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THERMAL DECOMPOSITION OF ANIONIC ORGANOALUMINUM COMPOUNDS

V. THE PREPARATION AND CRYSTAL STRUCTURE OF THE (ISOPROPYLIDENEAMINO)DIMETHYLALUMINUM DIMER

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Summary

The thermolysis of $K[Al_2(CH_3)_6SCN]$ at 120° leads to the formation of $[(CH_3)_2AlNC(CH_3)_2]_2$. Verification of the dimeric configuration of (isopropylidenamino)dimethylaluminum has been obtained from three-dimensional X-ray data measured by counter methods. $[(CH_3)_2AlNC(CH_3)_2]_2$ crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions a 7.027(4), b 7.760(4), c 8.583(4) Å, α 115.70(5)°, β 105.72(5)°, γ 92.38(5)°, and ρ_{calc} 0.94 g/cm³ for $Z = 1$. Least-squares refinement gave a final conventional R value of 0.058 for 1230 independent reflections. Proposed structures of the parent 2/1 complex, as well as mechanisms for the formation of (isopropylidenamino)dimethylaluminum are discussed.

Introduction

The thermolysis of anionic organoaluminum compounds of the type $M[Al_2(CH_3)_6X]$ [1—3] and $M[Al(CH_3)_3X]$ [4] (where M = alkali metal, tetramethylammonium ion; X = halide, pseudohalide) has been shown to produce a range of new compounds. In particular, $K[Al_2(CH_3)_6SCN]$ decomposes to (isopropylidenamino)dimethylaluminum according to the reaction sequence:

$$KSCN + 2Al(CH_3)_3 \rightarrow K[Al_2(CH_3)_6SCN] \xrightarrow{120^\circ} \{(CH_3)_3Al{-}NC{-}CH_3\} \rightarrow [(CH_3)_2AlNC(CH_3)_2]_2$$

Trimethyl(acetonitrile)aluminum was not isolated in this case, but its presence was confirmed in the related reaction of tetraisocyanatogermanium and trimethylaluminium [5]. The final step of the scheme given above involves the well-known thermal nitrile rearrangement proposed by Wade et al. [6] (eqn. 1).

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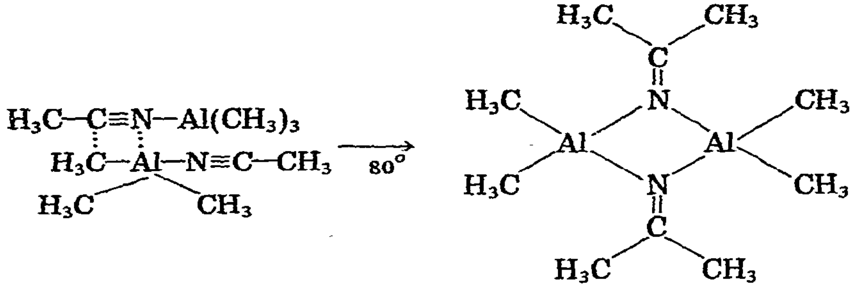
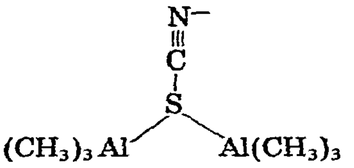


In the solid state the anion of $K[Al_2(CH_3)_6SCN]$ is believed to exist as the purely *S*-bonded species (I) on the basis of spectroscopic studies [7, 8] an



(I)

by analogy to the known structure of $K[Al_2(CH_3)_6N_3]$ [9, 10]. We report here final confirmation of the structure of $[(CH_3)_2AlNC(CH_3)_2]_2$ and new evidence bearing on the structure of the $[Al_2(CH_3)_6SCN]^-$ anion in the melt.

Experimental

(Isopropylidenamino)dimethylaluminum was prepared by the thermolysis of $K[Al_2(CH_3)_6SCN]$ in the manner previously described [1]. The compound is the same in every respect as that synthesized by the reaction of trimethylaluminum and acetonitrile [6].

