apparent. A significant difference between the two P–P bond distances would probably have been detected in the electron diffraction study.[10] Coupling between this motion and the P–C symmetric modes seems to provide a reasonable alternative. The effect of such coupling was illustrated[29] in a study of the frequencies for the P–X and P=S modes in some organophosphorus compounds. If the X substituent is a methyl group, it is found that the P–C stretch and P=S stretch interact very strongly with a "repulsion" of the two energy levels. Thus, the symmetric P–C stretch was found to be shifted by as much as 135 cm^{-1} by this type of interaction. Assuming the P–P stretch for the trans isomer is slightly higher than the 448 cm^{-1} observed for the symmetric PC_2 stretch, the interaction could shift the frequency 10 or 20 cm^{-1} resulting in the 486-cm^{-1} band which should be compared with the 455-cm^{-1} frequency observed for the P–P stretch for the *trans*-$P_2(CH_3)_4$. Similarly, the gauche isomer is expected to have a P–P stretching frequency somewhat lower than the PC_2 stretch (this mode was observed at 429 cm^{-1} in *gauche*-$P_2(CH_3)_4$) so the shift would be expected to be in the opposite direction by 10 or 20 cm^{-1} which is consistent with the observed frequency of 404 cm^{-1}. In addition, there is a shoulder on the high-frequency side of the PC_2 antisymmetric stretching mode which disappears with solidification which can be attributed to the PC_2 stretch of the *gauche* isomer. Thus the 80-cm^{-1} difference in the two P-P stretching modes may be the result from a small coupling with the phosphorus–carbon stretches.

This study reiterates the necessity of recording the vibrational spectrum in the solid state[2-8] if the presence or absence of conformers is to be determined by this technique for this type of molecule. The failure to observe a second isomer in the vibrational studies of H_2PPF_2 and $(CF_3)_2PPF_2$ seems surprising when one considers the P-P bond distance.[30] Both molecules had Raman bands near 404 cm^{-1} which were attributed to PF_2I impurity; infrared and Raman studies of the solids should be carried out to verify the presence of a single conformer for these molecules in the fluid states. Since two of the energy levels for the molecular orbitals of the X_2Y_4 molecules are highly dependent upon the molecular symmetry,[31] it may turn out that all of the unsymmetrical biphosphines will exist in only the trans conformation. Since both $P_2(CF_3)_4$ and $P_2(CH_3)_4$ were found to have appreciable concentrations of the gauche isomers, a study of the conformations of $(CH_3)_2PP(CF_3)_2$ should indicate the importance of the symmetry in the stabilization of the gauche isomer. Such studies are currently being undertaken in our laboratory.

Registry No. $(CF_3)_2PP(CF_3)_2$, 2714-60-5; $(CF_3)_2PH$, 460-96-8.

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Contribution from the Department of Polymer Science,
Faculty of Science, Osaka University, Toyonaka, Osaka, 560, Japan

Proton Magnetic Resonance Studies on Pentaalkyldialuminum Alkali Metal Oxides and Related Complexes[1]

TAKANOBU AOYAGI, TAKEO ARAKI,* NOBUKI OGUNI, and HISAYA TANI

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The nmr spectra of R_5Al_2ZM in aromatic hydrocarbon solutions can be explained by the structure of donor–acceptor type binuclear complexes of the type $[R_2AlZM][AlR_3]$ with nonequivalent Al atoms for R = Et, *i*-Bu; Z = O; M = Na, K, at the temperatures studied. This structure is also predominant for R = Et, Z = O, NPh, M = Li; R = Et, Z = S, M = Na; R = Et, Z = O, M = Cs; R = *i*-Bu, Z = O, M = Cs. However, at higher temperatures in benzene, intramolecular alkyl exchange through a cyclic intermediate is important for R = Et, Z = O, NPh, M = Li. The alkyl-exchange reaction is highly predominant for R = *i*-Bu, Z = O, NPh, M = Li. The complexes containing Cs seem to have a cyclic ionic structure. One of the factors determining the structure appears to be a combination effect of ionization energy and ionic radii of the alkali metals. The complex has weak interaction with toluene, predominantly at the Al atom of the R_2AlZM moiety. A tetrahydrofuran molecule can preferentially coordinate on the same aluminum atom.

Introduction

Recent works have shown that the reaction products of trialkylaluminums with alkali metal hydroxides[2-4] and N-substituted lithium amides[2b,3,5] in a molar ratio of 1:0.5 can be used as active catalysts for the highly stereospecific polymerization of acetaldehyde. Information about the catalyst structure in solution for the purified organoaluminum compounds obtained from the catalyst system is required in order to elucidate the stereocontrolling factor of the polymerization reaction. Synthetic studies[6] have indicated that the series of organoaluminum products can be rationalized as donor-ac-

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[1] The investigation on the oxygen analogs constitutes a part of the Ph.D. thesis of Dr. T. Aoyagi, Osaka University, 1967.

[2] (a) H. Tani, T. Aoyagi and T. Araki, *J. Polym. Sci., Part B*, 2, 921 (1964); (b) H. Tani, T. Araki, N. Oguni, and T. Aoyagi, *ibid.*, 4, 97 (1966).

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[5] H. Tani and N. Oguni, *J. Polym. Sci., Part B*, 3, 123 (1965).

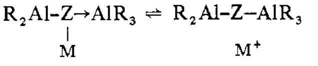
[6] T. Aoyagi, T. Araki, N. Oguni, M. Mikumo, and H. Tani, *Inorg. Chem.*, in press.

Table I. Nmr Spectral Data of Pentaethyldialuminum Sodiooxide, $[Et_2AlONa][AlEt_3]^a$

Solvent	Temp, °C	$CH_2{}^C$	$CH_2{}^A$	$CH_3{}^D$	$CH_3{}^B$	$\Delta\delta_{CH_3}$,[b] Hz	$\Delta\delta_{CH_2}$,[c] Hz	$\Delta\delta_{CH_3\text{-}CH_2}$, Hz: $\lvert\delta_{CH_3}{}^D - \delta_{CH_2}{}^C\rvert$	$\Delta\delta_{CH_3\text{-}CH_2}$, Hz: $\lvert\delta_{CH_3}{}^B - \delta_{CH_2}{}^A\rvert$
PhH	35	6 H, −0.77 ppm, quartet	4 H, −0.95 ppm, quartet	9 H, 0.84 ppm, triplet	6 H, 0.66 ppm, triplet	+11	+11.5	97	97
PhH	60	6 H, −0.79 ppm, quartet	4 H, −0.95 ppm, quartet	9 H, 0.80 ppm, triplet	6 H, 0.66 ppm, triplet	+9.5	+10	95.5	96
PhH	70	6 H, −0.82 ppm, quartet	4 H, −0.98 ppm, quartet	9 H, 0.77 ppm, triplet	6 H, 0.63 ppm, triplet	+8.5	+9	95	95.5
PhH	80	6 H, −0.82 ppm, quartet	4 H, −0.97 ppm, quartet	9 H, 0.76 ppm, triplet	6 H, 0.62 ppm, triplet	+8	+8	95	95
PhMe	−38	6 H, −0.82 ppm, quartet	4 H, −1.08 ppm, quartet	9 H, 0.84 ppm, triplet	6 H, 0.64 ppm, triplet	+12	+15.5	99.5	104
PhMe	0	6 H, −0.63 ppm, quartet	4 H, −0.86 ppm, quartet	9 H, 1.00 ppm, triplet	6 H, 0.82 ppm, triplet	+10.5	+13	98	103.5
PhMe	35	6 H, −0.65 ppm, quartet	4 H, −0.78 ppm, quartet	9 H, 0.96 ppm, triplet	6 H, 0.85 ppm, triplet	+7	+9	96	97
PhMe	60	6 H, −0.64 ppm, quartet	4 H, −0.77 ppm, quartet	9 H, 0.95 ppm, triplet	6 H, 0.84 ppm, triplet	+6.3	+8.5	95	97
PhMe	80	6 H, −0.57 ppm, quartet	4 H, −0.70 ppm, quartet	9 H, 1.02 ppm, triplet	6 H, 0.92 ppm, triplet	+6	+8	95	96.5
PhMe	100	6 H, −0.47 ppm, quartet	4 H, −0.58 ppm, quartet	9 H, 1.11 ppm, triplet	6 H, 1.02 ppm, triplet	+5.5	+7	94.2	96
PhH-THF[d]	35	6 H, −0.70 ppm, quartet	4 H, −0.86 ppm, quartet	9 H, 0.86 ppm, triplet	6 H, 0.71 ppm, triplet	+9.5	+9.2	94.5	94.0
PhH-THF[e]	35	6 H, −0.55 ppm, quartet	4 H, −0.59 ppm, quartet	9 H, 0.92 ppm, triplet	6 H, 0.83 ppm, triplet	+5.5	+1.5	88.5	84.5
PhH-THF[e]	60	10 H, −0.46 ppm, quartet		9 H, 1.03 ppm, triplet	6 H, 0.96 ppm, triplet	+5	±1	89	84
PhH-THF[e]	70	10 H, −0.38 ppm, quartet		9 H, 1.27 ppm, triplet	6 H, 1.04 ppm, triplet	+4.5	±1	89	84.5

