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The Redistribution Reaction of Ethyl Groups and Chlorine Atoms in the Ethylaluminum Chloride + Ether System*[1]

Ryokichi TARAO and Saburo TAKEDA

Research Center, Chisso Co., Ltd., Kanazawa-ku, Yokohama

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The redistribution reactions of ethyl groups and chlorine atoms in the $2AlEt_nCl_{3-n}$+ether system were studied by the Raman spectroscopic method. It was found that the reaction of $AlEtCl_2$ with Et_2O (molar ratio, 2 : 1) gave rise to $AlEt_2Cl$ and $AlCl_3 \cdot Et_2O$, although not quantitatively. On the contrary, the reaction of $AlEt_2Cl$ with Et_2O (molar ratio, 2 : 1) did not produce any $AlEt_3$ or $AlEtCl_2 \cdot Et_2O$ at all. These and several related observations demonstrate that, by the reaction between $AlEt_nCl_{3-n}$ and $AlEt_mCl_{3-m} \cdot Et_2O$ (n, m=0, 1, 2, 3), $AlEt_2Cl$ is preferentially produced as long as there is any possibility of its formation.

In 1963 Zambelli and his co-workers reported that a redistribution reaction*[2] of ethyl groups and chlorine atoms (Eq. (1)) took place in the $2AlEtCl_2$+electron donor (e.g., pyridine) system to produce $AlEt_2Cl$ and $AlCl_3 \cdot$donor complex:[1)]

$$2AlEtCl_2 + D \rightarrow AlEt_2Cl + AlCl_3 \cdot D \qquad (1)$$

(D=an electron donor substance)

It is still uncertain, however, whether or not the reaction (1) takes place with donor substances in general. For example, in 1965 McConnell and his co-workers reported that the reaction (1) did not take place when hexamethylphosphoramide (HPT) was used as D; they based this conclusion on their study of the infrared spectrum of the $2AlEtCl_2$+HPT system.[2)]

This study will do the following things concerning these redistribution reactions using the Raman spectroscopic method, which is far more suited than the infrared method to examining these systems, which are very sensitive to air and moisture;

i) Measure the Raman spectra of $AlEtCl_2$ and $AlEt_{1.5}Cl_{1.5}$ (sesquiethylaluminum chloride).

ii) Make sure that the reaction (1) really takes place when pyridine is used as D, and examine whether or not the reaction (1) also takes place when donor substances other than pyridine are used.

iii) Clarify such points as this: $AlEt_2Cl$ and $AlEtCl_2$ have been considered to form the equimolar complexes $AlEt_2Cl \cdot Et_2O$ and $AlEtCl_2 \cdot Et_2O$ respectively with Et_2O.[3)] By taking into consideration the fact that the reaction (1) takes place, however, it may still be possible that the $AlEtCl_2 \cdot Et_2O$ complex is actually an equimolar mixture of the $AlEt_2Cl \cdot Et_2O$ and $AlCl_3 \cdot Et_2O$ complexes.

iv) See whether reactions similar to the redistribution reaction (1), for example, the reaction (1′), take place or not, by using Et_2O as D.

$$2AlEt_2Cl + D \rightarrow AlEt_3 + AlEtCl_2 \cdot D \qquad (1')$$

Our results will be described below.

Experimental

Materials. Commercial $AlEt_3$, $AlEt_2Cl$, $AlEt_{1.5}Cl_{1.5}$ and $AlEtCl_2$ were distilled in vacuo just before use. Commercial $AlCl_3$ was used without further purification. Hexamethyldisiloxane ($Me_3SiOSiMe_3$), pyridine, and Et_2O were purified by the usual methods.

Measurement of Spectra. The Raman spectra were measured in the 3000—130 cm^{-1} region in the liquid state with a Shimadzu GRS Raman spectrophotometer. All the samples were distilled into Raman tubes under a high vacuum; the tubes were then sealed off under reduced pressure to prevent contamination with air and moisture. It was necessary in most cases to heat the sample (maximum: 100°C) to distil it, even under a high vacuum (10^{-3}—10^{-4} mmHg).

