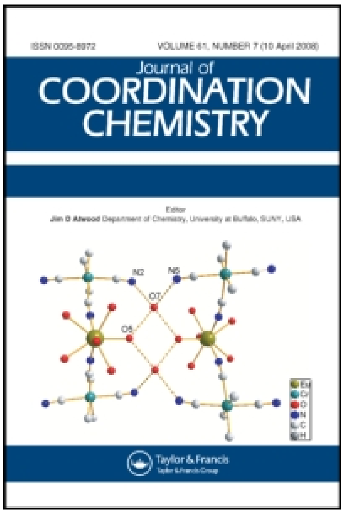

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Reaction of Diisobutylaluminum Chloride with *N,N'*-Bis(3-Aminopropyl)Ethylenediamine. Synthesis and Molecular Structure of $[C1_2Al\text{-}C_8H_{20}N_4][A1(C_4H_9)_2]$

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REACTION OF DIISOBUTYLALUMINUM CHLORIDE WITH *N,N'*-BIS(3-AMINOPROPYL)ETHYLENEDIAMINE. SYNTHESIS AND MOLECULAR STRUCTURE OF $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_4H_9)_2]$

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Reaction of diisobutylaluminum chloride with the tetradentate open-chain amine *N,N'*-bis(3-aminopropyl)ethylenediamine in a pentane-methylene chloride solution affords the crystalline organoaluminum complex $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_4H_9)_2]$. The title compound crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 10.722(2)$, $b = 22.292(4)$, $c = 9.810(3)$ Å, $\beta = 101.26(2)°$, $V = 2299.6(8)$ Å^3, and $\rho = 1.19$ g/cm^3 for $Z = 4$. Full-matrix least-squares refinement based on 2465 observed reflections with intensities ($I > 3\sigma(I)$) in the range $3.50 < 2\theta < 45.0°$ converged at $R = 0.048$, $R_w = 0.069$. The terminal primary amine units of the ligand are bridged by a dichloroaluminum unit and a diisobutylaluminum unit thus constituting an Al_2N_2 four-membered ring. The Al···Al contact of 2.808(2) Å does not suggest significant metal-metal interaction. The mean Al–Cl bond distance is 2.380(3) Å while the mean Al–N bond distance is 1.973(4) Å. The central aluminum atom of the title compound is six-coordinate, bonding to two chlorine atoms in addition to each nitrogen atom of the amine.

Keywords: Aluminum alkyl, amine, octahedral, structure, X-ray

INTRODUCTION

The coordination chemistry of aluminum, traditionally held to be rather unremarkable, is currently being shown to be quite intriguing. Although four-coordinate tetrahedral remains the predominant coordination mode of aluminum, workers have recently demonstrated that aluminum, under appropriate conditions, will readily exceed the usual coordination number of four and achieve five-[1–5] or even six-coordinate species.[6–8] Multidentate open-chain amines examined in this laboratory have proven to be particularly fruitful in this regard.[9–12] Indeed, the tetradentate open-chain amine *N,N'*-bis(3-aminopropyl)ethylenediamine, $C_8H_{22}N_4$, has emerged as a very effective ligand for the stabilization of higher coordination numbers for aluminum. Herein we report the synthesis and molecular structure of $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_4H_9)_2]$, isolated from reaction of diisobutylaluminum chloride with *N,N'*-bis(3-aminopropyl)ethylenediamine. Importantly, the central aluminum atom of the title compound is six-coordinate residing in an octahedral environment.

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EXPERIMENTAL

General

Standard Schlenk technique was employed in conjunction with an inert atmosphere dry box (Vacuum Atmospheres HE-43 Dri-Lab). Solvents were distilled under purified argon prior to use. Diisobutylaluminum chloride and *N,N'*-bis(3-aminopropyl)ethylenediamine, both purchased from Aldrich Chemical Co., were used as received. Single crystal X-ray data were collected on a Nicolet R3m/V diffractometer. ^1H NMR data were recorded on a JOEL-FX90Q NMR spectrometer.

Synthesis of $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_4H_9)_2]$

Inside the dry box a reaction vessel was charged with *N,N'*-bis(3-aminopropyl)-ethylenediamine (8.2 mmol) and a pentane–methylene chloride solvent mixture (10 cm^3 and 5 cm^3, respectively). Diisobutylaluminum chloride (16.4 mmol) was slowly added *via* syringe. Reaction was immediate and exothermic. The reaction vessel was removed from the dry box and heated in an oil bath (90°C) for 24 hr. Throughout the heating cycle the reaction vessel was vented periodically to release isobutane which was eliminated during the course of the reaction. Upon cooling, a multitude of small, colourless, extremely air-sensitive crystals were obtained. ^1H NMR ($CDCl_3$): δ 0.070 (d with sh, 4H, Al-CH_2-$CH(CH_3)_2$), 0.890 (d with sh, 12H, Al-CH_2-$CH(CH_3)_2$), 1.912 (m, 2H, Al-CH_2-CH-$(CH_3)_2$), 1.75, 2.92, 3.51 (m, 16H, N-$(CH_2)_3$-N-$(CH_2)_2$-N-$(CH_2)_3$-N).

