Reaction of Trimethylaluminum with a Macrocyclic Tetradentate Secondary Amine. Synthesis and Molecular Structure of $[Al(CH_3)]_2[C_{10}H_{20}N_4][Al(CH_3)_3]_2$

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Reaction of trimethylaluminum with the macrocyclic tetradentate secondary amine 1,4,8,11-tetraazacyclotetradecane in toluene affords $[Al(CH_3)]_2[C_{10}H_{20}N_4][Al(CH_3)_3]_2$. The title compound, characterized by single-crystal X-ray diffraction, crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters $a = 8.152$ (6) Å, $b = 13.783$ (9) Å, $c = 11.018$ (8) Å, $\beta = 90.18$ (6)°, and $D_{calcd} = 1.14$ g cm^{-3} for $Z = 2$. Least-squares refinement based on 1240 observed reflections with intensities $I \geq 3\sigma(I)$ in the range $3.0° \leq 2\theta \leq 45.0°$ led to a final R factor of 0.055 ($R_w = 0.078$). The compound resides on a crystallographic center of symmetry while the central cavity of the macrocycle is occupied by a Al-N-Al-N four-membered ring. The Al_2N_2 ring is planar and slightly asymmetric with independent Al-N distances of 1.959 (4) and 1.913 (4) Å. The Al···Al distance of 2.735 (2) Å does not indicate any significant interaction between the aluminum atoms.

Introduction

The interaction of macrocyclic ligands with metal ions resulting in stable complexes has been an active area of research for many years. Although the chemistry of oxygen-based macrocyclic ligands (i.e., crown ethers) has been extensively developed,[1-5] interest in macrocyclic ligands with donor species other than oxygen, such as sulfur and nitrogen, is significant. Perhaps most notable is the ability of sulfur-[6-9] and nitrogen-based crown ethers[10-18] to form complexes with various first- and second-row transition-metal ions. For example, the macrocyclic tetradentate secondary amine 1,4,8,11-tetraazacyclotetradecane (Figure 1),[19] first reported by Van Alphen,[20] has been shown to form complexes with various transition-metal ions including Ni(II),[10] Co(III),[11,12] and Rh(III).[12,13]

Macrocyclic ligands are of interest to us due to the fact that AlR_3 has been shown to react with crown ethers (CE) yielding $[AlR_3]_n[CE]$ complexes.[21-23] These $[AlR_3]_n[CE]$ complexes are important because they have frequently been shown to serve as precursors to the nonstoichiometric liquid inclusion compounds known as liquid clathrates.[24] The macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane thus offered convenient access to liquid clathrates based on transition metals. Herein, we report the synthesis and structure of $[Al(CH_3)]_2[C_{10}H_{20}N_4][Al(CH_3)_3]_2$ isolated from the reaction of trimethylaluminum with 1,4,8,11-tetraazacyclotetradecane in toluene. The title compound represents the first report of a macrocyclic amine-group IIIA (13)[25] metal alkyl complex.

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(19) The macrocyclic tetradentate secondary amine 1,4,8,11-tetraazacyclotetradecane is also known as 14-ane-N_4[7] and, perhaps more commonly as, cyclam.[11] Unless one is already familiar with the ligand, these trivial names may not prove very informative as to the structure of the macrocycle. Owing to its resemblance to crown ethers, we have sought to refer to the ligand using crown ether nomenclature: in our laboratory we use the trivial name tetraaza-14-crown-4, thus denoting a 14-membered ring containing four nitrogen atoms. Herein, however, we have used the IUPAC notation.
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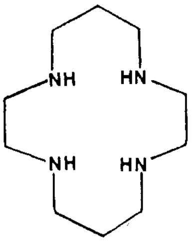

Figure 1. 1,4,8,11-Tetraazacyclotetradecane.

Experimental Section

General Comments. The extreme air and water sensitivity of reactants and products warranted concerted effort to exclude oxygen and moisture from the synthesis and subsequent manipulations. Thus, standard Schlenk technique was employed in conjunction with an inert atmosphere glovebox (Vacuum Atmospheres HE-43 Dri-Lab). Toluene was distilled under prepurified nitrogen from sodium/benzophenone immediately prior to use. Trimethylaluminum and 1,4,8,11-tetraazacyclotetradecane, both purchased from Aldrich Chemical Co., were used as received.