Single crystals of (isopropylidenamino)dimethylaluminum were grown by slow sublimation and sealed in thin-walled glass capillaries. Preliminary unit cell parameters were determined by precession (CuK_α) photographs. Final lattice parameters as determined from a least-squares refinement of the angular settings of 12 reflections accurately centered on a diffractometer are given in Table 1. A Delauney reduction confirmed that this was, in fact, the reduced cell.

TABLE 1

CRYSTAL DATA

Mol. formula: $[(H_3C)_2AlNC(CH_3)_2]_2$
Mol. wt: 226.3
Linear abs. coeff μ: 15.0
Calcd. density: 0.94 g/cm^3
Max crystal dimensions: 0.12 mm × 0.22 mm × 0.60 mm
Space group: triclinic, $P\bar{1}$
Molecules/unit cell: 1
Cell constants: a 7.027(4), b 7.760(4), c 8.583(4) Å;
α 115.70(5), β 105.72(5), γ 92.38(5)°; v = 399 Å^3

Data were taken on an Enraf-Nonius CAD-4 diffractometer with Ni-filtered copper radiation. The general details of the data collection process and the method of determination of standard deviations of the intensities have been reported [5]. A complete sphere of data was measured out to $2\theta = 140°$, and after averaging, yielded 1230 reflections deemed observed by the criterion that $I > \sigma_I$. The intensities were corrected in the usual manner for Lorentz and polarization effects but not for absorption. (Because of the small value of the linear absorption coefficient ($\mu = 15.0$), the minimum and maximum transmission factors are estimated to differ by 5%).

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]. 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 [13] for Al, N and C. Those for H were from ref. 14. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE [15] program. Crystal structure illustrations were obtained with the program ORTEP [16].

Solution and refinement of the structure

Statistical tests based on normalized structure factors did not allow a clear decision as to the space group, but structure solution, accomplished by direct methods [17], eventually upheld the centric $P\bar{1}$ as the correct choice. Several cycles of isotropic refinement led to an R value given by $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.13$. Conversion to anisotropic temperature factors, location of the hydrogen atoms, application of a weighting scheme [18] (based on essentially unit weights), and further least-squares refinement led to $R_1 = 0.058$ and $R_2 = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2\}^{1/2} = 0.058$. The hydrogen atom coordinates were not refined, and 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 feature greater than 0.3 $e^-/\text{Å}^3$. The standard deviation of an observation of unit weight was 2.00. The values of the positional and thermal parameters are given in Table 2*.

Discussion

It is at the outset quite surprising to find that the 120° thermolysis of the 2/1 complex of trimethylaluminum with potassium thiocyanate yields (isopropylidenamino)dimethylaluminum (eqn. 2). (K[(CH$_3$)$_2$AlS] was not iso-

$$2K[Al_2(CH_3)_6SCN] \xrightarrow[120°]{} [(CH_3)_2AlNC(CH_3)_2]_2 + 2K[(CH_3)_2AlS] \qquad (2)$$

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* The table of structure factors has been deposited as NAPS Document No. 02382, 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.