The Reaction of $AlEtCl_2$ with Pyridine. To 20.0 g of $AlEtCl_2$, 6.2 g of pyridine were added drop by drop under an atmosphere of nitrogen at the temperature of a dry ice-methanol mixture (molar ratio, $AlEtCl_2$: pyridine=2 : 1). A considerable evolution of heat was observed. The reaction mixture was then distilled *in vacuo* (2.5 mmHg).

Distillate (bp 40—47.5°C)	9.2 g
Residue	17.0 g
Total	26.2 g

The distillate, a colorless liquid, was distilled into a 6 *ml* Raman tube and sealed off; this fraction did not freeze at the temperature of a dry ice-methanol mixture.

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*[1] Presented at the Symposium on Organometallic Compounds, Osaka, October, 1966.

*[2] The term "dismutation" has often been employed. In this paper, however, the term "redistribution reaction" will be preferred in order to emphasize the more general nature of the reaction.

1) A. Zambelli, J. Dipietro and G. Gatti, *J. Poly. Sci.*, **A1**, 403 (1963).

2) R. L. McConnell, M. A. McCall, G. O. Cash, Jr., F. B. Joyner and H. W. Coover, Jr., *ibid.*, **A3**, 2135 (1965).

3) S. Takeda and R. Tarao, This Bulletin, **38**, 1567 (1965).

The distillation residue crystallized to white crystals at room temperature.

The Analyses of the Lower-boiling Fraction of the $2AlEtCl_2+Et_2O$ System. To 11.0 g of $AlEtCl_2$, 3. 2g of Et_2O was added drop by drop under an atmosphere of nitrogen with cooling (molar ratio, $AlEtCl_2 : Et_2O=2 : 1$). The reaction mixture (11.2 g) was fractionated by distillation into a lower-boiling fraction (3.0 g, bp 95.5—96.5°C/7 mmHg) and a higher-boiling fraction (6.1 g, bp 128—134°C/17 mmHg). The distillation residue and the amount lost were about 2 g. Aluminum and chlorine analyses of the lower-boiling fraction were then carried out. Found: Al, 21.4; Cl, 43.3%. By using the datum of chlorine analysis as a basis, and by postulating that the lower-boiling fraction was a mixture of $AlEt_2Cl$ and $AlEtCl_2$, the $AlEt_2Cl$ content of this fraction was calculated. The calculated $AlEt_2Cl$ content was 48.8 mol per cent. (Calcd for $AlEt_2Cl$: Al, 22.38; Cl, 29.41%. Calcd for $AlEtCl_2$: Al, 21.25; Cl, 55.86%.)

The Synthesis of $AlCl_3 \cdot Et_2O$. Substantially the method reported by Frankforter and Daniels was adopted.[4] The purification of the product, $AlCl_3 \cdot Et_2O$, was accomplished by distillation *in vacuo*; a distillate with bp 84—85°C/3×10^{-2} mmHg was thus obtained. The complex was white crystals with a mp of 36—38.5°C; the value agreed very well with the values listed in the literature.[4-6]

Found: Al, 13.25; Cl, 51.25%. Calcd for $AlCl_3 \cdot Et_2O$: Al, 13.00; Cl, 51.27%.

Results and Discussion

The Raman Spectra of $AlEt_3$, $AlEt_2Cl$, $AlEt_{1.5}Cl_{1.5}$ and $AlEtCl_2$. Among these four organoaluminum compounds, $AlEt_3$ and $AlEt_2Cl$ have been studied Raman-spectroscopically by several investigators; the tentative assignments of the main Raman lines in the skeletal vibration region have also been made.[7,8] As no Raman spectroscopic study has been reported for $AlEt_{1.5}Cl_{1.5}$ and $AlEtCl_2$, however, the present authors have measured their Raman spectra in the present study; the spectra obtained (in the skeletal vibration region) are shown in Figs. 1c and 1d. The spectra of $AlEt_3$ and $AlEt_2Cl$, also obtained in this study, are shown in Figs. 1a and 1b; these spectra agree precisely with those given by Hoffmann[7] and Yamamoto.[8] It was found that the spectrum of $AlEt_{1.5}Cl_{1.5}$ was a superposition of those of $AlEt_2Cl$ and $AlEtCl_2$. The tentative assignments of the main Raman lines of $AlEtCl_2$ in the skeletal vibration region were made as are shown below by taking the assignments given for $AlEt_2Cl$ and $AlCl_3$ into consideration. (The chlorine bridge structure was assumed for the dimer of $AlEtCl_2$ in assigning these lines.)

