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Spectroscopic Studies of Dialkylaluminum Alkoxides and the Trialkylaluminum-Ether Complex. I. Structures and Symmetries*1

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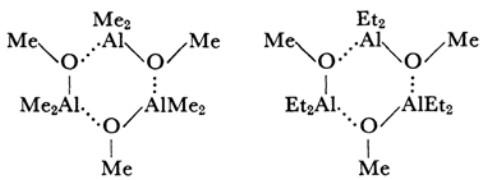
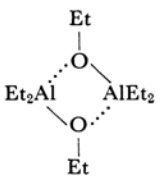
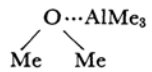
The infrared and Raman spectra of $[Al(CH_3)_2OCH_3)]_3$, $[Al(C_2H_5)_2OCH_3]_3$, $[Al(C_2H_5)_2 \cdot OC_2H_5]_2$, and $Al(CH_3)_3 \cdot (CH_3)_2O$ have been measured in the 3000—300 cm^{-1} region, and the infrared absorption bands and the Raman lines in the skeletal vibration region (720—300 cm^{-1}) have been compared. For $[Al(CH_3)_2OCH_3]_3$ and $[Al(C_2H_5)_2OCH_3]_3$, the results are consistent with trimeric structures with symmetry D_{3h}. For $[Al(C_2H_5)_2OC_2H_5]_2$, the results are consistent with a dimeric structure with symmetry V_h. Thus, the structures with the oxygen bridge proposed by Hoffmann for these polymeric compounds have been confirmed by spectroscopic measurements. The structures with alkyl bridges are very unlikely. For $Al(CH_3)_3 \cdot (CH_3)_2O$, the results do not contradict the postulated structure, with symmetry C_s.

It has been suggested, although there has been no direct experimental evidence, that dimethylaluminum methoxide $[Al(CH_3)_2OCH_3]_3$, diethylaluminum methoxide $[Al(C_2H_5)_2OCH_3]_3$, and diethylaluminum ethoxide $[Al(C_2H_5)_2OC_2H_5]_2$ have the molecular structures of the dimeric or trimeric bridge forms represented by[1,2]:





and that the trimethylaluminum - dimethyl ether complex, $Al(CH_3)_3 \cdot (CH_3)_2O$, has the structure with symmetry C_s represented by[3]:



Structures with the alkyl bridges, as in the case of trimethylaluminum, however, also appear to be possible for these three dialkylaluminum alkoxides. In the present study, in order to

*1 Presented in part at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

1) E. G. Hoffmann, *Ann.*, **629**, 104 (1960).

2) N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

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

TABLE I. DIALKYLALUMINUM ALKOXIDES AND THE TRIMETHYLALUMINUM - DIMETHYL ETHER COMPLEX

Compond	B.p., °C/mmHg	Al %		Mol. wt.	
		Calcd.	Found*1	Calcd.	Found*2
$(AlMe_2OMe)_3$*3	75.6—76.8/4	30.7	30.3	264.2	294.7
$(AlEt_2OMe)_3$	70.5—72.0/5	23.2	23.0	348.4	361.1
$(AlEt_2OEt)_2$*4	59.0/1.5	20.7	20.4	260.3	278.7
$AlMe_3 \cdot Me_2O$*4	41.5/10	22.8	22.7	118.2	121.6

*1 Analysis was carried out by volumetric method (oxine complex salt method).
*2 Molecular weights were determined by measuring freezing point depression of benzene solution; values listed are mean values of several measurements.
*3 Me=CH_3, Et=C_2H_5. These abbreviations are used throughout Tables I—II.
*4 Cited from Ref. 3.

obtain some positive evidences of these proposed structures, the infrared and Raman spectra of these three dialkylaluminum alkoxides and the trimethylaluminum - dimethyl ether complex have been measured, and the infrared absorption bands and the Raman lines in the skeletal vibration region (720—300 cm^{-1}) have been compared. Some conclusions have been reached from these spectra as to the structures of these compounds.

