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Thermal Decomposition of 1:1 R_3Al:en Adducts (R = Me, Et; en = Ethylenediamine): Synthesis and Structure of a Novel Intermediate, $Al[(HNCH_2CH_2NH)AlMe_2]_3$

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The thermal decomposition of the 1:1 adducts of ethylenediamine (en) with the trialkylaluminum compounds R_3Al (R = Me, Et) in aromatic hydrocarbon solvents leads to the formation of insoluble polymeric solids whose composition corresponds approximately to the formula $[RAl(en\text{-}2H)]_n$. These thermolysis reactions proceed through a series of intermediates which were identified with the aid of ^1H, ^{13}C, and ^{27}Al NMR spectroscopy. In the case of Me_3Al–en, a crystalline intermediate, $Al[(HNCH_2CH_2NH)AlMe_2]_3$, was isolated from the decomposition of the 1:1 Me_3-Al:en adduct in toluene solution, and its molecular structure was characterized by means of a single-crystal XRD study (space group $Pca2_1$; $a = 19.151$ (4) Å, $b = 10.864$ (1) Å, $c = 21.035$ (3) Å; $V = 4376.3$ (9) Å^3; $Z = 8$). Full-matrix least-squares refinement converges at $R = 0.044$ and $R_w = 0.047$ based on 2753 reflections with $F > 4\sigma(F)$. The molecule has an AlN_6 pseudooctahedral core with the en-2H units both chelating and bridging to 6- and 4-coordinated Al atoms. The ^{27}Al NMR spectrum of this compound shows two peaks, at 160 and 40 ppm, attributed to the 4-coordinated and 6-coordinated Al atoms, respectively. The pyrolysis pathways for the 1:1 AlR_3:en adducts in benzene solution were investigated by means of NMR, FT-IR, GC, DSC, TGA, and elemental analyses of the intermediate and final products.

Introduction

The chemistry of organoaluminum amides and imides derived from the interaction of ammonia, or primary or secondary organic amines, with organoaluminum compounds of the type R_3Al (R = alkyl or aryl groups) has been the subject of intensive research for many years, in part due to the novel molecular structures that have been generated through Al–N–Al bridging interactions.[1] These interactions often lead to oligomerization, forming rings or cages which contain two or more Al atoms bridged by NR_2 or NR groups. The factors which determine the ring size, the geometry, and the extent of cluster formation have been of interest in this work as well as the chemistry leading to these structures. The reactions of chelating bi- or polydentate amines with the R_3Al compounds have extended further the range of novel structures exhibited by the organoaluminum amides and imides, by allowing a wider range of Al coordination environments and extent of cluster formation.[3]

The research activity in this area has been enhanced recently by the discovery that such organoaluminum–nitrogen compounds have potential utility as precursors to aluminum nitride,[4] a refractory ceramic material of much current interest for both electronic and structural applications.[5] Such precursors offer the prospect of improvements in processability, by virtue of the volatility, solubility, and/or thermoplasticity characteristic of molecular systems.

The factors influencing the formation of chelated monomers versus open-chain dimers in organoaluminum amides derived from the reaction of a 1:1 ratio of R_3Al with various diamines of the type $HRN(CH_2)_nNR'R''$ (R = H, Me, Et, Ph; R′, R″ = Me, Et), have been investigated by Beachley and co-workers.[2c,d] They found that the equilibria between the monomer and dimer forms were influenced by steric effects due to the R, R′, and R″ substituents, as well as the ligand base strength and the chelate ring size. The interaction of triethylaluminum with ethylenediamine (en) in a 1:1 ratio was previously studied by Gilbert and Smith.[6] They reported that the initially formed liquid adduct undergoes two successive decomposition processes at 50 and 130 °C, respectively, leading to a soluble polymeric solid of the composition $[EtAl(HNCH_2CH_2NH)]_x$. However, the detailed structural analysis of the final and intermediate products of these decomposition processes was not described nor was the pyrolysis of the compounds to a ceramic product performed.

Recently, we reported the results of studies carried out on the 2:1 and 3:2 R_3Al:en systems which have yielded a hydrocarbon-

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(1) (a) Laubengayer, A. W. *Inorganic Polymers*; Special Publication; The Chemical Society: London, 1961. (b) Mole, T.; Jeffrey, E. A. *Organoaluminum Compounds*; Elsevier: London, 1972; p 236. (c) Lappert, M. F.; Power, P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood/Wiley: New York, 1980; p 99. (d) Cesari, M.; Cucinella, S. Aluminum-Nitrogen Rings and Cages. In *The Chemistry of Inorganic Homo and Heterocycles*; Haiduc, I., Sowerby, B., Eds.; Academic Press: London, 1987; p 167.

(2) (a) Interrante, L. V.; Sigel, G. A.; Garbauskas, M.; Hejna, C.; Slack, G. A. *Inorg. Chem.* **1989**, *28*, 252. (b) Sauls, F. C.; Czekaj, C. L.; Interrante, L. V. *Inorg. Chem.* **1990**, *29*, 4688. (c) Beachley, O. T., Jr.; Racette, K. C. *Inorg. Chem.* **1975**, *14*, 2534. (d) Beachley, O. T., Jr.; Racette, K. C. *Inorg. Chem.* **1976**, *15*, 2110.

(3) (a) Perego, G.; Del Piero, G.; Corbellini, M.; Bruzzone, M. *J. Organomet. Chem.* **1977**, *136*, 301. (b) Robinson, G. H.; Moise, F.; Pennington, W. T.; Sangokoya, S. A. *Polyhedron* **1989**, *8*, 1279. (c) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1987**, *109*, 6892. (d) Robinson, G. H.; Sangokoya, S. A.; Moise, F.; Pennington, W. T. *Organometallics* **1988**, *7*, 1887. (e) Goedken, V. L.; Ito, H.; Ito, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1453.

(4) (a) Interrante, L. V.; Carpenter, L. E.; Whitmarsh, C. K.; Lee, W.; Slack, G. A. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 359. (b) Tebbe, F. N.; Bolt, J. D.; Young, R. J., Jr.; Van Busbirk, O. R.; Mahler, W.; Reddy, G. S.; Chowdry, U. *Adv. Ceram.* **1989**, *26*, 63. (c) Bolt, J. D.; Tebbe, F. N. *Adv. Ceram.* **1989**, *26*, 69. (d) Tebbe, F. N. U.S. Patent 4696968. (e) Boyd, D. C.; Haasch, R. T.; Mantell, P. R.; Schulze, R. K.; Evans, J. F.; Gladfelter, W. L. *Chem. Mater.* **1989**, *1*, 119. (f) Interrante, L. V.; Lee, W.; McConnell, M.; Lewis, N.; Hall, E. *J. Electrochem. Soc.* **1989**, *136*, 472. (g) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1988**, *27*, 4335. (h) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1987**, *26*, 4341.

(5) (a) Kuramoto, N.; Taniguchi, H.; Aso, I. *Adv. Ceram.* **1989**, *26*, 107. (b) Lee, R.-R. *J. Am. Ceram. Soc.* **1991**, *74*, 2242. (c) Virkar, A. V.; Jackson, T. B.; Cutler, R. A. *J. Am. Ceram. Soc.* **1991**, *72*, 2031. (d) Iwase, N.; Anzai, K.; Shinozaki, K. *Solid State Technol.* **1986** (Oct), 135.

(6) Gilbert, J. K.; Smith, J. D. *J. Chem. Soc. A* **1968**, 233.

0020-1669/92/1331-4815$03.00/0

soluble liquid polymer suitable for the preparation of AlN thin films[7] as well as various intermediates with novel structures containing 4- and 5-coordinated Al atoms.[7,8] We have now extended this study to include the 1:1 system originally investigated by Gilbert and Smith[6] and report here an overall analysis of the thermolysis chemistry occurring in solutions containing these $\mathrm{R_3Al}$–en mixtures and the results of a molecular structure determination carried out on a novel intermediate isolated from the 1:1 system.

Experimental Section

General Procedures. All syntheses and manipulations were performed by using Schlenk techniques under dry N_2 or in a N_2-filled drybox. Ethylenediamine was refluxed and distilled from KOH under N_2; benzene and toluene were refluxed overnight over sodium and distilled under N_2 before use. Triethylaluminum was purified by vacuum distillation. Trimethylaluminum (99% pure) and deuterated benzene (C_6D_6, 99.5% D) were used as received.

NMR spectra were obtained at ambient temperature on a Varian XL200 NMR spectrometer. Chemical shift values for both ^{1}H and ^{13}C NMR spectra were determined relative to C_6D_6 as internal reference (δ = 7.15 ppm for ^{1}H NMR utilizing residual protonated solvent and δ = 128.0 ppm for ^{13}C NMR). ^{27}Al NMR spectra were obtained on the same spectrometer with a delay time of 2 s. $AlCl_3$ aqueous solution was used as an external standard (δ = 0). All of the NMR samples were prepared in the glovebox as clear solutions or suspensions in C_6D_6. The effects of heating on the NMR spectra were examined by heating the sample in a flask to the desired temperature for a designated time, cooling to room temperature, and then loading the sample into the NMR tube along with C_6D_6. IR spectra were obtained on a Perkin-Elmer FT-1800 infrared spectrometer. DSC and TGA measurements of the compounds were carried out with a Perkin-Elmer TAS7 DSC/TGA thermal analysis system at a heating rate of 10 °C/min. Both the TGA and DSC samples were loaded under inert atmosphere. The purging gas in the TGA experiments was either nitrogen which had been passed through a BTS catalyst (BASF Co.) and a molecular sieve column to remove O_2 and H_2O, respectively, or electronic grade ammonia. Gaseous decomposition products were analyzed on a Shimadzu GC-9A gas chromatograph with a 6-ft VZ-10 column (AllTECH Associates Inc.). Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories and Galbraith Laboratories, Inc.

