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UNSATURATED COMPOUNDS OF THE MAIN GROUP ELEMENTS: THE MOLECULAR STRUCTURE OF THE REACTION PRODUCT OF 1,3-CYCLOOCTADIENE WITH TRIMETHYLALUMINUM AND POTASSIUM

ARLENE MOOTZ McPHERSON and GALEN STUCKY*
Department of Chemistry and Materials Research Laboratory
University of Illinois, Urbana, Illinois 61801 (U.S.A.)
and
H. LEHMKUHL
Max Planck Institut für Kohlenforschung, Mülheim/Ruhr,
Mülheim, Germany
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Summary

1,3-Cyclooctadiene reacts with trimethylaluminum and potassium according to the equation

$$4K + 4Al(CH_3)_3 + 2C_8H_{12} \xrightarrow[0°]{THF} 3K[Al(CH_3)_4]+K[(C_8H_{12})_2Al]$$

to give potassium bis(3,8-cis-cyclooctenyl)aluminate. The compound can be described as a bicyclo derivative of cyclooctene formed by the 1,4 addition to 1,3-cyclooctadiene. The structure of the complex was determined from 4500 unique data measured by single crystal X-ray diffractometer techniques. Full matrix least squares refinement gave final agreement factors of $R_1 = 0.043$ (observed data) and $R_2 = 0.045$ (all data) in the monoclinic space group $P2_1/c$ ($a = 9.658(6)$, $b = 12.220(8)$ and $c = 14.150(9)$Å; $\beta = 113.85(1)°$; $V = 1527.43$ Å; $Z = 4$ for $\rho_{calc} = 1.23$ g cm^{-3}).

Introduction

The reaction of trialkylaluminum compounds with unsaturated[1] organic fragments is an important part of the extensive industrial chemistry of organoaluminum catalysis. It has been shown in previous work that trialkylaluminum compounds react with unsaturated or aromatic hydrocarbons in the presence of a reducing metal such as sodium or potassium according to the general equation:

$$2R_3Al + 2M + ArH \rightarrow M[R_2AlArH] + M[R_4Al]$$

where M is sodium or potassium.

It was originally thought that the R_2Al group was coordinated via a bicyclo configuration to two carbon atoms of a 1,3-diene or aromatic ring. Thus, a bicyclo-structure was first postulated for the anion, dimethyl-1,4-dihydro-1,4-naphthalene-aluminate.[2] The 1,4 attack of the metal atom was subsequently confirmed, and the dimeric nature of the naphthalene and authracene organoluminates was revealed in two subsequent X-ray structural investigations.[3,4] In these two systems, the coordination around the aluminum atom is very nearly tetrahedral and the sodium-carbon atom distances to the aromatic portions of these rings are consistent with an ion-pair description of the interaction between two disolvated sodium ions and the organoaluminum and an organoaluminum diene ion. In order to further investigate the ion pairing in alkali metal organoaluminates and also to establish the nature of the interaction of the aluminum atom with non-aromatic dienes, crystallographic investigations were initiated on the products of the reactions of M (M=Na or K), R_3Al (R=methyl or ethyl), and olefins and dienes, including styrene, stilbene, 1,3-cyclooctadiene, and 1,3-butadiene. Of these compounds, crystals suitable for X-ray diffraction were obtained for the potassium bis(3,8-cis-cyclooctenyl)-aluminate. The characterization of this complex by X-ray analysis is described in this paper.

Experimental

Potassium bis(3,8-cis-cyclooctenyl)aluminate is prepared by the reaction of trimethylaluminum with potassium metal and 1,3-cyclooctadiene in tetrahydrofuran at 0° according to the following equation:[5]

$$4K + 4Al(CH_3)_3 + 2C_8H_{12} \xrightarrow[0°]{THF} 3K[Al(CH_3)_4] + K[(C_8H_{12})_2Al].$$

Since the compound slowly decomposes in THF, it was recrystallized from benzene and diethyl ether. The crystals tend to be twinned; thus the recrystallization was effected over a period of six months from a minimum amount of solvent in a closed container. A single crystal that measured approximately 0.43 x 0.64 x 0.27 mm was obtained. This crystal was mounted in a thin-walled glass capillary and sealed off to exclude air and moisture. These preparations were carried out in an inert atmosphere box.