[a] $J_{AB} = J_{CD} = 7.5$ Hz. [b] $\Delta\delta_{CH_3} = \delta_{CH_3}{}^B - \delta_{CH_3}{}^D$. [c] $\Delta\delta_{CH_2} = \delta_{CH_2}{}^A - \delta_{CH_2}{}^C$. [d] $[Et_2AlONa][AlEt_3]$:THF = 4:1 (mol/mol). [e] $[Et_2AlONa][AlEt_3]$:THF = 1:1 (mol/mol).

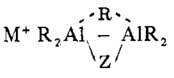
ceptor type binuclear complex compounds $[R_2AlZM][AlR_3]$ (1), where Z = O, NR′, or S and M = alkali metal. One of the other possible structures, *i.e.*, ate complexes of the type $[RM][R_2AlZAlR_2]$, was excluded because attempts to prepare the complex from bis(diethylaluminum) oxide[7] and ethyllithium gave only Et_4AlLi in a very low yield. The third possible structure, which is ionic in nature, $M^+[R_2AlZAlR_3]^-$,[8] is acceptable when a polarization equilibrium is considered[9]



$$\underset{\mathbf{1}}{R_2Al\text{-}\underset{\substack{|\\M}}{Z}\text{→}AlR_3} \rightleftharpoons \underset{\mathbf{2}}{R_2Al\text{-}Z\text{-}\bar{A}lR_3 \quad M^+}$$

1 2

On assuming complete dissociation, the structure of the anion can be compared with the dimer structure of trialkylaluminums. The most plausible ionic structure 2 is one where the anion is stabilized by formation of a cyclic conjugated anion involving a bridged alkyl group (**2a**).



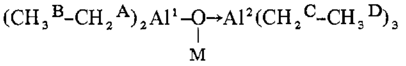
2a

When the bond angle of Al-Z→Al is relatively small, the nonionic complex **1** can also have a similar cyclic structure **1c** (see a later section). These cyclized states would give equivalent alkyl signals in their nmr spectrum under conditions where rapid alkyl exchanging occurs, *e.g.*, at higher temperature. In contrast, the open complex **1** would show nonequivalent alkyl signals in a 2:3 ratio.

This report is concerned with nmr spectroscopic studies on the individual binuclear organoaluminum complexes in aromatic hydrocarbons, in order to estimate the predominant structures and to examine the possibility of coordination of added donor molecules to the complexes.

Results and Discussion

Pentaethyldialuminum Sodiooxide, $[Et_2AlONa][AlEt_3]$. The nmr spectra of this complex at 60 and 100 MHz in benzene at room temperature are shown in Figures 1a and 1b, respectively. Finely resolved signals can readily be analyzed to be CH_3-C double triplets (signal groups at lower field) and CH_2-Al double quartets (signal groups at higher field). Assignments of signals are listed in Table I where notations of protons are based on the formula



$$(CH_3{}^B\text{-}CH_2{}^A)_2Al^1\text{-}\underset{\substack{|\\M}}{O}\text{→}Al^2(CH_2{}^C\text{-}CH_3{}^D)_3$$

The triplet at the lower field (centered at ~0.8 ppm) can be due to H^D protons and that at higher field (centered at ~0.6 ppm) to H^B protons, because the relative intensity of these triplets is nearly equal to 3:2. Similarly, the two quartets, one at higher field (centered at ~−1.0 ppm) and one at lower field (centered at ~−0.8 ppm), can be assigned to H^A protons and H^C protons, respectively. These results can reasonably be interpreted based on the type-**1** structure containing nonequivalent alkyl groups. The fact that H^A protons are observed at higher field than H^C protons indicates the electron density on the Al^1 atom is lower than that on the Al^2 atom.

A somewhat different spectrum was observed in toluene (Figure 1c); the methyl signal group was composed of a quartet and that of the methylene signal a quintet. The spectra

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[7] H. Tani, T. Araki, N. Oguni, and N. Ueyama, *J. Amer. Chem. Soc.*, 89, 173 (1967).

[8] K. Ziegler in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold, New York, N. Y., 1960, p 206.

[9] The facts that dissociation of the complex containing a sulfur atom (1, Z = S) occurs[6] readily to result in R_2AlSNa and AlR_3 and that R_4AlM is not produced from R_5Al_2ZM exclude a possibility of dissociation where R^- and M^+ are formed simultaneously: $R_5Al_2ZM \rightleftharpoons R^- + M^+ + R_2AlZAlR_2$.

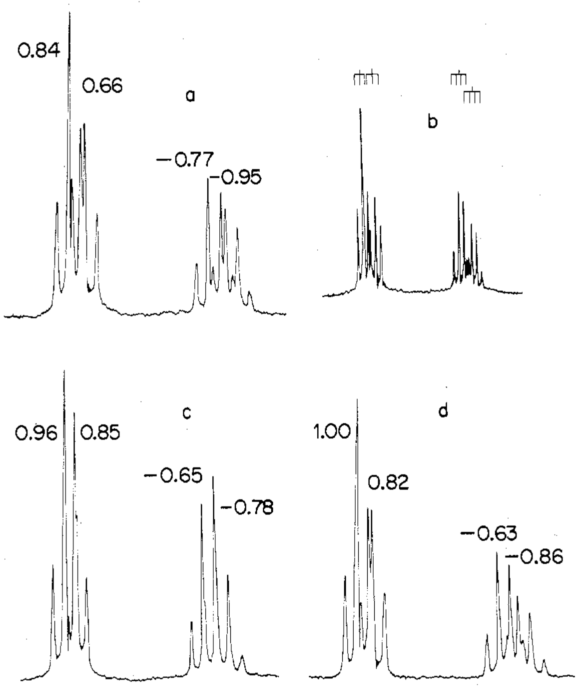
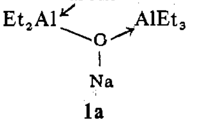


Figure 1. Nmr spectra of [Et_2AlONa][$AlEt_3$]: (a) 60 MHz, in benzene at 35°; (b) 100 MHz, in benzene at 35°; (c) 60 MHz, in toluene at 35°; (d) 60 MHz, in toluene at 0°.

can be analyzed as double triplets and double quartets of the same coupling constant, respectively. This was confirmed by lowering the temperature to 0°. The methyl quartet was resolved into a sextet (double triplets) and the methylene quintet into an octet (double quartets) (Figure 1d). In the whole range of temperatures studied, only the spectra due to the type-**1** structure were observed.

