Journal of Organometallic Chemistry, 47 (1973) 321–329

THE SYNTHESIS AND STRUCTURE OF POTASSIUM CYANOTRIMETHYLALUMINATE

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(Received June 20th, 1972)

SUMMARY

The reaction of KCN with $Al(CH_3)_3$ to form $K[Al(CH_3)_3CN]$ is greatly facilitated by the presence of an aromatic solvent: for *p*-xylene a solid complex, $K[Al(CH_3)_3CN] \cdot C_6H_4(CH_3)_2$, has been isolated. The crystal structure of potassium cyanotrimethylaluminate has been determined from three-dimensional X-ray data measured by counter methods. $K[Al(CH_3)_3CN]$ crystallizes in the monoclinic space group $C2/c$ with cell dimensions $a = 19.902(7)$, $b = 9.211(4)$, $c = 9.615(4)$ Å, $\beta = 107.74(5)°$, and $\rho_{calcd.} = 1.09$ g cm^{-1} for $Z = 8$. Least squares refinement gave a conventional weighted R factor of 4.9% for 807 independent reflections. The monomeric $[Al(CH_3)_3CN]^-$ units possess no crystallographic symmetry, and the packing in the unit cell is such that the nitrogen atoms on three such units approach the potassium atom to within 3.11 Å. The average aluminum–methyl carbon bond distance is 1.971 (7) Å, while the aluminum–cyano carbon distance is 2.047 (7) Å. This significant lengthening is attributed to partial electron deficiency in the aluminum–cyano carbon bond.

INTRODUCTION

Alkali metal halides react with trialkylaluminum compounds to form 1/1, $M[AlR_3X]$, and 2/1, $M[Al_2R_6X]$, complexes[1]. From a tabulation of the physical properties of substances of both types, Lehmkuhl[2] has concluded that complexation occurs most readily for the cases in which the ionic radius of the alkali metal is large, the alkyl chain is short, and the complex anion is small. The essential considerations are therefore the lattice energies of MX and $M[AlR_3X]$ or $M[Al_2R_6X]$. The same trend in reactivities holds also for the alkali metal thiocyanates[3,4] and azides[5]. Only the 2/1 complex of tetramethylammonium cyanide and trimethylaluminum has been reported[4], apparently because of the higher lattice energy of the Group Ia cyanides compared to Group Ia thiocyanates and azides[5].

No structural data has been thus far presented on any alkali metal pseudohalide complex of an alkylaluminum, although serious questions as to the nature of the complex anion have arisen[6,7]. Recent reports of unexpected thermal behavior for compounds of this general type[6,8] also make it desirable to place the stereo-

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chemistry of anionic organoaluminum compounds on a firm basis. We therefore report here the synthesis and structure of $K[Al(CH_3)_3CN]$, and the isolation of an intermediate in the preparation, $K[Al(CH_3)_3CN]\cdot C_6H_4(CH_3)_2$.

EXPERIMENTAL

The preparation of potassium cyanotrimethylaluminate was attempted in two ways. 1/1 molar ratios of KCN and $(CH_3)_3Al$ were placed in a bomb tube within an inert atmosphere box and later sealed under a vacuum of 10^{-4} mmHg. No reaction was observed after many days of heating at temperatures in excess of 180°. (With NaCN similar results were obtained, but with RbCN a small quantity of product was isolated after a reaction time of many weeks). The second method of preparation involved the addition of an aromatic hydrocarbon in a quantity such that the molar ratio in the sealed tube was 1/1/1. Reaction then proceeded rapidly at 100° for benzene, toluene, or *p*-xylene. In all cases an oxygen- and water-sensitive complex was isolated containing a stoichiometric amount of the aromatic molecule. The complex of *p*-xylene is a white powder which elemental analysis showed to be $K[Al(CH_3)_3CN]\cdot C_6H_4(CH_3)_2$. (Found: C, 59.29; H, 8.25; Al, 11.03; K, 15.65; N, 5.74. $K[Al(CH_3)_3CN]\cdot C_6H_4(CH_3)_2$ calcd.: C, 59.30; H, 7.83; Al, 11.11; K, 16.08; N, 5.76%.) Potassium cyanotrimethylaluminate was obtained solvent free from tetrahydrofuran solution of $K[Al(CH_3)_3CN]\cdot C_6H_4(CH_3)_2$.