Systematic absences ($h0\ell$: $\ell = 2n+1$ and $0k0$: $k = 2n+1$) which were observed on precession and Weissenberg photographs uniquely defined the monoclinic space group $P2_1/c$ (centric). The crystal was mounted on the diffractometer goniometer with the crystallographic b-axis coincident with the diffractometer ϕ-axis. Lattice constants and their standard deviations were obtained by a least-squares refinement of the angular settings of twelve reflections which were carefully selected and centered after data collection on a Picker four-circle diffractometer. The unit cell with four molecules has the dimensions: a = 9.658(6), b = 12.220(8), and c = 14.150(9) Å, β = 113.85(1)°, volume= 1527.6 Å^3. The calculated density is 1.23 g cm^{-3}.

The crystal was offset 2.4° so that the crystallographic b-axis would no longer coincide with the diffracometer ϕ-axis. After careful recentering of the crystal, an orientation matrix was calculated and a take-off angle of 1.5° was chosen to collect approximately 75% of the intensity of a representative, high intensity.

Two quadrants ($\bar{h}k\ell$, $hk\ell$ and $\bar{h}k\bar{\ell}$, $hk\bar{\ell}$) of intensity data were collected using the θ-2θ scan technique with a scan rate of 2° min^{-1}; a scan width of 1.2° was sufficient to collect all the peak intensity. Stationary crystal-stationary counter background counts of 10 seconds were taken both at the beginning and end of each scan. The quadrant, $\bar{h}k\ell$, $hk\ell$, of intensity data was collected to 60°, whereas the second quadrant, $hk\bar{\ell}$, $\bar{h}k\bar{\ell}$, was collected only to 35° in 2θ using MoKα (λ = 0.7107 Å) radiation and copper foil attenuators. Three peaks were chosen as standards and were monitored every fifty reflections. Some difficulty was encountered with the mechanical stability of the crystal in the capillary and it was necessary to recollect the first quadrant of data to 35° along with about 100 reflections beyond 35°. The intensities of the standards associated with the data thus collected did not vary more than 4%.

4500 unique reflections were measured for the first quadrant; of these 2150 were observed. The raw intensities were corrected for backgrounds, Lorentz and polarization effects. The systematic absences were checked and deleted along with the negative F(obs) resulting in a data set of about 3700 reflections. The estimated standard deviations $\sigma(F)$ of the structure factors are based on counting statistics.[3,4]

Solution and Refinement of the Structure

The structural solution was begun using a direct methods approach.[6] Six E-maps were generated using the sets of phases with the highest figures of merit. Although none of these maps directly revealed the structure, a recurring feature was the presence of atoms on two distinct centers of inversion, along with a pseudo-mirror at $y = 1/4$ (actually a c-glide). An examination of the Harker line and planes on a Patterson map revealed the position of only one aluminum atom (0.06, 0.25, 0.142). A least-squares cycle on the aluminum atom was run and a Fourier map calculated with the subsequent set of phases disclosed atoms on the two special positions, (000) and $(00\frac{1}{2})$.

A Fourier calculation based on three "aluminum atoms" in the above positions revealed an additional six atoms and indicated that the atoms on the special positions were in fact potassium atoms. This Fourier map also exhibited pseudo mirror symmetry at $y = \frac{1}{4}$ and a pseudo inversion center at $(0\ \frac{1}{4}\ 0)$. The remaining part of the structure was solved by the usual Fourier refinement techniques. In the initial stages of solution and refinement, unit weights were used and 2150 reflections with $I(\mathrm{obs}) \geq 2\sigma_c(I)$ constituted the data set. Scattering factors for the hydrogen atoms were the best spherical form factors of Stewart, *et al.*,[7] while those for potassium, aluminum, and carbon were taken from the compilation of Hanson, *et al.*[8] Two cycles of isotropic least-squares refinement on the nonhydrogen atom parameters (sigma weights) yielded values of $R_1 = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$ of 0.127 and $R_2 = \Sigma\omega||F_o|-|F_c||^2/\Sigma\omega F_o^{\,2}$ of 0.135. Converting all of the nonhydrogen atom thermal parameters from isotropic to anisotropic and varying all six β_{ij} lowered R_2 to 0.051. At this stage in the refinement, the two forms of data to 35° were averaged and inserted in the data set comprised of the $\bar{h}k\ell$, $hk\ell$ form to 60° in 2θ. This data set (observed and unobserved) was used in the final stages of refinement. A least-squares cycle on the positions and β's of the nonhydrogen atoms was run, and followed by a few cycles in which the positional parameters and isotropic thermal parameters (B's) of the hydrogen atoms were varied. The H(7A)-C(7) and H(7B)-C(7) bond lengths were 0.87 and 1.08 Å, while the C(3)-H(3) bond distance was 0.89 Å. The remaining C-H bond distances varied from 0.95 to 1.00 Å. The positions of the hydrogen atoms bonded to C(7) were recalculated at a bond distance of 0.95 Å, and the refinement of all hydrogen parameters was discontinued.