More detailed information in relating the solvent effect on the organoaluminums can be obtained by using values of internal chemical shift: $\Delta\delta_{CH_3}$ ($=\delta_{CH_3{}^B} - \delta_{CH_3{}^D}$), $\Delta\delta_{CH_2}$ ($=\delta_{CH_2{}^A} - \delta_{CH_2{}^C}$), $\Delta\delta_{(CH_3\text{-}CH_2)_1}$ ($=\delta_{CH_3{}^D} - \delta_{CH_2{}^C}$), and $\Delta\delta_{(CH_3\text{-}CH_2)_2}$ ($=\delta_{CH_3{}^B} - \delta_{CH_2{}^A}$) (Table I). In benzene solution $\Delta\delta_{CH_3}$ and $\Delta\delta_{CH_2}$ increased slightly (~3.5 Hz) with lowering of temperature, accompanied by slight increase (~2 Hz) in $\Delta\delta_{(CH_3\text{-}CH_2)}$'s. Analogous trends were also observed in toluene solution. Increases in $\Delta\delta_{CH_2}$ and $\Delta\delta_{(CH_3\text{-}CH_2)_1}$ were larger than those of $\Delta\delta_{CH_3}$ and $\Delta\delta_{(CH_3\text{-}CH_2)_2}$, respectively. This indicates that the strongest solvent effect is exerted upon the H^A protons which are attached to the Al^1 atom of lower electron density. The organoaluminum molecule would be surrounded by toluene molecules under a weak interaction.[10] This is indicated by the existence of more or less shielding effect on all of the protons at lower temperatures. Our results suggest that the concentration of toluene molecule is higher around the Al^1 atom than at the Al^2 atom. For convenience, we prefer to formulate this as a structure **1a**.[11]



1a

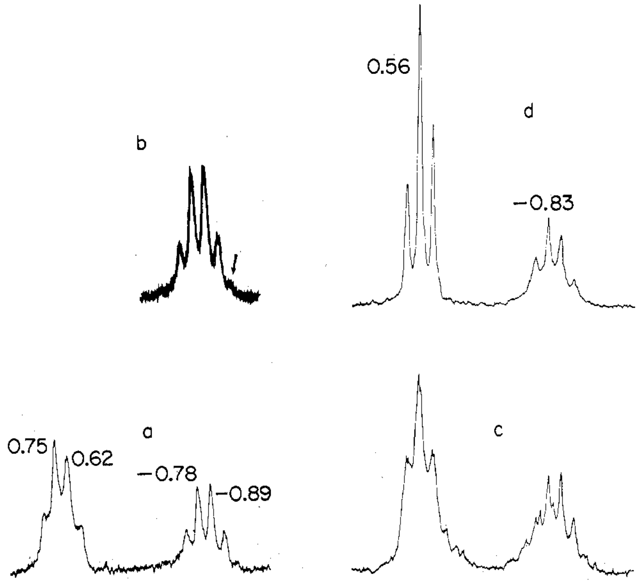
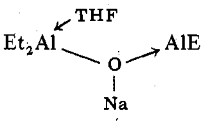


Figure 2. Nmr spectra of [Et_2AlOLi][$AlEt_3$]: (a) in toluene-d_8 at 35°; (b) confirmation of quintet in CH_2-Al protons; recorded with five scans on a Varian T-60 spectrometer under unlocked condition; (c) in benzene at 35°; (d) in benzene at 80°.

Addition of 1 molar equiv of tetrahydrofuran to [Et_2AlONa][$AlEt_3$] in benzene resulted in a remarkable downfield shift of the $CH_2{}^A$ protons (Tables I and II). This can be due to an increase in the electron density on the Al^1 atom by coordination of a tetrahydrofuran molecule preferentially on the atom (**1b**). Even at higher temperature no further significant shift was observed. Formation of a complex between these molecules without any serious skeletal changes in the binuclear aluminum structure is thereby suggested. A_2X_2 resonances due to tetrahydrofuran protons were retained after coordination. This indicates that ring opening[12,13] of tetrahydrofuran is not involved in the system.



1b

Pentaethyldialuminum Lithiooxide, [Et_2AlOLi][$AlEt_3$]. For this compound a satisfactory nmr spectrum was obtained when the sample was prepared under a vacuum,[14] rather than prepared under argon atmosphere. Figure 2a shows its spectrum (in toluene-d_8), in which the methyl protons consisted of a quartet and the methylene protons of a quintet, respectively. Low solubility of the compound in toluene caused some ambiguity in the methylene signals, but the quintet could be detected by a five-scanned recording (Figure 2b). By the aid of spin-tickling techniques, the spectrum can be analyzed as for a type-**1** structure (Table II). The pattern of the spectrum, which is unchanged up to 60°, is quite similar to that of [Et_2AlONa][$AlEt_3$] in toluene.

In benzene, multiplicity (due essentially to type-**1** structure) in the spectrum at room temperature (Figure 2c) converted into a single methyl triplet and a single methylene quartet at 60-80° (Figure 2d). This is rationalized in terms of equivalent ethyl groups at higher temperature, presumably due to rapid intramolecular alkyl exchange through bridging between

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(10) Since steep increases in $\Delta\delta CH_2$ and $\Delta\delta CH_3$ were observed below 35°, the solvent effect can be related with coordination—presumably π-electron donation—of the toluene molecule with the organoaluminum complex.

(11) This type of interaction of an aromatic compound (toluene > benzene, in this case) with the organoaluminum complex may be responsible for the observation that the last *ca.* 1 molar equiv of aromatic solvent was difficult to remove under reduced pressure.

(12) E. C. Ashby and W. E. Foster, *J. Amer. Chem. Soc.*, 88, 3248 (1966).

(13) P. C. Keller, *Inorg. Chem.*, 11, 256 (1972).

(14) S. Tachibana, M.Sc. Thesis, Osaka University, 1970.

Table II. Nmr Spectral Data of Pentaethyldialuminum Lithiooxide, $[\mathrm{Et_2AlOLi}][\mathrm{AlEt_3}]$[a]

Solvent	Temp, °C	$\mathrm{CH_2}^{\mathrm{C}}$	$\mathrm{CH_2}^{\mathrm{A}}$	$\mathrm{CH_3}^{\mathrm{D}}$	$\mathrm{CH_3}^{\mathrm{B}}$	$\Delta\delta_{\mathrm{CH_3}}$,[b] Hz	$\Delta\delta_{\mathrm{CH_2}}$,[c] Hz	$\Delta\delta_{\mathrm{CH_3-CH_2}}$, Hz: $\lvert\delta_{\mathrm{CH_3}}{}^{\mathrm{D}} - \delta_{\mathrm{CH_2}}{}^{\mathrm{C}}\rvert$	$\Delta\delta_{\mathrm{CH_3-CH_2}}$, Hz: $\lvert\delta_{\mathrm{CH_3}}{}^{\mathrm{B}} - \delta_{\mathrm{CH_2}}{}^{\mathrm{A}}\rvert$
PhH	35	6 H, −0.78 ppm, multiplet	4 H, −0.83 ppm	9 H, 0.63 ppm, multiplet	6 H, 0.60 ppm	+2	+5	85	85.5
PhH	60	10 H, −0.78 ppm, quartet		15 H, 0.62 ppm, triplet		0	0	83.5	83.5
PhH	70	10 H, −0.86 ppm, quartet		15 H, 0.53 ppm, triplet		0	0	83.5	83.5
PhH	80	10 H, −0.83 ppm, quartet		15 H, 0.56 ppm, triplet		0	0	83.5	83.5
PhMe	−50	6 H, −0.97 ppm, quartet	4 H, −1.07 ppm, quartet	9 H, 0.65 ppm, triplet	6 H, 0.50 ppm, triplet	+9	+6	97	94
PhMe	−30	6 H, −0.89 ppm, quartet	4 H, −0.98 ppm, quartet	9 H, 0.71 ppm, triplet	6 H, 0.58 ppm, triplet	+7	+5.5	95	94
PhMe-d_8	35	6 H, −0.78 ppm, quartet	4 H, −0.89 ppm, quartet	6 H, 0.75 ppm, triplet	6 H, 0.62 ppm, triplet	+8	+8	92	92
PhMe-d_8	80	6 H, −0.53 ppm, quartet	4 H, −0.60 ppm, quartet	9 H, 0.79 ppm, triplet	6 H, 0.74 ppm, triplet	+2.5	+4	89.5	81
THF	−30	6 H, −0.77 ppm, quartet	4 H, −0.71 ppm, quartet	15 H, 0.63 ppm, triplet		±1	−3.5	83.5	80
THF	0	6 H, −0.68 ppm, quartet	4 H, −0.61 ppm, quartet	15 H, 0.73 ppm, triplet		±1	−3.5	84	80

