Figure 9. Absorption and CD spectra of [Co(α-CDX^{2-})(cyclen)]$^+$ (---) and [Co(β-CDX^{2-})(cyclen)]$^+$ (—).

clodextrin, the spectral similarity indicates that cyclodextrins coordinate to cobalt(III) ion through the O$^-$(2) and O$^-$(3) groups of one glucose unit in the same way as they do in [Co(α- or β-CDX^{2-})(en)$_2$]Cl.

Syntheses and Properties of Cyclodextrinato Complexes. The preparations of CDX complexes were successfully carried out by the reaction of *trans*-[CoCl$_2$N$_4$]$^+$ or [CoCO$_3$N$_4$]$^+$ and CDX neutralized with 2 equiv of alkali. However, the properties of the present CDX complexes in a neutral aqueous solution largely depend upon the remaining amine ligands. For example, the violet

band of [Co(CDX^{2-})(NH$_3$)$_4$]Cl was temporarily formed by the reaction of [CoCl(H$_2$O)(NH$_3$)$_4$]Cl and CDX neutralized with 2 equiv of NaOH in an ammoniacal solution at room temperature but soon decomposed to give brown species. Even in the cyclen complexes, partial decomposition into an aqua or diaqua complex was observed. The complexes of Δ- and Λ-[Co(CDX^{2-})(en)$_2$]$^+$ were, however, stable and showed no indication of isomerization or decomposition. Thus, the complex stability decreases in the order (en)$_2$ > cyclen > (NH$_3$)$_4$.

Preparations of anionic CDX complexes were also attempted. Both complexes [Co(α-CDX^{2-})(acac)$_2$]$^-$ and [Co(α-CDX^{2-})(edda)]$^-$ where acac and edda denote acetylacetonate(1-) and ethylenediamine-*N,N'*-diacetate(2-) were successfully prepared and separated by using a column of QAE-Sephadex A-25. But they easily lost their optical activities and decomposed to neutral species in an aqueous solution.

The CDX complexes have generally high solubilities, and sometimes an organic solvent was used for the isolation of the complex. The CDX complexes tend to contain such organic solvent and a small amount of inorganic salts used for the column elution because they preserve the intrinsic properties arising from cyclodextrin, that is, the cavities to include various kinds of substrates. This trend was observed in other cobalt(III)–cyclodextrin complexes.[7]

Since the present complexes carry a positive charge, they can be adsorbed on ion-exchange resins. This means the facile preparation of a column containing a cyclodextrinato complex. The column will be applicable to optical resolution of neutral and anionic metal complexes. Experiments are now in progress.

Safety Notes. Perchlorate salts of metal complexes with organic ligands are potentially explosive. In general, when noncoordinating agents are required, every attempt should be made to substitute anions such as the fluoro sulfonates for the perchlorates. If a perchlorate must be used, only small amounts of material should be prepared and this should be handled with great caution. Cf. ref 18.

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Organometallic Precursors to AlN: Synthesis and Crystal Structures of [(CH₃)₂AlNH₂]₃ and the Planar Species [(t-C₄H₉)₂AlNH₂]₃

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The reaction of the trialkylaluminum compounds (CH$_3$)$_3$Al and (*t*-C$_4$H$_9$)$_3$Al with ammonia gas in hydrocarbon solvents followed by heating affords the trimeric species [(CH$_3$)$_2$AlNH$_2$]$_3$ (**1**) and [(*t*-C$_4$H$_9$)$_2$AlNH$_2$]$_3$ (**2**) in moderate yield. The crystal and molecular structures of these compounds have been determined by X-ray diffraction methods in connection with their investigation as precursors to aluminum nitride. Both aluminum and nitrogen atoms in these two ring compounds exhibit distorted tetrahedral geometries with the greatest deviation occurring at N. This deviation from tetrahedral geometry about N is reflected largely in the endocyclic Al–N–Al angle, which averages 122° for **1** and 134° for **2**. The (AlN)$_3$ ring in **1** is in a skew-boat conformation with no unusual intermolecular contacts. Unlike the case of **1**, the *tert*-butyl derivative **2** features an unprecedented planar (AlN)$_3$ ring. All six atoms of alternating Al and N are coplanar, as required by crystallographic 3-fold symmetry axes. The effects of the Al and N substituents on the (AlN)$_x$ ring size and conformation, as well as on the endocyclic Al–N–Al bond angles, are discussed in the context of the structural results obtained for these and other (AlN)$_x$ heterocycles. Crystallographic data with Mo Kα radiation (λ = 0.710 69 Å): C$_6$H$_{24}$N$_3$Al$_3$ (**1**), *a* = 12.105 (4) Å, *b* = 8.853 (2) Å, *c* = 14.343 (4) Å, β = 108.26 (2)°, *Z* = 4, monoclinic, space group *P2$_1$/c*, *R* = 0.066; C$_{24}$H$_{60}$N$_3$Al$_3$ (**2**), *a* = 10.401 (3) Å, *c* = 50.783 (39) Å, α = β = 90°, γ = 120°, *Z* = 6, rhombohedral, space group *R3c*, *R* = 0.038.