Structural solution and refinement

A single crystal of $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_4H_9)_2]$ was mounted in a thin-walled glass capillary under an inert atmosphere of argon in the dry box. Cell dimensions and an orientation matrix from the setting angles of 48 carefully centred reflections in the range $27.17 < 2\theta < 42.66°$ corresponded to a monoclinic cell. The space group was determined to be $P2_1/c$. The structure was solved by direct methods and refined, based on 2465 observed reflections ($I > 3\sigma(I)$), using SHELXTL.[13] Hydrogen atoms were located by standard difference Fourier techniques; those bonded to carbon atoms of the isobutyl groups were included in the structure factor calculations at idealized positions ($d_{C-H} = 0.95$ Å) assuming a staggered confirmation for the methyl groups. All other hydrogen atoms were refined using isotropic thermal parameters. An isotropic group thermal parameter ($U_{iso} = 0.081(3)$Å^2) was employed for the isobutyl hydrogen atoms. Refinement converged at $R = 0.048$, $R_w = 0.069$. Relevant crystallographic data are given in Table I.

RESULTS AND DISCUSSION

For some time this laboratory has had an interest in the interactions of organoaluminum species with various amine functions. Although initially concerned with organoaluminum-macrocyclic amine complexes,[14-17] our attention has recently shifted towards the corresponding chemistry of organoaluminum-multidentate open-chain amine complexes.[4-7,18] These systems, characterized by the cleavage of N–H

TABLE I

Summary of crystallographic data for $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_4H_9)_2]$.

Empirical formula	$C_{16}H_{38}N_4Al_2Cl_2$
Molecular weight	411.44
Colour; habit	colourless; parallelpiped
Space group	$P2_1/c$
a, Å	10.722(2)
b, Å	22.292(4)
c, Å	9.810(3)
β (deg)	101.26(2)
Cell volume, $Å^3$	2299.6(8)
Z	4
ρ g/cm^3	1.19
Diffractometer	Nicolet R3m/V
Radiation	Mo-Kα (λ = 0.71073 Å)
Temperature	21°C
2θ Range, deg	3.50 to 45.0
Reflections collected	3296
Reflections observed	2465
GOF	1.97
R	0.048
R_w	0.069

and Al–R bonds and the elimination of alkane, result in reaction products possessing extensive Al–N association. The organoaluminum complex $[Cl_2Al{\cdot}C_8H_{20}N_4]$ $[Al(C_4H_9)_2]$ was isolated from reaction of diisobutylaluminum chloride with *N*,*N′*-bis(3-aminopropyl)ethylenediamine. The X-ray crystal structure of the title compound is given in Figure 1. Final atomic coordinates are given in Table II while selected bond distances and angles are provided in Table III.

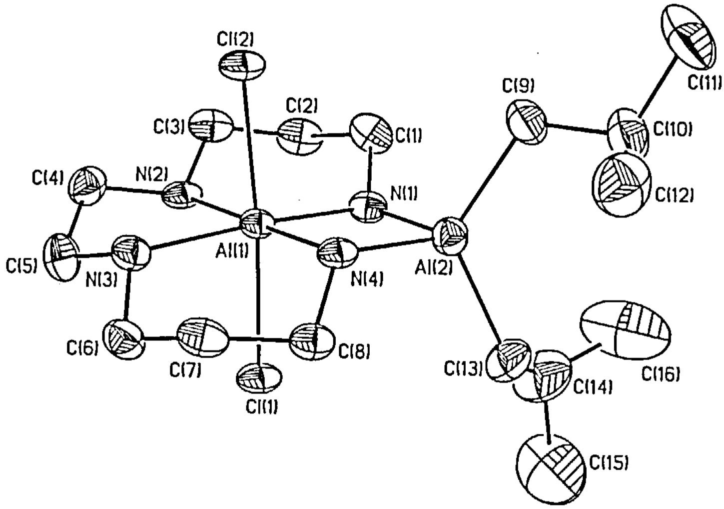

FIGURE 1 A view of the $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_4H_9)_2]$ molecule showing the atom labelling scheme. Thermal ellipsoids show 35% probability levels; hydrogen atoms have been omitted.

TABLE II

Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_4H_9)_2]$.

