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THERMAL DECOMPOSITION OF ANIONIC ORGANOALUMINUM COMPOUNDS

IV. THE FORMATION OF ALKALI METAL TETRAMETHYLALUMINATES AND THE CRYSTAL STRUCTURE OF $Rb[Al(CH_3)_4]$

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SUMMARY

Thermolytic or photolytic decomposition of $M[Al_2(CH_3)_6N_3]$ in aromatic solvents produces quantitative yields of $M[Al(CH_3)_4]$. The crystal structure of $Rb[Al(CH_3)_4]$ has been determined from three-dimensional X-ray data measured by counter methods. Rubidium tetramethylaluminate crystallizes in the tetragonal space group $I4_1/amd$ with cell dimensions (T23°) $a=b=9.931(3)$, $c=8.031(3)$Å, and $\rho_{calc}=1.45\ g\cdot cm^{-3}$ for $Z=4$. Least squares refinement gave a conventional R factor of 0.048 for 214 independent observed reflections. In the distorted tetrahedral anion the two independent carbon–aluminum–carbon angles are 106.0(2)° and 115.6(3)°, and the carbon–aluminum bond length is 2.006(8)Å.

INTRODUCTION

The 1/1 complex of tetramethylammonium iodide and trimethylaluminum has been shown to yield upon thermolysis[1] the trimethylamine complex of iododimethylaluminum:

$$[N(CH_3)_4][Al(CH_3)_3I] \xrightarrow{280^\circ} (CH_3)_3N\cdot Al(CH_3)_2I + C_2H_6$$

On the other hand, the 2/1 complex of trimethylaluminum and potassium thiocyanate behaves in a different manner[2,3].

$$K[Al_2(CH_3)_6SCN] \xrightarrow{120^\circ} [(CH_3)_2CN\cdot Al(CH_3)_2]_2 + \text{decomposition products}$$

With these reactions in mind and in view of the notorious thermolytic and photolytic reactivity of organic azides[4] it seemed likely that new preparative routes might be found via compounds of the type $M[Al_2(CH_3)_6N_3]$ and $M[Al(CH_3)_3N_3]$. Weller and Dehnicke[5] have previously mentioned the high temperature conversion of the 2/1 into the 1/1 complex:

$$[N(CH_3)_4][Al_2(CH_3)_6N_3] \xrightarrow{180-190^\circ} [N(CH_3)_4][Al(CH_3)_3N_3] + Al(CH_3)_3$$

We wish to report the thermal decomposition of the benzene and toluene complexes[6] of $Rb[Al_2(CH_3)_6N_3]$ and $K[Al_2(CH_3)_6N_3]$ to give the corresponding tetramethylaluminates:

$$M[Al_2(CH_3)_6N_3] \xrightarrow{180^\circ} M[Al(CH_3)_4] + N_3Al(CH_3)_2$$

The results of a single-crystal X-ray structural investigation of $Rb[Al(CH_3)_4]$ are also discussed[7].

EXPERIMENTAL

A. *Preparations**

The air-sensitive complex of $M[Al_2(CH_3)_6N_3]$ with either benzene or toluene was prepared by the sealed tube reaction[6] of 0.01 mole MN_3 with 0.02 mole $Al(CH_3)_3$ in an excess of aromatic hydrocarbon (≈ 0.10 mole). At 80° with toluene, for example, the liquid complex $M[Al_2(CH_3)_6N_3] \cdot n\ C_6H_5CH_3$, where $n \approx 2 \rightarrow 5$, was quickly obtained. The substance was then removed from the excess toluene and transferred to a tube for thermolysis. Heating at 180° for 10 days produced a quantitative yield of $K[Al(CH_3)_4]$, while the reaction with the rubidium salt reached completion in a much shorter period of time (≈ 2 days). In each case, the tetramethylaluminate was identified by complete elemental analysis and by single-crystal X-ray precession photographs. A pale-yellow, viscous liquid also produced was suspected of being a polymeric material based on $N_3Al(CH_3)_2$. The infrared spectrum of the substance was almost identical to that reported for $[N_3Al(CH_3)_2]_3$[8,9]. The tetramethylaluminate may be separated from dimethylaluminum azide by repeated washing with hydrocarbon solvents. $K[Al(CH_3)_4]$ and $Rb[Al(CH_3)_4]$ were also obtained by photolysis at 3000 or 2537 Å of the parent 2/1 complexes in benzene or toluene.