Anisotropic refinement of all nonhydrogen atoms converged with the final R-factors: R_1 (observed data only) = 0.043 and R_2 (all data) = 0.045. The final ERF was 1.67 and the scale factor (for the F's) was 3.38. A final difference Fourier map revealed no peaks over 0.5 e $Å^{-3}$.*

The final positional and anisotropic thermal parameters for the nonhydrogen atoms are reported in Tables 1 and 2, respectively, along with the standard deviations in these parameters. Table 3 reports the positional and isotropic thermal parameters for the hydrogen atoms. Selected interatomic distances and bond angles are listed in Tables 4 and 5.

Discussion

The structural aspects of the hydrocarbon products which are formed in the reaction:

$$2R_3Al + 2M + R' \rightarrow M[R_4Al] + M[R_2AlR']$$

(M = alkali metal, R' = bifunctional unsaturated hydrocarbon)

are now reasonably well established.[1-4] The R_2Al group is always added at the position of highest charge density

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*The table of structure factors has been deposited as a NAPS Document. Please contact ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017.

Table 1

Positional Parameters for the Nonhydrogen Atoms in $K[(C_8H_{12})_2Al]$

Atom	x	y	z
K(1)	0	0	0
K(2)	0	0	0
Al	0.05569(6)[a]	0.24948(6)	0.14005(4)
C(1)	0.2028(2)	0.2974(2)	0.0768(2)
C(2)	0.2698(2)	0.1865(2)	0.0745(2)
C(3)	0.2753(2)	0.1122(2)	0.1442(2)
C(4)	0.2076(2)	0.1351(2)	0.2207(2)
C(5)	0.3255(3)	0.1798(2)	0.3239(2)
C(6)	0.3690(3)	0.2994(3)	0.3239(2)
C(7)	0.4359(3)	0.3346(3)	0.2511(3)
C(8)	0.3288(3)	0.3767(2)	0.1428(2)
C'(1)	-0.0435(2)	0.3621(2)	0.1979(2)
C'(2)	-0.1804(3)	0.3864(2)	0.1006(2)
C'(3)	-0.2314(2)	0.3132(2)	0.0246(2)
C'(4)	-0.1560(2)	0.2023(2)	0.0401(2)
C'(5)	-0.2353(2)	0.1198(2)	0.0853(2)
C'(6)	-0.2694(3)	0.1611(2)	0.1761(2)
C'(7)	-0.1333(3)	0.1948(2)	0.2732(2)
C'(8)	-0.0859(3)	0.3160(2)	0.2834(2)

[a] Errors in the lattice parameters are included in these and all other estimated standard deviations.

of the hydrocarbon anion. Furthermore, the thermal stability and ease of formation of the complex anion, $[R_2AlR']^-$ increases with increasing electron affinity of the hydrocarbon, R'. The situation for a 1,3 diene can be envisioned as shown below, where the charge distributions have been estimated by simple Hückel molecular orbital theory.