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)*
Cl(1)	215(1)	−189(1)	2020(1)	46(1)
Cl(2)	4702(1)	67(1)	2796(1)	44(1)
Al(1)	2497(1)	−100(1)	2446(1)	32(1)
Al(2)	2734(1)	−1236(1)	3707(1)	42(1)
N(1)	2551(3)	−930(1)	1821(3)	39(1)
N(2)	2310(3)	237(1)	508(3)	41(1)
N(3)	2288(3)	764(1)	3021(3)	40(1)
N(4)	2715(3)	−414(1)	4337(3)	35(1)
C(1)	3325(4)	−1070(2)	773(4)	55(2)
C(2)	2906(4)	−707(2)	−559(4)	56(2)
C(3)	3072(4)	−37(2)	−437(4)	50(2)
C(4)	2448(4)	893(2)	594(4)	53(2)
C(5)	1816(4)	1122(2)	1743(5)	55(2)
C(6)	1563(4)	876(2)	4138(4)	49(2)
C(7)	2049(4)	512(2)	5437(4)	48(1)
C(8)	1920(3)	−162(2)	5273(4)	41(1)
C(9)	4420(4)	−1622(2)	4273(5)	59(2)
C(10)	4573(5)	−2078(2)	5450(5)	70(2)
C(11)	5884(5)	−2387(3)	5690(7)	104(3)
C(12)	4321(6)	−1793(3)	6766(6)	93(3)
C(13)	1144(4)	−1637(2)	3964(5)	63(2)
C(14)	497(6)	−2076(3)	2880(8)	103(3)
C(15)	−856(7)	−2173(3)	2914(12)	180(6)
C(16)	1175(4)	−2653(3)	2956(7)	179(5)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

The absence of diisobutylaluminum chloride fragments in the title compound is significant and may be accounted for by considering the disproportionation of the diisobutylaluminum chloride dimer. The disproportionation of alkylaluminum halide dimers, in the presence of sufficiently strong Lewis bases, to provide the stronger Lewis acid species and a trialkylaluminum species has been previously noted in this laboratory.[14,19] Necessarily, as Ziegler noted,[20] such a process must proceed through the transient existence of a mixed alkyl-halo bridged species. Thus, the reactive organoaluminum species in this system were triisobutylaluminum and isobutylaluminum dichloride. During the course of the reaction two N–H bonds were cleaved from the amine while one isobutyl group was cleaved from each of the two organoaluminum units thus eliminating two units of isobutane. The reaction is illustrated in equation (*1*).

$$(C_4H_9)_3Al + (C_4H_9)AlCl_2 + C_8H_{22}N_4 \longrightarrow [Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_4H_9)_2] + 2C_4H_{10} \qquad (1)$$

Several points are worthy of note regarding structure and bonding in $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_4H_9)_2]$. The title compound contains two aluminum fragments: one dichloroaluminum unit and one diisobutylaluminum unit. Particularly

TABLE III

Selected bond distances (Å) and angles (deg) for $[Cl_2Al\cdot C_8H_{20}N_4][Al(C_4H_9)_2]$.

Atoms	Distance	Atoms	Distance
Cl(1)-Al(1)	2.408(1)	Cl(2)-Al(1)	2.351(1)
Al(1)-N(1)	1.953(3)	Al(1)-N(2)	2.018(3)
Al(1)-N(3)	2.032(3)	Al(1)-N(4)	1.954(3)
Al(2)-N(1)	1.946(3)	Al(2)-N(4)	1.935(3)
Al(2)-C(9)	1.981(4)	Al(2)-C(13)	1.984(5)
N(1)-C(1)	1.475(6)	N(2)-C(3)	1.482(5)
N(2)-C(4)	1.469(5)	N(3)-C(5)	1.489(5)
N(3)-C(6)	1.484(6)	N(4)-C(8)	1.481(5)
C(1)-C(2)	1.528(6)	C(2)-C(3)	1.504(7)
C(4)-C(5)	1.512(7)	C(6)-C(7)	1.514(5)
C(7)-C(8)	1.515(6)	C(9)-C(10)	1.523(7)
C(10)-C(11)	1.542(7)	C(10)-C(12)	1.510(8)
C(13)-C(14)	1.511(8)	C(14)-C(15)	1.473(10)
C(14)-C(16)	1.472(8)		