654 cm^{-1}	(m)	ν(AlC).
505 cm^{-1}	(mb)	ν(AlCl) terminal
346 cm^{-1}	(vs)	ν_s(AlCl) bridge

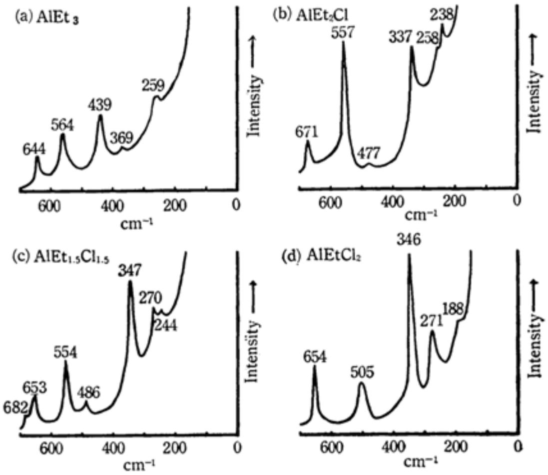

Fig. 1. The Raman spectra of $AlEt_3$, $AlEt_2Cl$, $AlEt_{1.5}Cl_{1.5}$ and $AlEtCl_2$ in the skeletal vibration region.

From Figs. 1b and 1d it is apparent that the strong line of $AlEt_2Cl$ at 557 cm^{-1} (assigned to ν(AlC) A_{1g} in the literature[7,8]) can be used as a key band of $AlEt_2Cl$, for $AlEtCl_2$ has no Raman line near 557 cm^{-1}.

The Presence of $AlEt_2Cl$ in the $2AlEtCl_2+$ Electron Donor System. Zambelli and his coworkers reported that they had distilled the product of the reaction between $2AlEtCl_2$ and pyridine *in vacuo* and confirmed that the distillate was $AlEt_2Cl$ by the use of the results of aluminum and chlorine analyses of it.[1] The present authors repeated this

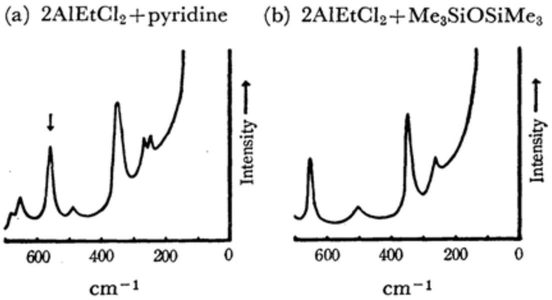

Fig. 2. The Raman spectra of the distillates from the systems
(a) $2AlEtCl_2$+pyridine
(b) $2AlEtCl_2+Me_3SiOSiMe_3$.

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[4] G. B. Frankforter and E. A. Daniels, *J. Am. Chem. Soc.*, **37**, 2560 (1915).

[5] W. Menzel and M. Fröhlich, *Ber.*, **75B**, 1055 (1942).

[6] G. Briegleb and W. Lauppe, *Z. Phys. Chem.*, **B35**, 42 (1937).

[7] E. G. Hoffmann, *Z. Elektrochem.*, **64**, 616 (1960).

[8] O. Yamamoto, This Bulletin, **35**, 619 (1962).

TABLE 1. OBSERVED RAMAN FREQUENCIES OF $AlEt_nCl_{3-n}\cdot Et_2O$ ($n=0, 1, 2, 3$) AND VIBRATIONAL ASSIGNMENTS[*1,*2]