Introduction

Although the structures and properties of the alkylaluminum amides R$_2$AlNR′R″ have been the subject of considerable attention for many years,[1-6] there has been renewed interest recently due

to the application of certain of these compounds as precursors to aluminum nitride and to AlN-containing ceramics.[7-9] A key issue

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in the consideration of potential AlN precursors has been the ability to generate AlN in high purity and in the desired final form, e.g., powders for ceramic substrates,[10,11] thin films as coatings for electronic devices,[12-16] and fibers for high-temperature structural composites.[8,9] Therefore, the physical properties (volatility, solubility, thermoplasticity, etc.) and the thermolysis chemistry of these precursors, as well as the relationship between these properties and the precursor molecular structure, are of particular concern.

Previous work on the structures and properties of the alkylaluminum amides has focused largely on the alkyl- and arylamine derivatives $R_2AlNR'R''$, where both R' and R'' are organic groups or where one of these substituents is hydrogen. Unlike the corresponding boron compounds, where monomeric compounds of this type have been identified,[17] the aluminum derivatives show a strong tendency to oligomerize through formation of Lewis acid–base complexes. Therefore, these compounds are generally found in the form of oligomers of the type $[R_2AlNR'R'']_n$, with either four- ($n = 2$) or six-membered ($n = 3$) $(AlN)_n$ rings. The ring size and conformation appear to be intimately dependent on entropic factors (favoring the larger number of molecules, e.g., dimers), ring strain, and substituent steric interactions.[18,19]

In the case where both R' and R'' are organic groups, steric interactions between the 1,2 Al and N substituents generally prevail over ring strain to yield a dimeric unit with a planar four-membered $[AlN]_2$ ring. Among the few exceptions are the derivatives of organic cyclic amines, where a structure solution of the R', R'' = CH_2CH_2 compound has revealed a trimeric unit with a skew-boat conformation for the six-membered $[AlN]_3$ ring,[2] and molecular weight and ^{1}H NMR studies have suggested that the corresponding R', R'' = $(CH_2)_3$ compound exists in solution as an equilibrium mixture of the dimer and trimer.[20] Similarly, replacement of the aluminum alkyl substituents by hydrogen (i.e., R = H and R', R'' = CH_3) allows formation of a trimer with two methyl groups on nitrogen.[3] In this case, the six-membered $(AlN)_3$ ring was found to occur in a chair conformation. When one or both of the two N substituents are hydrogen, both trimeric (R = CH_3, R' = H, R'' = CH_3)[1] and dimeric (R = CH_3, R' = H, R'' = $Si(CH_3)_3$;[21] R = $Si(CH_3)_3$ and R', R'' = H[4]) species have been identified, depending, apparently, on the steric bulk of the

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Table I. Crystallographic Data for $[(CH_3)_2AlNH_2]_3$ and $[(t\text{-}C_4H_9)_2AlNH_2]_3$

chem formula	$C_6H_{24}N_3Al_3$	$C_{24}H_{60}N_3Al_3$
fw	219.22	417.69
space group	$P2_1/c$	$R3c$
temp, K	297	297
λ, Å	0.710 64	0.710 64
ρ(calcd), g/cm³	1.00	0.99
μ, cm⁻¹	2.3	1.4
a, Å	12.105 (4)	10.401 (3)
b, Å	8.853 (2)	10.401 (3)
c, Å	14.343 (4)	50.783 (39)
α, β, γ, deg	90, 108.26 (2), 90	90, 90, 120
V, Å³	1459.8	4757.7
Z	4	6
$R(F)$	0.066	0.038
$R_w(F)$	0.074	0.036

N and Al substituents.

We report here the preparation of a new *tert*-butylaluminum amide as well as the results of structural studies carried out on both the $(CH_3)_2AlNH_2$ and $(t\text{-}C_4H_9)_2AlNH_2$ compounds. The $(CH_3)_2AlNH_2$ compound was previously reported by Wiberg,[22] who indicated that is was dimeric in liquid ammonia. Wiberg obtained this compound by the controlled thermolysis of the adduct $(CH_3)_3Al\cdot NH_3$, an intermediate in the following series of reactions: $R_3Al + NH_3 \rightarrow R_3Al\cdot NH_3$ (adduct); $R_3Al\cdot NH_3 \xrightarrow{\Delta} R_2AlNH_2$ (amide) + RH; $R_2AlNH_2 \xrightarrow{\Delta}$ "RAlNH" (imide) + RH; RAlNH $\xrightarrow{\Delta}$ AlN + RH.

As part of a detailed study of these reactions, we have confirmed the formation of a crystalline $(CH_3)_2AlNH_2$ intermediate as well as the eventual formation of AlN on thermolysis above 400 °C; however, several new features of this chemistry relating to the structure of the $(CH_3)_2AlNH_2$ intermediate and the conditions required to obtain pure AlN as the final product of the thermolysis have been noted.[7]

A similar reaction sequence pertains to other choices of the Al substituent R, although the only other case for which the initial Lewis acid–base adduct was isolated was when R = $t\text{-}C_4H_9$. As with R = CH_3, this adduct yields a crystalline R_2AlNH_2 compound as the initial product of thermolysis. For the other systems investigated, i.e., R = C_2H_5 and $i\text{-}C_4H_9$, the corresponding adduct was not isolated. Instead, alkane was eliminated at room temperature on addition of ammonia to a solution of the trialkylaluminum compound, yielding, on removal of the solvent, a liquid R_2AlNH_2 derivative.