Preparation of the 1:1 $\mathbf{Me_3Al{:}en}$ Adduct $\mathbf{H_2NCH_2CH_2NH_2AlMe_3}$ (1M). To a solution of 14.4 g of trimethylaluminum (0.2 mol) in 40 mL of toluene cooled at –40 °C was added 40 mL of a toluene solution containing 12.02 g of ethylenediamine (0.2 mol). The resulting suspension was stirred at 0 °C for 1 h and then evacuated at this temperature until all the toluene was removed, leaving 26.03 g (98.5% yield) of a colorless solid (**1M**). This material was not stable at room temperature, so it was stored at –30 °C. ^{1}H NMR (C_6D_6): δ –0.488 (s, 9H, $\mathrm{Al(C}H_3)_3$), 0.753 (broad, 4H, $\mathrm{N}H_2$), 1.753 (multiplet, 4H, $\mathrm{C}H_2\mathrm{C}H_2$). ^{13}C{^{1}H} NMR ($C_6D_6$): δ 41.50 (s, $C\mathrm{H_2}C\mathrm{H_2}$), –8.51 (broad, $\mathrm{Al(}C\mathrm{H_3)_3}$).

Preparation of the 1:1 $\mathbf{Et_3Al{:}en}$ Adduct $\mathbf{H_2NCH_2CH_2NH_2Al(CH_2CH_3)_3}$ (1E). A 12.02-g sample of ethylenediamine (0.2 mol) was slowly added to 22.8 g of triethylaluminum (0.2 mol) cooled in a dry ice–2-propanol bath (–55 °C), resulting in 33.95 g (97.5% yield) of a colorless oil (**1E**). Like its trimethylaluminum analog, it was unstable at room temperature; therefore, it was stored at –30 °C. ^{1}H NMR (C_6D_6): δ 1.42 (triplet, J = 8.20 Hz, 9H, $\mathrm{AlCH_2C}H_3$), 0.12 (quartet, J = 8.2 Hz, 6H, $\mathrm{AlC}H_2\mathrm{CH_3}$), 0.90 (broad, 4H, $\mathrm{N}H_2$), 1.81 (broad, 4H, $\mathrm{C}H_2\mathrm{C}H_2$). ^{13}C{^{1}H} NMR ($C_6D_6$): δ 41.36 (s, $C\mathrm{H_2}C\mathrm{H_2}$), 10.89 (s, $\mathrm{AlCH_2}C\mathrm{H_3}$), 0.15 (broad, $\mathrm{Al}C\mathrm{H_2CH_3}$). ^{27}Al NMR: δ 164 (broad, $Al\mathrm{CH_2CH_3}$).

Preparation of $\mathbf{Al[(HNCH_2CH_2NH)AlMe_2]_3}$ (5M). A solution of 9.02 g of ethylenediamine (0.15 mol) in 30 mL of toluene in a Schlenk flask connected to a N_2 bubbler was added dropwise to 45 mL of a toluene solution containing 14.4 g of trimethylaluminum (0.2 mol) that was cooled in a dry ice–2-propanol bath (–40 °C). The resulting colorless suspension was then heated at 80 °C for 5 h, leaving a milky white suspension. This mixture, after removal of toluene by evacuation at less than 60 °C, yielded an off-white powder. Upon sublimation (125 °C, 0.015 Torr), 11.0 g of a colorless crystalline material, $\mathrm{Al[(HNCH_2CH_2NH)AlMe_2]_3}$ (**5M**), was obtained. Yield: 59%. Mp: 148–151 °C. Anal. Calcd for $\mathrm{Al_4C_{12}N_6H_{36}}$: Al, 29.03; C, 38.71; N, 22.58; H, 9.68. Found: Al, 29.59; C, 38.02; N, 22.10; H, 9.09. ^{1}H NMR (C_6D_6): δ –0.68 (s, 3H, $\mathrm{AlC}H_3$), –0.67 (s, 3H, $\mathrm{AlC}H_3$), –0.61 (s, 3H, $\mathrm{AlC}H_3$), –0.57 (s, 3H, $\mathrm{AlC}H_3$), –0.53 (s, 6H, $\mathrm{AlC}H_3$), –0.29 (broad, $\mathrm{N}H$), 0.18 (broad, $\mathrm{N}H$), 0.60 (broad, $\mathrm{N}H$), 1.70 (multiplet, $\mathrm{C}H_2\mathrm{C}H_2$), 2.15 (multiplet, $\mathrm{C}H_2\mathrm{C}H_2$), 2.40 (multiplet, $\mathrm{C}H_2\mathrm{C}H_2$). ^{13}C{^{1}H} NMR ($C_6D_6$): δ 46.13 (s, $C\mathrm{H_2}$), 43.20 (s, $C\mathrm{H_2}$), 41.81 (s, $C\mathrm{H_2}$), 41.58 (s, $C\mathrm{H_2}$), 41.46 (s, $C\mathrm{H_2}$), 38.63 (s, $C\mathrm{H_2}$), –13.0 (broad, $\mathrm{Al}C\mathrm{H_3}$), –10.5 (broad, $\mathrm{Al}C\mathrm{H_3}$), –9.0 (broad, $\mathrm{Al}C\mathrm{H_3}$). ^{27}Al NMR: δ 40.5 (sharp, $Al\mathrm{[(HN(CH_2)_2NH)Al(CH_3)_2]_3}$), 159.5 (broad, $\mathrm{Al[(HN(CH_2)_2NH)}Al\mathrm{(CH_3)_2]_3}$).

Crystallographic Analysis. A single-crystal X-ray study of $\mathrm{Al[(HNCH_2CH_2NH)AlMe_2]_3}$ (**5M**) was carried out on a Siemens-Nicolet R3m diffractometer using Cu Kα radiation (graphite monochromator; λ = 1.541 78 Å). A Wyckoff scan mode was used for data collection {ω range = 1.70 ° + [$2\theta(K\alpha_1) - 2\theta(K\alpha_2)$]; 2θ range = 3–125°}. Intensities of four standard reflections were monitored after every 60 data points. A total of 3058 reflections were collected, of which 2753 reflections were uniquely observed ($F > 4\sigma(F)$) for the crystal. The attenuation coefficient was 2.016 mm^{-1}. An attempt was made to improve the R value by applying an empirical absorption correction to the data sets. This did not succeed because the ψ-scan reflections with high 2θ values were not collected due to the collision limit of the diffractometer. Therefore, the final results are reported with no absorption correction applied.

Crystals for X-ray diffraction were grown by slow cooling of a hexane solution under an atmosphere of nitrogen. A suitable crystal was sealed in a thin-walled capillary in a N_2-filled glovebox and mounted on a goniometer head. The positions of Al atoms were identified from a Patterson vector map. Three Fourier cycles allowed all of the non-hydrogen atoms of the asymmetric unit to be recognized. Atomic coordinates and anisotropic temperature factors of all non-hydrogen atoms were refined by means of a full-matrix least-squares refinement procedure. All isotropic hydrogen atoms were included in calculated positions. The refinement converged at R = 4.4% and R_w = 4.7%. The highest peak in the difference electron density map is 0.20 e Å^{-3}. All atomic scattering factors were taken from ref 9. These values are incorporated in the software of the computer programs. SHELXTL PLUS (Release 4.21/V) computer programs were used for data reduction and all other calculations.

NMR Studies of the Decomposition of the 1:1 $\mathbf{Me_3Al{:}en}$ Adduct (1M) in Benzene Solution. A suspension containing 5 g of the 1:1 adduct (**1M**) and 30 mL of benzene in a 100-mL round-bottomed flask connected to a N_2 bubbler was heated under reflux (80 °C) for 40 min. The flask was connected to an oil bubbler to allow the gaseous decomposition products (only methane was detected by GC) to escape. After 20 min of heating, a colorless, clear solution was obtained. Shortly after this, some white solid was generated; its amount increased with increased heating time. This decomposition process was investigated by ^{1}H NMR spectroscopy. The product of complete decomposition for the above reaction was obtained by refluxing a toluene solution with the same adduct concentration at 120 °C for 12 h, followed by filtration, washing, and evacuation at 70 °C; this was found to be an off-white solid (**6M**) which was insoluble in hydrocarbon solvents. Anal. Found: Al, 27.30; N, 29.43; C, 33.92; H, 8.09 (corresponding to $\mathrm{Al_{1.0}N_{2.1}C_{2.8}H_{8.1}}$).

