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Synthesis and Crystal Structure of the Novel Organoaluminum Complex $[Al(CH_3C(CH_2NH)_3)_2(Al(CH_3)_2)_3]$

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Summary: The syntheses, structures, and reactions of organoaluminum amide and imide complexes have been the subject of ongoing investigation.[1–10] *Recently, we synthesized the novel organoaluminum amide* $[Al(CH_3)_2]_3Al[CH_3C(CH_2NH)_3]_2$, *tris(dimethylaluminio)aluminum bis(ethylidynetris(methanamide)), the first example involving a tripodal ligand*[11,12] *of an organoaluminum compound. The complex crystallized in the tetragonal space group* $P4_12_12$, *with cell parameters* $a = 10.235(3)$ *and* $c = 24.45(1)$ Å, $V = 2562(2)$ Å^3, $D_{calc} = 1.106$ g/cm^3, $Z = 4$, *and* $R = 0.045$. *The molecular symmetry of the complex is* C_2. *Both four- and six-coordinated Al atoms were observed in these complexes, with the tripodal NH groups serving as both chelating and bridging ligands. The four aluminum atoms of the complex all lie in a plane, with three aluminum atoms forming an equilateral triangle around the fourth central aluminum atom. The central* AlN_6 *unit of the complex has an octahedral symmetry, and the other three Al atoms are in a tetrahedral environment. The central Al atom is connected to the terminal Al atom by two bridging nitrogen atoms of the tripodal ligand, forming three four-membered rings.*

Introduction

Prior studies showed that the organoaluminum amides of the general formula $R_2AlNR'R''$, where $NR'R''$ is a simple, monofunctional amide group, occur as cyclic or oligomeric species with either four- or six-membered $(AlN)_n$ rings.[1–10,14] In these structures, both N and Al are typically four-coordinate in a distorted tetrahedral geometry analogous to that found in crystalline AlN. On the other hand, with multidentate amines, more complicated structures are formed in which the coordination number of Al is 4, 5, or 6.[15–18] Beachley and Racette[18] investigated the steric effect affecting the formation of chelated monomeric or unchelated dimeric organoaluminum–nitrogen compounds. The tripodal ligand 1,1,1-tris(aminomethyl)ethane is a tridentate ligand and is often used to coordinate to transition metals, e.g. Fe, Co, Ni, Cu, and Zn.[11,19,20] Because of intramolecular bonds in the N_3 tripodal ligand, the three nitrogen atoms always occupy adjacent positions around the metal ion. Herein we report a novel, highly symmetric organoaluminum compound with a tripodal ligand.

Experimental Section

Apparatus and Materials. All manipulations were carried out in a N_2-flushed glovebag, drybox, or vacuum system. Solvents were distilled and degassed prior to use. All ^1H, ^{13}C, and ^{27}Al NMR spectra were measured on a Varian VXR-300 spectrometer. Chemical shifts are referenced relative to either TMS (^1H) or benzene-d_6 (^1H, δ 7.15; $^{13}C\{^1H\}$, δ 128.00), while ^{27}Al NMR spectra were referenced relative to $Al(H_2O)_6^{3+}$. Mass spectral data were obtained on a VG-7025 GC/MS/MS spectrometer. IR spectra were recorded as Nujol mulls between KBr disks on a FT-IR spectrometer.