[a] $J_{\mathrm{AB}} = J_{\mathrm{CD}} = 7.5$ Hz. [b] $\Delta\delta_{\mathrm{CH_3}} = \delta_{\mathrm{CH_3}}{}^{\mathrm{B}} - \delta_{\mathrm{CH_3}}{}^{\mathrm{D}}$. [c] $\Delta\delta_{\mathrm{CH_2}} = \delta_{\mathrm{CH_2}}{}^{\mathrm{A}} - \delta_{\mathrm{CH_2}}{}^{\mathrm{C}}$.

Table III. Nmr Spectral Data of Pentaethyldialuminum Compounds, $[\mathrm{Et_2AlZM}][\mathrm{AlEt_3}]$[a]

Z	M	Solvent	Temp, °C	$\mathrm{CH_2}^{\mathrm{C}}$	$\mathrm{CH_2}^{\mathrm{A}}$	$\mathrm{CH_3}^{\mathrm{D}}$	$\mathrm{CH_3}^{\mathrm{B}}$	$\Delta\delta_{\mathrm{CH_3}}$,[b] Hz	$\Delta\delta_{\mathrm{CH_2}}$,[c] Hz	$\Delta\delta_{\mathrm{CH_3-CH_2}}$, Hz: $\lvert\delta_{\mathrm{CH_3}}{}^{\mathrm{D}} - \delta_{\mathrm{CH_2}}{}^{\mathrm{C}}\rvert$	$\Delta\delta_{\mathrm{CH_3-CH_2}}$, Hz: $\lvert\delta_{\mathrm{CH_3}}{}^{\mathrm{B}} - \delta_{\mathrm{CH_2}}{}^{\mathrm{A}}\rvert$
O	K	PhH	35	6 H, −0.73 ppm, quartet	4 H, −0.89 ppm, quartet	9 H, 0.88 ppm, triplet	6 H, 0.77 ppm, triplet	+7.5	+10	96.5	99.5
O	Cs	PhH	35	6 H, −0.45 ppm, quartet	4 H, −0.39 ppm, quartet	9 H, 1.10 ppm, triplet	6 H, 1.07 ppm, triplet	+1.5	−3.5	92	86.5
NPh	Li	PhH	70	10 H, −0.68 ppm, quartet		15 H, 0.61 ppm, triplet		0	0	78	78
S	Na	PhH	35	10 H, 0.15 ppm, quartet (broad)		15 H, 1.40 ppm, triplet (sharp)		0	±2–3	75	75

[a] $J_{\mathrm{AB}} = J_{\mathrm{CD}} = 7.5$ Hz. [b] $\Delta\delta_{\mathrm{CH_3}} = \delta_{\mathrm{CH_3}}{}^{\mathrm{B}} - \delta_{\mathrm{CH_3}}{}^{\mathrm{D}}$. [c] $\Delta\delta_{\mathrm{CH_2}} = \delta_{\mathrm{CH_2}}{}^{\mathrm{A}} - \delta_{\mathrm{CH_2}}{}^{\mathrm{C}}$.

two aluminum atoms. The lower value of $\Delta\delta_{(\mathrm{CH_3}-\mathrm{CH_2})}$ of this compound in benzene, compared with that in toluene, corresponds to the increase in the electron density[15] of the aluminum atoms in the former solution. The increase in the electron density can be related to the intramolecular coordination of the alkyl group. Since toluene has higher basicity than benzene,[16] toluene molecules interact with the aluminum atoms more strongly than benzene molecules do. As a result, intramolecular alkyl bridging in the organoaluminum compound would be considerably hindered in toluene.

Upon addition of tetrahydrofuran, a pronounced downfield shift of $\mathrm{CH_2}^{\mathrm{A}}$ protons, which resulted in inversion in the sign of $\Delta\delta_{\mathrm{CH_2}}$, and a decrease in $\Delta\delta_{(\mathrm{CH_3}-\mathrm{CH_2})}$ (Table II) were observed. These observations are quite similar to the case above and can also be interpreted in terms of coordination of the tetrahydrofuran molecule at the Al^1 atom. Since there was no significant change in the values of internal chemical shift with lowering of temperature, further coordination of tetrahydrofuran molecules would not be involved.

Pentaethyldialuminum Potassiooxide, $[\mathrm{Et_2AlOK}][\mathrm{AlEt_3}]$. The nmr spectrum of this compound in benzene at room temperature resembles those of $[\mathrm{Et_2AlONa}][\mathrm{AlEt_3}]$ and $[\mathrm{Et_2AlOLi}][\mathrm{AlEt_3}]$ in toluene; *i.e.*, the methyl protons and the methylene protons showed as a quartet and a quintet, respectively. This pattern can be analyzed on the basis of a type-**1** structure as the latter cases (Table III).

Pentaethyldialuminum Cesiooxide, $[\mathrm{Et_2AlOCs}][\mathrm{AlEt_3}]$. At room temperature in benzene, a single methyl triplet and two methylene quartets were observed (Table III). A type-**1** structure can be deduced, in which the electron density on the two aluminum atoms in the molecule differs only slightly. Close similarity in the electron density of the two aluminums suggests a possibility that this compound may be converted into an ionic type-**2a** structure rather readily.

The ionic radii and ionization energies of the alkali metals[17] (Table IV) appear to exert an effect on the structure of $[\mathrm{Et_2AlOM}][\mathrm{AlEt_3}]$ in aromatic hydrocarbon solutions. Concerning the alkali metals whose ionization energies are higher than 100 kcal/mol (Li, Na, K), only the compound containing lithium (the metal having the smallest radius) showed an indication of a cyclic structure. It is not reasonable to consider that a compound containing lithium (the metal having the highest ionization energy) has an ionic structure, while the compounds containing sodium or potassium (metals having lower ionization energies) have a nonionic structure. We prefer, alternatively, the idea that the intramolecular bridging of the ethyl group is hindered with the increasing radii of the alkali metals. On this basis, a nonionic structure **1c** seems more plausible.[18,19] Although an attempt to determine the conductivity of $[\mathrm{Et_2AlOLi}][\mathrm{AlEt_3}]$ resulted in failure be-

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(15) E. G. Hoffmann, *Z. Anal. Chem.*, 170, 177 (1959); T. Takeshita and W. E. Frankle, *Tetrahedron Lett.*, 5913 (1968); K. Hatada and H. Yuki, *ibid.*, 213 (1968).