NMR Studies of the Decomposition of the 1:1 $\mathbf{Et_3Al{:}en}$ Adduct (1E) in Solution. In a manner similar to that used for the study of the 1:1 $\mathrm{Me_3Al}$:en system, a 30-mL benzene solution containing 7.5 g of the 1:1 $\mathrm{Et_3Al}$:en adduct (**1E**) was heated at 65 °C for 40 min under reflux. A gas evolved from the solution, which was identified as ethane by GC. After 30 min, a white solid appeared in the solution; the amount of this solid increased with increased heating time. ^{1}H, ^{13}C, and ^{27}Al NMR spectra of these products at various stages were taken to elucidate the decomposition pathway. In order to isolate the product of complete decomposition from the above reaction, 20 mL of toluene solution with the same adduct concentration was refluxed at 120 °C for 12 h, yielding an off-white suspension. After filtration, washing with toluene, and evacuation at less than 70 °C, an off-white solid (**6E**) was obtained. Anal. Found: Al, 24.83; N, 25.02; C, 39.39; H, 9.85 (corresponding to $\mathrm{Al_{1.0}N_{1.9}C_{3.6}H_{10.6}}$). This material was virtually insoluble in hydrocarbon solvents.

Results and Discussion

Synthesis and Characterization of $\mathbf{Al[(HNCH_2CH_2NH)AlMe_2]_3}$ (5M).

During our initial studies of the thermolysis of the 1:1

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[7] Jiang, Z.; Interrante, L. V. *Chem. Mater.* **1990**, *2*, 439.

[8] Jiang, Z.; Interrante, L. V.; Kwon, D.; Tham, F. S.; Kullnig, R. *Inorg. Chem.* **1991**, *30*, 995.

[9] Ibers, J. A.; Hamilton, W. C. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

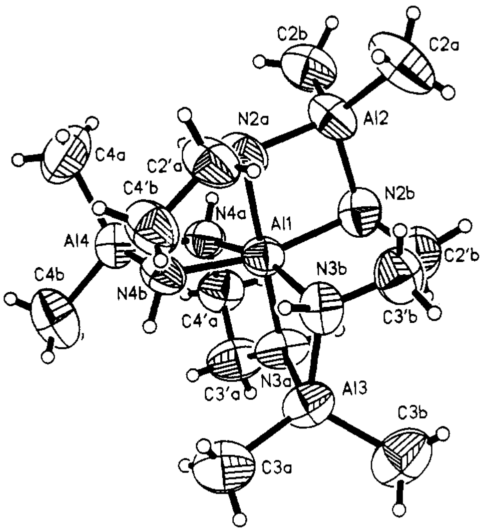
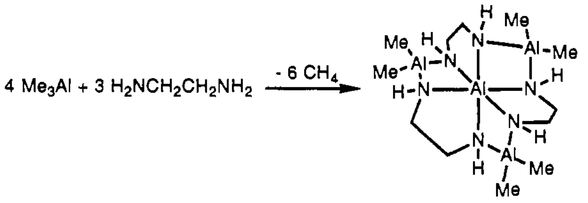


Figure 1. ORTEP plot (50%) probability thermal ellipsoids of the molecular structure of $Al[(HNCH_2CH_2NH)AlMe_2]_3$ (**5M**) with the numbering scheme.

Me_3Al:en adduct in benzene solution, a crystalline intermediate was isolated from the solution on cooling. The ^{27}Al NMR spectrum of this compound indicated both 4- and 6-coordinate Al environments, suggesting further study of the structure by single-crystal X-ray diffraction methods. As is described below, the results of this X-ray diffraction study indicated that the structure had a 4:3 Al:en ratio; therefore, this compound can be made more effectively by mixing Me_3Al and en in a 4:3 ratio in benzene solution, followed by heating at 80 °C for 5 h, according to eq 1.



(5M)

(1)

The single-crystal study of compound **5M** indicates an asymmetric unit containing two unique molecules, which reside in general positions. The two molecules are almost identical in conformation and absolute configuration but differ slightly in bond distances and angles. No symmetric element can be found in these structures. Figure 1 shows an ORTEP drawing of one of the molecules. The crystal data and atomic coordinates for all non-hydrogen atoms are listed in Tables I and II, and the bond distances and angles, in Tables III and IV. The molecule contains three AlN_2C_2 five-membered rings and three Al_2N_2 four-membered rings. The mode of bonding of the three ethylenediamine ligands to the central aluminum atom is typical of that seen for metals coordinated with three bidentate ligands. The three $Al(CH_3)_2$ units bridge the ethylenediamine ligands, forming the additional three four-membered rings. The trans N(2a)–Al(1)–N(3a) bond angle is 175.5 (2)°, which is much larger than the N(2b)–Al(1)–N(4b) bond angle (160.7 (2)°) or N(3b)–Al(1)–N(4a) bond angle (162.8 (2)°). Therefore, the core AlN_6 structure can be described as a distorted octahedron. Presumably, the distortion is due to the geometric constraints imposed by the interconnected six rings. The cis N–Al–N bond angles are in the range 79.7 (2)–104.3 (2)°. The Al(1)–N bond distances from the central aluminum atom vary from 2.011 (5) to 2.042 (5) Å, which are slightly longer than those (1.899 (6)–1.943 (5) Å) from the 4-coordinate aluminum atoms Al(2), Al(3), and Al(4). The nonbonding Al–Al distances (2.868 (3)–2.888 (3) Å) are in the same range as those in the related $MeAl[(HNCH_2CH_2NH)AlMe_2]_2$ (**4M**) structure.[8]

Table I. Crystallographic Data for $Al[(HN(CH_2)_2NH)AlMe_2]_3$ (**5M**)

formula	$C_{12}H_{36}Al_4N_6$
mol wt	372.4
color	white
space group	$Pca2_1$
a, b, c (Å)	19.151 (4), 10.864 (1), 21.035 (3)
cell vol (Å^3)	4376.3 (9)
Z	8
d_{calcd} (g/cm^3)	1.131
crystal dimens (mm)	0.48 × 0.54 × 0.54
scan speed (deg/min)	variable; 4.50–29.30 in ω
scan range (ω) (deg)	1.70
2θ range (deg)	3.0–125.0
abs coeff (mm^{-1})	2.016
$F(000)$ (e)	1616
index ranges	$0 \le h \le 20$ $0 \le k \le 11$ $-22 \le l \le 0$
no. of unique data	3058
no. of obsd data ($F > 4\sigma(F)$)	2753
R	0.044
R_w	0.047
goodness of fit	2.34
largest diff peak (e Å^{-3})	0.20

The most closely related structural analog among the previously studied organoaluminum compounds is $\{[(Me_3Si)_2N]_2Al(NH_2)_2\}_3$-Al,[10] where a central aluminum atom is surrounded by the six NH_2 groups in an octahedral configuration and the other three aluminum atoms are coordinated by four nitrogen atoms in a tetrahedral configuration. Replacing each pair of cis N–H groups in this structure with a NCH_2CH_2N group would effectively lead to the structure of **5M**. It is noted that the three trans N–Al–N bond angles in $\{[(Me_3Si)_2N]_2Al(NH_2)_2\}_3Al$ are all about 176.0°, indicating that this structure is closer to the idealized octahedral geometry than that of compound **5M**, presumably due to the absence of the $-CH_2CH_2-$ linking groups.

Parts a and b of Figure 2 show the ^1H and ^{13}C NMR spectra, respectively, of **5M**. The ^{13}C NMR spectrum indicates that each C atom of the CH_2 groups from these three ethylenediamine units results in a separate peak; furthermore, the H atoms of these six $AlCH_3$ groups give rise to five peaks in the ^1H NMR spectrum with an integration ratio of 2:1:1:1:1, suggesting that two of the six methyl groups appear as one peak (−0.528 ppm). The relatively complicated nature of both spectra is consistent with the fact that compound **5M** possesses a highly unsymmetrical structure.

The ^{27}Al NMR spectrum (Figure 2c) of compound **5M** shows two distinct peaks (160 and 40 ppm). The 160 ppm peak position is characteristic of 4-coordinate Al atoms such as those in the $[R_2AlR']_x$ (R = Me, Et; R' = NEt_2, OMe_2, OEt_2, etc.) compounds[11] and is therefore assigned to Al(2–4). The 40 ppm resonance is assigned to the 6-coordinate Al1. Although apparently no ^{27}Al NMR spectra for compounds with AlN_6 structural units have been previously reported, studies of ^{27}Al NMR of Al alkoxides and $Al(acac)_3$ with AlO_6 units have indicated that the ^{27}Al NMR peaks for the 6-coordinate Al atoms generally appear in the range 0–10 ppm.[12] The relatively symmetrical environment for this octahedral AlN_6 species makes its ^{27}Al NMR peak much sharper than that of the rather unsymmetrical, 4-coordinated $Al(N)_2(C)_2$ atoms in the $Al[(HNCH_2CH_2NH)AlMe_2]_3$ (**5M**) structure (Figure 2c). Also,

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(10) Paciorek, K. J. L.; Nakahara, J. H.; Hoferkamp, L. A.; George, C.; Flippen-Anderson, J. L.; Gilardi, R.; Schmidt, W. R. *Chem. Mater.* **1991**, *3*, 82.

(11) Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janssen, E.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *10*, 779.