Preparation of $[Al(CH_3)_2]_3Al[CH_3C(CH_2NH)_3]_2$, Tris(dimethylaluminio)aluminum Bis(ethylidynetris(methanamide)). The title complex was prepared in high yield (90%) by the reaction of $[Al_2(NEt_2)_2Me_4]$[13] with an excess of 1,1,1-ethylidynetris(methanamine) in ether at 22 °C for 2 h under nitrogen (eq 1). Sublimation of the reaction mixture at 120 °C in a vacuum line gave the pure desired complex, which was resublimed at 188 °C. MS: characteristic fragmentation ions occur at *m/z* (EI, 30 eV, assignment in parentheses) 425 $(M - H)^+$, 411 $(M - Me)^+$, 395 $(M - (2Me + H))^+$, 379 $(M - (3Me + 2H))^+$, 339 $(M - (AlMe_2 + 2Me))^+$, 310 $(M - ((AlMe_2)_2 + 2H)^+$, 225 $(Al(CH_3C(CH_2NH)_3)^+$, 241 $(Al(CH_3C(CH_2NH)_3) - Me + H)^+$, 198 $(Al(CH_3C(CH_2NH)_3)AlMe_2)^+$, 182 $(Al(CH_3C(CH_2NH)_3)AlMe - H)^+$, 57 $(AlMe_2)^+$.

Crystallographic Measurements. A suitable single crystal of $[Al(CH_3)_2]_3Al[CH_3C(CH_2NH)_3]_2$ was chosen for the structural analysis. Intensity data were collected on a CAD4 diffractometer. Relevant crystallographic data are given in Table 1. Atomic parameters of non-hydrogen atoms are listed in Table 2.

Results and Discussion

Tris(dimethylaluminio)aluminum bis(ethylidynetris(methanamide)) was produced by reacting $[Al_2(NEt_2)_2Me_4]$[13] with excess 1,1,1-ethylidynetris(methan-

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Table 1. Crystallographic Data Refinement Details for $[AlMe_2]_3Al[CH_3C(CH_2NH)_3]_2$

formula	$C_{16}H_{42}N_6Al_4$
fw	426.47
diffractometer used	CAD4
space group	$P4_12_12$
cryst syst	tetragonal
a, Å	10.235(3)
c, Å	24.45(1)
V, Å^3	2562(1)
Z	4
D_{calc}, Mg·M^{-3}	1.106
λ(Mo Kα), Å	0.710 73
F(000)	928
unit cell detn: no.; 2θ range, deg	25; 16.72–20.32
scan type	$\theta/2\theta$
2θ scan width, deg	$2(0.65 + 0.35 \tan\theta)$
2θ range, deg	2–50
μ(Mo Kα), cm^{-1}	1.89
cryst size, mm	0.50 × 0.63 × 0.73
temp, K	298
no. of rflns measured	2567
no. of unique rflns	1379
no. of rflns $I_0 > 2.0\sigma(I_0)$	1052
no. of refined params	120
R_m	0.038
R, R_w[a]	0.045, 0.049
minimized function	$\sum w\|\|F_o\| - \|F_c\|\|^2$
weighting scheme	$1/[\sigma^2(F_o)^2 + 0.0001F_o^2]$
10^4g (second ext coeff)	0.32
transm factors (min, max)	0.96, 1.00
$(\Delta/\delta)_{max}$	0.0116
$(\Delta/\rho)_{max,min}$, e Å^{-3}	−0.210, 0.200
GoF	2.27
computation program	NRCVAX[b]

[a] $R = [\sum(|F_o| - |F_c|)/F_o]$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2)]^{1/2}$; $\sigma^2(F_o)$ from counting statistics. [b] NRCVAX: Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

Table 2. Atomic Parameters x, y, z, and B_{iso}[a]

	x	y	z	B_{iso}, Å^2
A11	0.06658(13)[b]	0.06658	0	2.81(6)
A12	−0.13040(14)	−0.13040	0	3.42(7)
A13	0.24929(16)	0.08184(15)	0.08769(6)	3.97(7)
N1	−0.0787(3)	0.0077(3)	0.04934(14)	3.18(17)
N2	0.1243(4)	0.2003(3)	0.05539(14)	3.19(17)
N3	−0.0518(4)	0.1974(4)	−0.03609(14)	3.30(17)
C1	−0.0986(6)	−0.3067(5)	0.02938(23)	5.6(3)
C2	0.4288(6)	0.1444(6)	0.07428(23)	5.9(3)
C3	0.2017(7)	0.0340(6)	0.16284(22)	6.6(3)
C4	−0.1167(5)	0.2507(4)	0.06189(19)	3.64(22)
C5	−0.1720(5)	0.1119(5)	0.06546(21)	4.43(24)
C6	0.0175(5)	0.2595(4)	0.08786(19)	4.19(24)
C7	−0.1099(5)	0.2956(5)	0.00184(22)	4.39(24)
C8	−0.2092(6)	0.3431(5)	0.09228(24)	5.5(3)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid. [b] Values in parentheses are the error of standard deviation.

