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THE CRYSTAL STRUCTURE OF CESIUM AZIDOTRIMETHYLALUMINATE

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Summary

The crystal structure of Cs[Al$(CH_3)_3N_3$] has been determined from single-crystal X-ray diffraction data collected by counter methods. Cesium azidotrimethylaluminate crystallizes in the orthorhombic space group *Pbcm* with cell dimensions a = 8.027 (9), b = 10.504 (9), c = 10.307 (9) Å, and ρ_{calc} = 1.89 g cm^{-1} for Z = 4. Least-squares refinement gave a final R value of 0.046 for 556 independent observed reflections. The anion lies on a crystallographic mirror plane; the Al—N bond length is 1.97 (1) Å. Within the azide ion the two nitrogen—nitrogen lengths are distinctly different: 1.13 (2) and 1.21 (2) Å.

Introduction

Alkali metal halides and pseudohalides are known to react with trialkylaluminum compounds to form 1/1, M[AlR_3X], and 2/1, M[Al_2R_6X], complexes [1-3]. Many of these substances have now been shown to exhibit unusual thermolytic [2, 4, 5], photolytic [6], and solution behavior [7, 8]. X-ray crystallographic studies have been reported on three 2/1 complexes, K[$Al_2(C_2H_5)_6F$] [9], K[$Al_2(CH_3)_6F$] · C_6H_6 [10], and K[$Al_2(CH_3)_6N_3$] [8], and on several 1/1 halide complexes [11, 12]. The 1/1 pseudohalide complexes are of structural interest in that the coordination mode of the pseudohalide ligand itself may be clearly revealed as in the case of K[Al$(CH_3)_3$CN] [13] and of [$(CH_3)_2$Tl][Al$(CH_3)_3$NCS] [14].

We report here the preparation and three-dimensional structure of Cs[Al$(CH_3)_3N_3$], a 1/1 complex containing the azide ion.

Experimental

Cesium azidotrimethylaluminate was prepared by the slow decomposition of the liquid complex of Cs[$Al_2(CH_3)_6N_3$] with benzene [7]. Single crystals of

TABLE 1

CRYSTAL DATA

Mol. formula: $Cs[Al(CH_3)_3N_3]$

Mol. wt.: 247.01

Linear abs. coeff. μ: 43.55 cm^{-1}

Calc. density: 1.89 g cm^{-3}

Max. crystal dimensions: 0.15 × 0.15 × 0.70 mm

Space group: orthorhombic, *Pbcm*

Molecules/unit cell: 4

Cell constants[a]: a = 8.027 (9), b = 10.504 (9), c = 10.307 (9) Å

Cell volume: 869.0 $Å^3$

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[a] Mo-K_α radiation, λ = 0.71069 Å. Ambient temperature of 23 ± 1°C.

the colorless, air-sensitive compound were sealed in thin-walled glass capillaries. Preliminary unit cell parameters were determined by Weissenberg and precession (Cu-K_α) photographs. Final lattice parameters as determined from a least-squares refinement of the angular settings of 14 reflections accurately centered on a diffractometer are given in Table 1.

Data were taken on an Enraf—Nonius CAD-4 diffractometer with graphite crystal monochromated molybdenum radiation. The crystal was aligned such that the needle 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 3.5°. The scan rate was variable and was determined by a fast 20° min^{-1} prescan. Calculated speeds for the slow scan (based on the net intensity gathered in the prescan) ranged from 7 to 0.6° min^{-1}. Moving-crystal–moving-counter backgrounds were collected for 25% of the total scan width 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 = 0.8° and B = 0.2°. Aperture settings were determined in a like manner with A = 4 mm and B = 4 mm. Other diffractometer parameters and the method of estimation of standard deviations have been described previously [15]. As a check on the stability of the instrument and crystal, three reflections were measured after every 40 reflections; no significant variation was noted.

One independent octant of data was measured out to 2θ = 54°; a slow scan was performed on a total of 556 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 20 was obtained in the prescan. Based on these considerations, the data set of 556 reflections (used in the subsequent structure determination and refinement) was considered observed, and consisted in the main of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorenz, polarization, and absorption effects [16]. The transmission factors ranged from 0.38 to 0.80.

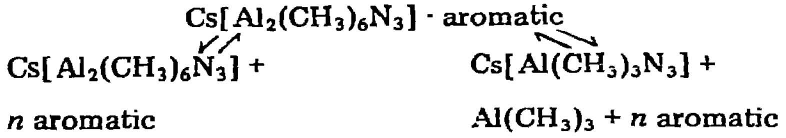
Fourier calculations were made with the ALFF [17] program. The full-matrix, least-squares refinement was carried out using the Busing and Levy programs ORFLS [18]. The function $w(|F_o|-|F_c|)^2$ was minimized. No corrections were made for extinction or anomalous dispersion. Neutral atom scattering factors were taken from the compilations of Cromer and Waber [19] for Cs, Al, N, and C; those for hydrogen were from "International Tables for X-ray Crystallography" [20]. The scattering by cesium was corrected for the real and imaginary components of anomalous dispersion using Cromer's table [21]. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin and Levy ORFFE program [21]. Crystal structure illustrations were obtained with the program ORTEP [23].