Synthesis of $[Al(CH_3)]_2[C_{10}H_{20}N_4][Al(CH_3)_3]_2$. A 150-mL reaction vessel was charged with 1,4,8,11-tetraazacyclotetradecane (5.00 mmol) and taken inside the glovebox where toluene (20 mL) was added. At this point trimethylaluminum (20 mmol) was slowly added via syringe. Reaction was exothermic, although not violently so. The reaction tube was removed from the glovebox and heated in an oil bath (120 °C) for 24 h. Upon cooling to room temperature, a multitude of colorless, rectangular, extremely air-sensitive, crystals deposited on the walls of the reaction vessel. ^1H NMR (C_6D_6): δ -0.380 (s, 3 H, $AlCH_3$), -0.395 (s, 9 H, $Al(CH_3)_3$), 0.605 (d of q, 4 H, $CH_2CH_2CH_2$), 1.835 (d of t, 2 H, NCH_2CH_2N), 2.152–2.916 (m, 8 H, $NCH_2CH_2CH_2N$). Crystalline samples of the product were mounted in thin-walled glass capillaries (in the glovebox) and subjected to X-ray diffraction analysis.

Structure Solution and Refinement. Preliminary X-ray examination of several crystalline specimens revealed pseudo-orthorhombic symmetry. However, careful examination of X-ray axial photographs indicated a monoclinic unit cell with orthorhombic twinning. After several unsuccessful attempts to obtain an untwinned specimen for analysis, intensity data were collected on a twinned crystal. X-ray intensity data were collected on a Nicolet R3m diffractometer using an ω-scan technique with Mo Kα radiation (λ = 0.71073 Å) at -100 °C. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 8.152 (6) Å, b = 13.783 (9) Å, c = 11.018 (8) Å, β = 90.18 (6)°, and V = 1237 (5) Å^3, for Z = 2. The structure was solved by direct methods and refined, based on 1240 observed reflections with intensities $I \geq 3\sigma(I)$, using SHELXTL.[26] Hydrogen atoms, located from difference Fourier maps, were placed in idealized positions with fixed isotropic temperature factors. Refinement converged at R = 0.15. Further refinement using RAELS86[27] on the twinned structure converged at R = 0.055 (R_w = 0.078) for a nonstatistical 5:1 twinning model. The nature of the twinning phenomenon is further addressed later in the paper. Relevant crystallographic data are given in Table I.

Results and Discussion

The reaction of AlR_3 with MX (M = alkali-metal ion or tetraalkylammonium ion; X = halide or pseudohalide ion) resulting in 1:1 (eq 1) and 1:2 (eq 2) compounds has been previously reported.[28] When prepared in aromatic sol-

$$MX + AlR_3 \rightarrow M[AlR_3X] \quad (1)$$

$$MX + 2AlR_3 \rightarrow M[Al_2R_6X] \quad (2)$$

vents the 1:2 complex yields the liquid inclusion compounds referred to as liquid clathrates.[24] Recently, we have employed the metal ion coordinating ability of crown ethers to expand the range of MX moieties exhibiting liquid clathrate behavior. We have since reported the synthesis and structure of several $[AlR_3]_n[CE]$ complexes.[21-23] Two points became obvious in these organoaluminum macrocyclic complexes: (a) the flexibility of the crown ethers and (b) the extensive interaction of AlR_3 with the oxygen atoms of the crown. The Al–O interaction was so strong in these complexes that the crown ethers were essentially turned "inside out" as the oxygen atoms were pulled from the interior of the central cavity toward the outward perimeter. In the presence of MX species $[AlR_3]_n[CE]$ complexes have been found to give the desired liquid inclusion compounds. Essentially, the crown ethers serve as a transport for the AlR_3 to the X^- moiety.[29] Thus, $[AlR_3]_n[CE]$ complexes enhance the formation of liquid clathrates with certain MX species. The overall process is given by (eq 3).

Table I. Summary of the Crystallographic Data for $[Al(CH_3)]_2[C_{10}H_{20}N_4][Al(CH_3)_3]_2$

empirical formula	$C_{18}H_{44}N_4Al_4$
color; habit	colorless Prisms
size	0.25 × 0.20 × 0.20
space group	monoclinic, $P2_1/n$
unit cell Dimens	
a, Å	8.152 (6)
b, Å	13.783 (9)
c, Å	11.018 (8)
β, deg	90.18 (6)
V, Å^3	1237 (5)
molecules/cell	2
mol wt	424.6
D(calcd), g/cm^3	1.14
diffractometer	Nicolet R3
radiatn	Mo Kα (λ = 0.71073 Å)
temp, °C	-100
2θ range, deg	3.0–45.0
reflctns collected	1824
reflctns obsd	1240 ($I > 3\sigma(I)$)
GOF	1.57
data to parameter ratio	10.5:1
R	0.055
R_w	0.078

$$nAlR_3 + CE \rightarrow [AlR_3]_n[CE] \xrightarrow{MX} [M{\cdot}CE][Al_2R_6X] \quad (3)$$