The infrared spectra of diethylaluminum ethoxide and the trimethylaluminum-dimethyl ether complex were reported in the previous paper,[3] but those of dimethylaluminum methoxide and diethylaluminum methoxide and the Raman spectra of these four compounds have not yet been reported as far as the author is aware.

Experimental

Dimethylaluminum methoxide was prepared by the reaction of trimethylaluminum with methanol. Diethylaluminum methoxide was prepared by the reaction of triethylaluminum with methanol. Diethylaluminum ethoxide was prepared by the reaction of triethylaluminum with ethanol. The trimethylaluminum - dimethyl ether complex was prepared by the reaction of trimethylaluminum with dimethyl ether. Table I shows the boiling points, aluminum contents, and molecular weights of these four compounds.*2

The infrared spectra were measured in the 3000—300 cm^{-1} region in the liquid state with a Japan Spectroscopic Co., Model DS-402G infrared spectrophotometer. The procedure described in the previous paper was used.[3] The Raman spectra were measured in the same region and in the liquid state with a Shimadzu GRS Raman spectrophotometer. All the samples were distilled into Raman tubes, which were then sealed off under reduced pressure to prevent contamination with air or moisture. Figure 1 shows the Raman spectra observed. The Raman spectrum of dimethylaluminum methoxide was also measured in a 10 volume per cent benzene solution. The spectrum obtained was merely a superposition of the spectrum of pure dimethylaluminum methoxide on that of benzene. No Raman line of dimethylaluminum methoxide shifted to either a higher or a lower frequency.

*2 The author is indebted to Mr. Hitoshi Shinkoda for his aluminum analysis.

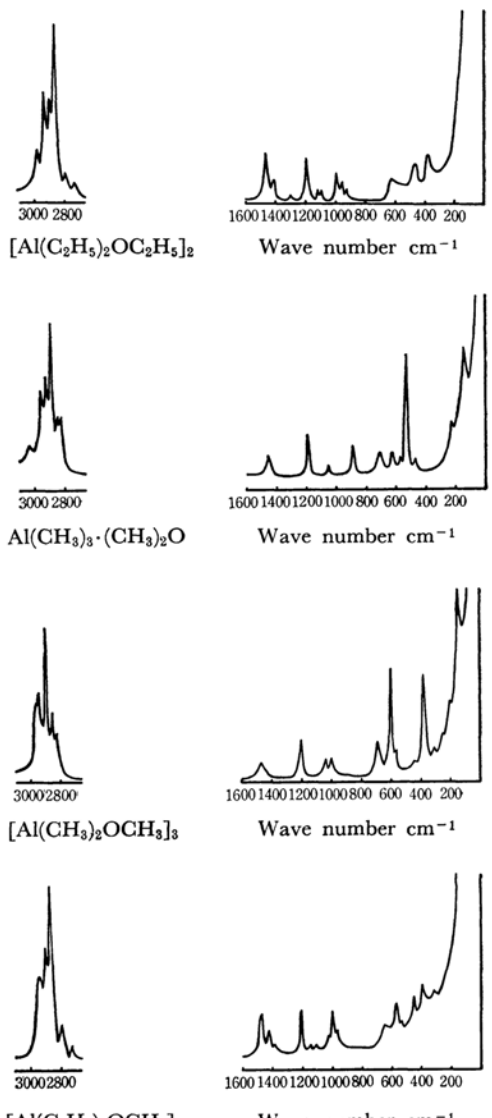


Fig. 1. The Raman spectra of dialkylaluminum-alkoxides and the trimethylaluminum - dimethyl ether complex.