Solution and refinement of structure

Statistical tests were used to establish the space group as the centric *Pbcm*. Density calculations led to the inference of four molecules in the unit cell, and the Patterson map was interpreted in terms of the cesium atom on a crystallographic two-fold axis (a position which allows four cesium atoms per unit cell). An electron density map phased on the cesium atom position ($R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.38$) led to the location of the remaining six non-hydrogen atoms in the asymmetric unit. Isotropic refinement afforded a reliability index, $R_1 = 0.091$. Anisotropic refinement yielded $R_1 = 0.062$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(F_o)^2]^{1/2} = 0.066$. Location of the hydrogen atoms on a difference Fourier map, followed by further anisotropic refinement gave final values of $R_1 = 0.046$ and $R_2 = 0.051$. Hydrogen atom coordinates were not refined. The weighting scheme was based on essentially unit weights; unobserved reflections were not included. 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 unaccounted electron density. The final value for the standard deviation of an observation of unit weight was 1.67. The final values of the positional and thermal parameters are given in Table 2*.

Discussion

Cesium azidotrimethylaluminate was prepared from the room temperature decomposition of the benzene liquid clathrate of the 2/1 compound $Cs[Al_2(CH_3)_6 \cdot N_3]$. It is therefore seen that the parent may react in two ways [8]:



$Cs[Al_2(CH_3)_6N_3] \cdot$ aromatic

$Cs[Al_2(CH_3)_6N_3]$ + n aromatic

$Cs[Al(CH_3)_3N_3]$ + $Al(CH_3)_3$ + n aromatic

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* The table of structure factors has been deposited as NAPS Document, No. 02548, with National Auxiliary Publications Service, c/o Microfiche Publications, 440 Park Ave. So., New York, New York 10016. 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 2

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS[a] FOR CESIUM AZIDOTRIMETHYLALUMINATE

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs	0.1469(1)	0.2500	0.0000	0.0177(2)	0.0067(1)	0.0088(1)	0.0000	0.0000	0.0000
Al	0.7221(6)	0.3135(4)	0.2500	0.0135(7)	0.0056(4)	0.0060(4)	0.0003(5)	0.0000	0.0000
N1	0.8924(14)	0.1789(13)	0.2500	0.0099(20)	0.0080(14)	0.0084(13)	0.0002(13)	0.0000	0.0000
N2	0.8594(15)	0.0672(10)	0.2500	0.0139(19)	0.0053(12)	0.0064(11)	−0.0000(14)	0.0000	0.0000
N3	0.8344(18)	−0.0390(13)	0.2500	0.0223(30)	0.0069(13)	0.0122(18)	0.0006(18)	0.0000	0.0000
C1	0.5087(24)	0.2253(21)	0.2500	0.0157(28)	0.0141(33)	0.0258(36)	−0.0014(24)	0.0000	0.0000
C2	0.7594(16)	0.4191(10)	0.0925(13)	0.0251(24)	0.0066(10)	0.0114(14)	0.0025(14)	0.0002(16)	0.0008(10)
H1(C1)	0.398	0.278	0.250[b]						
H2(C1)	0.487	0.159	0.185						
H3(C2)	0.864	0.465	0.042						
H4(C2)	0.678	0.407	0.085						
H5(C2)	0.762	0.384	0.052						

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Hydrogen atom coordinates were not refined, and isotropic B was set at 5.5 Å^2.

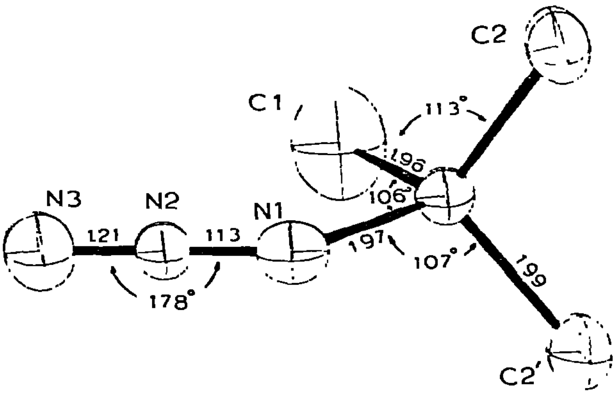
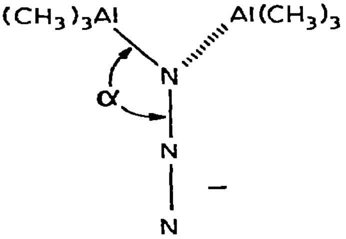


Fig. 1. Structure of the azidotrimethylaluminum anion with the atoms displayed as their 40% probability ellipsoids for thermal motion. The standard deviations of the bond distances are less than 0.02 Å, and the bond angles, 1°. The carbon—hydrogen bond lengths (not shown) ranged from 0.85 to 1.10 Å.