In an attempt to further extend the range of MX species exhibiting liquid clathrate behavior beyond alkali-metal salts, we have begun to examine (eq 3) with respect to macrocyclic ligands that have been shown to form stable complexes with transition-metal ions. The ease with which the nitrogen-based macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane forms stable complexes with transition-metal ions[10-13] made it a logical macrocycle to investigate.

During the course of the reaction of $Al(CH_3)_3$ with 1,4,8,11-tetraazacyclotetradecane, shown in (eq 4), four methyl groups were cleaved from two $Al(CH_3)_3$ units. Additionally, all four N–H bonds of the macrocycle were cleaved. This all resulted in an Al_2N_2 four-membered ring occupying the central cavity of the macrocycle. Thus, although not isolated, methane is included in (eq 4) for mass balance.

$$4Al(CH_3)_3 + H_2[C_{10}H_{20}N_4]H_2 \xrightarrow{120\ °C} [Al(CH_3)]_2[C_{10}H_{20}N_4][Al(CH_3)_3]_2 + 4CH_4 \quad (4)$$

Indeed, the release of alkane from the reaction of AlR_3 with R_2N–H and the subsequent formation of Al_2N_2 fragments has been previously noted. Earlier work by

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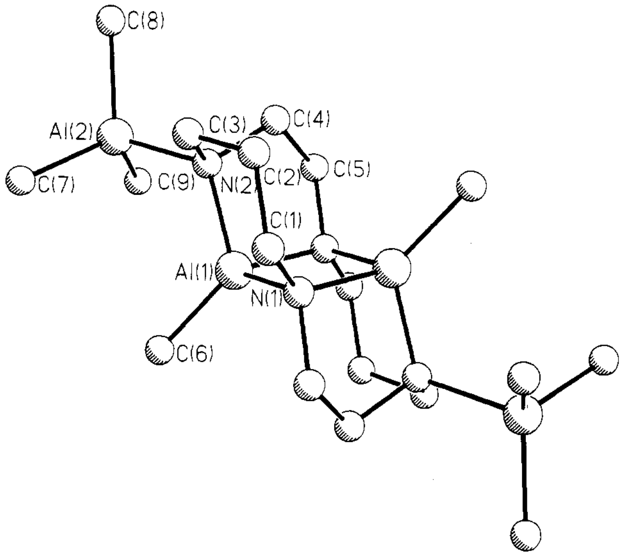

Figure 2. Structure of $[Al(CH_3)]_2[C_{10}H_{20}N_4][Al(CH_3)_3]_2$.

Table II. Final Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[Al(CH_3)]_2[C_{10}H_{20}N_4][Al(CH_3)_3]_2$

atom	*x/a*	*y/b*	*z/c*	*U*[a]
Al(1)	640 (2)	5912 (1)	124 (1)	24
Al(2)	−1058 (2)	8052 (1)	166 (1)	32
N(1)	769 (5)	4880 (3)	−1094 (4)	33
C(1)	506 (6)	5210 (4)	−2370 (4)	37
C(2)	−1091 77)	5792 (4)	−2526 (5)	44
C(3)	−1140 (6)	6737 (4)	−1856 (5)	40
N(2)	−1104 (5)	6667 (3)	−491 (4)	35
C(4)	−2643 (6)	6189 (3)	−87 (6)	39
C(5)	−2375 (6)	5687 (4)	1133 (5)	40
C(6)	2717 (6)	6450 (4)	626 (5)	37
C(7)	843 (9)	8677 (5)	−688 (6)	65
C(8)	−3180 (7)	8622 (4)	−308 (5)	50
C(9)	−753 (7)	7951 (4)	1938 (5)	44

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Smith[30] on the reaction of amines with aluminum alkyls indicated that temperature is a critical factor in determining the structure of the reaction product. Smith reported that amines having N-H bonds react with aluminum alkyls at low temperature to form 1:1 addition compounds. Furthermore, if such addition compounds are subsequently exposed to higher temperatures (120 °C), alkane would be evolved as a result of cleavage of N-H and Al-R bonds. Characteristically, these reaction products possessed Al_2N_2 fragments. Smith referred to these reactions as intermolecular condensations.