(12) Kritz, O.; Gasensky, B.; Lycka, A.; Fusek, J.; Hermanek, S. *J. Magn. Reson.* **1984**, *60*, 375.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $Al[(HN(CH_2)_2NH)AlMe_2]_3$ (**5M**)

	x	*y*	*z*	*U*(eq)[a]
Al(1)	2515 (1)	507 (1)	−1791	60 (1)
Al(2)	1197 (1)	1724 (2)	−1987 (1)	76 (1)
C(2a)	796 (4)	3231 (6)	−1621 (4)	118 (1)
C(2b)	634 (3)	828 (6)	−2616 (4)	101 (1)
N(2a)	1547 (3)	550 (5)	−1399 (3)	79 (1)
C(2′a)	1646 (3)	582 (7)	−731 (3)	93 (1)
N(2b)	2117 (3)	1893 (4)	−2333 (3)	73 (1)
C(2′b)	2543 (4)	3024 (5)	−2221 (3)	87 (1)
Al(3)	3928 (1)	1375 (2)	−1623 (1)	75 (1)
C(3a)	4439 (3)	351 (7)	−1014 (3)	97 (1)
C(3b)	4464 (4)	2702 (6)	−2026 (4)	115 (1)
N(3a)	3439 (2)	424 (5)	−2243 (3)	75 (1)
C(3′a)	3559 (3)	−721 (6)	−2525 (4)	90 (1)
N(3b)	3015 (3)	1900 (4)	−1324 (2)	68 (1)
C(3′b)	2743 (4)	3103 (6)	−1532 (3)	85 (1)
Al(4)	2354 (1)	−2078 (2)	−1556 (1)	76 (1)
C(4a)	1437 (4)	−2720 (6)	−1322 (4)	129 (1)
C(4b)	3064 (4)	−3359 (6)	−1595 (4)	112 (1)
N(4a)	2317 (2)	−1048 (4)	−2302 (2)	62 (1)
C(4′a)	2857 (3)	−1214 (6)	−2799 (3)	78 (1)
N(4b)	2650 (2)	−675 (4)	−1058 (2)	63 (1)
C(4′b)	2224 (3)	−299 (7)	−504 (3)	95 (1)
Al(5)	10092 (1)	4543 (2)	864 (1)	55 (1)
Al(6)	9987 (1)	7167 (2)	732 (1)	69 (1)
C(6a)	10724 (4)	8438 (5)	768 (4)	98 (1)
C(6b)	9048 (3)	7822 (6)	552 (3)	100 (1)
N(6a)	9950 (2)	6023 (4)	1437 (2)	57 (1)
C(6′a)	10517 (3)	6110 (5)	1919 (3)	68 (1)
N(6b)	10269 (3)	5840 (4)	190 (2)	65 (1)
C(6′b)	9829 (3)	5592 (6)	−384 (3)	83 (1)
Al(7)	11462 (1)	3521 (2)	652 (1)	68 (1)
C(7a)	12010 (3)	4572 (6)	65 (3)	95 (1)
C(7b)	11932 (3)	2064 (6)	982 (4)	98 (1)
N(7a)	11022 (2)	4431 (4)	1316 (3)	64 (1)
C(7′a)	11180 (3)	5607 (5)	1618 (3)	71 (1)
N(7b)	10534 (2)	3183 (4)	331 (2)	63 (1)
C(7′b)	10198 (3)	1989 (6)	477 (3)	79 (1)
Al(8)	8730 (1)	3444 (2)	1011 (1)	77 (1)
C(8a)	8215 (3)	4342 (6)	1684 (4)	103 (1)
C(8b)	8277 (4)	2074 (7)	588 (5)	129 (1)
N(8a)	9128 (2)	4686 (5)	472 (2)	68 (1)
C(8′a)	9231 (3)	4727 (7)	−220 (3)	87 (1)
N(8b)	9650 (2)	3120 (4)	1343 (2)	63 (1)
C(8′b)	10011 (4)	1964 (6)	1179 (3)	83 (1)

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

the chemical shift value for this $\mathit{Al}\mathrm{N}_6$ atom is at lower field than that typical of $\mathit{Al}\mathrm{O}_6$ (ca. 0 ppm),[12] which is understandable in view of the electronegativity difference between N and O. The FT-IR spectrum of **5M** shows four sharp peaks in the N–H stretching region (3278, 3300, 3320, 3330 cm^{-1}), which are attributed to the stretching vibrations of the six N–H groups.

Thermolysis of the 1:1 Me_3Al:en Adduct (1M) in Solution. The 1:1 Me_3Al:en adduct (**1M**) is a colorless solid, which slowly decomposes into a polymeric glass at room temperature, releasing methane, which was identified by GC. The DSC of **1M** shows an exothermal peak starting at 30 °C and ending at 150 °C, which is attributed to the decomposition process in which methane and a new Al–N linkage are produced from the reaction of AlMe and N–H groups.

In order to study the decomposition pathway of **1M**, as well as the structures of any intermediates formed during the decomposition, the ^{1}H NMR spectra of a suspension of sparingly soluble **1M** in benzene heated at 80 °C for varying amounts of time were determined (Figure 3). These spectra indicate that the relative intensity of the peak attributed to **1M** (−0.49 ppm, $H_2NCH_2CH_2NH_2Al(C\mathit{H}_3)_3$, labeled as a) decreases with increased heating time; concurrently, new peaks at −0.57 and −0.74 ppm (labeled as b) appear. With further heating, another set of peaks (−0.53, −0.57, −0.61, −0.67, and −0.68 ppm, labeled as c) appears. On the basis of the chemical shift values and relative intensities of these new peaks, the first set of peaks is attributed to the $AlMe_2$ groups of $MeAl[(HNCH_2CH_2NH)AlMe_2]_2$ (**4M**)[8] and the second one is assigned to the $AlMe_2$ groups of **5M**.

Table III. Bond Distances (Å) for $Al[(HN(CH_2)_2NH)AlMe_2]_3$ (**5M**)

Al(1)–Al(2)	2.879 (3)	Al(1)–N(2a)	2.030 (5)
Al(1)–N(2b)	2.036 (5)	Al(1)–Al(3)	2.888 (3)
Al(1)–N(3a)	2.011 (5)	Al(1)–N(3b)	2.042 (5)
Al(1)–Al(4)	2.868 (3)	Al(1)–N(4a)	2.038 (5)
Al(1)–N(4b)	2.023 (5)	Al(2)–C(2a)	1.966 (7)
Al(2)–C(2b)	1.965 (8)	Al(2)–N(2a)	1.899 (6)
Al(2)–N(2b)	1.915 (5)	N(2a)–C(2′a)	1.419 (9)
C(2′a)–C(4′b)	1.539 (10)	N(2b)–C(2′b)	1.493 (8)
C(2′b)–C(3′b)	1.501 (10)	Al(3)–C(3a)	1.958 (7)
Al(3)–C(3b)	1.962 (8)	Al(3)–N(3a)	1.911 (6)
Al(3)–N(3b)	1.943 (5)	N(3a)–C(3′a)	1.398 (9)
C(3′a)–C(4′a)	1.559 (9)	N(3b)–C(3′b)	1.473 (8)
Al(4)–C(4a)	1.954 (7)	Al(4)–C(4b)	1.946 (7)
Al(4)–N(4a)	1.929 (5)	Al(4)–N(4b)	1.934 (5)
N(4a)–C(4′a)	1.480 (8)	N(4b)–C(4′b)	1.481 (8)
Al(5)–Al(6)	2.872 (2)	Al(5)–N(6a)	2.027 (5)
Al(5)–N(6b)	2.027 (5)	Al(5)–Al(7)	2.884 (2)
Al(5)–N(7a)	2.024 (5)	Al(5)–N(7b)	2.039 (5)
Al(5)–Al(8)	2.884 (3)	Al(5)–N(8a)	2.028 (5)
Al(5)–N(8b)	2.029 (5)	Al(6)–C(6a)	1.977 (7)
Al(6)–C(6b)	1.970 (6)	Al(6)–N(6a)	1.936 (5)
Al(6)–N(6b)	1.915 (5)	N(6a)–C(6′a)	1.489 (7)
C(6′a)–C(7′a)	1.520 (8)	N(6b)–C(6′b)	1.498 (8)
C(6′b)–C(8′a)	1.521 (9)	Al(7)–C(7a)	1.984 (7)
Al(7)–C(7b)	1.948 (7)	Al(7)–N(7a)	1.906 (5)
Al(7)–N(7b)	1.936 (5)	N(7a)–C(7′a)	1.459 (8)
N(7b)–C(7′b)	1.480 (8)	C(7′b)–C(8′b)	1.521 (10)
Al(8)–C(8a)	1.981 (8)	Al(8)–C(8b)	1.940 (8)
Al(8)–N(8a)	1.920 (6)	Al(8)–N(8b)	1.928 (5)
N(8a)–C(8′a)	1.470 (8)	N(8b)–C(8′b)	1.475 (8)

It was observed that the starting suspension became a clear solution when heated at 80 °C for 17 min (stage 3d) and this solution again became a suspension by stage 3e (80 °C, 25 min). The above observation can be explained by the hypothesis that at stage 3d, all the sparingly soluble **1M** has converted into the highly soluble compound **4M**. However, when the solution is further heated to stage 3e, a significant amount of **5M** is generated, which has a relatively low solubility, therefore yielding a suspension again. When the suspension is heated further, an insoluble solid is produced and its relative amount increases with the heating time, whereas the relative amount of **4M** and **5M** decreases at the same time.