$$KCN + Al(CH_3)_3 + C_6H_4(CH_3)_2 \xrightarrow{100^\circ} K[Al(CH_3)_3CN]\cdot C_6H_4(CH_3)_2 \xrightarrow{THF}$$
$$\longrightarrow K[Al(CH_3)_3CN] + C_6H_4(CH_3)_2$$

Single crystals of $K[Al(CH_3)_3CN]$ were grown by slow evaporation of a tetrahydrofuran solution and sealed in thin-walled glass capillaries. Preliminary unit cell parameters were determined by precession (Cu-$K\alpha$) photographs. The crystal system is monoclinic. Systematic absences allow the space group to be $C2/c$ or Cc. The lattice parameters as determined from a least-squares refinement of $(\sin\theta/\lambda)^2$ values of 10 reflections are: $a = 19.902(7)$, $b = 9.211(4)$, $c = 9.615(4)$ Å, $\beta = 107.74(5)°$, $V = 1679$ Å^3. The calculated density is 1.09 g·cm^{-3} with $Z = 8$. Data were taken on an ENRAF–NONIUS CAD-4 diffractometer with Ni filtered copper radiation. The crystal, a block of dimensions 0.15 mm × 0.10 mm × 0.10 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 $\omega - 2\theta$ scan technique with a take-off angle of 1.5°. 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 0.4° 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 $A = 0.9°$ and $B = 0.5°$. Aperture settings were determined in a like manner with $A = 4$ mm and $B = 3$ mm. The crystal-to-source and crystal-to-detector distances were 21.6 and 20.8 cm, respectively. The lower level and upper level discriminators of the pulse height analyzer were set to obtain a 95% window centered on the Cu-$K\alpha$ peak. As a check on the stability of the diffractometer and the crystal, three standard peaks were measured periodically during data collection. No significant variation in the intensity of the standards was noticed.

The standard deviations of the intensities, σ_I were estimated from the formula:

$$\sigma_I = \{[C_N + (T_C/2T_B)^2 \cdot (B_1 + B_2)] + 0.03\,[C_N + (T_C/2T_B)^2 \cdot (B_1 + B_2)]^2\}^{\frac{1}{2}}$$

where C_N is the counts collected during scan time T_C, and B_1 and B_2 are background intensities, each collected during the background time T_B. Two symmetry related quadrants of data were measured out to $2\theta = 100°$, and one quadrant to $2\theta = 120°$. A total of 1813 reflections were collected of which 807 were unique and had intensities greater than background.

The intensities were then corrected in the usual manner for Lorentz and polarization effects but not for absorption because of the moderate size of the linear absorption coefficient ($\mu = 57.7\ \mathrm{cm}^{-1}$) and the magnitude of the crystal dimensions.

Fourier calculations were made with the ALFF[9] program. The full-matrix, least-squares refinement was carried out using the Busing and Levy Program ORFLS[10]. 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 Ibers[11] for K, Al, N, C, and H. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE[12] program. Crystal structure illustrations were obtained with the program ORTEP[13].