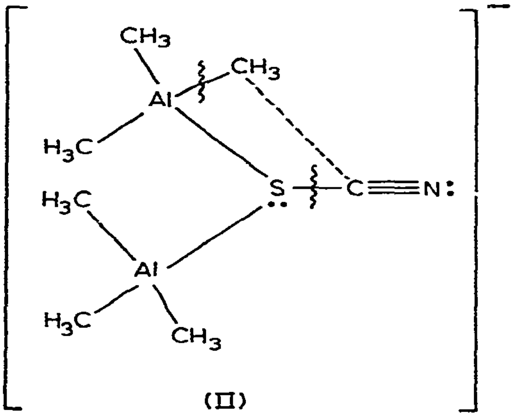
TABLE 2

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS[a] FOR (ISOPROPYLIDENAMINO)DIMETHYLALUMINUM DIMER

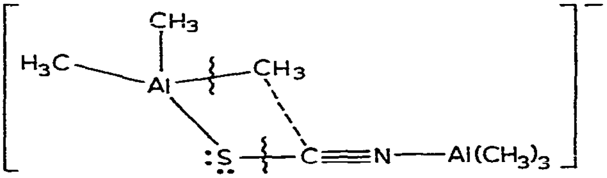
Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	−0,0089(1)	0.9096(1)	−0.6880(1)	337(3)	326(3)	195(2)	105(2)	88(2)	110(2)
N	0,0946(3)	0.8708(3)	−0,4754(3)	298(6)	300(6)	235(5)	100(5)	80(4)	130(5)
C(1)	0,1979(4)	0.7484(5)	−0.4510(4)	306(8)	356(9)	320(8)	88(7)	72(6)	173(7)
C(2)	0,2531(6)	0.5918(6)	−0.6043(6)	570(14)	436(12)	486(12)	285(11)	189(11)	150(10)
C(3)	0,2745(6)	0.7509(7)	−0.2689(6)	506(13)	660(16)	439(11)	195(11)	95(10)	396(12)
C(4)	−0,2374(6)	0.7042(6)	−0.8766(5)	558(14)	441(12)	310(9)	31(10)	−27(9)	90(9)
C(5)	0,2119(6)	0.9928(7)	−0.7566(6)	551(14)	684(17)	499(12)	222(12)	323(11)	362(12)
H(1)	0,187[b]	0.593	−0.718						
H(2)	0,218	0.468	−0.625						
H(3)	0,398	0.625	−0.585						
H(4)	0,219	0.625	−0.281						
H(5)	0,219	0.812	−0.188						
H(6)	0,398	0.719	−0,227						
H(7)	−0,312	0.688	−0.812						
H(8)	−0,281	0.719	−0.969						
H(9)	−0,188	0.594	−0.906						
H(10)	0,187	1.062	−0.812						
H(11)	0,251	0.883	−0,820						
H(12)	0,312	1.062	−0.656						

[a] Anisotropic thermal parameters X 10^4 defined by exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Hydrogen atom coordinates were not refined, and isotropic B was set at 5.0 Å^2.

lated from the yellow-red viscous residue, but is shown for material balance). The thiocyanate moiety normally behaves as a unit in inorganic reactions; there is to our knowledge no precedent for cleavage of the sulfur—carbon bond in any environment at such a low temperature. It is, however, possible to construct a mechanism for the formation of the observed products if one admits the likelihood of $(CH_3)_3Al—NC—CH_3$ as an intermediate [5]. In a multistep, roundabout fashion the decomposition may take place as in II with the formation of a molecule of acetonitrile which then seeks out a free trimethylaluminum molecule in the melt to form trimethyl(acetonitrile)aluminum. The temperature is well above the 80° necessary for the rearrangement of two molecules of $(CH_3)_3Al—NC—CH_3$ into $[(CH_3)_2AlNC(CH_3)_2]_2$. This assumes the *S*-bridged structure for the anion; considerable simplification would be experienced if $[Al_2(CH_3)_6SCN]^-$ possessed a head-to-tail bridged thiocyanate group (III). Here the acetonitrile adduct of trimethylaluminum is produced directly. The step-wise mechanism we propose therefore involves an intramolecular rearrangement based on the well-known ability of the trimethylaluminum group to function as an alkylating agent (Scheme 1).



