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THE INTERACTION OF AROMATIC HYDROCARBONS WITH ORGANOMETALLIC COMPOUNDS OF THE MAIN GROUP ELEMENTS

III. THE CRYSTAL STRUCTURE OF $K[Al_2(CH_3)_6F]\cdot C_6H_6$

J.L. ATWOOD and W.R. NEWBERRY III

Department of Chemistry, University of Alabama, University, Alabama 35486 (U.S.A.)

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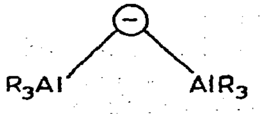
Summary

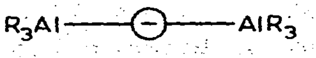
The crystal structure of $K[Al_2(CH_3)_6F]\cdot C_6H_6$ has been determined from three-dimensional X-ray data measured by counter methods. The compound crystallizes in the orthorhombic space group *Pnma* with cell dimensions a = 14.071(5), b = 14.404(5), c = 8.862(3) Å and ρ_{calc} = 1.04 $g\cdot cm^{-3}$ for $Z = 4$. Least squares refinement gave a conventional weighted R factor of 0.037 for 973 independent observed reflections. In the fluorine-bridged anion, the aluminum—fluorine—aluminum bond angle is fixed at 180° by crystallographic symmetry. The aluminum—fluorine bond length of 1.782(2) Å is compared to other halogen-bridged systems. The potassium ion coordination sphere contains six methyl groups at distances from 3.23 to 3.47 Å; the benzene functions as a molecule of crystallization with 3.947(7) Å as the shortest benzene carbon—potassium ion approach.

Introduction

In the preceding paper in this series [1], we enumerated a number of factors of importance in the formation of liquid complexes of compounds of the form $M[Al_2(CH_3)_6X]$ with aromatic molecules. The dominant consideration is that the anionic charge be localized and quite available for interaction with the positive ion. Compounds (such as $K[Al_2(CH_3)_6N_3]$) which exhibit this solution behaviour are all believed to possess an angular anionic structure that shows a sepa-



(A)



(B)

ration of organic and inorganic regions (A). A geometry of this nature affords ample opportunity for strong cation—anion interactions and for a liquid orientation of anions in a manner such as to trap aromatic molecules. On the other hand, a symmetrical anionic structure (B) does not produce the same solution effects. We report here the structural parameters of a molecule of this type, $K[Al_2(CH_3)_6F]\cdot C_6H_6$, and point out the difference between molecules of solvation commonly found in a wide range of systems and the liquid complex formation.

Experimental

$K[Al_2(CH_3)_6F]\cdot C_6H_6$ was prepared by the sealed tube reaction of 0.01 mole of KF and 0.02 mole of $Al(CH_3)_3$ in 0.10 mole of benzene. Reaction began immediately and went rapidly to completion at 80°; no evidence of the liquid layering effect [1,2] was noted.

Single crystals of the colorless, air-sensitive product were selected from the benzene solution and sealed in thin-walled glass capillaries. The crystal system is orthorhombic and systematic absences allow the space group to be *Pnma* or *Pna*2_1. However, statistical tests based on normalized structure factors show that the correct choice is the centric *Pnma*. The lattice parameters as determined from a least-squares refinement of the angular settings of 12 reflections accurately centered on an Enraf-Nonius CAD-4 diffractometer are: $a = 14.071(5)$, $b = 14.404(5)$, $c = 8.862(3)$ Å, $\rho_{calc} = 1.04$ g·cm^{-3} for $Z = 4$. Data were collected on the CAD-4 diffractometer with graphite crystal monochromated copper radiation ($\lambda = 1.54051$ Å). The crystal, a rectangular block of dimensions 0.40 mm × 0.50 mm × 0.40 mm, was aligned on the diffractometer such that no symmetry axis was coincident with the ϕ axis of the diffractometer.

The diffracted intensities were collected by the ω—2θ scan technique with a take-off angle of 3.0°. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 0.5° min^{-1}. Background counts were collected for 25% of the total scan time at each end of the scan range. For each intensity the scan width was determined by the equation: scan range = $A + B\tan\theta$, where $A = 0.85°$ and $B = 0.45°$. Aperture settings were determined in a like manner with $A = 4$ mm and $B = 4$ mm. Other diffractometer parameters and the method of calculating standard deviations have been described previously [3]. As a check on the stability of the instrument and the crystal, one standard peak was measured periodically during data collection. No significant decrease in intensity was noted.