Atoms	Angle	Atoms	Angle
Cl(1)-Al(1)-Cl(2)	175.4(1)	Cl(1)-Al(1)-N(1)	87.6(1)
Cl(2)-Al(1)-N(1)	96.0(1)	Cl(1)-Al(1)-N(2)	87.5(1)
Cl(2)-Al(1)-N(2)	89.5(1)	N(1)-Al(1)-N(2)	93.5(1)
Cl(1)-Al(1)-N(3)	87.9(1)	Cl(2)-Al(1)-N(3)	88.4(1)
N(1)-(Al(1)-N(3)	175.3(1)	N(2)-Al(1)-N(3)	84.9(1)
Cl(1)-Al(1)-N(4)	93.7(1)	Cl(2)-Al(1)-N(4)	89.3(1)
N(1)-Al(1)-N(4)	87.3(1)	N(2)-Al(1)-N(4)	178.5(1)
N(3)-Al(1)-N(4)	94.3(1)	N(1)-Al(2)-N(4)	88.1(1)
N(1)-Al(2)-C(9)	109.6(2)	N(4)-Al(2)-C(9)	112.8(2)
N(1)-Al(2)-C(13)	110.4(2)	N(4)-Al(2)-C(13)	108.8(2)
C(9)-Al(2)-C(13)	121.9(2)	Al(1)-N(1)-Al(2)	92.1(1)
Al(1)-N(1)-C(1)	118.3(2)	Al(2)-N(1)-C(1)	128.5(2)
Al(1)-N(2)-C(3)	118.0(2)	Al(1)-N(2)-C(4)	109.1(2)
C(3)-N(2)-C(4)	112.7(3)	Al(1)-N(3)-C(5)	108.2(2)
Al(1)-N(3)-C(6)	117.8(2)	C(5)-N(3)-C(6)	113.0(3)
Al(1)-N(4)-Al(2)	92.4(1)	Al(1)-N(4)-C(8)	118.4(2)
Al(2)-N(4)-C(8)	127.0(2)	N(1)-C(1)-C(2)	111.8(3)
C(1)-C(2)-C(3)	116.6(3)	N(2)-C(3)-C(2)	112.9(4)
N(2)-C(4)-C(5)	108.9(3)	N(3)-C(5)-C(4)	108.6(3)
N(3)-C(6)-C(7)	112.9(3)	C(6)-C(7)-C(8)	115.6(3)
N(4)-C(8)-C(7)	113.0(3)	Al(2)-C(9)-C(10)	117.3(3)
C(9)-C(10)-C(11)	111.9(5)	C(9)-C(10)-C(12)	110.9(4)
C(11)-C(10)-C(12)	111.6(4)	Al(2)-C(13)-C(14)	119.4(4)
C(13)-C(14)-C(15)	113.5(6)	C(13)-C(14)-C(16)	112.1(5)
C(15)-C(14)-C(16)	110.4(5)		

significant is the coordination of the central aluminum atom, Al(1). In addition to being bonded to two chlorine atoms it is also bonded to each of the nitrogen atoms of the tetradentate amine. The mean Al-Cl bond distance is 2.380(3) Å while the mean Al-N bond distance is 1.973(4) Å. The Cl(1)-Al(1)-Cl(2) bond angle is 175.4(1)° whereas the mean Cl-Al-N bond angle in the title compound is 89.99(3)°. With these values and other relevant data in Table II, one may describe the coordination of the central aluminum atom in $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_4H_9)_2]$ as six-coordinate octahedral.

The tetradentate amine *N,N'*-bis(3-aminopropyl)ethylenediamine has previously been shown to be effective in stabilizing higher coordination numbers of aluminum. This laboratory has recently reported the synthesis and molecular structure of $[Al(CH_3)][C_8H_{19}N_4][Al(CH_3)_2]$,[10] isolated from reaction of this amine with trimethylaluminum. The central aluminum atom in this organoaluminum complex was shown to be five-coordinate, bonding to each nitrogen atom of the amine in addition to a methyl carbon atom. The geometry about the five-coordinate aluminum atom was shown to be trigonal bipyramidal. The isolation of this product prompted us to examine the reaction of this amine with the alkylaluminum halide diethylaluminum chloride. The product of this reaction, $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$,[12] proved to be quite interesting as the coordination number of the central aluminum atom was shown to be six. The present study was undertaken in an effort to assess the effects of increased steric bulk of the aluminum species as a function of coordination number of the central aluminum atoms in these systems.

The increased steric demands of diisobutylaluminum chloride has little overall effect (relative to the ethyl analogue) as the coordination number of the central aluminum atom of the title compound remained six. Indeed, the mean Al–Cl and Al–N bond distances of 2.380(3) Å and 1.973(4) Å, respectively, for the title compound compare well with corresponding values of 2.394(1) Å and 1.971(4) Å for the six-coordinate ethyl derivative described above. It appears that multidentate open-chain amines present interesting possibilities with regard to the stabilization of higher coordination numbers of aluminum. Forthcoming contributions will address this topic with related multidentate open-chain amines.

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SUPPLEMENTARY MATERIAL AVAILABLE

Summary of data collection and refinement, molecular plots, tables of bond distances and angles, final fractional coordinates, and thermal parameters (15 pages) and a listing of observed and calculated structure factors (11 pages) are available from G.H.R.

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