amine). The structure of $[Al(CH_3)_2]_3Al[CH_3C(CH_2NH)_3]_2$ was determined by X-ray diffraction and is consistent with the data obtained from ^1H, ^{13}C, and ^{27}Al NMR and mass spectra. The overall reaction is given in eq 1.

$$2Al_2(NEt_2)Me_4 + 2CH_3C(CH_2NH_2)_3 \rightarrow Al[(CH_3C(CH_2NH)_3)_2(AlMe_2)_3] + 4Et_2NH + 2MeH \quad (1)$$

Crystallographic Data. The molecular and crystal structures of the complex were determined by X-ray crystallography. The exact molecular symmetry is C_2 with the 2-fold axis passing through Al(1) and Al(2). This axis coincides with the crystallographic 2-fold symmetry along [110]. There are two tripodal ligands coordinated to the four aluminum atoms (see Figure 1).

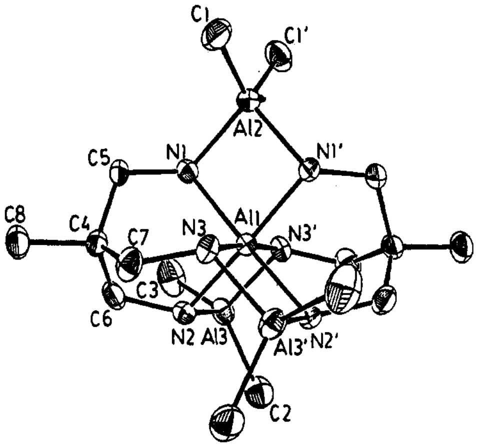

Figure 1. Molecular structure of $[Al(CH_3C(CH_2NH)_3)_2(Al(CH_3)_2)_3]$.

Table 3. Selected Bond Lengths and Angles for $[AlMe_2]_3Al[CH_3C(CH_2NH)_3]_2$

	Bond Lengths (Å)		
Al(1)–N(1)	2.007(4)	Al(3)–C(2)	1.973(6)
Al(1)–N(2)	2.014(4)	Al(3)–C(3)	1.963(6)
Al(1)–N(3)	2.010(4)	N(1)–C(5)	1.485(6)
Al(2)–N(1)	1.932(4)	C(4)–C(5)	1.532(6)
Al(2)–C(1)	1.969(5)	C(4)–C(6)	1.517(7)
Al(3)–N(2)	1.931(4)	C(4)–C(7)	1.540(7)
Al(3)–N(3)	1.935(4)	C(4)–C(8)	1.530(7)
	Bond Angles (deg)		
N(1)–Al(1)–N(1′)	85.2(2)	Al(1)–N(3)–Al(3)	92.5(2)
N(1)–Al(1)–N(2)	91.0(1)	N(2)–Al(3)–N(3)	89.7(2)
N(1)–Al(1)–N(2′)	174.6(2)	Al(1)–N(1)–C(5)	114.9(3)
N(1)–Al(1)–N(3)	91.0(2)	N(1)–Al(2)–C(1)	111.0(2)
N(1)–Al(1)–N(3′)	92.8(2)	C(5)–C(4)–C(7)	110.3(4)
Al(1)–N(1)–Al(2)	92.7(2)	C(5)–C(4)–C(8)	108.5(4)
Al(1)–N(2)–Al(3)	92.5(2)		