One unique octant of data was measured out to $2\theta = 120°$; 973 reflections with intensities greater than background were recorded. The intensities were corrected in the usual manner for Lorentz and polarization effects, but not for absorption because of the moderate value of the linear absorption coefficient ($\mu = 29.3$ cm^{-1}); the estimated transmission factors differ by less than 5%.

Fourier calculations were made with the ALFF [4] program. The full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS [5]. The function $\Sigma W(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction or anomalous dispersion. Neutral atom scattering factors were taken from the compilations of Cromer and Waber [6]. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE [7] program. The crystal structure illustrations were obtained with the program ORTEP [8].

Structure determination and refinement

The position of the potassium and fluorine atoms were deduced from the Patterson map with the use of the symmetry demanded by the presence of 4 molecules in the unit cell. An electron density map phased on these positions revealed the location of all nonhydrogen atoms in the asymmetric unit. Isotropic refinement led to a reliability index of

$$R_1 = \frac{\Sigma(|F_o| - |F_c|)}{\Sigma|F_o|} = 0.090$$

Conversion to anisotropic refinement together with the application of a weighting scheme ($W = 1/\sigma^2$) yielded $R_1 = 0.058$. At this point a difference Fourier map was calculated, and the hydrogen atom coordinates were determined. Further anisotropic refinement of nonhydrogen atoms and refinement of the hydrogen atom positional parameters led to final values of $R_1 =$ 0.038 and

$$R_2 = \left\{\frac{\Sigma W(|F_o| - |F_c|)^2}{\Sigma W(F_o)^2}\right\}^{1/2} = 0.037$$

The largest parameter shifts in the final cycle of refinement were less than 0.05 of their estimated standard deviations. A final difference Fourier map showed no feature greater than 0.3 $e/\text{Å}^3$. No systematic variation of $W(|F_o| - |F_c|)^2$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was observed. The final values of the positional and thermal parameters are given in Table 1*.

Discussion

Two features of the structure of the anion (Fig. 1) are worth particular note. Since the fluorine atom resides on a crystallographic center of inversion, the aluminum—fluorine—aluminum bond angle is 180°. The observed aluminum—fluorine bond distance, 1.782(2) Å, would by past standards be regarded as quite short even for a singly bonded fluorine atom [9]. The same situation was found for the closely related compound $K[Al_2(C_2H_5)_6F]$ [10], where the aluminum—fluorine distance is 1.820(3) Å. Allegra and Perego postulated *sp* hybridization of the fluorine atom to explain the exact linear coordination of the two aluminum atoms. The aluminum—fluorine bond distance was accounted for by a degree of overlap between filled fluorine *p* orbitals and empty aluminum

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* The table of structure factors has been deposited as NAPS Document No. 02235, with ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th Street, New York, New York 10017. A copy may be secured by citing the document and remitting 1.50 for microfiche or 5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 1

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS [a,b] FOR $K[Al_2(CH_3)_6F] \cdot C_6H_6$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
F	0.5000	0.0000	0.0000	103(2)	107(2)	198(5)	24(2)	58(3)	− 8(3)
K	0.6598(1)	0.2500	0.5218(1)	73(1)	44(1)	223(2)	0	37(1)	0
Al	0.4390(1)	0.0372(1)	0.1657(1)	48(1)	51(1)	122(1)	4(1)	7(1)	11(1)
C(1)	0.4044(3)	−0.0766(3)	0.2708(6)	75(3)	78(3)	231(8)	− 9(2)	−12(4)	51(4)
C(2)	0.5330(4)	0.1105(3)	0.2737(7)	91(3)	68(3)	320(10)	−14(2)	−38(5)	2(4)
C(3)	0.3292(3)	0.1058(3)	0.0859(5)	85(3)	74(3)	197(7)	25(3)	−26(4)	5(4)
C(4)	0.3750(6)	0.2500	0.6924(9)	91(7)	169(10)	346(21)	0	−12(9)	0
C(5)	0.3446(4)	0.3321(4)	0.6356(8)	106(5)	119(5)	379(15)	−13(4)	45(7)	−51(8)
C(6)	0.2837(4)	0.3306(4)	0.5157(7)	145(6)	102(4)	315(13)	19(5)	44(7)	2(7)
C(7)	0.2533(7)	0.2500	0.4594(9)	155(9)	138(8)	243(16)	0	−17(9)	0
H(1)	0.4038(29)	−0.1291(29)	0.2150(40)	*c*					
H(2)	0.3513(27)	−0.0785(29)	0.3026(45)						
H(3)	0.4351(29)	−0.0887(26)	0.3589(42)						
H(4)	0.5786(26)	0.0749(27)	0.3160(42)						
H(5)	0.5508(27)	0.1639(29)	0.2225(42)						
H(6)	0.5128(28)	0.1490(30)	0.3147(47)						
H(7)	0.3084(26)	0.0822(28)	0.0002(43)						
H(8)	0.3488(27)	0.1693(30)	0.0369(46)						
H(9)	0.3019(27)	0.1374(28)	0.1556(45)						
H(10)	0.3968(40)	0.2500	0.7809(58)						
H(11)	0.3657(25)	0.3950(27)	0.6900(41)						
H(12)	0.2587(27)	0.3910(28)	0.4811(39)						
H(13)	0.2109(39)	0.2500	0.3744(61)						