The X-ray crystal structure of $[Al(CH_3)]_2[C_{10}H_{20}N_4]$-$[Al(CH_3)_3]_2$ is shown in Figure 2. Final fractional atomic coordinates are given in Table II while selected bond distances and angles are given in Table III. Several points are worthy of note regarding structure and bonding. First of all, it is important to note the severe distortion experienced by the macrocycle due to the aluminum alkyl units. Furthermore, a particular point of interest is the fact that the molecule resides upon a crystallographic center of symmetry. The most striking feature of the title compound, however, is the Al_2N_2 four-membered ring occupying the central cavity of the macrocycle. A view of the molecule showing only the Al-N framework is shown in Figure 3. Each aluminum atom in the Al_2N_2 ring is

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Al(CH_3)]_2[C_{10}H_{20}N_4][Al(CH_3)_3]_2$

	Bond Distances		
Al(1)–N(1)	1.959 (4)	Al(1)–N(2)	1.886 (4)
Al(1)–C(6)	1.928 (5)	Al(1)···Al(1A)	2.735 (2)
Al(1)–N(1A)	1.913 (4)	Al(2)–N(2)	2.042 (4)
Al(2)–C(7)	1.991 (6)	Al(2)–C(8)	1.969 (5)
Al(2)–C(9)	1.972 (5)	N(1)–C(1)	1.493 (6)
N(1)–Al(1A)	1.913 (4)	N(1)–C(5A)	1.525 (6)
C(1)–C(2)	1.538 (7)	C(2)–C(3)	1.498 (7)
C(3)–N(2)	1.507 (6)	N(2)–C(4)	1.486 (6)
C(4)–C(5)	1.527 (8)	C(5)–N(1A)	1.525 (6)
	Bond Angles		
N(1)–Al(1)–N(2)	101.3 (2)	N(1)–Al(1)–C(6)	115.3 (2)
N(2)–Al(1)–C(6)	123.4 (2)	N(1)–Al(1)–Al(1A)	44.4 (1)
N(1)–Al(1)–N(1A)	90.1 (2)	N(2)–Al(1)–N(1A)	93.6 (2)
C(6)–Al(1)–N(1A)	126.0 (2)	N(2)–Al(2)–C(8)	105.3 (2)
N(2)–Al(2)–C(7)	104.5 (2)	N(2)–Al(2)–C(9)	106.7 (2)
C(7)–Al(2)–C(8)	112.1 (3)	C(8)–Al(2)–C(9)	113.5 (3)
C(7)–Al(2)–C(9)	113.8 (3)	Al(1)–N(1)–Al(1A)	89.9 (2)
Al(1)–N(1)–C(1)	114.6 (3)		

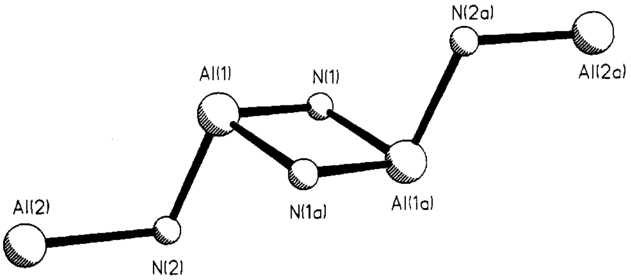

Figure 3. Al-N fragment of $[Al(CH_3)]_2[C_{10}H_{20}N_4][Al(CH_3)_3]_2$.

bonded to three nitrogen atoms. The Al_2N_2 ring is planar and slightly asymmetric with independent Al-N distances of 1.959 (4) and 1.913 (4) Å for Al(1)-N(1) and Al(1)-N(1A), respectively. The Al(1)-C(6) distance is 1.928 (5) Å in the methylaluminum fragment while the average Al-C distance is 1.977 Å for the independent trimethylaluminum unit. The Al(1)-N(1)-Al(A) angle of 89.9 (2)° compares well with the N(1)-Al(1)-N(A) angle of 90.1 (2)° in the Al_2N_2 ring (Al(1) and N(1) are related to Al(1A) and N(1A) through the center of symmetry). The Al(1)-N(2) distance of 1.886 (4) Å is the shortest Al-N interaction in the compound while the Al(2)-N(2) distance of 2.042 (4) Å is the longest. The Al···Al distance of 2.735 (2) Å does not indicate any significant metal-metal interaction. All of these Al-N bond distances are in good agreement with a wide range of Al-N compounds.[31-33]

The nature of the twinning mechanism (in addition to the near orthorhombic crystal symmetry) is such that there is a pseudo-mirror plane passing through the plane containing the crystallographic center of symmetry, the four aluminum atoms, as well as N(2) and N(2A) (this essentially consists of the Al-N framework shown in Figure 3). This serves to slightly disorder the locations of C(1), C(2), C(3), C(4) and C(5). The twinning is also apparent in the pseudomirror plane shown in the *c* direction on the axial photographs.