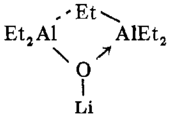
(16) For example, H. C. Brown and J. D. Brady, *J. Amer. Chem. Soc.*, 74, 3570 (1952).

(17) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, pp 96, 526.

Table IV. Ionization Energy and Ionic Radii of Alkali Metals[17]

	Ionization energy, kcal/mol	Ionic radii (M^+), Å
Li	125.8	0.607
Na	120.0	0.958
K	101.6	1.331
Cs	91.3	1.656

cause of its very low conductivity, this fact may support the assumption of a nonionic structure. For the compounds containing cesium (the metal having the lowest ionization energy), on the other hand, the possibility of an ionic structure appears to be reasonable.



1c

Pentaethyldialuminum Lithioanilide, $[Et_2AlNPhLi][AlEt_3]$. The nmr spectrum of this compound varied with temperature similarly to the case of $[Et_2AlOLi][AlEt_3]$ in benzene (Figure 3). The discussion for the latter compound can be applied. However, the internal chemical shift $\Delta\delta_{(CH_3-CH_2)}$ was smaller in the nitrogen compound by a value of *ca.* 20 Hz than in the oxygen compound. This difference may be due to a combination of the deshielding effect of the phenyl group attached to the N atom and the electronic effect associated with the higher electron density on the Al atom of this compound.

Bond angles in metal-X-metal alternating structures have been determined for $Me_3SiNHSiMe_3$ (131°) and $Me_3SiOSiMe_3$ (150°) by Kriegsmann.[20] It is reasonable to assume that the Al-N→Al bond angle is smaller than that of Al-O→Al, when the tetragonal configuration of the nitrogen atom is compared with the trigonal configuration of the oxygen. A decrease in the bond angle would be advantageous for intramolecular alkyl bridging,[21] by which the electron density on the Al^2 atom would be decreased and in turn that on Al^1 would be increased.

Pentaethyldialuminum Sodiosulfide, $[Et_2AlSNa][AlEt_3]$.[24] The characteristic feature of the spectrum of this compound in benzene (*ca.* 10% solution) is that the methylene signals are broadened in contrast with the sharp triplet of the methyl signal. The broadening of the methylene signal may be due to slight differences in the electron densities of the two Al atoms. This analysis may suggest a type-**1** structure. For this compound there is neither an origin of intramolecular deshielding effect by the phenyl group nor a structural requirement for increased bending in the Al-S→Al bond. In this respect, the low $\Delta\delta_{(CH_3-CH_2)}$ value may be ascribed to an effect by the electrons around the sulfur atom. A similar effect of a sulfur atom has been observed for the compounds $(C_2H_5)_nX$, where X = O, N, and S, in studies on the relationship between chemical shift and electronegativity of X.[25,26]

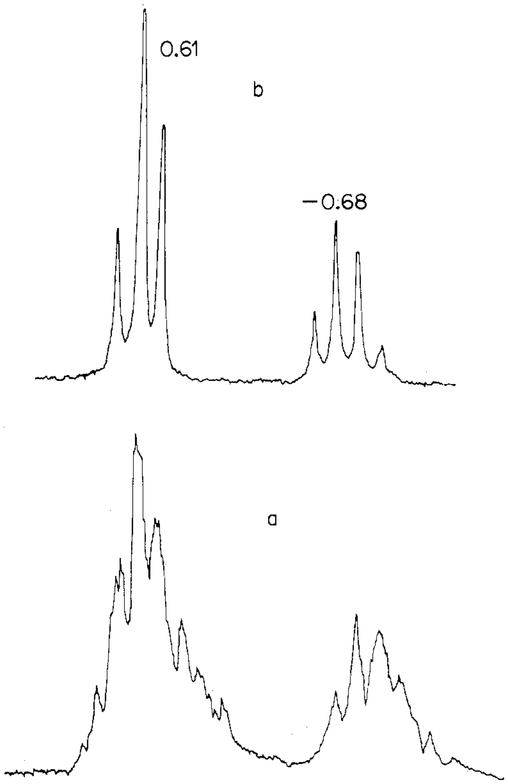


Figure 3. Nmr spectra of $[Et_2AlNPhLi][AlEt_3]$: (a) in benzene at 35°; (b) in benzene at 70°.

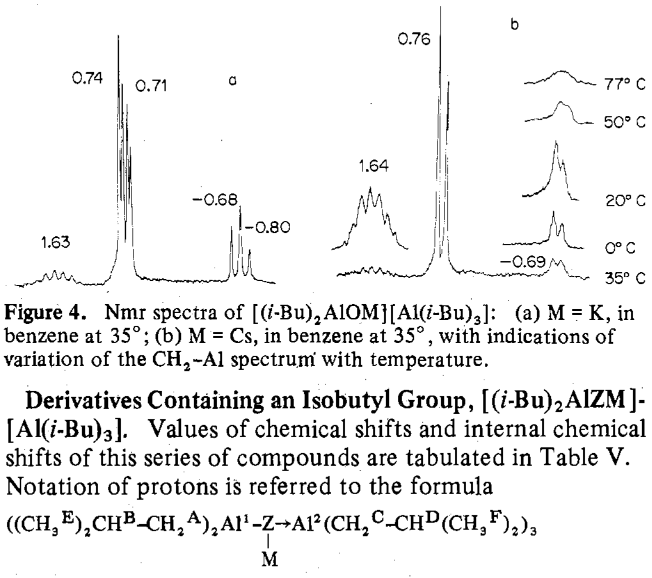
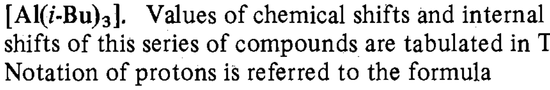


Figure 4. Nmr spectra of $[(i\text{-}Bu)_2AlOM][Al(i\text{-}Bu)_3]$: (a) M = K, in benzene at 35°; (b) M = Cs, in benzene at 35°, with indications of variation of the CH_2-Al spectrum with temperature.

Derivatives Containing an Isobutyl Group, $[(i\text{-}Bu)_2AlZM]$-$[Al(i\text{-}Bu)_3]$. Values of chemical shifts and internal chemical shifts of this series of compounds are tabulated in Table V. Notation of protons is referred to the formula



$$((CH_3{}^{E})_2CH^{B}\text{-}CH_2{}^{A})_2Al^1\text{-}\underset{\displaystyle M}{\underset{|}{Z}}\rightarrow Al^2(CH_2{}^{C}\text{-}CH^{D}(CH_3{}^{F})_2)_3$$

In cyclohexane-benzene solution the nmr spectrum of $[(i\text{-}Bu)_2AlONa][Al(i\text{-}Bu)_3]$ was analyzed as a type-**1** structure. On increasing the concentration of benzene, a most remarkable increase in the internal chemical shift was observed with respect to the A protons. This observation can be rationalized when the interaction of benzene molecules with the Al^1 atom is assumed to be the strongest.

The nmr spectrum of $[(i\text{-}Bu)_2AlOLi][Al(i\text{-}Bu)_3]$ in benzene at room temperature showed a simple pattern of isobutyl protons, while that of $[(i\text{-}Bu)_2AlOK][Al(i\text{-}Bu)_3]$ (Figure 4a) showed a double pattern due to a type-**1** structure at temperatures 35-77°. The methylene signal of $[(i\text{-}Bu)_2AlOCs]$[Al-

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(18) Slow alkyl-exchange processes were detected in a study of the reaction of the complexes with acetaldehyde below room temperature.[19]

(19) T. Araki, K. Hayakawa, T. Aoyagi, Y. Nakano, and H. Tani, *J. Org. Chem.*, in press.

