_2O-$ in the signal of the methyl group of $(AlRR'OCH_2CH_2NMe_2)_2$ attached to the N atom. Although this observation no doubt supports formula I for $(AlRR'OCH_2CH_2NMe_2)_2$, the details will be described in the forthcoming publication.

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