Table 2

Anisotropic Thermal Parameters for

Nonhydrogen Atoms in

$K[(C_8H_{12})_2Al]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K(1)	0.0146(1)	0.0048(1)	0.0091(1)	-0.0006(1)	0.0047(1)	-0.0027(1)
K(2)	0.0212(2)	0.0053(1)	0.131(1)	-0.0023(1)	0.0097(1)	-0.0038(1)
Al	0.0081(1)	0.00335(4)	0.00383(4)	0.0003(1)	0.00246(4)	-0.00012(4)
C(1)	0.0120(3)	0.0048(2)	0.0052(2)	0.0002(2)	0.0044(2)	0.0003(1)
C(2)	0.0115(3)	0.0071(2)	0.0056(2)	0.0006(2)	0.0041(2)	-0.0009(2)
C(3)	0.0103(3)	0.0044(2)	0.0066(2)	0.0014(2)	0.0025(2)	-0.0007(1)
C(4)	0.0098(3)	0.0044(2)	0.0051(2)	0.0002(2)	0.0027(2)	0.0008(1)
C(5)	0.0132(4)	0.0093(3)	0.0052(2)	0.0011(3)	0.0018(2)	0.0008(2)
C(6)	0.0165(4)	0.0116(3)	0.0066(2)	-0.0042(3)	0.0016(3)	-0.0031(2)
C(7)	0.0162(5)	0.0125(3)	0.0105(3)	-0.0080(3)	0.0045(3)	-0.0048(3)
C(8)	0.0152(4)	0.0058(2)	0.0095(2)	-0.0029(2)	0.0069(3)	-0.0004(2)
C'(1)	0.0130(3)	0.0037(1)	0.0053(2)	0.0002(2)	0.0038(2)	-0.0009(1)
C'(2)	0.0133(4)	0.0041(2)	0.0067(2)	0.0026(2)	0.0054(2)	0.0010(1)
C'(3)	0.0096(3)	0.0062(2)	0.0055(2)	0.0025(2)	0.0028(2)	0.0016(2)
C'(4)	0.0099(3)	0.0051(2)	0.0035(1)	0.00002(2)	0.0021(2)	-0.0003(1)
C'(5)	0.0105(3)	0.0052(2)	0.0066(2)	-0.0009(2)	0.0031(2)	-0.0004(2)
C'(6)	0.0153(4)	0.0067(2)	0.0085(2)	-0.0005(2)	0.0080(3)	0.0011(2)
C'(7)	0.0197(5)	0.0073(2)	0.0059(2)	0.0014(3)	0.0073(2)	0.0012(2)
C'(8)	0.0168(4)	0.0061(2)	0.0051(2)	0.0014(2)	0.0048(2)	-0.0005(2)

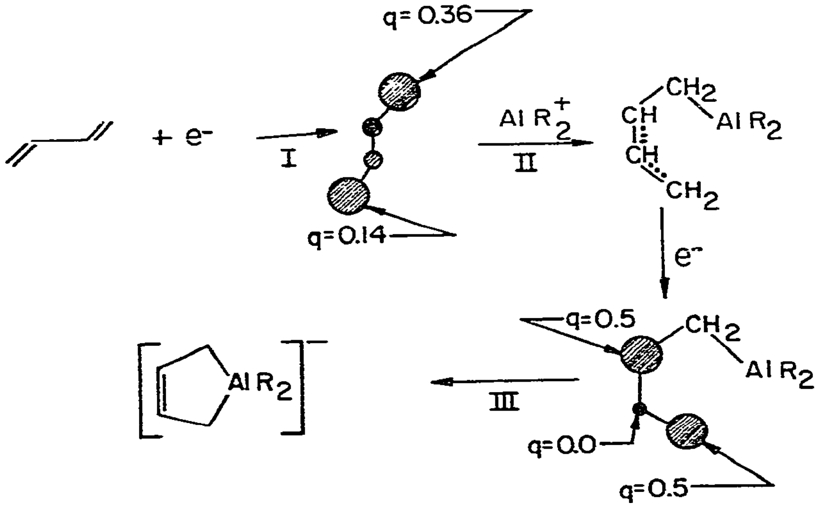


Table 3

Positional and Isotropic Parameters for the Hydrogen Atoms in $K[(C_8H_{12})_2Al]$[b]

Atom	x	y	z	B
H(1)	0.158	0.329	0.006	3.4
H(2)	0.314	0.173	0.023	4.6
H(3)	0.323	0.051	0.146	3.7
H(4)	0.166	0.066	0.237	2.8
H(5A)	0.416	0.139	0.351	4.8
H(5B)	0.289	0.172	0.381	5.9
H(6A)	0.449	0.310	0.400	6.2
H(6B)	0.279	0.353	0.307	6.2
H(7A)[a]	0.489	0.274	0.240	8.4
H(7B)[a]	0.505	0.392	0.283	7.2
H(8A)	0.283	0.440	0.156	5.3
H(8B)	0.387	0.394	0.104	4.4
H'(1)	0.014	0.430	0.223	3.3
H'(2)	-0.230	0.453	0.091	4.6
H'(3)	-0.320	0.329	-0.038	3.4
H'(4)	-0.169	0.175	-0.027	2.6
H'(5A)	-0.172	0.055	0.108	3.5
H'(5B)	-0.330	0.099	0.032	3.7
H'(6A)	-0.321	0.102	0.194	4.0
H'(6B)	-0.346	0.224	0.155	4.7
H'(7A)	-0.047	0.145	0.279	3.4
H'(7B)	-0.157	0.174	0.332	4.6
H'(8A)	-0.171	0.361	0.287	4.0
H'(8B)	0.002	0.327	0.350	2.9

[a] Calculated values.