(20) H. Kriegsmann, *Z. Elektrochem.*, 61, 1088 (1957).

(21) For compounds having mixed bridging alkyl groups in relation to N or O compounds, see ref 22 and 23, respectively.

(22) V. R. Magnuson and G. D. Stucky, *J. Amer. Chem. Soc.*, 91, 2544 (1969).

(23) E. C. Ashby, J. Laemmle, and G. E. Parris, *J. Organometal. Chem.*, 19, P24 (1969).

(24) M. Mikumo, M.Sc. Thesis, Osaka University, 1966.

(25) P. T. Narasimhan and M. T. Rogers, *J. Amer. Chem. Soc.*, 82, 5983 (1960).

(26) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 35, 722 (1961).

Table V. Nmr Spectral Data of Pentaisobutyldialuminum Compounds $[(i\text{-Bu})_2AlZM][Al(i\text{-Bu})_3]$[a]

Z	M	Solvent	Temp, °C	CH_3^F	CH_3^E	CH_2^C	CH_2^A	CH^{B+D}	$\Delta\delta_{CH_3}$,[b] Hz	$\Delta\delta_{CH_2}$,[c] Hz	$\Delta\delta_{CH_3-CH_2}$, Hz: $\lvert\delta_{CH_3}{}^C - \delta_{CH_3}{}^F\rvert$	$\Delta\delta_{CH_3-CH_2}$, Hz: $\lvert\delta_{CH_3}{}^A - \delta_{CH_2}{}^E\rvert$
O	Na	CH-PhH[d]	35	18 H, 0.81 ppm, doublet	12 H, 0.86 ppm, doublet	6 H, −0.51 ppm, doublet	4 H, −0.56 ppm, doublet	5 H, 1.71 ppm, multiplet	−3	+3	79.5	85.5
O	Na	CH-PhH[e]	35	18 H, 0.77 ppm, doublet	12 H, 0.81 ppm, doublet	6 H, −0.62 ppm, doublet	4 H, −0.74 ppm, doublet	5 H, 1.60 ppm, multiplet	−3	+7	83.5	93.5
O	Na	CH-PhH[f]	35	30 H, 0.70 ppm, doublet		6 H, −0.79 ppm, doublet	4 H, −1.00 ppm, doublet	5 H, 1.54 ppm, multiplet	0	+13	88.5	101.5
O	Na	PhH-THF[g]	35	18 H, 0.82 ppm, doublet	12 H, 0.84 ppm, doublet	6 H, −0.24 ppm, doublet	4 H, −0.21 ppm, doublet	5 H, 1.88 ppm, multiplet	−1.5	−2	63.5	62.5
O	Li	PhH	35	30 H, 0.51 ppm, doublet		10 H, −0.86 ppm, doublet		5 H, 1.20 ppm, sextet	0	0	82.5	82.5
O	K	PhH	35	18 H, 0.74 ppm, doublet	12 H, 0.71 ppm, doublet	6 H, −0.68 ppm, doublet	4 H, −0.80 ppm, doublet	5 H, 1.63 ppm, multiplet	+2	+7	85	90
O	K	PhH	77	18 H, 0.68 ppm, doublet	12 H, 0.64 ppm, doublet	6 H, −0.69 ppm, doublet	4 H, −0.80 ppm, doublet	5 H, 1.58 ppm, multiplet	+2.5	+6.5	82.5	86.5
O	K	PhH-THF[g]	35	18 H, 0.84 ppm, doublet	12 H, 0.86 ppm, doublet	6 H, −0.24 ppm, doublet	4 H, −0.20 ppm, doublet	5 H, 1.88 ppm, multiplet	−2	−1.5	64.5	63.5
O	Cs	PhH	35	30 H, 0.76 ppm, doublet (sharp)		10 H, −0.69 ppm, doublet (broad)		5 H, 1.64 ppm, multiplet	0	2	87.5	87.5
O	Cs	PhH	77	30 H, 0.74 ppm, doublet (sharp)		10 H, −0.64 ppm, singlet (broad)		5 H, 1.64 ppm, multiplet	0	?	84	84
NPh	Li	PhH	35	30 H, 0.49 ppm, doublet		10 H, −0.91 ppm, doublet		5 H, 1.10 ppm, sextet	0	0	83.5	83.5

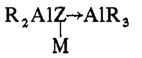
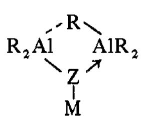
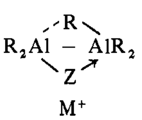
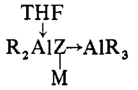
[a] $J_{AB} = J_{CD} = J_{BE} = J_{DF} = 6.5$ Hz. [b] $\Delta\delta_{CH_3} = \delta_{CH_3}{}^E - \delta_{CH_3}{}^F$. [c] $\Delta\delta_{CH_2} = \delta_{CH_2}{}^A - \delta_{CH_2}{}^C$. [d] CH = cyclohexane. $[(i\text{-Bu})_2AlONa][Al(i\text{-Bu})_3]$:PhH = 1:0.64 (mol/mol). [e] $[(i\text{-Bu})_2AlONa][Al(i\text{-Bu})_3]$:PhH = 1:1.04 (mol/mol). [f] CH:PhH = ~1:1. [g] PhH:THF = 3:1.

Table VI. Nmr Spectral Data of Pentaalkyldialuminum Oxides Containing Methyl Groups[a]

Compound	Solvent	CH_2^A	CH_3^B	CH_3^C	CH_3^C: Ppm	CH_3^C: Rel intens	$\delta_A - \delta_C$, Hz	$\lvert\delta_{CH_3}{}^B - \delta_{CH_2}{}^A\rvert$, Hz
$[Et_2AlONa][AlMe_3]$	PhMe	4 H, −0.81 ppm, quartet	6 H, 0.75 ppm, triplet	9 H	−1.41 −1.45 −1.49	0.45 1.00 0.55	−36.5 −39 −41	93.5
$[Et_2AlONa][AlMe_3]$	PhMe	4 H, −0.84 ppm, quartet	6 H, 0.75 ppm, triplet	9 H	−1.38 −1.43 −1.49	0.60 1.00 1.15	−34.5 −36.5 −40	94.5
$[Et_2AlOLi][THF][AlMe_3]$ (route a)	PhH	4 H, −0.37 ppm, quartet	6 H, 0.90 ppm, triplet	9 H	−0.94 −1.02 −1.07	0.89 1.00 0.96	−33.5 −38.5 −41.5	76.5
$[Et_2AlOLi][AlMe_3][THF]$ (route b)	PhH	4 H, −0.40 ppm, quartet	6 H, 0.88 ppm, triplet	9 H	−0.96 −1.04 −1.14	0.93 1.00 0.47	−33.5 −38.5 −44	77
$[Me_2AlOLi][AlMe_3]$ + THF (1:4)	PhH	CH_3^A 6 H, −1.20 ppm, singlet		9 H, singlet	−1.32		−7.6	
$[Me_2AlOLi][AlMe_3]$	THF	6 H, −1.45 ppm		9 H	−1.47		−1~2	

[a] Temperature is 35°. Notations of protons are based on the formulas $(CH_3{}^B\text{-}CH_2{}^A)_2Al\text{-}\underset{\underset{M}{|}}{O}\rightarrow Al(CH_3{}^C)_3$ and $(CH_3{}^A)_2Al\text{-}\underset{\underset{M}{|}}{O}\rightarrow Al(CH_3{}^C)_3$.