SOLUTION AND REFINEMENT OF THE STRUCTURE

Statistical tests based on normalized structure factors clearly indicated that the space group was $C2/c$. The potassium atom was located with the initial three-dimensional Patterson function, and several electron density maps preceded by partial least-squares refinement cycles revealed all the non-hydrogen atoms in the asymmetric unit. Subsequent isotropic refinement led to a reliability index ($R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$) of 9.5%. A difference Fourier map now indicated the positions of the hydrogen atoms. Anisotropic refinement of the non-hydrogen atoms and refinement of the positional parameters of the hydrogen atoms with isotropic temperature factors fixed at 4.0 led to $R_1 = 6.1\%$. Inclusion of a weighting scheme ($W = 1/\sigma^2$) and additional cycles of refinement produced a final $R_1 = 4.9$ and $R_2 = [\Sigma W(|F_o| - |F_c|)^2/\Sigma(F_o)^2]^{\frac{1}{2}} \times 100 = 4.9\%$. (The assumption that the nitrogen of the cyanide group was bonded to the aluminum atom led to an $R_2 = 5.3\%$. More significantly, however, the isocyano model gave the unreasonable result of a smaller isotropic temperature factor for the terminal atom than for the bridging atom.) Unobserved reflections and eleven reflections which appeared to suffer from secondary extinction were not included. The largest non-hydrogen parameter shifts in the final cycle of refinement were less than 0.20 of their estimated standard deviations. A final difference Fourier map showed no feature greater than 0.3 e$^-$/Å^3. The value of ERF was 1.49. No systematic variation of $W(|F_o| - |F_c|)^2$ *vs.* $|F_o|$ or $\sin\theta/\lambda$ was observed. 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.

DISCUSSION

The reactivity of alkali metal cyanides toward alkyl aluminum compounds

TABLE 1

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR POTASSIUM CYANOTRIMETHYLALUMINATE

H	K	OBS	CAL	H	K	OBS	CAL	H	K	OBS	CAL	H	K	OBS	CAL	H	K	OBS	CAL
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 2

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS[a,b] FOR POTASSIUM CYANOTRIMETHYLALUMINATE

Atom	*x/a*	*y/b*	*z/c*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0.0890(1)	0.1177(1)	0.1725(1)	26(1)	130(2)	138(2)	−10(1)	21(1)	−16(2)
Al	0.3576(1)	0.1639(2)	0.2892(2)	28(1)	96(2)	128(3)	−5(1)	16(1)	−2(2)
N	0.4411(3)	0.3666(5)	0.5551(6)	34(2)	144(8)	141(9)	5(3)	21(3)	−2(1)
C1	0.4104(3)	0.2902(6)	0.4643(7)	27(2)	106(8)	129(10)	1(3)	15(3)	14(7)
C2	0.3669(5)	0.2785(9)	0.1227(9)	65(4)	170(12)	138(11)	−11(6)	30(6)	12(10)
C3	0.2599(4)	0.1504(9)	0.2953(10)	32(3)	242(15)	236(16)	−11(5)	12(5)	−16(12)
C4	0.4072(5)	−0.0244(8)	0.3130(12)	51(3)	109(10)	330(19)	6(5)	56(7)	−18(10)
H1(C2)	0.4099(32)	0.3020(71)	0.1230(74)	[c]					
H2(C2)	0.3472(33)	0.2396(67)	0.0359(75)						
H3(C2)	0.3376(30)	0.3752(65)	0.1075(65)						
H1(C3)	0.2634(34)	0.1078(67)	0.3874(75)						
H2(C3)	0.2235(31)	0.2467(63)	0.2468(64)						
H3(C3)	0.2347(32)	0.0900(61)	0.2123(67)						
H1(C4)	0.3879(33)	−0.0873(68)	0.3661(73)						
H2(C4)	0.4481(31)	−0.0135(71)	0.3103(75)						
H3(C3)	0.3876(32)	−0.0925(68)	0.2411(70)						

[a] Standard deviations in parentheses refer to last digit quoted. [b] Anisotropic thermal parameters × 10^4 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 thermal parameters for hydrogen atoms taken as 4.0 Å^2.