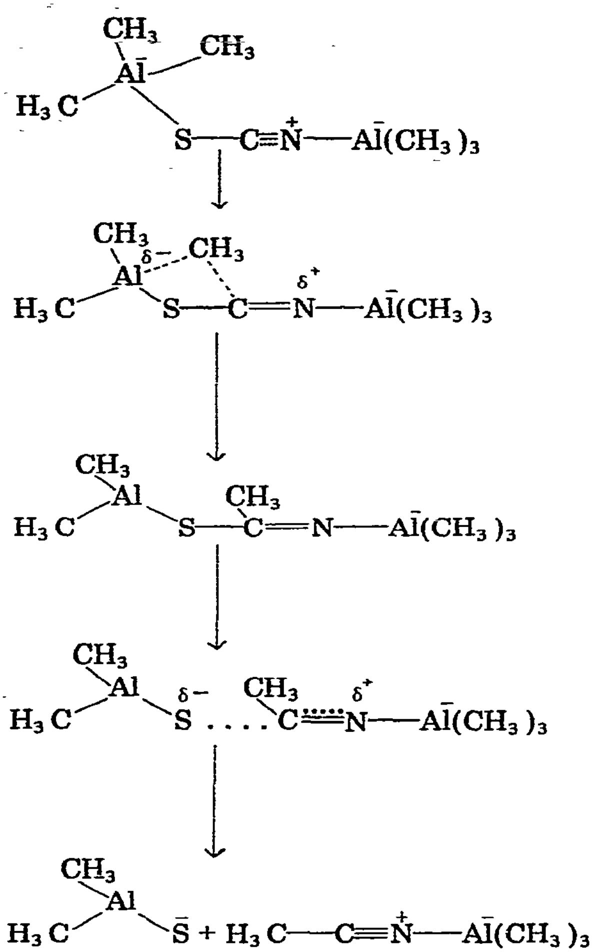
(II)



(III)

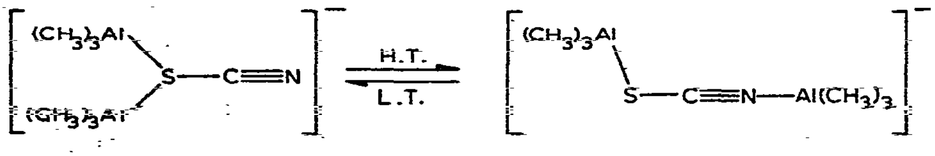
There is good reason to believe the solid state structure of $K[Al_2(CH_3)_6SCN]$ exhibits the *S*-bridged thiocyanate moiety [7—10]. On the other hand, one may cite two pieces of evidence that the head-to-tail bridged configuration lies only slightly higher in energy. The failure of $K[Al_2(C_2H_5)_6SCN]$ to form a liquid complex with benzene or toluene [19] is an indication of a different shape for the anion (in comparison with $K[Al_2(CH_3)_6SCN]$). Thus, the nonbonded repulsion of the ethyl groups appears to preclude the *S*-bridged structure. Secondly, the geometry of the anion has been shown to depend in a subtle fashion on the na-

SCHEME 1



ture of the cation. In K[Al$(CH_3)_3$SCN] the thiocyanate ion is *S*-bonded [7], while in [$(CH_3)_2$Tl] [Al$(CH_3)_3$NCS] it is *N*-bonded [20]. Therefore the difference in the donor ability of the sulfur vs. the nitrogen atom of the thiocyanate group is small enough to be offset by the "nonbonded" interaction of the cation.

In summary, it seems likely that the true structure of the [$Al_2(CH_3)_6SCN]^-$ ion is best represented by an equilibrium (eqn. 3), which at room temperature lies far to the left for the potassium salt, but at melt temperatures (>100°) lies well to the right. (The driving force is viewed as the increased steric interaction of the nonbonded methyl groups at higher temperatures.)