[b] Estimated standard deviations for these values are 1.1 (B) and 0.010 for positional coordinates.

The presence of R_2Al^+ has been ascribed to the autodissociation of $R_3Al \cdot D$[1] (D = donor molecule), i.e.,

$$2R_3AlD \rightleftarrows [R_2AlD_2]^+ + [R_4Al]^-$$

and in the present case, further exchange between the com-

Table 4

Interatomic Distances (Å) for the Nonhydrogen Atoms in $K[(C_8H_{12})_2Al]$

Atoms	Distance[a]		
Bonded Distances		Selected Nonbonded Distances (< 4.0 Å)	
Al-C(1)	2.047(2)		
Al-C(4)	2.014(2)		
Al-C'(1)	2.023(2)	Al-C(2)	2.699(3)
Al-C'(4)	2.043(2)	Al-C(3)	2.686(2)
C(1)-C(2)	1.508(3)	Al-C'(2)	2.698(2)
C(2)-C(3)	1.326(3)	Al-C'(3)	2.702(3)
C(3)-C(4)	1.500(3)	Al-K(1)	3.557(2)
C(4)-C(5)	1.544(3)	Al-K(2)	3.568(2)
C(5)-C(6)	1.520(4)		
C(6)-C(7)	1.484(4)	K(1)-C(3)	2.954(3)
C(7)-C(8)	1.549(4)	K(1)-C'(4)	3.066(3)
C(8)-C(1)	1.541(3)	K(1)-C(2)	3.298(3)
C'(1)-C'(2)	1.498(3)	K(1)-C'(5)	3.315(3)
C'(2)-C'(3)	1.331(3)		
C'(3)-C'(4)	1.511(3)	K(2)-C'(2)[b]	2.999(2)
C'(4)-C'(5)	1.553(3)	K(2)-C(1)	3.071(3)
C'(5)-C'(6)	1.535(3)	K(1)-C'(3)	3.310(3)
C'(6)-C'(7)	1.525(3)	K(2)-C(8)	3.354(3)
C'(7)-C'(8)	1.539(3)		
C'(8)-C'(1)	1.540(3)		

[a] Errors in the lattice parameters are included in the estimated standard deviations.

[b] The position of K(2) is the symmetry related position, 0 $\frac{1}{2}$ 0.

plex anions could lead to the product reported here via the reaction:

$$2K^+[R_2AlR']^- \underset{THF}{\rightarrow} K^+[R_4Al]^- + K^+[AlR'_2]^-$$

In agreement with the above, the compound with R' = C_8H_{12}, i.e., $K[(C_8H_{12})_2Al]$ can be described as a 1,4-bicyclo derivative of 2-cyclooctene formed by 1,4-addition to 1,3-cyclooctadiene. The geometry of the anion is shown in

Table 5
Selected Angles (degrees) for the Nonhydrogen Atoms in $K[(C_8H_{12})_2Al]$

Atoms	Angle[a]	Atoms	Angle
C(1)-Al-C(4)	88.32(9)	C'(1)-Al-C'(4)	88.0(9)
Al-C(1)-C(2)	97.6(1)	Al-C'(1)-C'(2)	98.9(1)
Al-C(1)-C(8)	115.6(2)	Al-C'(1)-C'(8)	112.8(2)
Al-C(4)-C(3)	98.7(1)	Al-C'(4)-C'(3)	97.8(1)
Al-C(4)-C(5)	112.3(2)	Al-C'(4)-C'(5)	114.8(1)
C(1)-C(2)-C(3)	119.1(2)	C'(1)-C'(2)-C'(3)	120.4(2)
C(2)-C(3)-C(4)	120.8(2)	C'(2)-C'(3)-C'(4)	119.1(2)
C(3)-C(4)-C(5)	112.2(2)	C'(3)-C'(4)-C'(5)	110.7(2)
C(4)-C(5)-C(6)	116.0(2)	C'(4)-C'(5)-C'(6)	116.2(2)
C(5)-C(6)-C(7)	118.5(3)	C'(5)-C'(6)-C'(7)	116.4(2)
C(6)-C(7)-C(8)	118.6(2)	C'(6)-C'(7)-C'(8)	117.4(2)
C(7)-C(8)-C(1)	116.0(2)	C'(7)-C'(8)-C'(1)	116.2(2)
C(8)-C(1)-C(2)	109.7(2)	C'(8)-C'(1)-C'(2)	112.1(2)
C(1)-Al-C'(1)	120.3(1)	C(3)-K(1)-C(3)*[b]	180.00(0)
C(1)-Al-C'(4)	117.1(1)	C'(4)-K(1)-C'(4)*	180.00(0)
C(4)-Al-C'(1)	126.9(1)	C(3)-K(1)-C'(4)	82.55(7)
C(4)-Al-C'(4)	119.5(1)	C(3)-K(1)-C'(4)*	97.45(7)
		C(2)-K(1)-C'(5)	98.52(7)
C'(2)-K(2)-C'(2)*	180.00(0)	C(2)-K(1)-C'(5)*	81.48(7)
C(1)-K(2)-C(1)*	180.00(0)		
C(1)-K(2)-C'(2)	82.44(7)		
C'(3)-K(2)-C(8)	98.16(7)		