The structures of both crystalline R_2AlNH_2 compounds (R = CH_3, $t\text{-}C_4H_9$) have now been determined, leading to an extension in the range of structural types exhibited by the organoaluminum amides as well as further information relating to the effect of Al and N substituents on ring size and conformation in this series of compounds.

Experimental Section

General Procedures. All reactions were performed by using either modified Schlenk techniques under an inert atmosphere of nitrogen or a N_2-filled HE-493 Vacuum Atmospheres drybox. Solvents were freshly distilled from sodium under nitrogen before use. Trimethylaluminum (98% purity) was used as purchased from Aldrich. High-purity ammonia gas was purchased from the USS Agri-chemicals Division of the U.S. Steel Corp. $(t\text{-}C_4H_9)_3Al$ was prepared by using a literature procedure.[23]

Physical Methods. Infrared spectra were recorded on a Perkin-Elmer 298 infrared spectrometer. ^{1}H NMR spectra were obtained by using a Varian 200-MHz NMR spectrometer. All values are given in parts per million (ppm) relative to C_6H_6 at δ 7.15. Mass spectral data were obtained with a Varian Mat 731 spectrometer (field ionization) and with a Hewlett-Packard 5386 GC/MS spectrometer (chemical ionization) for **1** and **2**, respectively. Carbon and hydrogen microanalyses were performed by Galbraith Laboratories.

$[(CH_3)_2AlNH_2]_3$ (**1**). Ammonia gas was bubbled through a solution of $(CH_3)_3Al$ (38 mL, 0.39 mol) in benzene (160 mL) at room tempera-

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Table II. Atom Coordinates (×10⁴)

atom	x	y	z
		Complex 1	
Al(1)	3271 (2)	4751 (2)	743 (1)
Al(2)	2091 (2)	7999 (2)	1136 (1)
Al(3)	2180 (2)	5060 (2)	2666 (1)
N(1)	2215 (4)	4181 (5)	1443 (3)
N(2)	3409 (4)	6915 (5)	975 (4)
N(3)	2103 (4)	7214 (5)	2386 (3)
C(1)	2537 (6)	4404 (8)	−663 (5)
C(2)	4756 (5)	3768 (8)	1379 (6)
C(3)	663 (5)	7332 (7)	139 (5)
C(4)	2387 (6)	10173 (6)	1249 (5)
C(5)	3682 (6)	4635 (8)	3661 (5)
C(6)	725 (6)	4431 (8)	2889 (5)
		Complex 2	
Al(1)	7996 (2)	8016 (1)	7500
N(1)	10023 (11)	8280 (6)	7501 (2)
H(1n)	9982 (74)	7683 (73)	7377 (10)
H(2n)	9923 (72)	7775 (72)	7644 (10)
C(1)	7025 (9)	7030 (9)	7159 (2)
C(2)	5353 (9)	6227 (11)	7200 (2)
C(3)	7574 (11)	8082 (11)	6921 (1)
C(4)	7265 (13)	5668 (11)	7120 (2)
C(5)	6984 (11)	7015 (11)	7833 (2)
C(6)	8016 (14)	7506 (15)	8062 (2)
C(7)	5821 (10)	7374 (10)	7920 (2)
C(8)	6453 (11)	5423 (11)	7845 (2)

Figure 1. Computer-generated thermal ellipsoid (probability level 50%) plot of **1**, illustrating skew-boat conformation. Pseudo-2-fold axes are along Al(1) and N(3). Hydrogen atoms are omitted for clarity.

Figure 2. Thermal ellipsoid (probability level 50%) plot of **2** with hydrogen atoms omitted for clarity except those on N.

ture for a period of 3.5 h at a flow rate of 0.2 scfh.[24] The solution was refluxed for 2 h and the solvent removed by distillation to afford a white material. Upon sublimation (0.01 Torr, 70 °C), colorless crystals were obtained: yield 20.3 g, 70%; mp 133–135 °C; ¹H NMR (C_6D_6 solution) δ 0.68 s (2 H, NH_2), −0.095 s (6 H, CH_3); IR ν(N–H) 3350, 3420 cm⁻¹; MS (EI) m/e (relative intensity, ion) 219 (3.2%, M), 204 (100%, M − 15). Redissolving **1** in heptane and cooling slowly afforded colorless crystals suitable for X-ray analysis. Adequate chemical analyses (C, H, N) were not obtained, presumably due to incomplete combustion and loss of alkane during analyses.

[(t-C₄H₉)₂AlNH₂]₃ (2). In a manner analogous to that described for **1**, ammonia was bubbled through a solution of (t-C_4H_9)₃Al (3.5 g, 17.6 mmol) in xylenes (25 mL) for a period of 2 h at 0.2 scfh.[24] Heating at 115 °C for 2 days followed by filtration of the mixture while hot and slow cooling afforded colorless plates suitable for X-ray studies: yield 1.4 g, 52%; mp 230–232 °C; ¹H NMR (C_6D_6 solution) δ 1.07 s (18 H, CH_3), 0.68 br (2 H, NH_2); IR ν(N–H) 3317, 3260 cm⁻¹; MS (CI) m/e (relative intensity, ion) 472 (0.5%, M + 1), 456 (3.2%, M − 15), 414 (100%, M − 57), 257 (10%, M − 214). Anal. Calcd: C, 61.09; H, 12.84; N, 8.91. Found: C, 61.42; H, 13.05; N, 8.77.