[a] Standard deviations in parenthese refer to last digit quoted.

[b] Anisotropic thermal parameters X 10^4 defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}hl)]$

[c] Isotropic thermal parameters set at 6.0 Å for all hydrogen atoms.

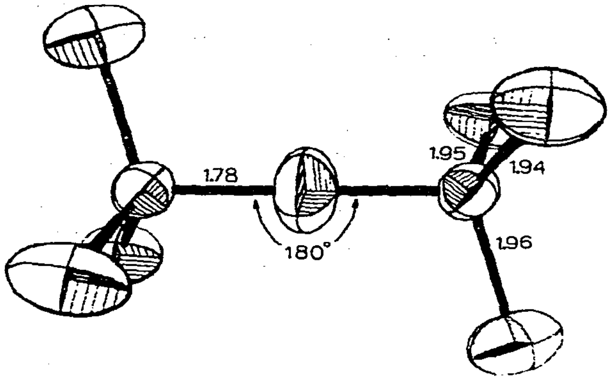
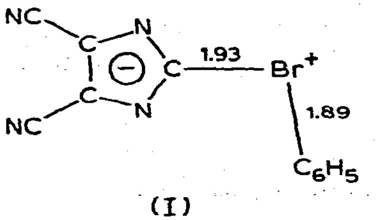


Fig. 1. Structure of the $[Al_2(CH_3)_6F]^-$ ion with the atoms presented as their 50% probability ellipsoids for thermal motion.

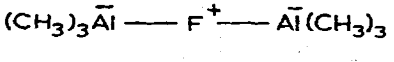
d orbitals. However, the meaning of bond distances in compounds of this type is far from straightforward. While it is true that a bridging halide ion may exhibit a longer bond length than a terminal one (i.e., in $[CH_3AlCl_2]_2$ the Al—Cl bridge separation is 2.25(1) Å compared to the Al—Cl terminal length of 2.05(1) Å [11]), factors other than intrinsic bond strength may play a large role. There now exist systems somewhat comparable to that of $[Al_2(CH_3)_6F]^-$ where the halogen-bonded element *cannot* use *d* orbitals. One such is the recently determined bromoylide structure (I) [12]. Here the two carbon—bromide bond lengths are not far different from that of bromobenzene (1.86(2) Å) [13]. Therefore, the use of aluminum *d* orbitals is not necessarily implied by the aluminum—fluorine bond distance in either $K[Al_2(C_2H_5)_6F]$ or $K[Al_2(CH_3)_6F]\cdot C_6H_5$.

Haaland and coworkers [14] have recently added to the literature the structure of a third fluorine-bridged organoaluminum compound: $[(CH_3)_2AlF]_4$. In the puckered Al_4F_4 ring, the aluminum—fluorine distance is 1.810(3) Å and the aluminum—fluorine—aluminum bond angle is 146(3)°. Thus it seems that in organoaluminum compounds of this sort, an aluminum—fluorine bond length of 1.80 Å should now be regarded as normal.

The coordination sphere of the potassium ion, which lies on a mirror plane, is shown in Fig. 2 and the packing in the unit cell is illustrated by Fig. 3. The nearest neighbors are six methyl groups in symmetry related pairs at 3.230(4), 3.302(3), and 3.472(4) Å. Since the closest aryl—carbon—potassium approach is 3.947(7) Å, the benzene molecule merely occupies a lattice site, and has no strong preferential interaction with cation or anion. This behavior appears to be quite common [15,16] and should not be confused with the type of interaction shown by the solution studies [1,2] on $K[Al_2(CH_3)_6N_3]$ and structurally related compounds.