$AlEt_3\cdot Et_2O$				$AlEt_2Cl\cdot Et_2O$			
2981	w	D	CH str.	2979	m	D	CH str.
2934	s	P		2937	s	P	
2894	sh			2896	vw		
2860	vs	P		2864	vs	P	
2784	m	D		2790	w	D	
2717	w			2727	w		
1461	m	D	CH_3 degenerate deform., CH_3 symmetric deform., CH_2 scissors (ether)	1454	m	D	CH_3 degenerate deform., CH_3 symmetric deform., CH_2 scissors (ether)
1409	w	D	CH_2 scissors ($-CH_2-Al$)	1411	w	D	CH_2 scissors ($-CH_2-Al$)
1328	w	D	CH_2 wag, CH_2 twist (ether)	1325	w	D	CH_2 wag, CH_2 twist (ether)
1189	m	P	CH_2 wag, CH_2 twist ($-CH_2-Al$), CH_3 rock	1197	m	P	CH_2 wag, CH_2 twist ($-CH_2-Al$), CH_3 rock
1093	w	P		1091	w	P	
1036	w		CO antisymmetric str.	1023	vw		CO antisymmetric str.
992	m	D	CC str.	993	m	D	CC str.
958	vw			954	vw		
899	w	D	CO symmetric str.	892	w	D	CO symmetric str.
834	w		CH_2 rock (ether)	835	w		CH_2 rock (ether)
				(803	vw)		
779	w			776	w		
638	w		AlC_3 degenerate str.	651	w	D	AlC_2 antisymmetric str.
489	s	P	AlC_3 symmetric str.	558	m	P	AlC_2 symmetric str.
				410	s	P	AlO str. + AlCl str.
333	vw			336	vw		

[*1] m, medium; s, strong; w, weak; v, very; b, broad.

[*2] P, polarized; D, depolarized.

$AlEtCl_2\cdot Et_2O$				$AlCl_3\cdot Et_2O$			
2985	s	D	CH str.	2989	s	D	CH str.
2940	vs	P		2942	s	P	
2903	vw						
2873	s	P		2877	w		
2785	w	D		2784	m	D	
2737	vw						
1455	m	D	CH_3 degenerate deform., CH_3 symmetric deform., CH_2 scissors (ether)	1453	m	D	CH_3 degenerate deform., CH_3 symmetric deform., CH_2 scissors
1409	w	D	CH_2 scissors ($-CH_2-Al$)	1400	w	D	
1330	w	D	CH_2 wag, CH_2 twist (ether)	1330	w	D	CH_2 wag, CH_2 twist
1290	vw						
1203	m	P	CH_2 wag, CH_2 twist ($-CH_2-Al$), CH_3 rock				
1095	m	P		1096	m	P	
999	mb	D	CO antisymmetric str., CC str.	993	mb	D	CO antisymmetric str., CC str.
962	vw						
889	w	D	CO symmetric str.	879	w	D	CO symmetric str.
838	w		CH_2 rock (ether)	836	w		CH_2 rock
(802	vw)			(804	vw)		
771	w			777	w		
639	m	D	AlC str.				
493	vw		$AlCl_2$ antisymmetric str.	546	wb	D	$AlCl_3$ degenerate str.
410	s	P	$AlCl_2$ symmetric str.				
355	vw			409	s	P	$AlCl_3$ symmetric str.
327	w	D					
276	w	P		324	s	P	$AlCl_3$ symmetric deform.

reaction under similar conditions and measured the Raman spectrum of the distillate. The results are shown in Fig. 2a. It was found that the distillate surely contains $AlEt_2Cl$; for the 557 cm^{-1} line of $AlEt_2Cl$ obviously appears (marked in Fig. 2a by an arrow). Therefore, there is no doubt that $AlEt_2Cl$ is produced in this system, as Zambelli and his co-workers stated. By comparing the intensities of the 557 cm^{-1} and 340 cm^{-1} lines with each other, it was found that the sample is not pure $AlEt_2Cl$ but approximately an equimolar mixture of $AlEt_2Cl$ and a considerable amount of $AlEtCl_2$.

As will be described below, when Et_2O was used as D in place of pyridine, similar results were obtained (Fig. 5b). When $Me_3SiOSiMe_3$ was used as D and treated with $AlEtCl_2$ (molar ratio, $AlEtCl_2 : Me_3SiOSiMe_3 = 2 : 1$), however, the spectrum of the distillate showed no line at 557 cm^{-1} (Fig. 2b). Thus it has been found that the reaction (1) sometimes takes place and sometimes does not, depending on the nature of D, and that the reaction (1) does not proceed quantitatively, but rather stops at the point by which about a half of the $AlEtCl_2$ initially present has turned to $AlEt_2Cl + AlCl_3 \cdot D$, even if pyridine or Et_2O is used as D.