(3)

As predicted by Wade and coworkers [6], (isopropylidenamino)dimethylaluminum exists as a dimer (Fig. 1) which resides on a crystallographic center of

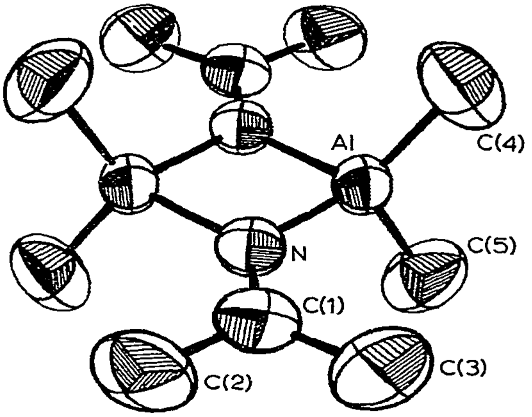


Fig. 1. Molecular structure of the (isopropylidenamino)dimethylaluminum dimer with the atoms displayed as their 50% probability ellipsoids for thermal motion.

inversion. The aluminum—nitrogen bond distance of 1.926(2) Å agrees well with those reported for other cyclic Al—N systems: 1.91(3) Å in $[(CH_3)_2AlN(CH_2)_2]_3$ [21] and 1.92(2) Å in $[(C_6H_5)_2AlNC(C_6H_5)(C_6H_4Br)]_2$ [22]. Likewise, the aluminum—carbon length, 1.973(3) Å, is quite close to the standards set in other well-determined organoaluminum structures [23, 24]. Other bond distances and angles within the molecule, given in Table 3, are in accord with those found in related (but less well-characterized) systems [22].

The intermolecular contacts (Fig. 2) are typical of a molecular compound of this type [5].

TABLE 3

BOND DISTANCES AND ANGLES FOR THE (ISOPROPYLIDENAMINO)DIMETHYLALUMINUM DIMER

Bond distances (Å)			
Al —N	1.930(2)	Al —N[a]	1.925(2)
Al —C(4)	1.969(4)	Al —C(5)	1.978(4)
C(1)—C(2)	1.512(5)	C(1)—C(3)	1.516(5)
N —C(1)	1.273(3)		
C(2)—H(1)	0.97[b]	C(3)—H(4)	0.98
C(2)—H(2)	0.90	C(3)—H(5)	0.93
C(2)—H(3)	0.99	C(3)—H(6)	0.85
C(4)—H(7)	0.90	C(5)—H(10)	0.86
C(4)—H(8)	0.83	C(5)—H(11)	0.88
C(4)—H(9)	0.90	C(5)—H(12)	0.89
Bond angles (°)			
N —Al —N[a]	83.7(1)	Al —N —Al[a]	96.3(1)
C(4)—Al —C(5)	120.1(2)	C(2)—C(1)—C(3)	115.8(3)
C(1)—N —Al	131.0(2)	C(1)—N —Al[a]	132.5(2)
N —Al —C(4)	121.4(2)	N —Al —C(5)	111.2(2)
N[a] —Al —C(4)	112.2(1)	N[a] —Al —C(5)	111.5(2)
N —C(1)—C(2)	121.9(3)	N —C(1)—C(3)	122.3(3)

[a] Related to atom listed in Table 2 by $(\bar{x}, \bar{y}, \bar{z})$ + unit cell translations along y and z. [b] Hydrogen atom positions were not refined, but a realistic standard deviation of these bond lengths is 0.1 Å.

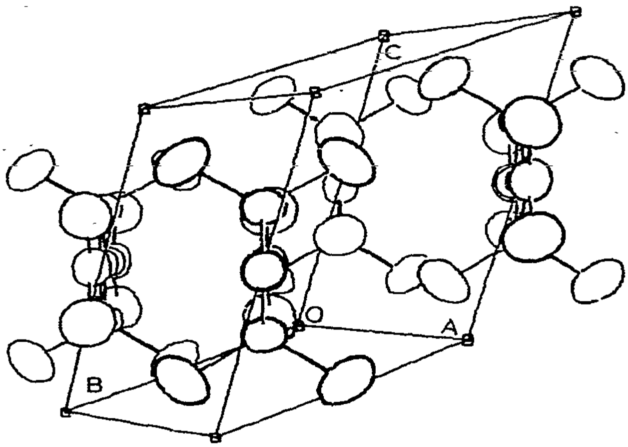


Fig. 2. Unit cell packing for the (isopropylidenamino)dimethylaluminum dimer.

Acknowledgements

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