Table VII. Summary of the Structures of Pentaalkyldialuminum Complexes in Solution

	Structure			
	 $R_2Al\underset{\mid}{Z}\rightarrow AlR_3$ (M below Z)			THF 
Compounds	**1**	**1c**	**2a**	**1b**
$[Et_2AlOLi][AlEt_3]$	Predominant	Possible	No	Identified
$[Et_2AlONa][AlEt_3]$	Almost	No	No	Identified
$[Et_2AlOK][AlEt_3]$	Almost	No	No	
$[Et_2AlOCs][AlEt_3]$	Predominant	Probably no	Possible	
$[Et_2AlNPhLi][AlEt_3]$	Predominant	Highly possible	No	
$[Et_2AlSNa][AlEt_3]^a$	Predominant	No?	No?	
$[(i\text{-}Bu)_2AlOLi][Al(i\text{-}Bu)_3]$	Possible?	Predominant	No	
$[(i\text{-}Bu)_2AlONa][Al(i\text{-}Bu)_3]$	Almost	No	No	
$[(i\text{-}Bu)_2AlOK][Al(i\text{-}Bu)_3]$	Almost	No	No	Identified
$[(i\text{-}Bu)_2AlOCs][Al(i\text{-}Bu)_3]$	Predominant	Probably no	Possible	
$[(i\text{-}Bu)_2AlNPhLi][Al(i\text{-}Bu)_3]$	Possible?	Predominant	No	
$[Me_2AlOLi][AlMe_3]$				Identified
$[Et_2AlOLi][AlMe_3]$				Identified

[a] A synthetic experiment shows that the equilibrium $[Et_2AlSNa][AlEt_3] \rightleftharpoons Et_2AlSNa + AlEt_3$ is important for this compound. This equilibrium must be taken into account in the nmr results. Further detailed structural aspects (**1** or **2**) of this compound are only in vague classifications.

$(i\text{-}Bu)_3]$ changed from double doublets at room temperature or below (Figure 4b) to a broad resonance at 77°. In this case isomerization from a type-**1** to a type-**2a** structure appears to occur.

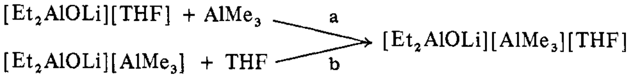
Since a parallelism in the nmr spectra of the isobutyl and ethyl derivatives with respect to the nature of the alkali metal is apparent, we prefer to assume a type-**1c** structure for $[(i\text{-}Bu)_2AlOLi][Al(i\text{-}Bu)_3]$ for the same reasons as discussed in the section on $[Et_2AlOLi][AlEt_3]$. Our observations indicate that the nature of alkali metal is the major factor in determining the structure of the organoaluminum compounds in solution. The alkyl group exerts an effect on the more detailed structure. For example, the type-**1c** structure appears to be more predominant in $[(i\text{-}Bu)_2AlOLi][Al(i\text{-}Bu)_3]$ than in $[Et_2AlOLi][AlEt_3]$.

An indication of the coordination of tetrahydrofuran to the Al^1 atom was obtained with $[(i\text{-}Bu)_2AlOK][Al(i\text{-}Bu)_3]$ (Table V). It is interesting to note that a considerable downfield shift was observed also for $CH_3{}^E$ protons. This corresponds to steric crowding in the coordinated state, where the tetrahydrofuran ring interacts with the methyl protons of the isobutyl group.

$[(i\text{-}Bu)_2AlNPhLi][Al(i\text{-}Bu)_3]$ showed a simple isobutyl signal in benzene at room temperature, similar to $[(i\text{-}Bu)_2AlOLi][Al(i\text{-}Bu)_3]$. This feature is identical with that encountered in the case of the corresponding ethyl derivatives.

Derivatives Containing a Methyl Group. The spectrum of $[Me_2AlOLi][AlMe_3]$ in benzene containing tetrahydrofuran showed two methyl signals in a relative intensity of 2:3. A weaker signal due to the Me_2AlOLi moiety (Al^1) is observed at lower field (Table VI).

Lithium compounds containing ethyl and methyl groups ($[Et_2AlOLi][AlMe_3][THF]$) obtained from two different routes (a and b) resulted in quite similar spectra, indicating identity in their chemical structures. The pattern of the signals consists of three Me–Al singlets. Similar spectra were observed with $[Et_2AlONa][AlMe_3]$ in toluene solution. Since the relative intensities of the three methyl signals varied with the synthetic routes, the multiplicity can be assumed as the result of intramolecular exchange of the alkyl groups between two aluminum atoms. The requirement for the exchange process (*i.e.*, the aluminum atom in the Et_2AlOLi moiety must be coordinatively unsaturated) is less fulfilled in the compound obtained by route a, compared with that obtained by route b. The signal at the highest field can tentatively be assigned as that of methyl group in an unexchanged species $[Et_2Al(THF)OLi][AlMe_3]$, because the intensity of this signal is higher in the compound obtained by route a than that of the compound obtained by route b. The signal at the lowest field is presumably due to the methyl group attached to Al^1 atom (exchanged species), because the signal shifts toward lower field in the presence of tetrahydrofuran, compared with the signal in the absence of tetrahydrofuran ($[Et_2AlONa][AlMe_3]$); see Table VI, $|\delta_A - \delta_C|$. The middle signal may be that of the bridging methyl group as has been detected for other organoaluminum systems.[27,28]



On summing up our nmr studies on the binuclear organoaluminum complexes, plausible structures in solution for individual complexes are listed in Table VII. It can be seen from the table that the structures of the complexes depend mainly upon the alkali metal and that the nature of the heteroatoms or the alkyl groups contributes to some minor variations in the structure.

Experimental Section

Materials. The organoaluminum compounds were prepared and purified according to the methods described previously.[6] All solvents were carefully dehydrated and purified under argon atmosphere.[6]

Proton Magnetic Resonance Spectroscopy. All but one spectrum were recorded at 60 MHz using a Varian A-60 nmr spectrometer at 35°, which is denoted as "room temperature" in the text. Temperatures were measured by the chemical shifts of methanol and ethylene glycol for low- and high-temperature experiments, respectively. The calibration curves in the operation manual of the spectrometer were applied for this purpose. Chemical shifts were measured relative to tetramethylsilane (TMS) external standard. Accuracy of chemical shift values in this paper is approximately ±0.05 ppm for δ and ±0.5 Hz for $\Delta\delta$, respectively. Because of higher accuracy in $\Delta\delta$ value than

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(27) (a) N. Muller and D. E. Pritchard, *J. Amer. Chem. Soc.*, 82, 248 (1960); (b) E. G. Hoffmann, *Trans Faraday Soc.*, 58, 642 (1962); (c) T. Mole and J. R. Surtess, *Aust. J. Chem.*, 17, 310 (1964); (d) T. Mole, *ibid.*, 18, 14 (1965); (e) K. C. Ramy, J. F. O'Brien, I. Hasegawa, and A. E. Borchart, *J. Phys. Chem.*, 69, 3418 (1965); (f) K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, 88, 5460 (1966).

(28) Further evidence will be necessary before more can be asserted concerning the origin of the middle signal.

in δ value, discussions in the text are mainly based on the latter values. Concentration of the sample was *ca.* 15% (wt/v) except for $[Et_2AlOLi][AlEt_3]$ (~2%) due to low solubility. The spectra showed no signals at δ 4-6 ppm due to oxidized species which might be produced by ill handling of the organoaluminums under argon atmosphere by syringes.

The spin-tickling experiment was performed using a Varian T-60 spectrometer with weak-field double irradiation in the frequency sweep mode. A Japan Optics Laboratory Co. Ltd. JNM-4H-100 spectrometer was used for the measurements at 100 MHz.