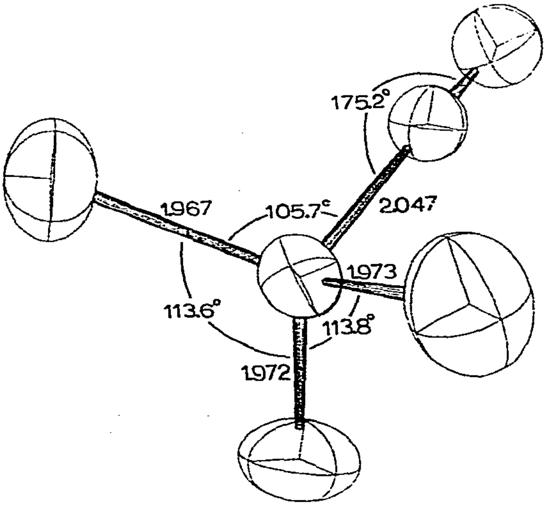

Fig. 1. Structure of the cyanotrimethylaluminate anion. The atoms are displayed as the 50% probability ellipsoids for thermal motion.

is greatly enhanced by the presence of an aromatic hydrocarbon. Formation of a well-defined complex in the case of the potassium cyanide/trimethylaluminum/*p*-xylene system indicates that the role of the aromatic solvent is more than that of a host medium. The behavior can be described in terms of an equilibrium:

$$KCN + Al(CH_3)_3 \rightleftharpoons K[Al(CH_3)_3CN] \xrightleftharpoons{C_6H_4(CH_3)_2} K[Al(CH_3)_3CN] \cdot C_6H_4(CH_3)_2$$

which lies far to the left at low temperatures (~ 100°) in the absence of *p*-xylene. Addition of the aromatic molecule could reasonably displace the equilibrium to the right by continually removing $K[Al(CH_3)_3CN]$ by complexation. Although the nature of the bonding of *p*-xylene to potassium cyanotrimethylaluminate is unknown, the dramatic effect the "solvent" has on the reaction strongly suggests the *p*-xylene is not merely a molecule of crystallization. Preliminary investigations[14] show that any methyl-substituted benzene derivative exhibits essentially the same effect on the reaction of KCN with $Al(CH_3)_3$. Additionally, complex formation involving an aromatic molecule and any of a range of compounds of the type $M[Al(CH_3)_3X]$ or $M[Al_2(CH_3)_6X]$ where M = alkali metal, tetramethylammonium ion; X = chloride, bromide, iodide, thiocyanate, azide ion has been observed.

The anion, $[Al(CH_3)_3CN]^-$, possesses no crystallographically imposed symmetry (Fig. 1). The aluminum–methyl carbon bond lengths of 1.972(8), 1.967(8), and 1.973(8) Å are all equivalent to within the quoted standard deviation, and compare well with the average single bond Al–C distances of 1.953(2), 1.98(1), and 1.986(11) Å found respectively in $[Al(CH_3)_3]_2$[15], $[Al(CH_3)_3]_2 \cdot C_4H_6O_2$[16], and $[Na(C_4H_8O)_2]_2$-$[Al(CH_3)_2(C_{10}H_8)]_2$[17]. The aluminum–cyano carbon bond distance, 2.047(7) Å, lies almost midway between the accepted Al–C single bond distance and the Al–C electron deficient bond distance, 2.124(2) Å, in $[Al(CH_3)_3]_2$[15]. It is significantly longer than that reported in $Li[Al(C_2H_5)_4]$[18], 2.023(6) Å, and is quite close to the average aluminum–naphthylenic carbon bond length, 2.065(10) Å, in $[Na(C_4H_8O)_2]_2[Al(CH_3)_2C_{10}H_8)]_2$[17]. The distortion could have its basis in either steric or electronic effects, but since in $K[Al(CH_3)_3CN]$ all other distances and angles are normal, an electronic origin seems more likely. No data exist on which to directly test the validity of a comparison of the aluminum–*sp*-hybridized carbon bond length