B. *X-ray data collection*

Single crystals of rubidium tetramethylaluminate were obtained from the residue of the photolysis experiment and sealed in thin-walled glass capillaries. Preliminary unit cell parameters were determined from precession (Mo-K_α) photographs. The crystal system is tetragonal, and systematic absences uniquely define the space group as $I4_1/amd$. The lattice constants as determined from a least-squares refinement of $(\sin\theta/\lambda)^2$ values of 12 reflections are: $a = b = 9.931(3)$, $c = 8.031(3)$ Å, and $\rho_{calc} = 1.45$ $g \cdot cm^{-3}$ for $Z = 4$. Data were taken on an Enraf–Nonius CAD-4 diffractometer with crystal monochromated Cu-K_α radiation. The crystal, a plate of dimensions 0.08 mm × 0.13 mm × 0.55 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 and the standard deviations determined in a manner previously described[3]. A total of 214 independent observed reflections ($I > 2\sigma(I)$) were measured out to 2θ 160° and corrected for absorption[10] (μ 97.0 cm^{-1}). The minimum and maximum transmission factors were 0.40 and 0.60, respectively.

Fourier calculations were made with the ALFF[11] program. The full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS[12].

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* None of the compounds identified herein have thus far proved to present an explosive hazard.

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[13]. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy program ORFFE[14] program. The crystal structure illustration was obtained with the program ORTEP[15].

C. Structure determination and refinement

The initial Fourier series phased on the rubidium and aluminum atoms in their

TABLE 1

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES FOR RUBIDIUM TETRAMETHYLALUMINATE