X-ray Crystallographic Studies. All X-ray data were collected by using a Nicolet P3F single-crystal diffractometer with Mo Kα radiation and a graphite monochromator. Calculations were carried out on a Data General Eclipse computer using SHELXTL, version 4, programs. Scattering factors and corrections for anomalous dispersion were from ref 25.

From a collection of colorless needles of [(CH₃)₂AlNH₂]₃ (1) obtained by slow cooling of a heptane solution, a single crystal was selected and sealed in a thin-walled capillary tube under nitrogen. Monoclinic lattice constants were determined by a least-squares fit of 20 accurately centered reflections with 20 < 2θ < 45°. The structure was solved by direct methods for the space group $P2_1/c$. The data were not corrected for absorption effects. In the final cycles of refinement all non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included at calculated positions. Further details of data collection and refinement are given in Table I.

Colorless plates of [(t-C₄H₉)₂AlNH₂]₃ (2) were obtained by slowly cooling a xylene solution to 0 °C. These were protected by hydrocarbon oil from air and moisture. A suitable crystal was then selected and mounted inside a thin-walled capillary tube for X-ray analysis. The
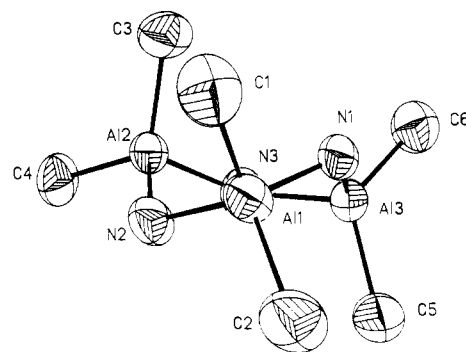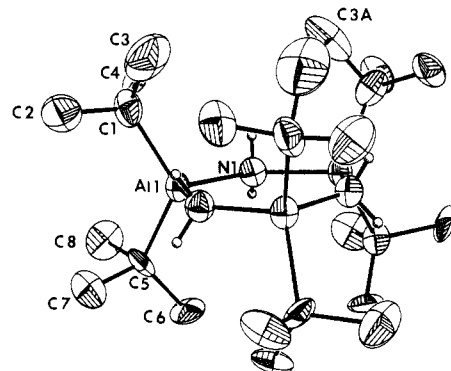
structure was solved by direct methods for the space group $R3c$. In the final cycles of refinement all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned at calculated positions with the exception of the hydrogens bonded to nitrogen. These hydrogens were located on the difference map and subsequently refined by using a riding model. Further details of data collection and refinement are given in Table I. Atom coordinates for **1** and **2** are given in Table II.

Results

Reaction of R₃Al (R = CH₃, t-C_4H_9) with ammonia in hydrocarbon solvents affords the adduct R₃Al·NH₃, which can be isolated by evaporation of the solvent.[24] Subsequent heating liberates 1 mol of alkane (CH_4 for **1** and i-C_4H_{10} for **2**), as detected by gas chromatography, to afford compounds **1** and **2** as trimeric species in the solid state. The mass spectra of [(CH₃)₂AlNH₂]₃ (**1**) and [(t-C₄H₉)₂AlNH₂]₃ (**2**) are consistent with the retention of the trimeric unit in the gas phase. For **1**, a weak peak at m/e (EI) 219 (relative abundance 3.5%) corresponds to the molecular weight for the trimer. The most abundant peak in the spectrum is M − 15, which corresponds to the loss of CH_3 at m/e 204 (100%). In the case of **2**, the mass spectrum showed a weak peak at m/e (CI) 472 (0.5%), corresponding to M + 1, and the most abundant peak at m/e 414 (100%), due to the elimination of one isobutyl fragment. Other fragment peaks were consistent with a trimeric formulation with no evidence of a dimeric mass peak in the case of either compound.

Structural Description. Pertinent bond distances and angles for [(CH₃)₂AlNH₂]₃ (**1**) are given in Table III. The structure of **1** as illustrated in Figure 1 consists of alternating (CH₃)₂Al and NH₂ units to form a six-membered (AlN₃) ring in a skew-boat conformation. This can readily be seen by viewing along the pseudo-2-fold axes through atoms Al(1) and N(3). The atoms N(1), Al(1), N(2), and N(3) are essentially coplanar with Al(2) 1.09 Å above and Al(3) 0.71 Å below the plane. Within the (AlN)₃ framework, dihedral N–AlN–Al angles range from 0.5 to 69.6° (Table III). The Al···Al and N···N distances average 3.382 (3) and 2.992 (10) Å and are similar to those values reported for *cis*- and *trans*-[(CH₃)₂AlNHCH₃]₃ and [(CH₃)₂AlNCH₂CH₂]₃ (Table IV). The shortest intramolecular 1,3 methyl–methyl

(24) The adducts R₃Al·NH₃ (R = CH₃, t-C_4H_9) can be isolated from these solutions if the temperature of the reaction mixture is maintained below the respective decomposition temperatures (ca. 55 °C for CH₃, 100 °C for t-C_4H_9)₃. For (t-C_4H_9)₃Al·NH₃: ¹H NMR (C_6D_6 solution) δ 1.09 s (27 H, CH₃), 0.89 br (3 H, NH₃); IR ν(N–H) 3357, 3278, 3170 cm⁻¹; MS (EI) m/e (ion, relative abundance) 215 (M, 0.5%), 198 (M − 17, 1%), 141 (M − 74, 88%), 84 (45%); mp 79–81 °C. Anal. Calcd: C, 66.91; H, 14.07; N, 6.50. Found: C, 66.16; H, 13.71; N, 6.36.