The Raman Spectra of $AlEt_nCl_{3-n} \cdot Et_2O$ ($n = 0, 1, 2, 3$). The infrared and Raman spectra of $AlEt_3 \cdot Et_2O$ were investigated by Hoffmann.7) The infrared spectrum of $AlCl_3 \cdot Et_2O$ was studied by Lewis and his co-workers,9) and the Raman spectrum, by Briegleb and Lauppe.6) The infrared spectra of $AlEt_2Cl \cdot Et_2O$ and $AlEtCl_2 \cdot Et_2O$ have been reported by the present authors,3) but their Raman spectra have never been reported. The Raman spectrum of $AlCl_3 \cdot Et_2O$ was studied by Briegleb and Lauppe about 30 years ago; it no longer seems very reliable. Therefore, in this study the Raman spectra of $AlCl_3 \cdot Et_2O$, $AlEt_2Cl \cdot Et_2O$, and $AlEtCl_2 \cdot Et_2O$ were reinvestigated to obtain more reliable data. The Raman spectra of those four compounds, $AlEt_3 \cdot Et_2O$, $AlEt_2Cl \cdot Et_2O$, $AlEtCl_2 \cdot Et_2O$, and $AlCl_3 \cdot Et_2O$, and the tentative assignments of the main Raman lines observed are shown in Table 1 and in Figs. 3a—3d. A detailed discussion with respect to the assignments has been given previously.3) The observed spectrum of $AlEt_3 \cdot Et_2O$ agrees precisely with that given by Hoffmann. The observed spectra of $AlEt_2Cl \cdot Et_2O$ and $AlEtCl_2 \cdot Et_2O$ correspond quite well with the infrared data. The observed frequencies of $AlCl_3 \cdot Et_2O$ are also given in Table 2, along with the Raman data of Briegleb and Lauppe and the infrared data of Lewis and his co-workers. Our data agree far more precisely with the infrared data than Briegleb and Lauppe's data do; therefore, our results are surely more reliable. For the sake of comparison the Raman spectrum of Et_2O measured by the present authors is shown in Fig. 4. It is well known that $AlEt_3$ and $AlCl_3$ form stable 1 : 1 coordination complexes with Et_2O, $AlEt_3 \cdot Et_2O$ and $AlCl_3 \cdot Et_2O$ respectively.4,10) Similarly, the present authors have considered that $AlEt_2Cl$ and $AlEtCl_2$ form stable 1 : 1 coordination complexes with Et_2O, $AlEt_2Cl \cdot Et_2O$ and $AlEtCl_2 \cdot Et_2O$ respectively.3) By taking into consideration the fact that the reaction (1) proceeds when $D = Et_2O$, however, there seems to be at least some possibility that the actual entity of the substance hitherto regarded as $AlEt_2Cl \cdot Et_2O$ is a $AlEt_3 \cdot Et_2O + AlEtCl_2 \cdot Et_2O$ or $2AlEt_3 \cdot Et_2O + AlCl_3 \cdot Et_2O$ mixture and that the entity of $AlEtCl_2 \cdot Et_2O$ is a $AlEt_2Cl \cdot Et_2O + AlCl_3 \cdot Et_2O$ or $AlEt_3 \cdot Et_2O + 2AlCl_3 \cdot Et_2O$ mixture. In order to clarify these points, the spectra obtained (Figs. 3a—3d, each sample was an equimolar mixture