The four aluminum atoms lie on a plane, with three aluminum atoms forming an equilateral triangle around the fourth central aluminum atom. The central aluminum atom, Al(1), is in an octahedrally coordinated geometry, whereas the other three aluminum atoms, Al(2), Al(3), and Al(3′), appear to be in tetrahedral geometries. The central Al(1) atom is bonded to each of the other three Al atoms through two N atoms of the tripodal ligand, thus forming the central AlN_6 unit. The other three Al atoms are in AlN_2C_2 units. Three Al_2N_2 four-membered ring fragments are characteristic of such a complex and are all planar with a typical Al–N–Al angle of 92° and N–Al–N of 85 and 90°, respectively, around the central Al(1) and the other terminal Al atom. Selected bond distances and angles are listed in Table 3. It is apparent that there are two kinds of Al atoms, one which is six-coordinate and another which is four-coordinate. This was confirmed by ^{27}Al NMR data. In six-coordinate Al(1) moiety the Al–N bond distance is 0.07 Å longer and the N–Al–N angle is 5° smaller than the analogous values of the four-coordinate Al moiety. These geometric differences may result from steric effects and the degree of electron donation from the alkyl groups. These results are similar to that of Interrante[21] but different from that of Robinson.[22]

Spectroscopic Data. The FT-IR spectrum of the complex showed three sharp peaks in the N–H stretching region (3325, 3345, 3360 cm^{-1}), which were attributed to

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Table 4. ^{1}H, ^{13}C, and ^{27}Al NMR Spectra of $[AlMe_2]_3Al[CH_3C(CH_2NH)_3]_2$ [δ, ppm (C_6D_6)]

	^{1}H	^{13}C	^{27}Al
$\underline{Al(CH_3)_2}$	−0.465 (s, 18H)	−9.956, −9.988	160
$\underline{Al}[L_2(AlMe_2)]_3$[a]			7
$\underline{CH_3}C(CH_2NH)_3$	0.012 (s, 6H)	22.510	
$CH_3\underline{C}(CH_2NH)_3$		33.337	
$CH_3C(\underline{CH_2}NH)_3$	2.102 (b, 6H)	52.645	
	2.616 (ddd, 6H)	52.645	
$CH_3C(CH_2\underline{NH})_3$	0.553 (b, 6H)		

[a] $L = CH_3(CH_2NH)_3$.

the stretching vibrations of six N–H groups. The ^{1}H, ^{13}C, and ^{27}Al NMR spectra of the complex are listed in Table 4. We assigned the ^{1}H NMR chemical shifts at 2.102 and 2.612 ppm to the two protons of the methylene group by using the 2D NMR-HETCOR (heteronuclear correlation) experiment. The explanation is reasonable for methylene carbon atoms, which should be further downfield than others and is also in accord with the NMR-DEPT technique. The direct proton decoupling NMR experiment gave interesting results. The low-frequency H–H coupling constants ^{4}J, ^{3}J, and ^{2}J of the methylene were 2 (W coupling), 8 (N–H coupling), and 14 (*gem*-coupling) Hz, respectively. The other one was complicated by the nuclear electric quadrupole moment of the aluminum atoms and the nitrogen atoms, as well as the coupling constrants of the NH group. The ^{27}Al NMR spectrum of the organoaluminum complex showed two distinct peaks at 160 and 7 ppm. The 160 ppm peak is characteristic of four-coordinate Al atoms when compared with the shift of four-coordinate Al atoms in complexes of $[R_2AlR']_x$ (R = Me, Et; R′ = NEt_2, OMe_2, OEt_2, etc.).[23] The 7 ppm resonance is assigned to the six-coordinate Al(1). It is apparent that the ^{27}Al NMR spectra for the six-coordinate Al atoms in the AlN_6 moieties have chemical shifts of 0–10 ppm.[24,25]

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Supplementary Material Available: Tables of anisotropic displacement coefficients, fractional coordinates, isotropic displacement coefficients and bond distances and angles (6 pages). Ordering information is given on any current masthead page. A list of structure factors is available upon request from the authors.

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