(25) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

Table III. Selected Distances (Å) and Angles (deg)[a]

Complex 1

Distances

Al(1)···Al(2)	3.335 (3)	Al(2)-N(2)	1.938 (5)
Al(1)···Al(3)	3.429 (3)	Al(2)-N(3)	1.921 (5)
Al(2)···Al(3)	3.383 (3)	Al(3)-N(1)	1.933 (5)
N(1)···N(2)	3.000 (9)	Al(3)-N(3)	1.942 (5)
N(1)···N(3)	3.025 (9)	Al(1)-C(1)	1.957 (7)
N(2)···N(3)	2.950 (10)	Al(1)-C(2)	1.947 (6)
Al(1)-N(1)	1.927 (6)	C(1)···C(3)	3.85 (1)
Al(1)-N(2)	1.940 (5)	C(2)···C(5)	3.96 (2)

Endocyclic Angles

N(1)-Al(1)-N(2)	101.7 (2)	Al(1)-N(1)-Al(3)	125.3 (2)
N(2)-Al(2)-N(3)	99.7 (2)	Al(1)-N(2)-Al(2)	118.6 (2)
N(1)-Al(3)-N(3)	102.7 (2)	Al(2)-N(3)-Al(3)	122.3 (3)

Exocyclic Angles

N(1)-Al(1)-C(1)	109.7 (3)	N(2)-Al(1)-C(2)	110.0 (2)
N(2)-Al(1)-C(1)	108.5 (3)		

Dihedral Angles within (AlN)$_3$ Ring

N(2)-Al(1)N(1)-Al(3)	36.3
N(3)-Al(2)N(2)-Al(1)	69.6
N(1)-Al(3)N(3)-Al(2)	0.5
Al(1)-N(1)Al(3)-N(3)	51.7
Al(2)-N(2)Al(1)-N(1)	30.8
Al(3)-N(3)Al(2)-N(2)	49.8

Complex 2

Distances

Al(1)···Al(1a)	3.592 (20)	N(1)-H(1n)	0.872 (70)
N(1)···N(1a)	3.118 (20)	N(1)-H(2n)	0.871 (62)
Al(1)-N(1)	1.985 (14)	C(4)···H(1n)	2.856
Al(1)-N(1a)	1.918 (10)	C(6)···H(2n)	2.820
N(1)-Al(1a)	1.918 (10)	C(7)···H(2na)[b]	2.897
Al(1)-C(1)	2.008 (10)	C(3)···C(3a)[c]	3.992
Al(1)-C(5)	1.990 (11)		

Endocyclic Angles

N(1)-Al(1)-N(1a)	106.1 (4)	Al(1)-N(1)-Al(1)'	133.9 (5)

Exocyclic Angles

C(1)-Al(1)-C(5)	117.8 (4)	Al(1)-C(1)-C(3)	113.7 (5)
C(1)-Al(1)-N(1)	107.5 (5)	H(1)-N(1)-Al(1)	103.3 (2.2)
C(1)-Al(1)-N(1a)	108.3 (5)	H(2)-N(1)-Al(1)	97.0 (5.2)
Al(1)-C(1)-C(2)	107.8 (6)	H(1)-N(1)-H(2)	103.0 (6.4)

[a] Additional distances and angles can be found in the supplementary material. [b] All other 1,2 nonbonded C–H distances are greater than 3.0 Å. [c] All other 1,2 nonbonded C–C distances are greater than 4.0 Å.

$(CH_3)Al$ nonbonded carbon distance is 3.89 Å for C(1) and C(3) (Table III) and is close to the sum of the van der Waals radii for two methyl groups (ca. 4.0 Å). The Al and N atoms exhibit distorted tetrahedral geometries, with the distortion from tetrahedral symmetry most apparent for N.

The structure of $[(t-C_4H_9)_2AlNH_2]_3$ (2) is illustrated in Figure 2. Pertinent bond distances and angles are given in Table III. The most conspicuous feature of **2** is the planar nature of the six-membered ring, which has D_{3h} symmetry. All Al and N atoms are coplanar and exhibit distorted tetrahedral geometries. Thus, the average Al–N bond distance is 1.952 Å and endocyclic N(1)-Al(1)-N(1a) and Al(1)-N(1)-Al(1a) bond angles are 106.1 (4) and 133.9 (5)°, while the C(1)-Al(1)-C(5) angle is 117.8 (4)°. The H(1n)-N(1) and H(2n)-N(1) bond distances are 0.872 (70) and 0.871 (62) Å, respectively, and the H(1n)-H(1)-H(2n) bond angle of 103.0 (6.4)° is about 5° less than that reported for NH_3.[26] Nonbonded 1,3 diaxial *tert*-butyl methyl–methyl carbon distances are equal to or greater than 4.0 Å, while the shortest C(Me) to H(N) distance of 2.86 (3) Å for H(1n) and C(4) is within range of the calculated van der Waals distance (3.2 Å).