In order to drive the above decomposition reaction to completion, a toluene solution of the 1:1 Me_3Al:en adduct was refluxed at 120 °C for 12 h, forming a suspension; the ^{1}H NMR spectrum of this suspension did not show any peaks, indicating that all of the starting material had been converted into an insoluble polymer. After filtering, washing with toluene, and evacuation at 70 °C, the polymeric solid **6M** was obtained; unfortunately, due to its insolubility in hydrocarbon solvents, its detailed characterization is difficult. The elemental analysis of this solid material indicates that the N:Al ratio is close to 2, suggesting that all of the original en has been reunited with the Al species. A nominal formula of $Al(CH_3)_{0.8}$(en-2.2H) is proposed on the basis of the elemental analysis, which suggests that about 2.2 mol of methane was eliminated from each 1:1 Me_3Al:en adduct during the reaction.

Therefore, on the basis of the above results, the decomposition pathway for the 1:1 Me_3Al:en adduct (**1M**) in solution shown in Scheme I is suggested, where the end product **6M** is a highly cross-linked polymer interconnected by N to Al donor interactions and containing various types of AlN_xC_y coordination environments. We presume that this polymer is formed by the decomposition reaction between free en and compound **5M**; however, it is possible that compound **4M** also takes part directly in the formation of the cross-linked polymer.

Table IV. Bond Angles (deg) for Al[(HN(CH_2)$_2$NH)$AlMe_2$]$_3$ (**5M**)

Al(2)–Al(1)–N(2a)	41.1 (2)	Al(2)–Al(1)–N(2b)	41.6 (2)	Al(6)–Al(5)–N(6a)	42.3 (1)	Al(6)–Al(5)–N(6b)	41.7 (1)
N(2a)–Al(1)–N(2b)	82.4 (2)	Al(2)–Al(1)–Al(3)	133.6 (1)	N(6a)–Al(5)–N(6b)	83.5 (2)	Al(6)–Al(5)–Al(7)	115.5 (1)
N(2a)–Al(1)–Al(3)	143.0 (2)	N(2b)–Al(1)–Al(3)	100.3 (2)	N(6a)–Al(5)–Al(7)	121.2 (1)	N(6b)–Al(5)–Al(7)	90.4 (2)
Al(2)–Al(1)–N(3a)	136.4 (2)	N(2a)–Al(1)–N(3a)	175.5 (2)	Al(6)–Al(5)–N(7a)	99.6 (2)	N(6a)–Al(5)–N(7a)	83.5 (2)
N(2b)–Al(1)–N(3a)	95.6 (2)	Al(3)–Al(1)–N(3a)	41.2 (2)	N(6b)–Al(5)–N(7a)	102.8 (2)	Al(7)–Al(5)–N(7a)	41.2 (2)
Al(2)–Al(1)–N(3b)	98.0 (2)	N(2a)–Al(1)–N(3b)	102.5 (2)	Al(6)–Al(5)–N(7b)	134.0 (2)	N(6a)–Al(5)–N(7b)	163.1 (2)
N(2b)–Al(1)–N(3b)	84.1 (2)	Al(3)–Al(1)–N(3b)	42.2 (1)	N(6b)–Al(5)–N(7b)	92.8 (2)	Al(7)–Al(5)–N(7b)	42.1 (1)
N(3a)–Al(1)–N(3b)	81.3 (2)	Al(2)–Al(1)–Al(4)	112.3 (1)	N(7a)–Al(5)–N(7b)	81.3 (2)	Al(6)–Al(5)–Al(8)	111.0 (1)
N(2a)–Al(1)–Al(4)	81.6 (2)	N(2b)–Al(1)–Al(4)	141.3 (2)	N(6a)–Al(5)–Al(8)	98.3 (1)	N(6b)–Al(5)–Al(8)	120.9 (2)
Al(3)–Al(1)–Al(4)	113.5 (1)	N(3a)–Al(1)–Al(4)	97.6 (2)	Al(7)–Al(5)–Al(8)	132.8 (1)	N(7a)–Al(5)–Al(8)	136.2 (2)
N(3b)–Al(1)–Al(4)	133.9 (2)	Al(2)–Al(1)–N(4a)	98.1 (1)	N(7b)–Al(5)–Al(8)	97.8 (1)	Al(6)–Al(5)–N(8a)	79.7 (2)
N(2a)–Al(1)–N(4a)	93.6 (2)	N(2b)–Al(1)–N(4a)	104.3 (2)	N(6a)–Al(5)–N(8a)	93.4 (2)	N(6b)–Al(5)–N(8a)	79.3 (2)
Al(3)–Al(1)–N(4a)	120.7 (2)	N(3a)–Al(1)–N(4a)	82.9 (2)	Al(7)–Al(5)–N(8a)	142.6 (2)	N(7a)–Al(5)–N(8a)	175.9 (2)
N(3b)–Al(1)–N(4a)	162.8 (2)	Al(4)–Al(1)–N(4a)	42.2 (1)	N(7b)–Al(5)–N(8a)	102.1 (2)	Al(8)–Al(5)–N(8a)	41.6 (2)
Al(2)–Al(1)–N(4b)	120.8 (2)	N(2a)–Al(1)–N(4b)	79.7 (2)	Al(6)–Al(5)–N(8b)	140.8 (2)	N(6a)–Al(5)–N(8b)	104.7 (2)
N(2b)–Al(1)–N(4b)	160.7 (2)	Al(3)–Al(1)–N(4b)	89.7 (1)	N(6b)–Al(5)–N(8b)	161.1 (2)	Al(7)–Al(5)–N(8b)	99.4 (1)
N(3a)–Al(1)–N(4b)	102.7 (2)	N(3b)–Al(1)–N(4b)	92.6 (2)	N(7a)–Al(5)–N(8b)	95.1 (2)	N(7b)–Al(5)–N(8b)	84.0 (2)
Al(4)–Al(1)–N(4b)	42.3 (1)	N(4a)–Al(1)–N(4b)	84.2 (2)	Al(8)–Al(5)–N(8b)	41.8 (1)	N(8a)–Al(5)–N(8b)	83.2 (2)
Al(1)–Al(2)–C(2a)	132.0 (2)	Al(1)–Al(2)–C(2b)	110.5 (2)	Al(5)–Al(6)–C(6a)	129.8 (2)	Al(5)–Al(6)–C(6b)	116.2 (2)
C(2a)–Al(2)–C(2b)	117.5 (3)	Al(1)–Al(2)–N(2a)	44.7 (2)	C(6a)–Al(6)–C(6b)	114.0 (3)	Al(5)–Al(6)–N(6a)	44.8 (1)
C(2a)–Al(2)–N(2a)	116.2 (3)	C(2b)–Al(2)–N(2a)	107.5 (3)	C(6a)–Al(6)–N(6a)	116.4 (3)	C(6b)–Al(6)–N(6a)	110.3 (3)
Al(1)–Al(2)–N(2b)	44.9 (2)	C(2a)–Al(2)–N(2b)	115.4 (3)	Al(5)–Al(6)–N(6b)	44.8 (2)	C(6a)–Al(6)–N(6b)	110.3 (3)
C(2b)–Al(2)–N(2b)	107.2 (3)	N(2a)–Al(2)–N(2b)	89.3 (2)	C(6b)–Al(6)–N(6b)	114.5 (3)	N(6a)–Al(6)–N(6b)	89.0 (2)
Al(1)–N(2a)–Al(2)	94.2 (2)	Al(1)–N(2a)–C(2′a)	106.3 (4)	Al(5)–N(6a)–Al(6)	92.9 (2)	Al(5)–N(6a)–C(6′a)	110.9 (3)
Al(2)–N(2a)–C(2′a)	132.5 (5)	N(2a)–C(2′a)–C(4′b)	112.8 (6)	Al(6)–N(6a)–C(6′a)	117.0 (3)	N(6a)–C(6′a)–C(7′a)	107.6 (5)
Al(1)–N(2b)–Al(2)	93.5 (2)	Al(1)–N(2b)–C(2′b)	108.4 (4)	Al(5)–N(6b)–Al(6)	93.4 (2)	Al(5)–N(6b)–C(6′b)	110.2 (4)
Al(2)–N(2b)–C(2′b)	121.4 (4)	N(2b)–C(2′b)–C(3′b)	109.8 (5)	Al(6)–N(6b)–C(6′b)	117.2 (4)	N(6b)–C(6′b)–C(8′a)	110.6 (5)
Al(1)–Al(3)–C(3a)	111.2 (2)	Al(1)–Al(3)–C(3b)	132.6 (2)	Al(5)–Al(7)–C(7a)	110.8 (2)	Al(5)–Al(7)–C(7b)	132.7 (2)
C(3a)–Al(3)–C(3b)	116.1 (3)	Al(1)–Al(3)–N(3a)	43.9 (2)	C(7a)–Al(7)–C(7b)	116.4 (3)	Al(5)–Al(7)–N(7a)	44.4 (1)
C(3a)–Al(3)–N(3a)	112.6 (3)	C(3b)–Al(3)–N(3a)	111.0 (3)	C(7a)–Al(7)–N(7a)	113.0 (3)	C(7b)–Al(7)–N(7a)	111.4 (3)
Al(1)–Al(3)–N(3b)	44.9 (1)	C(3a)–Al(3)–N(3b)	113.9 (3)	Al(5)–Al(7)–N(7b)	44.9 (1)	C(7a)–Al(7)–N(7b)	112.1 (3)
C(3b)–Al(3)–N(3b)	113.2 (3)	N(3a)–Al(3)–N(3b)	86.5 (2)	C(7b)–Al(7)–N(7b)	113.2 (3)	N(7a)–Al(7)–N(7b)	87.0 (2)
Al(1)–N(3a)–Al(3)	94.8 (2)	Al(1)–N(3a)–C(3′a)	112.7 (4)	Al(5)–N(7a)–Al(7)	94.4 (2)	Al(5)–N(7a)–C(7′a)	109.5 (3)
Al(3)–N(3a)–C(3′a)	133.7 (4)	N(3a)–C(3′a)–C(4′a)	108.7 (5)	Al(7)–N(7a)–C(7′a)	133.0 (4)	C(6′a)–C(7′a)–N(7a)	108.9 (4)
Al(1)–N(3b)–Al(3)	92.8 (2)	Al(1)–N(3b)–C(3′b)	110.4 (4)	Al(5)–N(7b)–Al(7)	93.0 (2)	Al(5)–N(7b)–C(7′b)	109.9 (4)
Al(3)–N(3b)–C(3′b)	118.9 (4)	C(2′b)–C(3′b)–N(3b)	109.1 (5)	Al(7)–N(7b)–C(7′b)	119.5 (4)	N(7b)–C(7′b)–C(8′b)	108.6 (5)
Al(1)–Al(4)–C(4a)	119.3 (2)	Al(1)–Al(4)–C(4b)	128.2 (2)	Al(5)–Al(8)–C(8a)	108.8 (2)	Al(5)–Al(8)–C(8b)	132.3 (3)
C(4a)–Al(4)–C(4b)	112.5 (3)	Al(1)–Al(4)–N(4a)	45.2 (1)	C(8a)–Al(8)–C(8b)	118.9 (3)	Al(5)–Al(8)–N(8a)	44.6 (1)
C(4a)–Al(4)–N(4a)	112.3 (3)	C(4b)–Al(4)–N(4a)	114.0 (3)	C(3a)–Al(8)–N(8a)	105.9 (3)	C(8b)–Al(8)–N(8a)	116.4 (3)
Al(1)–Al(4)–N(4b)	44.8 (1)	C(4a)–Al(4)–N(4b)	114.1 (3)	Al(5)–Al(8)–N(8b)	44.6 (1)	C(8a)–Al(8)–N(8b)	106.6 (3)
C(4b)–Al(4)–N(4b)	112.5 (3)	N(4a)–Al(4)–N(4b)	89.7 (2)	C(8b)–Al(8)–N(8b)	115.8 (3)	N(8a)–Al(8)–N(8b)	88.8 (2)
Al(1)–N(4a)–Al(4)	92.6 (2)	Al(1)–N(4a)–C(4′a)	110.1 (3)	Al(5)–N(8a)–Al(8)	93.8 (2)	Al(5)–N(8a)–C(8′a)	106.4 (3)
Al(4)–N(4a)–C(4′a)	118.5 (4)	C(3′a)–C(4′a)–N(4a)	107.5 (5)	Al(8)–N(8a)–C(8′a)	131.3 (4)	C(6′b)–C(8′a)–N(8a)	110.2 (5)
Al(1)–N(4b)–Al(4)	92.9 (2)	Al(1)–N(4b)–C(4′b)	110.8 (4)	Al(5)–N(8b)–Al(8)	93.5 (2)	Al(5)–N(8b)–C(8′b)	109.7 (4)
Al(4)–N(4b)–C(4′b)	118.8 (4)	C(2′a)–C(4′b)–N(4b)	108.9 (5)	Al(8)–N(8b)–C(8′b)	119.9 (4)	C(7′b)–C(8′b)–N(8b)	108.8 (5)