For the general case, $M[Al_2(CH_3)_6X]$, the direction which the decomposition takes appears to be a function of both temperature and lattice energy of $M[Al_2(CH_3)_6X]$ and of $M[Al(CH_3)_3X]$. Thus $Cs[Al_2(CH_3)_6N_3]$ · aromatic decomposes predominantly to the 1/1 compound, while $K[Al_2(CH_3)_6N_3]$ · aromatic reverts primarily to the 2/1 [8]. It should be noted also that once formed, it is very difficult to transform the 1/1 compound into the 2/1 liquid clathrate again.

The azidotrimethylaluminum anion, shown in Fig. 1, resides on a crystallographic mirror plane; the coordination about the aluminum atom is essentially tetrahedral. The two independent Al—C distances, 1.96(2) and 1.99(1), are normal for organoaluminum compounds in which the hydrogen atoms have been located [5, 13]. Aluminum—nitrogen bond lengths have been reported from 1.91 Å in $[(CH_3)_2AlN(CH_2)_2]_2$ [24] to 2.08 Å in $[(CH_3)_2Tl][Al(CH_3)_3NCS]$ [14], but the 1.97(1) Å value determined here should be regarded as the typical N→Al donor—acceptor length.

The coordination of the azide ion to the trimethylaluminum molecule is quite similar to that found for the 2/1 case [8]. In the two independent anions of $K[Al_2(CH_3)_6N_3]$, the Al—N—N angles, α, varied from 114.5(8)° to 117.2(6)°:



One can ascribe the depression from the expected sp^2 angle to nonbonded repulsions of the two $Al(CH_3)_3$ groups. In a like manner, the α angle in $Cs[Al(CH_3)_3N_3]$ is 123.2(9)° because of the nonbonded methyl—nitrogen repulsion (a structurally important factor in the absence of the more powerful effect described for $K[Al_2(CH_3)_6N_3]$).

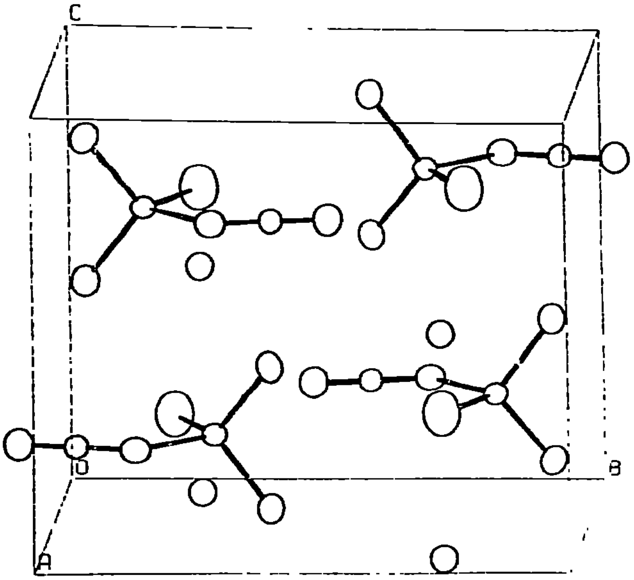


Fig. 2. Unit cell packing for cesium azidotrimethylaluminate.

Within the azide ion the two nitrogen—nitrogen bond lengths are distinctly different, in contrast to the equivalence found in both ionic [25] and head-to-tail bridged [26] structures. The terminal nitrogen—nitrogen length, 1.13(2) Å, is in good agreement with the average value from the $K[Al_2(CH_3)_6N_3]$ determination, 1.14 Å: so also is the bonded nitrogen—nitrogen distance (1.21(2) here compared to 1.23 Å [8]).

The packing (Fig. 2) appears to be typical of a compound of this type. The environment of the cesium ion consists of six groups (three pairs, each pair related by the two-fold axis) within 3.75 Å: an N1′ at 3.38(1) Å, an N3′ at 3.41(1) Å, and a C1′ at 3.72(1) Å*.

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* N1′ related to N1 in Table 2 by $(1-x, -y, \frac{1}{2}+z)$; N3′ related to N3 by $(1-x, y, z)$; C2′ related to C2 by $(1-x, -y, \frac{1}{2}+z)$.

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