Discussion

The observation of a trimeric molecular structure for the title compounds $[(CH_3)_2AlNH_2]_3$ (1) and $[(t-C_4H_9)_2AlNH_2]_3$ (2) both

in the solid state by X-ray diffraction methods and in the gas phase by mass spectrometry extends the number of structurally characterized examples of such heterocycles from 4 to 6, thereby allowing a more detailed assessment of the role of Al and N substituents in determining the ring size and conformation. The trimeric nature of the $(CH_3)_2AlNH_2$ derivative, although in apparent contradiction to the report of Wiberg,[22] is not surprising in the context of the earlier work on the other $R_2AlNR'R''$ compounds, where trimeric association was found for both $(CH_3)_2AlNHCH_3$[1] and the isomeric $H_2AlN(CH_3)_2$.[3] It is possible that the trimer reacts with liquid ammonia, yielding open-chain species with a lower effective molecular weight.

Bond distances in $[(CH_3)_2AlNH_2]_3$ (1) differ little from those that have been reported for the four previously studied trimers (Table IV), with an average Al–N bond length of 1.935 Å (as compared to average values of 1.90–1.96 Å for trimeric, dimeric, and cage-type $R_nAlNR'_n$ structures[27]) and an Al–C bond length of 1.958 Å. Both the Al–C (average 1.999 Å) and Al–N (average value 1.952 Å) bond distances are somewhat longer in the case of the $[(t-C_4H_9)_2AlNH_2]_3$ compound, perhaps reflecting the larger size of the *tert*-butyl substituent.

The chief differences in these two structures clearly lie in the endocyclic bond angles and overall ring conformation, both of which, in the case of the $[(t-C_4H_9)_2AlNH_2]_3$ compound, differ substantially from all prior observations on $(AlN)_n$ ring systems. Thus, the endocyclic N–Al–N bond angles in the $[(CH_3)_2AlNH_2]_3$ structure average 101.4°, whereas the C–Al–C bond angles average 118.3° and the Al–N–Al bond angle average is 122.1° (Table III). The $[(t-C_4H_9)_2AlNH_2]_3$ compound shows similar distortions from the idealized tetrahedral geometry about Al and N (Table III), where the bond angles about Al are similar to those in $[(CH_3)_2AlNH_2]_3$ but the endocyclic Al–N–Al angle is enlarged to 133.9°.

In a comparison of the six members of the series of structurally characterized $(AlN)_3$ ring compounds, the endocyclic Al–N–Al angle shows the most variability of all the bond angles, ranging from 115 (2)° in the $[H_2AlN(CH_3)_2]_3$ structure to 133.9 (2)° in the $[(t-C_4H_9)_2AlNH_2]_3$ compound (Table IV). The apparent extreme flexibility in this bond angle differs markedly from saturated carbon six-membered-ring systems, where appreciable deviations from tetrahedral bond angles are rarely observed.[28] However, bond angles of this magnitude have been observed in studies of halide[29] and oxygen-bridged[29,30] Al rings, where the bridging species have either no or, at most, one terminal substituent. This suggests that the small spatial requirements of the two hydrogen substituents in the case of the $[R_2AlN(CH_3)_2]_3$ compounds may be a factor in permitting expansion of the bridge bond angle. In addition, the appreciable electronegativity difference between Al and these bridging atoms (N, O, and halogen) implies a high degree of ionic character in the Al–X bonds, which would lead to relaxation in the constraint of sp^3 hybridization and greater flexibility in the bridging angle.

The skew-boat conformation observed for the $(AlN)_3$ ring in $[(CH_3)_2AlNH_2]_3$ could arise from crystal-packing interactions; however, there are no unusual intermolecular separations or interactions in this structure and the isomeric $H_2AlN(CH_3)_2$ compound was obtained in a chair conformation. A similar skew-boat conformation was observed for the $[(CH_3)_2AlN(CH_2CH_2)]_3$ compound, where the Al–N–Al bond angle was also around 120°, suggesting that the increase in these endocyclic bond angles may be driving this conformational change from a chair configuration. This conclusion is supported by the available data on the two $(AlO)_3$ heterocycles where similar bridge-bond angles were reported. Thus, the compound $[(CH_3)_2AlON(CH_3)_2]_3$, which was

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Table IV. Average Lengths (Å) and Angles (deg) for $(AlN)_x$ Heterocycles

compd	ring conformn[a]	Al···Al	N···N	Al–N	Al–C	N–Al–N	C–Al–C	Al–N–Al	ref
$[(CH_3)_2AlNH_2]_3$	sb	3.382 (3)	2.992 (10)	1.935 (5)	1.958 (7)	101.7 (2)	117.9 (4)	125.3 (2)	this work
						99.7 (2)	117.0 (3)	118.6 (2)	
						102.7 (2)	120.0 (3)	122.3 (3)	
$[(t\text{-}C_4H_9)_2AlNH_2]_3$	p	3.592 (20)	3.118 (20)	1.985 (14)	2.008 (10)	106.1 (4)	117.8 (4)	133.9 (5)	this work
$cis\text{-}[(CH_3)_2AlNHCH_3]_3$	c	3.403 (10)	3.014	1.940 (10)	1.973 (11)	101.9 (5)	117.6 (6)	122.4 (5)	1
						102.4 (4)	116.2 (6)	122.1 (4)	
$trans\text{-}[(CH_3)_2AlNHCH_3]_3$	sb	3.336 (8)	2.949 (18)	1.901 (1)	1.982 (19)	101.7 (6)	117.7 (9)	119.9 (6)	1
						100.1 (6)	117.4 (9)	129.9 (9)	
$[(CH_3)_2AlNCH_2CH_2]_3$	sb			1.91 (2)	1.96 (2)	100.8 (1.2)	114.6 (1.0)	120.4 (.9)	2
						102.4 (1.0)	114.4 (1.1)	121.2 (1.0)	
$[H_2AlN(CH_3)_2]_3$	c	3.3		1.93 (3)		108 (2)		115 (2)	3
$[(CH_3)_2AlN(CH_3)_2]_2$	p	2.809 (4)	2.726 (7)	1.958 (7)	1.951 (11)	88.3 (3)	115.7 (5)	91.7 (2)	1
$[\{(CH_3)_3Si\}_2AlNH_2]_2$	p	2.838 (1)		1.954 (2)	2.472 (1) (Al–Si)	86.9 (1)	123.6 (Si–Al–Si)	93.1 (1)	4
$[MeAlNMe]_7$	$(AlN)_3$ rings			1.96	1.97	111		120	27