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR POTASSIUM CYANOTRIMETHYLALUMINATE

Bond distances			
Al–C1	2.047(7)	K–C3	3.60(1)
Al–C2	1.972(8)	K–N	3.11(1)
Al–C3	1.967(8)	K–C1	3.30(1)
Al–C4	1.973(8)	K–C3	3.30(1)
N–C1	1.139(6)	K–C2	3.24(1)
K–N	2.83(1)	K–C1	3.35(1)
K–C1	3.62(1)	K–C2	3.65(1)
K–N	2.87(1)		

Bond angles			
C2–Al–C3	113.6(4)	C1–Al–C2	102.1(3)
C2–Al–C4	113.3(4)	C1–Al–C3	105.7(3)
C3–Al–C4	113.8(4)	C1–Al–C4	107.1(3)
Al–C1–N	175.2(5)		

to aluminum–sp^3-hybridized carbon bond lengths; however, the aluminum–sp-hybridized nitrogen bond distance in $(CH_3)_3Al \cdot NCCH_3$ (2.01 Å) falls well within the range of aluminum–sp^3-hybridized nitrogen distances[19]. It should also be noted that one would expect on the basis of classical arguments of resonance interaction, steric repulsion, and bond hybridization a shorter aluminum–carbon distance in the case of sp hybridization of the carbon atom.

For the structure of $(CH_3)_3SnCN$[20], the extremely long tin–cyano-carbon bond distance (2.49 Å) compared to the tin–methyl-carbon length (2.16 Å) was rationalized in terms of an arrangement of $(CH_3)_3Sn^+$ and CN^- ions. However, in the present study, perhaps the most useful description of the aluminum–cyano carbon bond is found with the application of Pauling's rule[21] for the correlation of bond order and bond length: the observed lengthening over the average sp^3 value corresponds to a bond order 0.75.

The C≡N bond length (1.139 Å) is in excellent agreement with the values found in numerous other cyanide-containing compounds[22], and the bond angles about the aluminum atom are as expected for the essentially tetrahedral coordination. The range of the nine independent carbon–hydrogen distances is 0.83 to 1.15 Å, and the average, 0.95 Å.

The coordination about the potassium atom, as shown in Fig. 2, consists basically of the cyanide groups of three anionic units. These nitrogen atoms, at distances of 2.83, 2.87, and 3.11 Å, are the only nitrogen atoms within 4.00 Å of the potassium atom. The sphere is filled out with four methyl groups, the carbon atoms of which lie at 3.24, 3.30, 3.60, and 3.65 Å from the potassium atom.

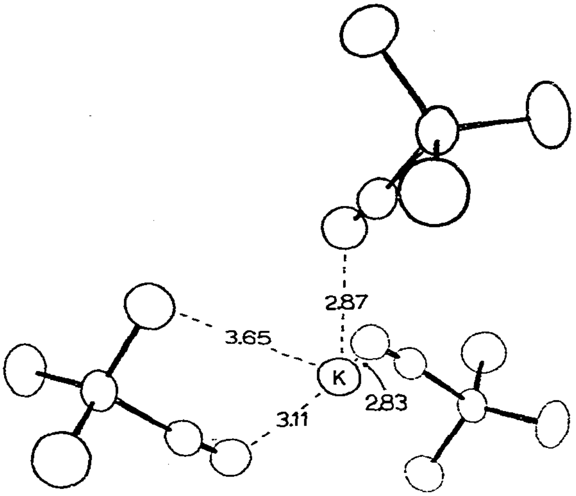

Fig. 2. Packing of the cyanotrimethylaluminate anions about the potassium ion.

ACKNOWLEDGEMENT

We are grateful to the National Science Foundation for support of this work under Grant GP-24852, and for departmental assistance in the purchase of the X-ray diffractometer. The authors also thank Mr. W. J. Cook and Dr. C. E. Bugg for aid in obtaining the crystal structure illustrations.

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