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VIBRATIONAL SPECTRA OF TETRAETHYLALUMINATE ANIONS

CHARLES A. WILKIE
Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233 (U.S.A.)

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SUMMARY

The vibrational spectra of $LiAlEt_4$ and $NaAlEt_4$ are reported. It is concluded that the former has D_{2d} symmetry and that the latter has T_d symmetry.

The X-ray crystal structures of several tetraalkylaluminum compounds[1,2] have been reported. $LiAl(C_2H_5)_4$[1] may be represented as an infinite chain with D_{2d} symmetry; $KAl(CH_3)_4$ has T_d symmetry[2]. Mach[3] has reported the infrared spectra of Li- and $NaAl(CH_3)_4$ and Li- and $NaAl(C_2H_5)_4$. He concludes tetrahedral symmetry for both ethyl compounds, and the two methyl compounds are analyzed in terms of C_{2v} symmetry. We have recently reported infrared and Raman studies on $LiAl(CH_3)_4$[4], which support the expected D_{2d} symmetry. We now wish to make known our results on $LiAl(C_2H_5)_4$ and $NaAl(C_2H_5)_4$.

TABLE 1

SELECTION RULES[a] FOR M SKELETAL VIBRATIONS OF MR_4

Point group	Stretching modes	Bending modes
T_d	$A(R)+T_2(I, R)$	$E(R)+T_2(I, R)$
$D_{2d}=V_d$	$A(R)+B_2(I, R)+E(I, R)$	$A(R)+B_1(R)+B_2(I, R)+E(I, R)$
C_{3v}	$2A(I, R)+E(I, R)$	$A(I, R)+2E(I, R)$
C_{2v}	$2A(I, R)+B_1(I, R)+B_2(I, R)$	$2A(I, R)+A_2(R)+B_1(I, R)+B_2(I, R)$

[a] I, IR active; R, Raman active.

Four possible symmetries may be considered for $MAlR_4^-$ compounds; the selection rules for these are tabulated in Table 1. The spectrum may be divided into three regions: ethyl vibrations (our results are in accord with Mach[3] and will not be given here); aluminum–carbon vibrations and cation active vibrations.

RESULTS AND DISCUSSION

$LiAl(C_2H_5)_4$

Absorptions at 618, 526 and 468 cm^{-1} in the Raman spectrum correspond to absorptions at 616 and 527 cm^{-1} in the IR and may be assigned as the aluminum–carbon stretching modes expected for D_{2d} symmetry. The bending vibrations occur at

279, 143, 109 and 95 cm^{-1} in the Raman spectrum. In the IR only the first two are predicted to be active; these are observed at 283 and 131 cm^{-1}. Two additional absorptions below 650 cm^{-1} are observed in the infrared. They show a lithium isotope effect and thus must represent Li–C modes. These occur at 256 and 312 cm^{-1} in ^{7}LiAl(C$_2$H$_5$)$_4$, moving to 262 and 326 cm^{-1} in ^{6}LiAl(C$_2$H$_5$)$_4$. These vibrations are absent in the Raman spectrum indicating that the lithium–carbon interaction is substantially ionic[5]. Lithium–carbon frequencies have been observed in the same frequency region in LiAl(CH$_3$)$_4$ and Li$_2$Zn(CH$_3$)$_4$ with the same lack of Raman activity[4].

Mach[3] has assigned the 615 cm^{-1} band as a CH$_2$ rocking mode and 526 cm^{-1} as the only infrared active aluminum–carbon frequency. He suggests tetrahedral symmetry, in opposition to the X-ray study. The results herein presented are in excellent agreement with D_{2d} symmetry, as expected from the X-ray study.

$NaAl(C_2H_5)_4$

The Raman and infrared spectra of this compound are substantially simpler than those of LiAl(C$_2$H$_5$)$_4$, indicating a higher symmetry for the sodium compound. Aluminum–carbon stretching frequencies occur at 556 cm^{-1} in the IR and 564 and 492 cm^{-1} in the Raman. The bending modes occur at 345 cm^{-1} in the IR and 340 and 302 cm^{-1} in the Raman. There is only one low frequency band, a very broad band centered at 132 cm^{-1} and this may be a lattice mode involving the sodium cation and the tetraethylaluminate anion. These results suggest T_d symmetry for NaAl(C$_2$H$_5$)$_4$, in agreement with Mach. All frequencies are collected and assigned in Table 2.

TABLE 2

INFRARED AND RAMAN SPECTRA OF LITHIUM AND SODIUM TETRAETHYLALUMINATES[a]

Assignment	^{7}LiAl(C$_2$H$_5$)$_4$		^{6}LiAl(C$_2$H$_5$)$_4$		NaAl(C$_2$H$_5$)$_4$	
	IR	Raman	IR	Raman	IR	Raman
ν(Al–C)	616sh	618m	616sh	618m		
ν(Al–C)	527s	526m	527s	526m	556s	564m
ν(Al–C)		468s		468s		492s
ν(Li–C)	312m		326m			
δ(Al–C)	283m	279m	283m	279m	345m	340m
ν(Li–C)	256m		262m			
δ(Al–C)	131m	143m	130m	143m		302m
ν(Na–C)						132brs
δ(Al–C)		109s		109s		
δ(Al–C)		95s		95s		

[a] In cm^{-1}; s=strong, m=medium, w=weak, br=broad.

The frequencies for the ethyl compounds are somewhat lower than the analogous frequencies in the methyl compounds, as has been observed for other metal alkyls[6]. The differences in the spectra of LiAl(C$_2$H$_4$)$_4$ and NaAl(C$_2$H$_5$)$_4$ indicate that the lithium cation is much more able than sodium to interact with the anion.

EXPERIMENTAL SECTION

Preparation of $LiAl(C_2H_5)_4$ and $NaAl(C_2H_5)_4$ was carried out by heating the metal with $Al(C_2H_5)_3$ in toluene at reflux under vacuum conditions. Filtration of the hot reaction mixture gave the desired compound[3]. The spectral samples samples were prepared in the dry-box using the Nujol technique. CsI plates and polyethylene plates were used for the infrared investigations. For Raman work the powered dry sample was sealed in a capillary tube. Spectra were obtained on a Beckman IR-12 (4000–200 cm^{-1}), a Hitachi–Perkin–Elmer FIS-3 (410–30 cm^{-1}), and a Spex Ramalog Double Spectrometer with an argon ion laser source.

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REFERENCES

1 R. L. Gerteis, R. E. Dickerson and T. L. Brown, *Inorg. Chem.*, 3 (1964) 872.
2 R. Wolfrum, G. Sauerman and E. Weiss, *J. Organometal. Chem.*, 18 (1969) 27.
3 K. Mach, *J. Organometal. Chem.*, 2 (1964) 410.
4 J. Yamamoto and C. A. Wilkie, *Inorg. Chem.*, 10 (1971) 1129.
5 J. H. B. George, J. A. Rolfe and L. A. Woodward, *Trans. Faraday Soc.*, 49 (1953) 375.
6 W. J. Lehmann, C. O. Wilson Jr. and I. Shapiro, *J. Chem. Phys.*, 28 (1958) 781.