^{a} Ring conformation described as skew-boat (sb), chair (c), and planar (p).

studied by single-crystal X-ray diffraction methods, was also found to have a skew-boat conformation[30] and the heterocycle [(C-H₃)₂AlOCH₃]₃, which was examined in the gas phase by electron diffraction, was also judged likely to have a boat or "twist-boat" conformation.[29]

On the other hand, the structural data on the two isomers of the [(CH₃)₂AlNHCH₃]₃ compound[1] suggest that the endocyclic bond angles are certainly not the whole answer to the question of conformation in these six-membered-ring compounds. Thus, whereas both the cis and trans isomers have Al–N–Al bond angles of around 120°, one ring (trans) has a skew-boat conformation and the other (cis) is in a chair configuration.

The planar conformation of the [(t-C₄H₉)₂AlNH₂]₃ ring has no precedent or analogue among other aluminum–nitrogen six-membered-ring heterocycles. The only close relative among group 13 and 15 compounds is the solid-state indium–arsenic compound [(CH₃)₂InAs(CH₃)₂]₃, which has been determined by X-ray crystallography to contain two independent molecules per asymmetric unit. One has a nearly planar (InAs)₃ ring while the other has a puckered ring conformation.[31] In this particular case, the heavier group 13 and 15 elements allow for a greater amount of flexibility within the (InAs)₃ six-membered rings.

The conformation of the *tert*-butyl compound might be appropriately viewed as the extreme extension of the distortion from a chair configuration brought about by 1,3 Al–Al substituent interactions and facilitated by the flexibility in the Al–N–Al bond angle. In this case the expansion in the Al–N–Al bond angle to 133.9° allows achievement of a planar conformation with only a slight adjustment in the endocyclic N–Al–N bond angle, relative to that in the (CH₃)₂AlNH₂]₃ compound. This angle (106.1°) is actually slightly larger than the average value in the [(C-H₃)₂AlNH₂]₃ compound, despite the presence of larger Al substituents, and is even closer to the idealized tetrahedral value.

A key question here, especially in the context of the recent structure solution of the corresponding [{(CH₃)₃Si}₂AlNH₂]₂ compound,[4] is why this compound is a trimer and not a dimer? Both steric and electronic factors can be invoked as potential answers to this question. First, it should be noted that the shortest nonbonded C–C distance involving the *tert*-butyl CH₃ groups on 1,3 Al atoms in the trimeric structure of this compound is 3.99 Å. This is close to the van der Waals diameter of two methyl groups (4.0 Å). Thus, it appears that the 1,3 *tert*-butyl group interactions are satisfactorily accommodated by the planar six-membered-ring structure. In the case of the 1,2 substituent interactions involving a methyl carbon and hydrogen on nitrogen, the shortest nonbonded distance is 2.86 Å, which also appears to be within normal limits for a van der Waals interaction.

The larger size of the (CH₃)₃Si groups in the case of the [{(CH₃)₃Si}₂AlNH₂]₂ compound may be sufficient to render these 1,3 or 1,2 interactions untenable in the hypothetical trimeric form of this compound; alternatively, the existence of two of these large
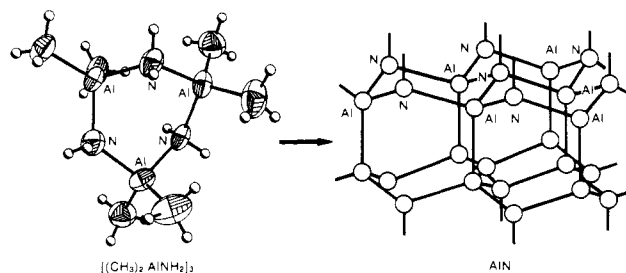

Figure 3. Drawing showing structural relationship between $(AlN)_3$ frameworks in the amide **1** and the final AlN wurtzite structure.

groups on the relatively small Al atoms may favor the smaller endocyclic N–Al–N bond angle required for the dimeric unit. In addition to such steric considerations, differences in the electronic structure of the Al atoms in these two structures arising from electronegativity differences in the respective substituents could also play a role in determining the observed structural differences. In accordance with Bent's rule,[32] the greater electronegativity of C relative to Si may favor the use of hybrid orbitals with a larger amount of s character in the bonding of the Al atoms in [(t-C₄H₉)₂AlNH₂]₃ to N, thus favoring the larger N–Al–N angle of the six-membered-ring structure over that required by a four-membered (AlN)₂ ring.[33]

In any case, it appears from structural and mass spectral data that even with *tert*-butyl groups on Al, the six-membered-ring structure is perferred over the four-membered dimeric alternative when the substituents on N are hydrogen. This suggests that the dominant factor which drives formation of the dimeric units in the case of the organoaluminum amides is the 1,2 steric interactions between the Al and N substituents and that, with less bulky N substituents, the trimeric form will generally be favored for dialkylaluminum amides.