Registry No. $[Et_2AlOLi][AlEt_3]$, 15407-37-1; $[Et_2AlONa][AlEt_3]$, 18347-70-1; $[Et_2AlOK][AlEt_3]$, 29467-77-4; $[Et_2AlOCs][AlEt_3]$, 38118-15-9; $[Et_2AlNPhLi][AlEt_3]$, 25136-39-4; $[Et_2AlSNa][AlEt_3]$, 38118-17-1; $[(i\text{-}Bu)_2AlOLi][Al(i\text{-}Bu)_3]$, 38194-35-3; $[(i\text{-}Bu)_2AlONa][Al(i\text{-}Bu)_3]$, 38118-18-2; $[(i\text{-}Bu)_2AlOK][Al(i\text{-}Bu)_3]$, 38118-19-3; $[(i\text{-}Bu)_2AlOCs][Al(i\text{-}Bu)_3]$, 38118-20-6; $[(i\text{-}Bu)_2AlNPhLi][Al(i\text{-}Bu)_3]$, 38194-36-4; $[Et_2AlONa][AlMe_3]$, 38118-21-7; $[Et_2AlOLi][AlMe_3][THF]$, 38118-22-8; $[Me_2AlOLi][AlMe_3][THF]$, 38118-23-9; $[Et_2AlOLi][AlEt_3][THF]$, 38118-24-0; $[Et_2AlONa][AlEt_3][THF]$, 38118-25-1; $[(i\text{-}Bu)_2AlOK][Al(i\text{-}Bu)_3][THF]$, 38118-26-2.

Acknowledgment. We wish to thank Mr. Masatoshi Mikumo for his experiments on the sulfur-containing compound, Mr. Shintaro Tachibana for the high-vacuum synthesis of $[Et_2AlOLi][AlEt_3]$, and Mr. Muneo Fukui for the synthesis of deuterated toluene. We also wish to express our appreciation to Dr. E. J. Vandenberg of Hercules Powder Co., for a gift of toluene-d_8. We are grateful to Mr. H. Naoki, Mr. M. Doi, and Miss Y. Kawashima for their running of nmr spectra.

Contribution No. 4240 from the Arthur Amos Noyes Laboratory of Chemical Physics,
California Institute of Technology, Pasadena, California 91109

Spectroscopic and Magnetic Properties of Heptacyanomolybdate(III). Evidence for Pentagonal-Bipyramidal and Monocapped Trigonal-Prismatic Structures

GEORGE R. ROSSMAN, F.-D. TSAY, and HARRY B. GRAY*

Received August 10, 1972

Several salts containing the $Mo(CN)_7{}^{4-}$ ion have been studied by a variety of spectroscopic and magnetic techniques. Infrared and Raman spectral data together with magnetic susceptibility measurements suggest a pentagonal-bipyramidal (D_{5h}) structure ($^2E_1{}''$-$(e_1{}'')^3$ ground state) for $Mo(CN)_7{}^{4-}$ in aqueous solutions of $K_4Mo(CN)_7 \cdot 2H_2O$. Anhydrous $K_4Mo(CN)_7$ and solid $Cs_4Mo(CN)_7 \cdot xH_2O$ also appear to contain pentagonal-bipyramidal anions. Solid $K_4Mo(CN)_7 \cdot 2H_2O$, however, exhibits infrared and Raman spectra that differ from the aqueous solution results. The esr spectrum of the dihydrate, which can be observed only below 150°K, gives $g_\parallel = 2.103$ and $g_\perp = 1.973$. The g values and a $\mu_{eff} = 1.73$ BM are consistent with a $^2A_1(a_2)^2(a_1)^1$ ground state of a monocapped trigonal-prismatic (C_{2v}) coordination geometry. Electronic spectral bands at 16,100, 20,900, and 22,500 cm^{-1} in crystalline $K_4Mo(CN)_7 \cdot 2H_2O$ are assigned respectively to the d-d transitions $^2A_1 \rightarrow {}^2A_2$, $^2A_1 \rightarrow {}^2B_2$, and $^2A_1 \rightarrow {}^2B_1$. The lowest spin-allowed d-d transition in D_{5h} $Mo(CN)_7{}^{4-}$ occurs at 24,900 cm^{-1}.

Introduction

The complex $K_4Mo(CN)_7 \cdot 2H_2O$ was reported by Young[1] in 1932 but to date has not been well characterized by physical methods. The compound is of considerable interest in view of the apparent seven-coordinate nature of the complex anion, $Mo(CN)_7{}^{4-}$, but it should be recognized that formulation as a higher coordinate species such as $Mo(CN)_7H_2O^{4-}$ is also possible.

In our laboratory we have been engaged in an investigation of the physical and chemical properties of various compounds containing the $Mo(CN)_7{}^{4-}$ ion. Although our attempts to establish the structure of $Mo(CN)_7{}^{4-}$ in several solid compounds by single-crystal X-ray methods have not yet been successful, we have been able to characterize thoroughly the complex anion by spectroscopic and magnetic measurements on both solid and aqueous solution samples. In the present paper we report magnetic susceptibility results and esr, infrared, Raman, and electronic spectral data for $K_4Mo(CN)_7 \cdot 2H_2O$ and $K_4Mo(CN)_7$. For comparison, certain preliminary results are also included for $Cs_4Mo(CN)_7 \cdot xH_2O$.

Experimental Section

Preparation of Compounds. Several batches of $K_4Mo(CN)_7 \cdot 2H_2O$ were prepared from K_3MoCl_6[2] and excess KCN by the literature method.[1] Shiny black flakes of 1-3-mm size and fine, dark olive green flakes were obtained in various batches. Recrystallization was accomplished by cooling concentrated solutions in oxygen-free water-ethanol mixtures and less conveniently by cooling saturated aqueous solutions. *Anal.* Calcd for $K_4Mo(CN)_7 \cdot 2H_2O$: K, 33.24; Mo, 20.39; C, 17.87; N, 20.84; H, 0.86. Found: K, 33.05; Mo, 20.47; C, 18.05; N, 20.39; H, 0.96.

Anhydrous $K_4Mo(CN)_7$ was prepared from the hydrate by heating it for 10-15 hr at 95° under high vacuum. It was also prepared in a finely divided form by lyopholyzing aqueous solutions of the dihydrate. *Anal.* Calcd for $K_4Mo(CN)_7$: K, 36.00; Mo, 22.08; C, 19.35; N, 22.57; H, 0.00. Found: K, 34.89; Mo, 22.33; C, 19.64; N, 22.22; H, 0.00.

Infrared spectra show that both $K_4Mo(CN)_7 \cdot 2H_2O$ and $K_4Mo(CN)_7$ decompose in air to KOH, $K_4Mo(CN)_8$, and K_2MoO_4. No evidence for what has been reported[3] to be $KMo(CN)_5$ was observed in the oxidation products. Although the solid dihydrate can be briefly exposed to dry air for purposes such as weighing without any sign of decomposition, it was generally handled in a nitrogen-purged glovebag and transferred to the appropriate nitrogen-filled containers. In a dry atmosphere, the flakes of the solid readily accumulate static electricity. The compound is soluble in water and slowly soluble in ethylene glycol but was found to be insoluble in common organic solvents. Since the solutions are extremely oxygen sensitive, all sample preparations of solutions for physical measurements were done in a high-vacuum line. The appropriate amount of degassed water was sublimed onto the solids in the sample vessel and the vessels were then closed either with stopcocks or by flame sealing under vacuum.

Physical Measurements. Absorption spectra in the region 210-2500 nm were obtained on a Cary 14 RI spectrophotometer equipped with quartz dewar for immersion of samples into liquid N_2.

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(1) R. C. Young, *J. Amer. Chem. Soc.*, **54**, 1402 (1932).

(2) R. J. Irving and M. C. Steele, *Aust. J. Chem.*, **10**, 490 (1957).

(3) M. C. Steele, *Aust. J. Chem.*, **10**, 404 (1957).