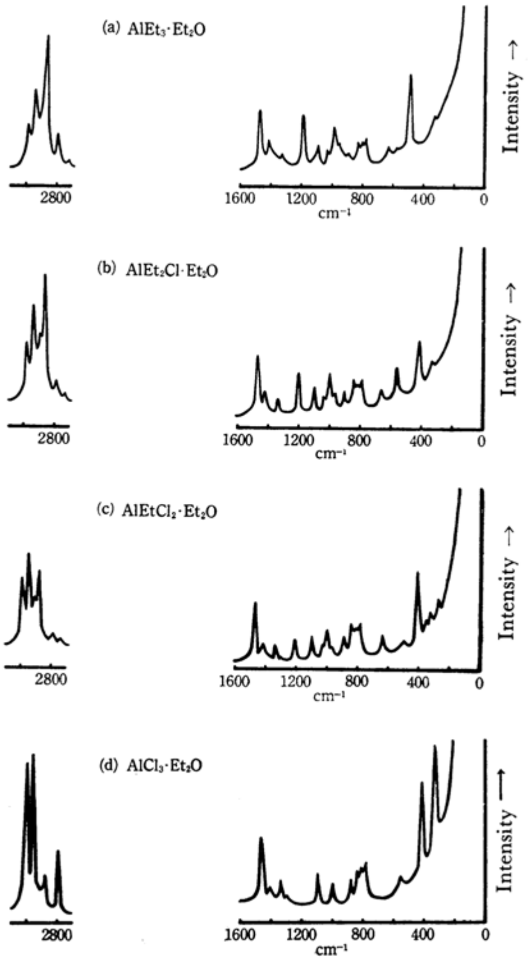

Fig. 3. The Raman spectra of $AlEt_3 \cdot Et_2O$, $AlEt_2Cl \cdot Et_2O$, $AlEtCl_2 \cdot Et_2O$ and $AlCl_3 \cdot Et_2O$.

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9) J. Lewis, J. R. Miller, R. L. Richards and A. Thompson, *J. Chem. Soc.*, **1965**, 5850.

10) E. B. Baker and H. H. Sisler, *J. Am. Chem. Soc.*, **75**, 4828 (1953).

TABLE 2. THE VIBRATIONAL SPECTRA OF $AlCl_3 \cdot Et_2O$

IR (Lewis *et al.*[9])		Raman (This study)		Raman (Briegleb *et al.*[6])	
2985	s	2989	s	2976	(10)
2940	w	2942	s		
2887	w	2877	w	2901	(10)
		2784	m		
1440	s	1453	m	1450	(5b)
1395	s	1400	w		
1334	m	1330	w		
1285	m			1262	(2)
1192	s			1206	(1)
1146	s				
1091	ms	1096	m		
				1054	(4)
1000	vs	993	mb		
876	s	879	w	891	(4)
834	m	836	w	823	(3)
790	w	804	vw		
765	s	777	w		
				690	(2b)
				625	(4)
535	s	546	wb	534	(6)
408	s	409	s	406	(10)
		324	s	310	(8)

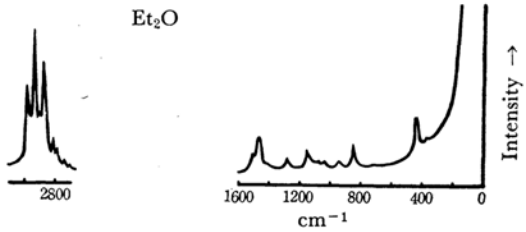

Fig. 4. The Raman spectrum of Et_2O.

of $AlEt_nCl_{3-n}$ and Et_2O) were compared with each other. The spectrum of $AlEt_2Cl \cdot Et_2O$ (Fig. 3b) is entirely different from the superposition of the spectra of Figs. 3a and 3c, or Figs. 3a and 3d. For example, the strong 489 cm^{-1} line of $AlEt_3 \cdot Et_2O$ (Fig. 3a) does not appear in Fig. 3b. Similarly, the spectrum of $AlEtCl_2 \cdot Et_2O$ (Fig. 3c) is entirely different from the superposition of the spectra of Figs. 3b and 3d, or Figs. 3a and 3d. These facts decisively suggest that an equimolar mixture of Et_2O and $AlEt_2Cl$ (or $AlEtCl_2$) forms a stable coordination complex, $AlEt_2Cl \cdot Et_2O$ (or $AlEtCl_2 \cdot Et_2O$).