H	K	CBS	CAL	H	K	CBS	CAL	H	K	OBS	CAL	H	K	CBS	CAL
******L= 0*******				3	12	10.8	10.5	2	7	25.7	25.4	8	0	8.1	7.2
2	0	171.9	192.2	******L= 2*******				4	7	20.9	21.3	10	0	3.3	3.1
4	0	148.0	154.1	2	0	66.5	61.5	8	7	12.0	12.0	1	1	79.9	80.3
6	0	133.0	127.7	4	0	29.2	27.9	1	8	21.1	21.6	3	1	71.2	68.3
8	0	74.4	71.5	6	0	3.5	0.5	3	8	11.8	11.9	5	1	64.0	60.2
10	0	52.0	49.7	8	0	13.9	12.4	0	9	10.7	11.3	7	1	47.0	45.0
12	0	33.8	33.1	10	0	4.5	5.0	1	10	15.8	14.5	6	2	9.1	9.1
2	2	102.8	108.0	12	0	2.7	0.2	******L= 4*******				3	3	59.7	59.2
4	2	109.8	108.7	1	1	139.9	151.3	0	0	94.6	77.4	5	3	51.1	52.3
6	2	104.4	100.3	3	1	143.8	142.2	2	0	110.4	104.3	7	3	39.6	39.6
8	2	58.8	57.3	5	1	106.6	103.7	10	0	33.6	32.5	9	3	24.8	27.0
10	2	42.7	40.3	7	1	80.8	77.0	2	2	120.0	125.8	6	4	6.8	6.3
12	2	26.9	28.0	9	1	56.8	53.0	8	2	60.4	57.2	5	5	42.6	45.4
4	4	93.5	97.5	11	1	33.7	33.4	10	2	36.7	36.2	7	5	32.3	34.7
6	4	84.9	85.4	4	2	3.2	5.2	1	3	6.8	6.5	7	7	26.0	26.5
8	4	51.5	52.1	6	2	18.5	17.3	0	4	68.1	65.2	6	8	4.7	4.5
10	4	37.6	36.5	10	2	1.1	1.5	2	4	96.2	101.8	1	9	29.4	30.6
6	6	72.6	75.2	12	2	4.8	3.2	4	4	83.9	84.2	******L= 7*******			
8	6	45.4	47.2	3	3	120.7	124.2	6	4	54.4	56.5	0	1	15.0	13.3
10	6	32.7	33.0	5	3	93.5	94.1	8	4	49.1	48.9	1	2	16.5	15.9
8	8	28.6	29.7	7	3	71.9	70.0	10	4	30.5	31.2	0	3	22.3	22.7
******L= 1*******				9	3	50.9	48.9	0	6	57.2	55.0	2	3	23.8	24.6
0	1	42.2	44.5	11	3	30.8	31.1	2	6	64.1	66.3	1	4	14.7	13.7
1	2	35.8	39.1	6	4	12.3	11.1	6	6	35.1	38.2	3	4	19.6	21.4
3	2	25.7	24.1	5	5	74.8	76.9	8	6	33.1	34.4	0	5	9.6	9.3
0	3	92.8	90.7	7	5	56.7	57.7	0	8	55.7	50.8	2	5	11.4	11.1
2	3	79.5	78.6	9	5	39.8	40.3	8	8	30.1	29.5	4	5	9.5	9.4
1	4	32.6	36.6	11	5	25.3	25.8	******L= 5*******				1	6	9.3	8.6
3	4	53.1	56.2	8	6	7.0	6.6	0	1	36.6	35.7	3	6	13.7	14.8
0	5	23.2	27.5	10	6	3.2	3.0	1	2	37.3	38.6	5	6	6.1	6.1
2	5	25.7	28.8	7	7	42.2	43.8	0	3	17.2	15.5	0	7	8.8	8.6
4	5	23.4	25.2	9	7	30.4	31.0	2	3	18.3	17.2	2	7	10.2	10.0
1	6	25.8	30.2	******L= 3*******				1	4	31.5	32.7	4	7	8.6	8.7
3	6	39.1	40.1	11	0	14.1	12.9	3	4	16.0	15.2	1	8	9.3	8.3
5	6	19.3	20.1	0	1	71.1	69.9	0	5	28.4	27.9	3	8	12.0	12.2
7	6	15.8	16.5	1	2	55.2	55.3	2	5	27.3	27.9	0	9	10.1	9.6
0	7	26.1	25.0	9	2	9.6	10.7	4	5	23.7	24.5	******L= 8*******			
2	7	24.8	24.1	11	2	13.0	11.8	1	6	20.7	21.8	0	0	66.7	61.2
4	7	19.7	20.5	0	3	22.0	23.9	3	6	9.7	10.1	2	0	51.9	49.0
1	8	18.9	19.3	2	3	21.9	22.1	5	6	16.4	17.4	2	2	37.3	37.6
3	8	25.9	26.7	4	3	18.4	19.1	0	7	20.2	18.4	4	2	33.1	33.8
5	8	14.3	14.2	10	3	9.0	8.3	2	7	20.3	18.6	6	2	30.9	32.7
7	8	11.8	11.9	1	4	41.2	43.5	4	7	16.7	16.3	0	4	40.7	43.9
0	9	28.5	25.0	5	4	31.0	31.9	6	7	11.7	11.8	4	4	26.4	30.5
2	9	26.8	22.4	9	4	8.4	9.4	1	8	19.2	17.6	6	4	24.7	29.4
4	9	21.9	19.4	11	4	11.3	10.3	3	8	10.8	9.4	0	6	38.0	40.7
6	9	17.1	15.8	0	5	41.1	41.7	5	8	13.9	13.7	******L= 9*******			
8	9	12.2	11.3	2	5	39.3	40.0	7	8	9.7	9.4	3	0	15.3	16.0
1	10	14.1	12.1	8	5	17.5	17.2	0	9	7.2	7.5	5	0	6.1	7.0
3	10	18.0	17.4	10	5	11.2	11.4	2	9	7.7	8.3	0	1	10.9	9.9
5	10	9.7	9.4	1	6	37.3	35.5	4	9	6.8	7.3	2	1	8.0	6.7
7	10	8.2	8.0	3	6	19.4	18.0	6	9	4.6	5.1	4	1	5.7	6.0
0	11	8.0	9.4	5	6	25.1	25.4	1	10	11.3	11.1	3	2	10.7	12.7
2	11	8.3	8.4	7	6	17.2	17.3	3	10	6.9	6.2	5	2	4.2	4.5
4	11	6.9	7.3	9	6	7.4	8.2	******L= 6*******				3	4	8.8	11.2
1	12	6.3	9.1	0	7	27.4	26.7	2	0	13.0	15.9				
								4	0	12.7	12.0				

symmetry-fixed positions ($\bar{4}2m$) yielded the coordinates of the carbon atom. Several cycles of isotropic refinement with weights based on $1/\sigma^2$ lowered the reliability index:

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

to 0.088. Conversion to anisotropic temperature factors reduced R_1 to 0.081. A difference Fourier clearly showed the positions of the two hydrogen atoms in the asymmetric unit, and the inclusion of their contributions followed by further anisotropic refinement of the rubidium, aluminum, and carbon atom parameters gave final R values of:

$$R_1 = 0.048$$

$$R_2 = \left\{\frac{\Sigma W(|F_o|-|F_c|)^2}{\Sigma W(F_o)^2}\right\}^{\frac{1}{2}} = 0.049$$

The largest parameter shifts in the final cycle of refinement were less than 0.07 of their estimated standard deviations. The only feature over 0.2 $e^-/Å^3$ in the last difference Fourier map was one of 0.8 $e^-/Å^3$ near the rubidium atom. The value of the standard deviation of an observation of unit weight was 1.60. Final observed and calculated structure factor amplitudes are listed in Table 1. The final values of the positional and thermal parameters are given in Table 2.