The IR spectrum of this solid (**6M**) indicates a broad N–H stretching band at around 3300 cm^{-1}. The rest of the absorption bands are relatively broad, consistent with expectations for a polymeric, presumably highly cross-linked, structure. TGA studies of this polymer under N_2 or NH_3 to 1000 °C show a 36.9% or 52.7% weight loss, respectively (the theoretical weight loss for decomposition of this compound to AlN is 57.7%).

Thermolysis of the 1:1 Et_3Al:en Adduct (1E) in Solution. The 1:1 Et_3Al:en adduct (**1E**) is a colorless oil which is unstable at room temperature. Like that for its trimethylaluminum counterpart, the DSC curve for the 1:1 Et_3Al:en adduct (**1E**) from 30 to 460 °C shows an exothermal decomposition peak from around 30 to 130 °C and a broad endothermal peak from around 320 to 450 °C. Its FT-IR spectrum shows a broad N–H stretching band at around 3200 cm^{-1}, suggesting the presence of hydrogen-bonded NH_2 groups. The ^{27}Al NMR spectrum of the adduct shows only one broad peak centered at 170 ppm, which is attributed to the 4-coordinated Al atom in the –NH_2AlEt_3 unit.

Its decomposition in solution was also studied by NMR spectroscopy. Figure 4 shows the ^{1}H NMR spectra of the 1:1 Et_3Al:en adduct (**1E**) and its reaction products after heating at 65 °C in benzene solution for various times. The spectra show a gradual decrease in the relative intensity of the peaks attributed to the adduct (1.42 and 0.12 ppm, labeled as a) and, at the same time, the appearance of a set of new peaks (2.40, 1.95, 1.30, 1.06, 0.06, and –0.13 ppm, labeled as b). After the solution had been heated at 65 °C for 17 min (stage 4d), all of the adduct had disappeared, and at this stage, the solution was still clear. Further heating of this solution for 30 min resulted in a suspension. At this point, the ^{1}H NMR spectrum (Figure 4e) is almost the same as in Figure 4d, except for the disappearance of the two broad peaks at around 0.60 and 2.35 ppm (labeled as c). The new set of peaks (labeled as b) are assigned to EtAl[($HNCH_2CH_2NH$)-$AlEt_2$]$_2$ (**4E**),[8] on the basis of their chemical shift values and relative intensities. As with the 1:1 Me_3Al:en system, free ethylenediamine will be released to the solution upon conversion to the 1:1 Et_3Al:en adduct to the intermediate **4E**. The two broad peaks labeled as c in Figure 4d are attributed to the NH_2 and CH_2 H atoms of ethylenediamine, respectively. Heating the solution from stage 4d to stage 4e results in a suspension; the solid material is presumably the further decomposition product of this 1:1 Et_3Al:en adduct.

The above thermolysis process was also studied by ^{13}C NMR spectroscopy. The ^{13}C NMR spectra of the adduct (labeled as a) and its thermolysis products (Figure 5) show that compound **4E** (labeled as b) is the only intermediate observed up to stage 5d, which is consistent with what was observed in the ^{1}H NMR spectra. When the solution was heated at 70 °C for 13 min, all of the adduct peaks had disappeared; however, a new peak at around 45.35 ppm (labeled as c) has developed, in addition to the peaks due to **4E**. This new peak is assigned to free ethylenediamine on the basis of a comparison with the ^{13}C NMR spectrum of a sample of pure en. Further heating from 5d to 5e causes the relative intensity of the en peak to decrease; at the same time, the clear solution develops a suspended white solid. Additional peaks of relatively low intensity are also discernible in Figure 5e

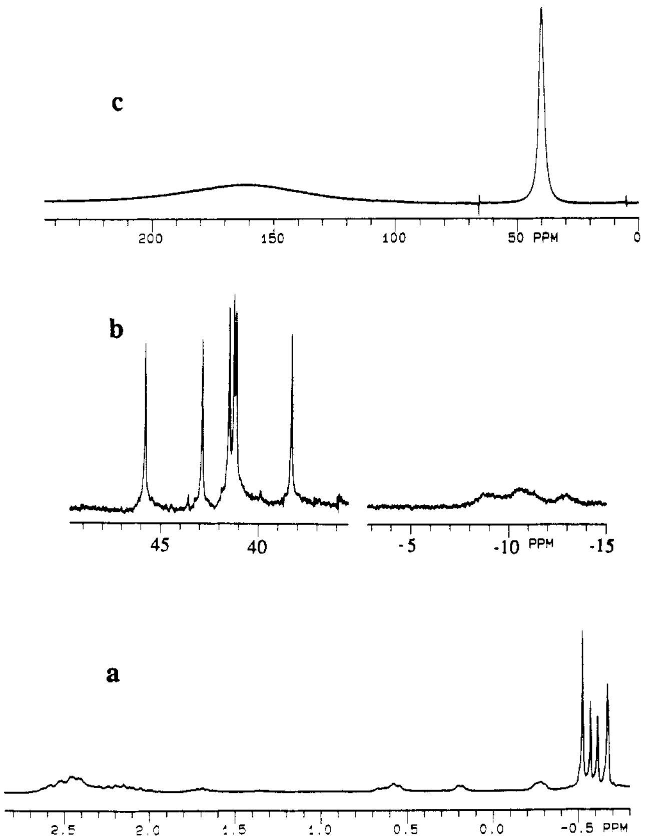
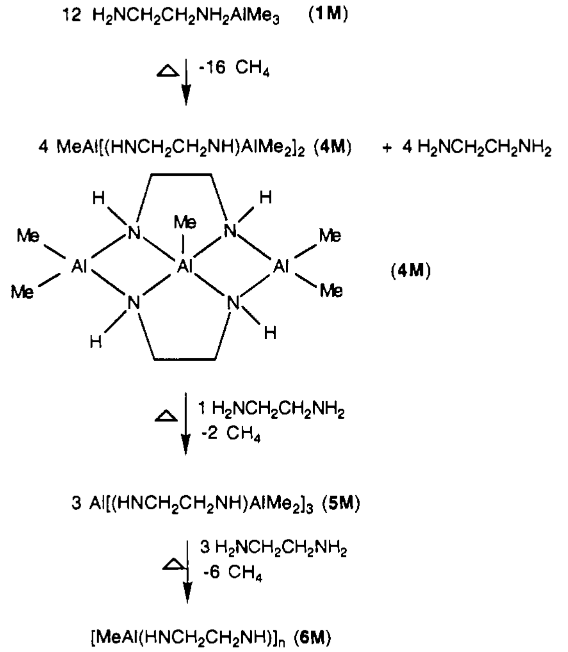