In connection with these findings, it was found that the following reactions, (2) and (3), proceeded quantitatively to the right:

$$AlEt_3 \cdot Et_2O + AlEtCl_2 \cdot Et_2O \rightarrow 2AlEt_2Cl \cdot Et_2O \qquad (2)$$

$$AlEt_2Cl \cdot Et_2O + AlCl_3 \cdot Et_2O \rightarrow 2AlEtCl_2 \cdot Et_2O \qquad (3)$$

The spectra of these systems were just the same as those of $AlEt_2Cl \cdot Et_2O$ (Fig. 3b)—reaction (2)—and $AlEtCl_2 \cdot Et_2O$ (Fig. 3c)—reaction (3).

The Redistribution Reaction of Ethyl Groups and Chlorine Atoms in the Ethylaluminum Chloride+Ether System. In an earlier section it was described that, when pyridine or Et_2O was used as D, the reaction (1) undoubtedly took place. To elucidate this phenomenon more thoroughly, the Raman spectra of several systems represented as $AlEt_nCl_{3-n} + AlEt_mCl_{3-m} \cdot Et_2O$ ($n, m = 0, 1, 2, 3$) were measured (shown in Figs. 5a—5f, and Figs. 6a and 6b); the results are summarized in Table 3. The following conclusions can be drawn from this table. The reaction (4) takes place, turning almost a half (48.8 per cent) of the $AlEtCl_2$ initially present into $AlEt_2Cl$ and giving a mixture of the four chemical species, $AlEtCl_2$, $AlEt_2Cl$, $AlEtCl_2 \cdot Et_2O$ and $AlCl_3 \cdot Et_2O$:

$$AlEtCl_2 + AlEtCl_2 \cdot Et_2O \rightarrow AlEt_2Cl + AlCl_3 \cdot Et_2O \qquad (4)$$

On the contrary, the similar reaction (5) does not take place at all:

$$AlEt_2Cl + AlEt_2Cl \cdot Et_2O \not\longrightarrow AlEt_3 + AlEtCl_2 \cdot Et_2O \qquad (5)$$

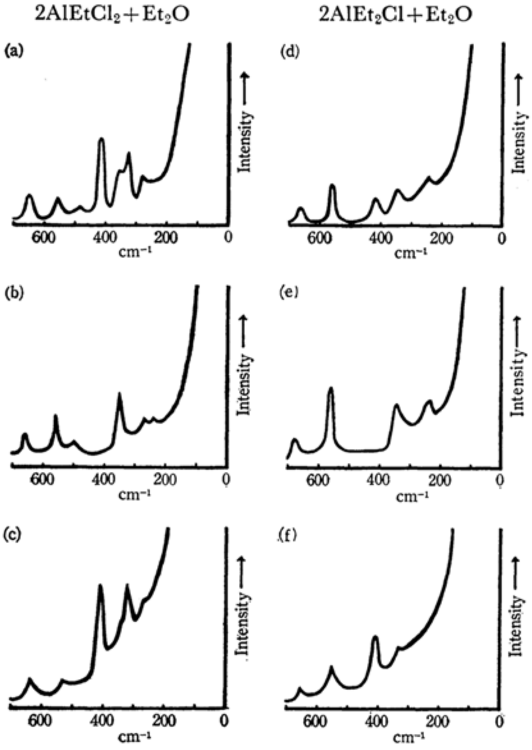

Fig. 5. The Raman spectra in the skeletal vibration region of the systems $2AlEtCl_2 + Et_2O$ (a, b, c) and $2AlEt_2Cl + Et_2O$ (d, e, f).
(a), (d): the total system
(b), (e): the lower boiling fraction
(c), (f): the higher boiling fraction

TABLE 3. THE RAMAN SPECTRA OF THE SYSTEMS $AlEt_nCl_{3-n} + AlEt_mCl_{3-m}\cdot Et_2O$ ($n, m=0, 1, 2, 3$)