(I)



$$(CH_3)_3\overset{-}{Al} — \overset{+}{F} — \overset{-}{Al}(CH_3)_3$$

(II)

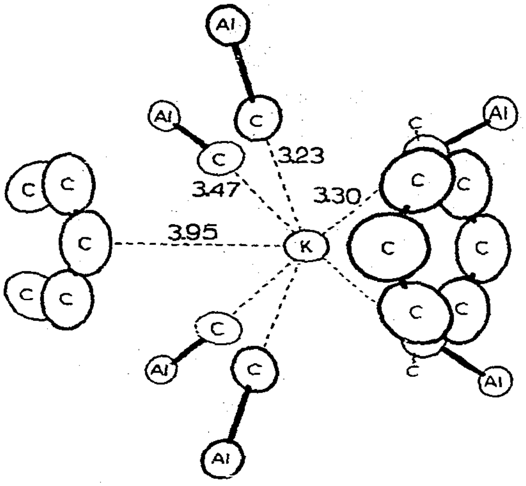


Fig. 2. Coordination sphere of the potassium ion in $K[Al_2(CH_3)_6F]\cdot C_6H_6$.

The aluminum—carbon bond lengths of 1.943(5), 1.946(5) and 1.965(4) Å fall near the values observed in other similar well-determined structures: 1.953(2) in $[Al(CH_3)_3]_2$ [17] and 1.971(4) in $K[Al(CH_3)_3CN]$ [16]. Within the aromatic ring the bond lengths and angles are normal for a benzene of solvation [18].

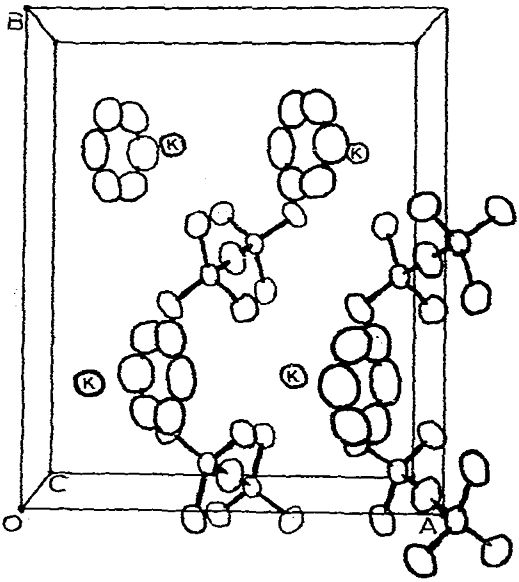


Fig. 3. Packing of four units of $K[Al_2(CH_3)_6F]\cdot C_6H_6$ shown with a superimposed unit cell.

TABLE 2

INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR K[Al$_2$(CH$_3$)$_6$F]·C$_6$H$_6$

Bond distances

Al—F	1.782(2)	Al—C(1)	1.946(5)
Al—C(2)	1.943(5)	Al—C(3)	1.965(4)
C(4)—C(5)	1.355(6)	C(5)—C(6)	1.364(6)
C(6)—C(7)	1.334(6)	C(3)—H(7)	0.88
C(1)—H(1)	0.90 [a]	C(3)—H(8)	1.05
C(1)—H(2)	0.80	C(3)—H(9)	0.86
C(1)—H(3)	0.91	C(4)—H(10)	0.84
C(2)—H(4)	0.90	C(5)—H(11)	1.07
C(2)—H(5)	0.93	C(6)—H(12)	0.99
C(2)—H(6)	0.87	C(7)—H(13)	0.96

Bond angles

C(1)—Al—C(2)	113.1(2)	C(1)—Al—F	105.2(1)
C(1)—Al—C(3)	113.5(2)	C(2)—Al—F	103.9(1)
C(2)—Al—C(3)	116.0(2)	C(3)—Al—F	103.5(1)
C(5)—C(4)—C(5) [b]	121.6(6)	C(5)—C(6)—C(7)	120.5(6)
C(4)—C(5)—C(6)	118.2(6)	C(6)—C(7)—C(6) [b]	121.0(6)

[a] Standard deviations of all carbon—hydrogen distances are 0.05 Å

[b] Related to C(5) and C(6) by the symmetry operation (x, ½−y, z).

Acknowledgements

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