Figure 2. NMR spectra of Al[(HNCH$_2$CH$_2$NH)AlMe$_2$]$_3$ (**5M**): (a) ^{1}H NMR; (b) ^{13}C NMR; (c) ^{27}Al NMR.

Scheme I. Decomposition Pathway for the 1:1 Me$_3$Al:en Adduct (**1M**) in Solution



at 38.10, 40.15, 40.21, 42.75, and 45.38 ppm (labeled as d). These new peaks are attributed to the ethyl analog (**5E**) of Al[(HNCH$_2$CH$_2$NH)AlMe$_2$]$_3$ (**5M**) on the basis of a comparison with the ^{13}C NMR spectrum of **5M** (Figure 2b), taking into account the change of methyl to ethyl groups. The peaks due to **5E** are not resolved in the corresponding ^{1}H NMR spectrum of the heated 1:1 Et$_3$Al:en adduct in benzene solution (Figure 4), presumably due to the relatively low concentration of this compound in solution compared to its precursor and successor species and overlap of the corresponding resonances.

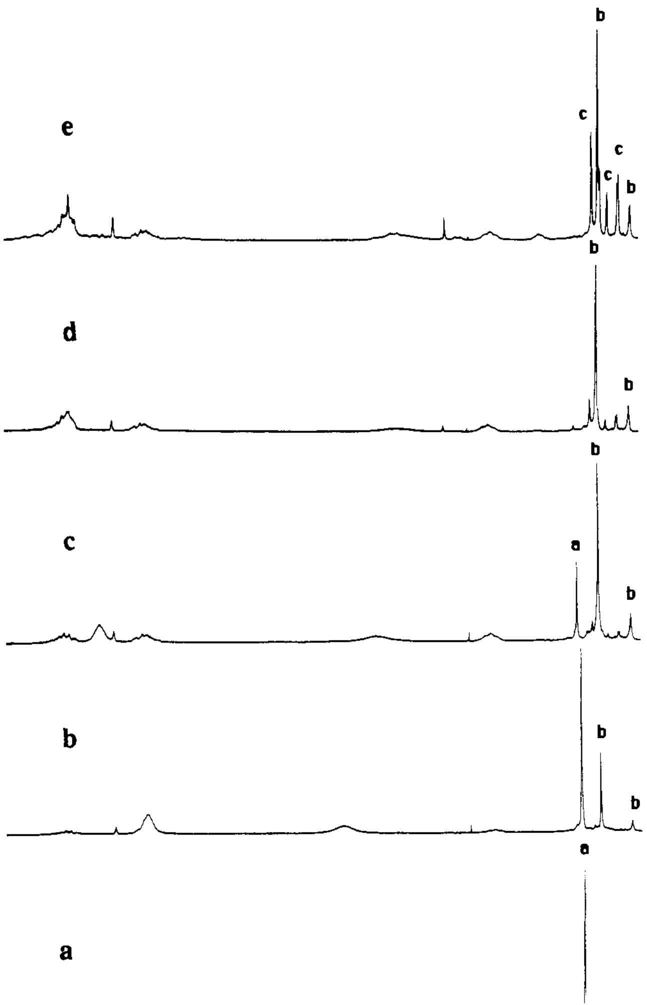


Figure 3. ^{1}H NMR spectra of the 1:1 Me$_3$Al:en (**1M**) solutions: (a) as prepared; (b) heated at 80 °C for 5 min; (c) heated at 80 °C for 10 min; (d) heated at 80 °C for 17 min; (e) heated at 80 °C for 25 min.

As its trimethylaluminum counterpart, compound **5E** is presumably formed from the reaction of **4E** and free ethylenediamine; furthermore, the insoluble polymer generated between 5d and 5e could be the product of the reaction between compound **5E** and amine. On the basis of the above observations, we conclude that the decomposition of the 1:1 Et$_3$Al:en adduct in solution follows a similar route to that proposed in Scheme I for the Me$_3$Al:en adduct, with variations in the relative concentration of the corresponding intermediates occurring, presumably due to differences in their relative stabilities and rates of production/elimination on thermolysis in solution. The complete decomposition of the 1:1 Et$_3$Al:en adduct in the insoluble polymer was carried out by refluxing a toluene solution of the 1:1 adduct at 120 °C for 12 h. The ^{1}H NMR spectrum of the resulting suspension does not show free amine or any other peaks. After filtration, washing, and evacuation, an essentially insoluble solid is obtained (**6E**). The elemental analysis indicates close to a 1:1 Al:en-2H ratio [Al(C$_2$H$_5$)$_{0.8}$(en-2.2H)]; the same formula as that of the 1:1 Me$_3$Al:en derivative, corresponding to a loss of 2.2 mol of ethane from each 1:1 adduct molecule. The FT-IR spectrum of this compound shows a broad, weak N–H stretching band at around 3300 cm^{-1}. The TGA studies of this polymer under N$_2$ and NH$_3$ show weight losses to 1000 °C of 44.7% and 49.1%, respectively. Even under NH$_3$, this weight loss is much less than the theoretical weight loss for conversion to AlN (62%), indicating

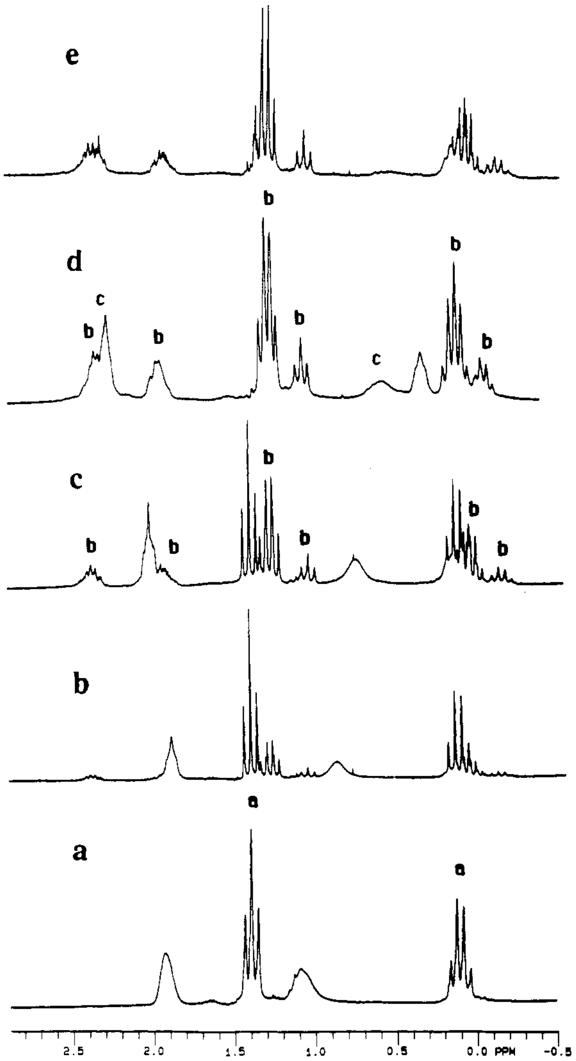


Figure 4. ^{1}H NMR spectra of the 1:1 Et_3Al:en (**1E**) solutions: (a) as prepared; (b) heated at 65 °C for 4 min; (c) heated at 65 °C for 10 min; (d) heated at 65 °C for 17 min; (e) heated at 65 °C for 30 min.

that some carbon is still left in the TGA residue. This conclusion is supported by the black color of the solid left from the TGA experiment.

It is noted from the spectra in Figure 5b,c that no peaks attributable to free amine are found, even though the proposed mechanism indicates that some ethylenediamine should be released on the formation of compound **4E**. However, it is observed that the peak (labeled as a, 41.36 ppm) attributed to the C atoms of the CH_2CH_2 unit (Figure 5a) of the adduct moves to lower field in Figure 5b (42.19 ppm) and appears at even lower field in Figure 5c (43.00 ppm). A similar effect is also found for the H atoms of CH_2CH_2 groups of the adduct in the ^{1}H NMR spectra (Figure 4). We attribute these observations to a fast intermolecular exchange process involving the free en and the adduct molecule during the formation of compound **4E**. This would result in the observation of one set of resonances due to the CH_2CH_2 groups, where the observed chemical shift values are determined by the relative amounts of the exchanging species. On this basis, we would expect (as is observed) that the resonance arising from the C atom in the CH_2CH_2 groups would move to lower fields as the relative concentration of free ethylenediamine increases from stage 5a to stage 5c. As soon as the adducts are completely converted to the intermediate (**3**), these free en molecules are released and appear in their normal position (45.35 ppm, peak c, Figure 5d).