[a] Errors in the lattice parameters are included in the estimated standard deviations.

[b] The starred atoms are those related by the center of inversion noted by the potassium position.

Figure 1. The aluminum-carbon bond distances in the anion are ~0.03 Å shorter than those observed in the naphthalene and anthracene aluminates.[3,4] The aluminum atom is four coordinate with the internal angles, C(1)-Al-C(4) and C'(1)-Al-C'(4), reduced from the tetrahedral value of 109° to 88.3(1)° and 88.0(1)°, respectively. The external angles

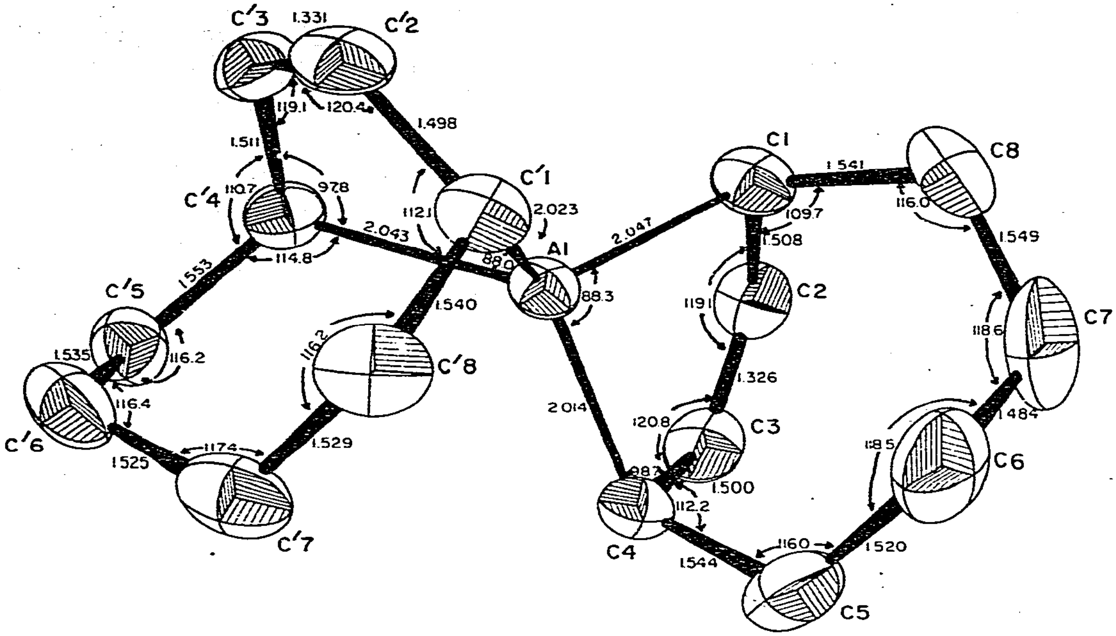


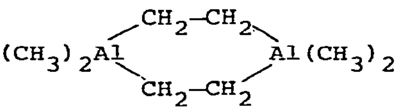
Figure 1. A Perspective View of the Anion of $K[(C_8H_{12})_2Al]$.

(e.g., C(1)-Al-C'(1)) are correspondingly increased to 117-127°. The carbon-carbon atom bond distances in the cyclooctenyl system are as predicted for the expected hybridization:[9,10] (sp^3-sp^3) expected, 1.54 Å; average 1.533(4) Å; (sp^3-sp^2) expected, 1.50 Å; average 1.504(4) Å; $(sp^2-sp^2+\pi)$ expected, 1.34 Å; average, 1.328(3) Å.