TABLE II. OBSERVED FREQUENCIES OF DIALKYLALUMINUM ALKOXIDES AND THE TRIMETHYLALUMINUM-DIMETHYL ETHER COMPLEX IN cm^{-1}

$(AlMe_2OMe)_3$		$(AlEt_2OMe)_3$		$(AlEt_2OEt)_2$		$AlMe_3 \cdot Me_2O$	
Raman	IR	Raman	IR	Raman	IR*	Raman	IR*
						3035 w	3028 w
	2988 sh		2989 sh	2974 w	2977 m	2989 vw	2983 m
2953 m	2954 sh					2957 m	2953 sh
2935 m	2934 s	2937 m	2941 s	2930 m	2939 s	2926 m	2925 s
2894 s	2895 w	2897 w	2901 s	2898 w	2901 s	2887 s	2889 m
2854 m	2853 m	2865 s	2865 s	2865 s	2864 s	2842 m	2847 w
2828 w	2829 vw					2820 m	2820 vw
		2792 m	2796 m	2791 w	2791 w		
		2730 vw	2731 w	2729 w	2727 w		
					1482 w		
			1467 m		1462 sh		
1458 w	1457 m	1464 s	1454 m	1458 s	1451 s	1460 m	1462 s
		1414 m	1411 m	1410 m	1409 s		
		1381 vw	1376 w		1394 s		
				1295 w	1288 m		
	1256 vw		1254 w		1254 w		1250 w
			1223 w		1222 w		
1201 m	1200 vs	1195 s	1197 s	1193 s	1193 s	1190 m	1185 vs
		1134 vw		1118 w			1153 m
		1099 w		1084 w	1100 s		
1018 m	1019 vw	1016 vw	1019 vw		1058 vs	1052 w	1046 vs
994 w	987 vs	988 s	984 vs	990 m	985 s		
		962 vw	956 w	955 w	948 m		
			918 m	928 w	914 w		
			885 w		894 s	894 m	891 s
			848 w		806 s		
687 m	686 vs	650 m	655 vs		652 vs	716 m	710 s
	642 s		632 m	634 m		625 m	622 m
596 s		568 s				576 w	
569 vw	567 vw	536 vw	540 vw			525 vs	525 m
					481 w		
440 vw	437 m	449 w	460 m	462 m		470 w	473 m
380 s		393 s		380 m			
309 vw	305 m	339 vw	351 m				

* Data in the 2000—300 cm^{-1} region are cited from Ref. 3.

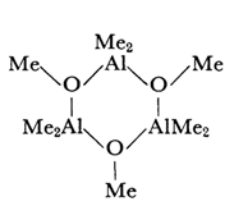
Dimethylaluminum Methoxide

Hoffmann found that this compound takes a trimeric structure in the benzene solution.[1] The similarity between the Raman spectrum in the liquid state and that in the benzene solution described above shows that the same trimeric structure remains also in the liquid state.

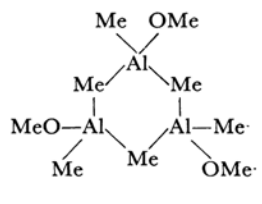
In the liquid state this compound has five infrared absorption bands and six Raman lines in the 720—300 cm^{-1} region; of those, four are both infrared and Raman active, as is shown in Table II.

There are two possible structural formulas, I and II, for this trimeric compound;

Formula I, with symmetry D_{3h}, has an oxygen bridge which would be formed by the coordination of lone-pair electrons in oxygen atoms with aluminum. Formula II, with symmetry C_{3v} or



I



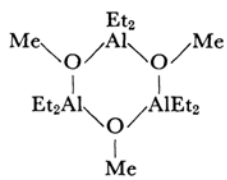
II

C_s, has an alkyl bridge which would be formed by the half bonds, as in the case of trimethylaluminum. Here the following postulations are made: the six atoms which constitute the oxygen bridge ring (model I) or the alkyl bridge ring (model II) are on a plane and occupy the six apices of a hexagon with D_{3h} symmetry; three methoxyl groups (model I) or three bridging alkyl groups (model II) lie on the ring plane, and

the plane containing two terminal alkyl groups (model I) or terminal methoxyl and alkyl groups (model II) and an aluminum atom is perpendicular to the ring plane. Model II requires that all skeletal vibrations be both infrared and Raman active. On the other hand, model I requires the skeletal vibrations of the species E′ to be both infrared and Raman active, those of the species A_2'' to be infrared active and Raman inactive, and those of the species A_1' and E″ to be infrared inactive and Raman active. The results described above support model I.