The title compound is easily compared to the Al_2N_2 ring compounds reported by Smith.[34-36] A comparison of mean

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Table IV. Comparison of Mean Bond Distances (Å) and Angles (deg) in Compounds Containing Al_2N_2 Four-Membered Rings

compd	Al–N	Al···Al	Al–N–Al	ref
$[(CH_3)_2AlN(CH_3)_2]_2$	1.958 (7)	2.809 (4)	91.7 (2)	*a*
$[\{(CH_3)_2AlN(CH_3)\}_2\text{-}\{(CH_3)AlN(CH_3)\}_6]$	1.910 (6)	2.683 (3)	88.4 (3)	*b*
cis-$[Al(CH_3)_2NHC(CH_3)_2]_2$	1.945 (5)	2.800	91.85 (2)	*c*
trans-$[Al(CH_3)_2NHC(CH_3)_2]_2$	1.959 (5)	2.789	90.8 (2)	*c*
$[Al(CH_3)]_2[C_{10}H_{20}N_4]\text{-}[Al(CH_3)_3]_2$	1.936 (4)	2.735 (2)	89.9 (2)	this study

[a] Reference 34. [b] Reference 35. [c] Reference 36.

bond distances and angles between the title compound and these Al_2N_2 condensation products is given in Table IV. It is important, however, to note the inherent difference between the title compound and the condensation products reported by Smith. The condensation products containing the Al_2N_2 fragments are the result of the reaction of AlR_3 with simpler amine units at high temperatures. The title compound is novel in that the macrocycle is essentially left unchanged. The Al_2N_2 ring, in fact, results from an intramolecular condensation specific to the interior cavity of the macrocycle.

The facile cleavage of Al–C and N–H bonds coupled with the novel structure of the title compound will serve as a benchmark in our studies as we explore the potential of nitrogen-based macrocycles in facilitating liquid clathrate behavior based on transition metals.

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Registry No. $[Al(CH_3]_2[C_{10}H_{20}N_4][Al(CH_3)_3]$, 107799-50-8; 1,4,8,11-tetraazacyclotetradecane, 295-37-4; trimethylaluminum, 75-24-1.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, and thermal parameters (8 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Is Thermal Stability of σ-Alkyl Transition-Metal Complexes Compatible with the Presence of Conformationally Free β-Hydrogens and Absence of Stabilizing Ligands? The Isolation of Novel and Unexpectedly Stable Four-Membered Cyclic (σ-Alkyl)palladium Complexes[1]

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A novel type of four-membered cyclic (σ-alkyl)palladium complexes has been isolated. These (2-aminoalkyl-*C,N*)palladium(II) complexes (or 2-azapalladacyclobutanes) are thermally semistable, although they lack the support of stabilizing ligands. Conformationally free β-hydrogens do not imply increased lability, and an X-ray structure of such a complex, chloro[2-(dimethylamino)-1-methylpropyl-*C,N*](dimethylamine)palladium(II) (4), has been obtained. The unexpected order of stability of the complexes provides new prospects on how to stabilize σ-alkyl transition-metal species.

Introduction

The thermal lability of σ-alkyl transition-metal complexes constitutes a persistent problem not only for organometallic chemists but also for synthetic chemists utilizing the expanding set of convenient and highly specific tools offered by modern organometallic chemistry.

One synthetically useful reaction, which illustrates this situation, is the transition-metal-catalyzed cross-coupling between organic halides and alkyl main-group-metal compounds outlined in a general form in eq 1.

$$RX + R'\text{–}m \xrightarrow[L]{M} R\text{–}R' + mX \tag{1}$$

R= aryl, vinyl, allyl
R'= aryl, alkyl, vinyl, allyl
X= Br, I
m= MgBr, Li, Zn, B, Al, Zr, Hg, Sn
M= Ni, Pd, Rh

From an origin of restricted scope (nickel-catalyzed coupling of aryl Grignard reagents with aryl or vinyl halides[2]) this reaction now, with the proper combination of reactants, appears as general as in eq 1.[3,4] However,

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