System	State[*1]	Sample volume ml	Raman spectrum Figure	Raman spectrum Interpretation[*2]
$AlEtCl_2 + AlEtCl_2\cdot Et_2O$	T	3	5a (=5b+5c)	1b + 1d + 3c + 3d
$AlEtCl_2 + AlEtCl_2\cdot Et_2O$	L	3	5b	1b + 1d
$AlEtCl_2 + AlEtCl_2\cdot Et_2O$	H	6	5c	3c + 3d
$AlEt_2Cl + AlEt_2Cl\cdot Et_2O$	T	3	5d (=5e+5f)	1b + 3b
$AlEt_2Cl + AlEt_2Cl\cdot Et_2O$	L	3	5e	1b
$AlEt_2Cl + AlEt_2Cl\cdot Et_2O$	H	6	5f	3b
$AlEt_3 + AlEtCl_2\cdot Et_2O$	T	6	— (=5d)	1b + 3b
$AlEt_2Cl + AlEt_3\cdot Et_2O$	T	6	6a	1b + 3a
$AlEt_3 + AlEt_2Cl\cdot Et_2O$	T	6	— (=6a)	1b + 3a
$AlEtCl_2 + AlEt_3\cdot Et_2O$	T	6	6b (=5d)	1b + 3b
$AlCl_3 + AlEtCl_2\cdot Et_2O$	L	3	—	1d

[*1] T, the total system; L, the lower-boiling fraction of the system;
H, the higher-boiling fraction of the system.

[*2] One of the spectra shown in Fig. 1a—1d and Fig. 3a—3d or some combination of them which agrees with the spectrum of the system studied.

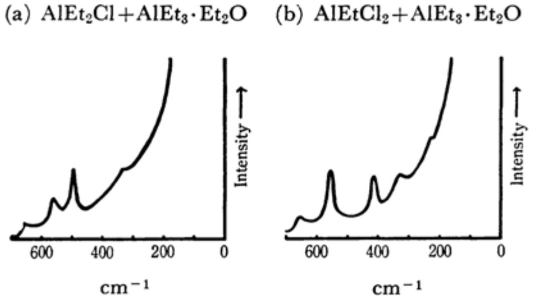

Fig. 6. The Raman spectra of the systems
(a) $AlEt_2Cl+AlEt_3\cdot Et_2O$
(b) $AlEtCl_2+AlEt_3\cdot Et_2O$.

The reverse reaction of the reaction (5), the reaction (5′), proceeds quantitatively to the right:

$$AlEt_3 + AlEtCl_2\cdot Et_2O \rightarrow AlEt_2Cl + AlEt_2Cl\cdot Et_2O \quad (5')$$

The reaction (6) does not take place at all, although Davidson and Brown reported that the analogous reaction, (6′), did take place:[11]

$$AlEt_2Cl + AlEt_3\cdot Et_2O \nrightarrow AlEt_3 + AlEt_2Cl\cdot Et_2O \quad (6)$$

$$AlMe_2Cl + AlMe_3\cdot Me_2O \rightarrow AlMe_3 + AlMe_2Cl\cdot Me_2O \quad (6')$$

The reverse reaction of the reaction (6), the reaction (6″), proceeds quantitatively to the right:

$$AlEt_3 + AlEt_2Cl\cdot Et_2O \rightarrow AlEt_2Cl + AlEt_3\cdot Et_2O \quad (6'')$$

The reactions (7) and (8) proceed quantitatively:

$$AlEtCl_2+AlEt_3\cdot Et_2O \rightarrow AlEt_2Cl + AlEt_2Cl\cdot Et_2O \quad (7)$$

$$AlCl_3+AlEtCl_2\cdot Et_2O \rightarrow AlEtCl_2 + AlCl_3\cdot Et_2O \quad (8)$$

As is apparent when one regards the redistribution reactions, (4), (5′), (6″), (7), and (8), by the reaction between $AlEt_nCl_{3-n}$ and $AlEt_mCl_{3-m}\cdot Et_2O$ ($n, m=0$, 1, 2, 3) $AlEt_2Cl$ is preferentially produced so long as there is a possibility of its formation, as in the cases of the reactions (4), (5′), (6″), and (7); if there is no possibility of $AlEt_2Cl$ formation, as in the case of the reaction (8), $AlEtCl_2$ is produced. The tendency to produce the most stable complex possible can not be observed at all. The driving force of these redistribution reactions is still uncertain. If it is postulated that the stability of a dimer of $AlEt_nCl_{3-n}$ increases in the order $(AlCl_3)_2$, $(AlEt_3)_2<(AlEtCl_2)_2<(AlEt_2Cl)_2$, the character of these redistribution reactions may be described as follows: the most stable possible dimer of $AlEt_nCl_{3-n}$ is produced.

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