The formation of an alumina-cyclopentane derivative, as opposed to an alumina-cyclopropane derivative, is consistent with the relatively small size of the aluminum atom. We also believe that in the case of the reaction:[1b]

$$2Li + 2(CH_3)_3Al \text{ THF } \xrightarrow{-10°} Li[(CH_3)_4Al] + Li[(CH_2-CH_2)Al(CH_3)_2]$$

it is much more probable that a dimeric



or polymeric species exists, in which the alumina-cyclopropane configuration is not present. A dimeric or oligomeric configuration can be expected whenever the charge distribution of the reduced hydrocarbon is unfavorable for chelation to the aluminum atom. This is found, for example, in the aromatic-containing anion $[R'AlR_2]_2^{2-}$, R' = naphthalene and anthracene.[3,4]

The nature of the organic species formed is also sensitive to the solvent and the alkali metal which are used. This is nicely illustrated by the reactions of butadiene with $(CH_3)_3Al$.[1b] The product in THF with sodium is analogous to that described here for cyclooctadiene. With sodium/diglyme or potassium/THF, an octadiene derivative is formed, via the anionic dimerization of two butadiene molecules. In hexamehtylphosphoramide a $(CH_3)_3Al$ butadiene-polymer results. Finally, with potassium amalgam in benzene, the product is of the form

$$K_2[R_3Al\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2AlR_3].$$

An important factor in understanding the above chemistry is the relative importance of ion-pair and solvent separated species. In the less basic solvents such as THF, both solvent and unsaturated groups are effective in competing for a coordination site at teh alkali metal, thus stabilizing any carbanions which may be present.[3,4] In solvents which are more basic or are chelating, so that solvent separated ion pairs become important, the resulting carbanions are more reactive. The consequences of this determine, to a large extent, not only the structural properties of the organometallic species which are formed, but also the selectivity and course of the chemical reactions which take place. For this reason the specific structural details of the alkali metal-unsaturated group interactions are important.

The average K^+-olefin carbon atom distance in $K[(C_8H_{12})_2Al]$ is 3.14 ± 0.17 Å. It is of interest to compare this value with the Na^+-acetylene carbon atom distance reported by Seff as observed in the structure of synthetic zeolite.[11] In this system the Na^+-C distances are in the range 2.6 - 3.0 Å. Using a value of 0.36 Å for the difference in Na^+ and K^+ radii[12] would correspond to an average Na^+-C distance of 2.8 Å in the structure of the sodium analog of the cyclooctene derivative described here, which is well within the range reported by Seff. The sodium-carbon atom distances in the previously mentioned naphthalene and anthracene dimethylaluminates range from 2.89 to 2.96 Å and 2.94 to 3.24 Å, respectively. The shortest distances from the sodium atom to the planes of the aromatic rings are 2.57 and 2.80 Å, respectively. The corresponding average Na-C distances are 2.91 and 3.07 Å, which are again compatible with the range of values observed both by Seff and in the present structure. The relatively large variation in metal atom-unsaturated carbon atom distances observed in the present structure (2.95-3.35 Å) and the above structures suggest that alkali-metal olefin bonding is largely charge-to-induced dipole in nature, as suggested by Seff.

The potassium ions and bis(3,8-cis-cyclooctenyl)-aluminate ions interact to form zig-zag chains along the b-direction of the crystal. Figure 2 is a view down the a-axis of the crystal. Only the two shortest contact distances between the potassium ions and the carbon atoms of the anion are drawn. The potassium-carbon atom distances are illustrated in Figure 3.