TABLE 2

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS[a,b] FOR RUBIDIUM TETRAMETHYLALUMINATE

Atom	*x/a*	*y/b*	*z/c*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rb	0.0000	0.2500	0.3750	0.0083(2)	0.0083(2)	0.0128(2)			
Al	0.5000	0.2500	0.6250	0.0065(5)	0.0065(5)	0.0082(5)			
C	0.3281(8)	0.2500	0.4935(9)	0.0114(9)	0.0114(9)	0.0099(10)		−0.0002(10)	
H(1)	0.32	0.17	0.43	[c]					
H(2)	0.23	0.2500	0.54						

[a] Standard deviations in parentheses refer to last digit quoted. [b] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}\cdot h^2+\beta_{22}\cdot k^2+\beta_{33}\cdot l^2+2\beta_{12}\cdot h\cdot k+2\beta_{13}\cdot h\cdot l+2\beta_{23}\cdot k\cdot l)]$. [c] Isotropic B set at 6.0 $Å^2$ for both hydrogen atoms.

DISCUSSION

The thermal decomposition of 2/1 anionic organoaluminum azides according to the equation:

$$M[Al_2(CH_3)_6N_3] \xrightarrow[\text{toluene}]{180°} M[Al(CH_3)_4]+N_3Al(CH_3)_2$$

points to the rather high stability of the azide group in this environment. Although in some circumstances a pressure build-up probably signaling the release of N_2 was noted, the major product is in all cases the tetramethylaluminate.

The substance given in the equation as $N_3Al(CH_3)_2$ was characterized primarily on the basis of very strong azido-group infrared absorptions at 2150 and 1220 cm^{-1}. The overall infrared spectrum was quite like that shown for the trimer $[N_3Al(CH_3)_2]_3$[8,9], and it seems likely that the pale yellow liquid is a polymer of higher order. At the time of generation of $N_3Al(CH_3)_2$, the reaction temperature was 180°; far above the 65° melting point reported for the trimer[8].

An important feature of the thermolysis and photolysis of the compounds under discussion is that all were done on the liquid complexes of $K[Al_2(CH_3)_6N_3]$ and $Rb[Al_2(CH_3)_6N_3]$ with benzene and toluene. A proposed mechanism of interaction of $M[Al_2(CH_3)_6X]$ with aromatic molecules has been briefly described[6,16], but the implications of the high temperature stability of these substances is now worth noting. Thus, the toluene complex of $K[Al_2(CH_3)_6N_3]$ is stable for many days at 180°, as evidenced by the appearance of the liquid-layering effect[6] in the presence of excess toluene. The force which holds the aromatic molecules in association with the ions must therefore be quite strong.

The crystal structure of $Rb[Al(CH_3)_4]$ has been previously determined from powder diffraction data by Weiss *et al.*[7]. Two features of the structure made it of interest to examine the structure of the anion in more detail. First, the very long aluminum–carbon distance of 2.06(10) Å, although not statistically significant because of the large standard deviation associated with it, fits well with the values found in other tetraalkylaluminates: 2.10(10)Å in $K[Al(CH_3)_4]$[7] and 2.023(6) Å in $Li[Al(C_2H_5)_4]$[17].

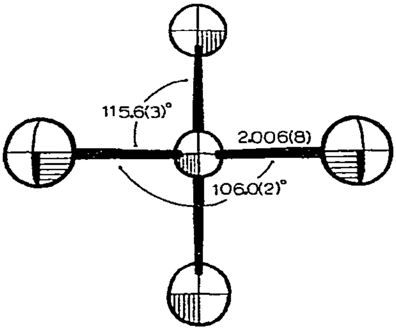

Fig. 1. Structure of the tetramethylaluminate anion in $Rb[Al(CH_3)_4]$. Atoms are displayed as their 50% probability ellipsoids for thermal motion.

The present single-crystal study has established the aluminum–carbon length at 2.006(8) Å. It is therefore only slightly longer than the average single bond Al–C distances in such compounds as $[Al(CH_3)_3]_2$[18], 1.953(2) Å, and $K[(CH_3)_3AlCN]$[19], 1.971 (5) Å.

The second noteworthy feature of the structure is the marked distortion from tetrahedral symmetry of the anion. The two independent values of the carbon–aluminum–carbon bond angles are 106.0(2)° and 115.6(3)°. Simple packing forces may be evoked to explain this deviation, but there are no data with which to rule out an electronic origin.

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