Diethylaluminum Methoxide

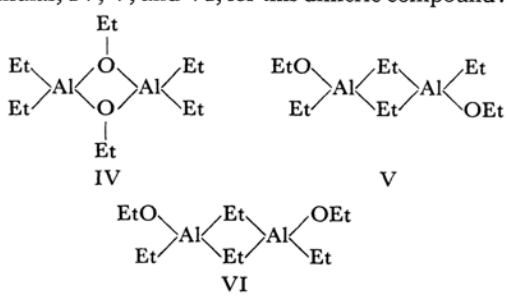
In the liquid state this trimeric compound has five infrared absorption bands and six Raman lines in the 720—300 cm^{-1} region; of these four are both infrared and Raman active, as is shown in Table II. These results are quite similar to those of dimethylaluminum methoxide. Analogous considerations lead to the conclusion that this compound is represented by the oxygen bridge model III:



III

Diethylaluminum Ethoxide

For this dimeric compound two infrared absorption bands and three Raman lines are observed in the liquid state in the 720—300 cm^{-1} region: the rule of mutual exclusion holds for these infrared absorption bands and Raman lines, as is shown in Table II. There are three possible structural formulas, IV, V, and VI, for this dimeric compound:



IV V

VI

Formula IV, with symmetry V_h, has an oxygen bridge. For diethylaluminum chloride, bromide, and iodide, a dimeric bridge structure over the halogen atoms with symmetry V_h (which corresponds to model IV) has been established by Yamamoto.[4] Formula V, with symmetry C_{2h}, corresponds to the "trans" form, in which two ethoxyl groups are present on opposite sides of the bridge plane, while formula VI, with symmetry C_{2v}, corresponds to the "cis" form, where the ethoxyl groups are on the same side of the bridge plane. In the latter two formulas, the alkyl bridge would be formed by the half bonds. Here the following postulation is made: the plane containing two terminal ethyl groups (model IV) or terminal ethoxyl and ethyl groups (models V and VI) and an aluminum atom is perpendicular to the bridge plane, as in the case of diethylaluminum halides (see also Ref. 4). The results described above eliminate the possibility of model VI, because model VI would require a majority of skeletal vibrations species (A_1, B_1, and B_2) to be both infrared and Raman active. The spectral data cannot be used to determine which of the remaining two forms, model IV and model V, exist in the liquid state, because the rule of mutual exclusion should hold for the skeletal vibrations in either case. If, however, we consider the conclusion of the preceding section that dimethylaluminum methoxide is represented by the oxygen bridge model I, model IV seems preferable.

The Trimethylaluminum - Dimethyl Ether Complex

For this complex four infrared absorption bands and five Raman lines are observed in the 720—300 cm^{-1} region; all of them are both infrared and Raman active, with the exception of a weak Raman line at 576 cm^{-1} which does not agree with any infrared band, as is shown in Table II. Though the possibility of the structure with a lower symmetry can not be eliminated, these results at least do not contradict the postulated structure with symmetry C_s.

Summary

The infrared and Raman spectra of dimethylaluminum methoxide, diethylaluminum methoxide, diethylaluminum ethoxide and the trimethylaluminum - dimethyl ether complex have been measured in the 3000—300 cm^{-1} region. For the three dialkylaluminum alkoxides, the results are consistent with the dimeric or trimeric structures with the oxygen bridge proposed by Hoffmann. For the trimethylaluminum - dimethyl ether complex, the results do not contradict the postulated structure with symmetry C_s.

The author is indebted to Professor Takehiko Shimanouchi of the University of Tokyo and to Mr. Saburo Takeda for their valuable discussions throughout this work, and to Dr. Hiroshi Suzuki of the University of Tokyo for reading the manuscript and for advice.

4) O. Yamamoto, This Bulletin, **35**, 619 (1962).