In the context of the balance of enthalpic and entropic factors cited by Coates[18] and others[1] as determinants of the degree of association, it appears that the enthalpic factor favors trimeric association and generally prevails over the entropic factor. The greater stability of the trimer over the dimer may relate to the smaller bond angles required for the dimer and the reluctance of N in particular to assume such a small bond angle when the substituents are hydrogen. In contrast, the expansion of this bond angle to values well in excess of even 120° does not seem to be much of a problem for the NH₂ group where relief of 1,3 substituent steric interactions is demanded by Al in the trimeric structure.

Precursors to AlN. In connection with the application of the R₃Al + NH₃ system as a source of AlN, it is noteworthy that the R₂AlNH₂ intermediate and the final AlN structure share a common feature, the existence of (AlN)₃ rings. The relatively facile conversion of these intermediates to AlN on heating may

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reflect the small amount of structural reorganization required for this conversion as well as the existence of a facile mechanism for the elimination of RH as a stable byproduct (Figure 3). A detailed study of the mechanism of this thermal decomposition process in the case of the trimethylaluminum–ammonia system is in progress.

Registry No. 1, 60363-54-4; **2**, 118142-16-8; $(CH_3)_3Al$, 75-24-1; $(t\text{-}C_4H_9)_3Al$, 4731-36-6.

Supplementary Material Available: Full listings of crystal data and summary of data collection and refinement, anisotropic thermal parameters, hydrogen coordinates, and bond distances and angles (Tables S1–S6) for $[(CH_3)_2AlNH_2]_3$ (1) and $[(t\text{-}C_4H_9)_2AlNH_2]_3$ (2) (8 pages); listings of observed and calculated structure factors (Tables S7 and S8) (7 pages). Ordering information is given on any current masthead page.

Contribution from the Departement d'Etude des Lasers et de la Physico-Chimie, Centre d'Etudes Nucléaires de Saclay, IRDI/DESICP/DLPC/SCM-UA CNRS 331, 91191 Gif Sur Yvette Cedex, France

Preparation, Characterization, and Crystal Structure of the Adducts WOF₄·nC₅H₅N (n = 1, 2)

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WOF₄·2C₅H₅N was prepared from the reaction of WOF₄ with an excess of pyridine, and WOF₄·C₅H₅N resulted from pumping of WOF₄·2C₅H₅N at room temperature or the reaction of stoichiometric amounts of WOF₄ and C₅H₅N in dichloromethane. The two adducts were characterized by elemental analyses, X-ray powder data, and vibrational spectroscopy. Solutions of the adducts in dichloromethane were studied by ¹⁹F and ¹H NMR spectroscopy. The crystal structures of WOF₄·2C₅H₅N and WOF₄·C₅H₅N have been determined by X-ray diffraction methods. Both adducts are of molecular type. In WOF₄·2C₅H₅N two nitrogen atoms of the pyridine ligands, one oxygen, and two fluorine atoms form a regular pentagon around the tungsten atom. Two other fluorine atoms, located at the apical positions, complete the pentagonal bipyramid of ligands. In WOF₄·C₅H₅N, the tungsten atom is surrounded by a distorted octahedron of ligands with the nitrogen of the pyridine ligand being trans to the oxygen atom and the equatorial plane made up of four fluorine atoms located at the corners of a regular rectangle. The space groups, unit cell parameters, and *R* factors are as follows: WOF₄·2C₅H₅N, monoclinic, C2/c, a = 8.248 (3) Å, b = 11.465 (3) Å, c = 13.507 (3) Å, β = 108.10 (2)°, V = 1296 Å³, Z = 4, and R = 0.031; WOF₄·C₅H₅N, monoclinic, P2₁/c, a = 7.757 (2) Å, b = 14.442 (3) Å, c = 7.859 (7) Å, β = 105.79 (4)°, V = 847 Å³, Z = 4, and R = 0.059.

Introduction

Oxide tetrafluorides of transition elements such as tungsten or molybdenum are known to be good electron acceptors,[1-17] and for instance their acid character has been demonstrated by their reactions with strong bases such as CsF[8] or NOF or ClOF₃.[7] All the adducts, except those obtained with XeF₂ or KrF₂,[9,10,12,14,15] have been found to be ionic and to contain the species $M_2O_2F_9^-$, MOF_5^-, or MOF_6^{2-} (M = W, Mo). As far as organic bases are concerned, their interaction with MoOF₄ or WOF₄, used as reactants or formed in situ, has been found[18-32] to yield either molecular or ionic species depending on the reaction conditions and/or bases. The data regarding the species of these organic base derivatives have been obtained mainly by ¹⁹F NMR spectroscopy, and no crystal data have been published so far.

Considering that the chemical properties of WF₆ and WOF₄ are closely related and also that Tebbe and Mutterties[18] had shown

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