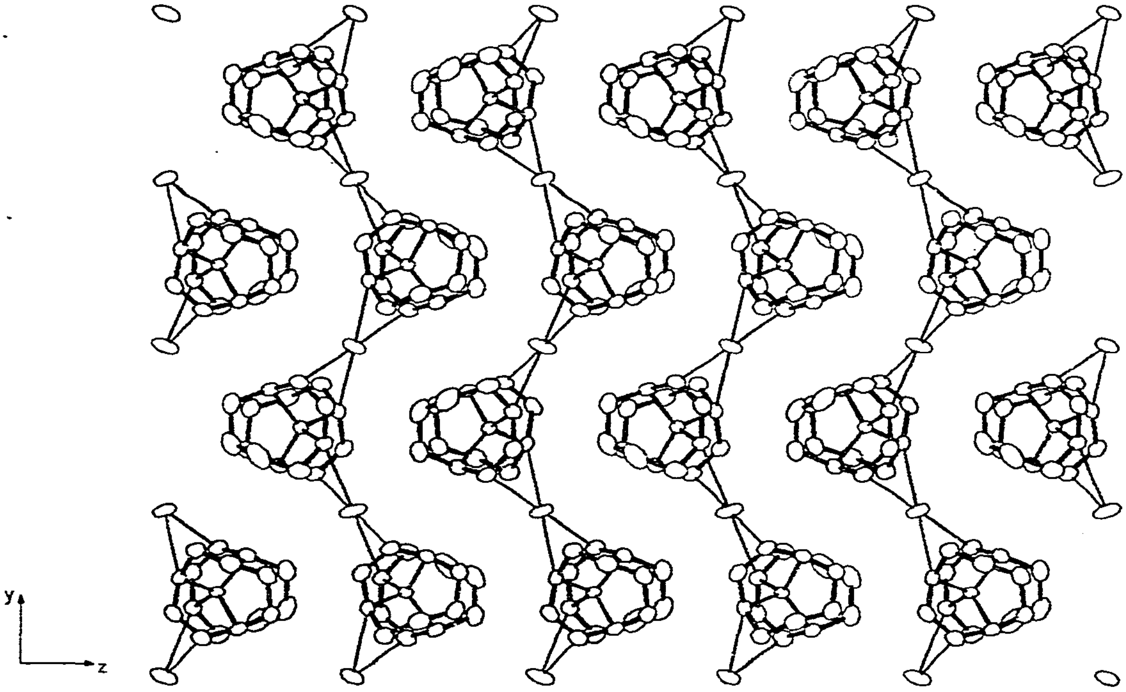


Figure 2. A Perspective View Down the Crystallographic a-axis of $K[(C_8H_{12})_2Al]$.

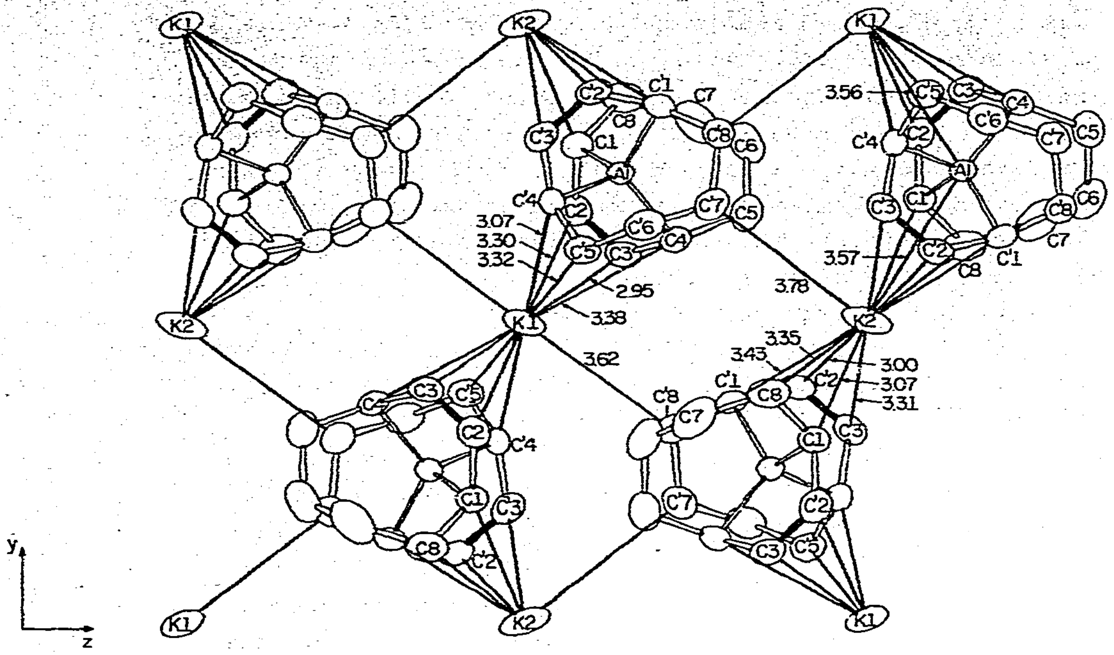


Figure 3. The Coordination Sphere Around the Potassium Ions in $K[(C_8H_{12})_2Al]$.

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