Comparison of the 1:1 and 2:1 R_3Al:en Systems. As is suggested in Scheme II, the thermolyses of the R_3Al–en adducts apparently

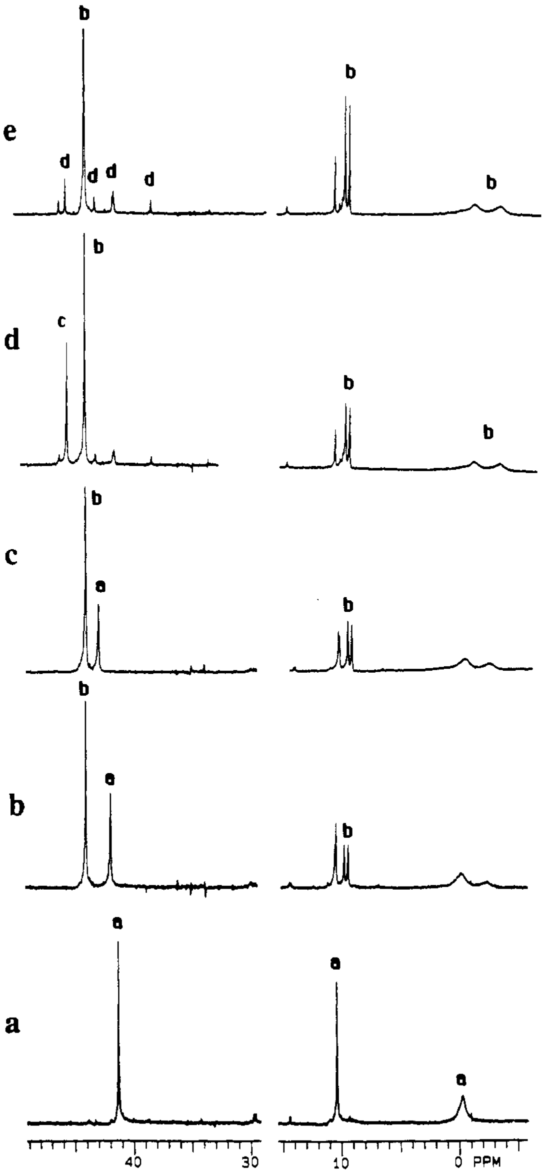
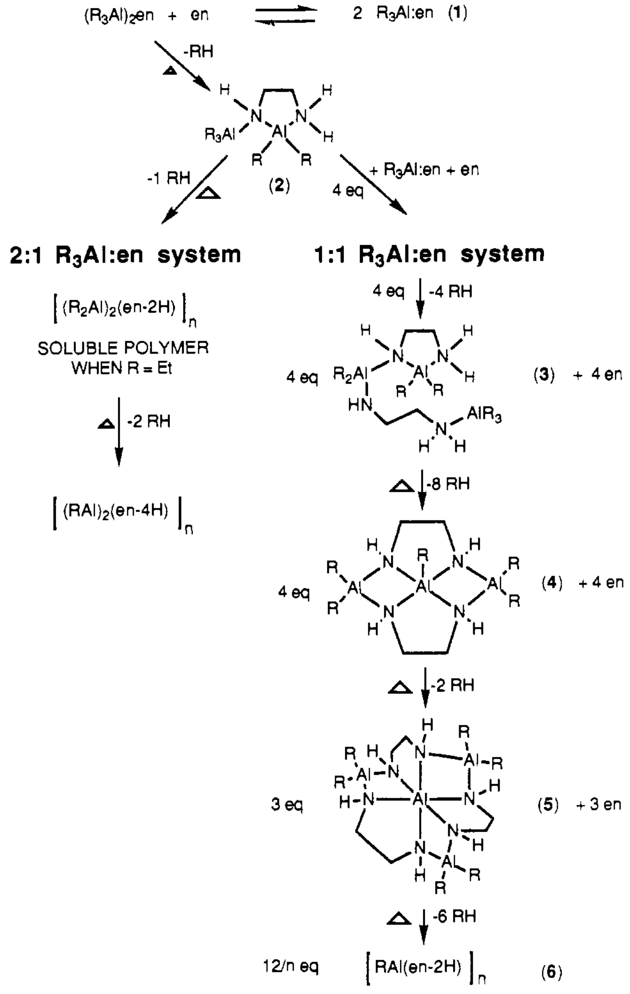


Figure 5. ^{13}C NMR spectra of the 1:1 Et_3Al:en (**1E**) solutions: (a) as prepared; (b) heated at 70 °C for 6 min; (c) heated at 70 °C for 9 min; (d) heated at 70 °C for 13 min; (e) heated at 70 °C for 20 min.

proceed through a common chelated Al(en-H) derivative, [(R_3Al)(en-H)(R_2Al)] (**2**). This species was evidenced by NMR spectroscopy in our prior study of the 3:2 R_3Al:en system as a precursor of the observed RAl[$(HNCH_2CH_2NH)AlR_2$]$_2$ (**4**) Al/en-2H cluster.[8] In the case of the 1:1 system, this species presumably reacts immediately with the additional 1:1 adduct in solution to yield **4** as the first identifiable intermediate. Whereas this is the final Al cluster intermediate identified in the case of the 3:2 adduct mixture, it goes on to form yet another novel Al/en-2H cluster (**5**) in the case of the 1:1 (or 4:3) system. Eventually, on continued heating, these Al/en-2H clusters presumably react with any additional en present, or just self-condense, to form cross-linked, insoluble polymers. Thus the final polymeric product in the case of the 1:1 system [RAl(en-2H)] (**6**) is likely to contain a mixture of Al clusters having Al coordination numbers of 4, (5?), and 6.

In contrast, a 2:1 ratio of R_3Al to en leads to a soluble amide polymer, [$(R_2Al)_2$(en-2H)]$_n$, through the same [(R_3Al)(en-H)(R_2Al)] intermediate (**2**); however, here the absence of appreciable 1:1 adduct and en in solution apparently allows this intermediate to polymerize directly, presumably through the R_3Al and NH_2 groups available on each monomer unit, to form a soluble, linear polymer, at least in the case of R = Et.[7] The presence of only

Scheme II. Comparison of the 2:1 and 1:1 R_3Al:en Systems



4-coordinated Al atoms in this product, as expected for such a linear polymer, has been verified by ^{27}Al NMR spectroscopy.[13] An important difference here is the bifunctional nature of the monomer units, quite unlike the polyfunctional Al/en-2H cluster species obtained in the case of the systems that contain an initial R_3Al:en ratio of <2:1, which lead to cross-linked polymeric products.

A key assumption in this reaction scheme is the presence of a rapid equilibrium, at least in the case of the systems with a R_3Al:en ratio of <2:1, involving the 1:1 and the 2:1 adducts and free en. Indeed, our NMR results, as well as the isolation of intermediate Al/en-2H cluster species having a R_3Al:en ratio higher than 1:1 from the thermolysis of the 1:1 adduct mixture, provide clear evidence for such an equilibrium in benzene solution. In the case of the 1:1 system, the additional en present in solution is eventually reunited with the Al/en-2H clusters to form what is almost certainly a very complex polymeric structure (**6**) with a deceptively simple [RAl(en-2H)] compositional formula. It is perhaps notable that Gilbert and Smith reported the formation of a benzene-soluble polymer of approximately the same composition by the thermolysis of a 1:1 mixture of neat Et_3Al and en at 130 °C.[6] It is possible that the difference in the reaction medium was responsible for the apparent dramatic difference in solubility properties; however, our own thermolysis studies of neat 1:1 R_3Al:en mixtures have yielded only insoluble polymers through the intermediacy of a series of, as yet, unidentified species.[14] Unfortunately, in the brief report of Gilbert and Smith on this particular system, no further information regarding the structure and properties of their soluble polymer is available.

As for the difference between the Me_3Al–en and Et_3Al–en systems, in general, they appear to follow very similar reaction pathways, except that the intermediates in the Me_3Al–en case appear to crystallize more readily and, in general, show lower solubilities than their Et_3Al–en counterparts. This observation, along with its tendency to form linear polymers, tends to favor the use of the 2:1 Et_3Al:en system as a means of generating processable AlN precursors for ceramic coatings or fibers.[7]

Acknowledgment. This work was supported by a grant from the Office of Naval Research.

Supplementary Material Available: Tables listing structure determination details, anisotropic displacement coefficients, and H atom coordinates and isotropic displacement coefficients (6 pages). Ordering information is given on any current masthead page.

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(13) A single, broad peak was observed for this polymer at ca. 155 ppm vs $AlCl_3$ aqueous solution: private communication from Dr. C. Whitmarsh, Chemistry Department, Rensselaer Polytechnic Institute.

(14) Jiang, Z. Ph.D. Thesis, Chemistry Department, Rensselaer Polytechnic Institute, 1990.