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Anionic and Neutral Aluminum Bis(*N,N′*-di-*tert*-butylethylenediamide) Complexes: $[Al\{[N(t\text{-}Bu)CH_2]_2\}_2]^-$ and $[Al\{[N(t\text{-}Bu)CH_2]_2\}_2]^\bullet$

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The reaction of the aluminum triamide $[\{HN(t\text{-}Bu)CH_2CH_2N\text{-}t\text{-}Bu\}Al\{N(t\text{-}Bu)CH_2\}_2]$ (**1**) with *n*-BuLi in hexane and diethyl ether gives the monomeric solvent-free lithium aluminum tetraamide $[Li\{N(t\text{-}Bu)CH_2CH_2N\text{-}t\text{-}Bu\}_2Al]$ (**2**), and the diethyl ether adduct $[Et_2O{\cdot}Li\{N(t\text{-}Bu)CH_2CH_2N\text{-}t\text{-}Bu\}_2Al]$ (**3**), respectively. The reaction of the diethyl ether adduct **3** with 2 equiv of the chelating nitrogen Lewis bases TMEDA (≡*N,N,N′,N′*-tetramethylethylenediamine) and *t*-Bu$_2$DAB (≡*N,N′*-di-*tert*-butyl-1,4-diazabutadiene) in diethyl ether affords the ionic complex $[Li(TMEDA)_2][Al\{[N(t\text{-}Bu)CH_2]_2\}_2]$ (**4**) and a mixture of the paramagnetic species $[Li(t\text{-}BuDAB)_2]$ and $[Al\{[N(t\text{-}Bu)CH_2]_2\}_2]$, which cocrystallize **5**, respectively. The reaction of the diethyl ether adduct **3** with 0.5 equiv of HgCl$_2$ yields the neutral paramagnetic species $[Al\{[N(t\text{-}Bu)CH_2]_2\}_2]$ (**6**). Crystals of **2** are triclinic, of space group $P\bar{1}$ (No. 2), with $a = 15.894(5)$ Å, $b = 15.473(5)$ Å, $c = 9.975(3)$ Å, $\alpha = 93.74(2)°$, $\beta = 91.97(2)°$, $\gamma = 102.07(3)°$, and $Z = 4$. Crystals of **3** are monoclinic, of space group $C2/c$ (No. 15), with $a = 15.835(5)$ Å, $b = 12.054(3)$ Å, $c = 16.456(5)$ Å, $\beta = 111.56(3)°$, and $Z = 4$. Crystals of **4** are orthorhombic, of space group *Pbca* (No. 61), with $a = 19.349(4)$ Å, $b = 22.227(7)$ Å, $c = 19.070(3)$ Å, and $Z = 8$. Crystals of **5** are orthorhombic, of space group *Pmmn* (No. 59), with $a = 13.874(4)$ Å, $b = 13.473(6)$ Å, $c = 12.717(3)$ Å, and $Z = 2$. Crystals of **6** are monoclinic, of space group $C2/c$ (No. 15), with $a = 16.721(4)$ Å, $b = 9.454(4)$ Å, $c = 16.460(8)$ Å, $\beta = 113.27(3)$, and $Z = 4$.

Introduction

In recent publications, we reported the preparation of aluminum amide complexes as an extension to our chemistry of the early group 13 hydrides.[1−3] We have focused on the reactions of various aluminum and gallium hydride sources with substituted ethylenediamines,[4−7] 1,4-diazabutadienes,[8−12] and related compounds,[13] as well as bulky monofunctional amines.[14,15] The target aluminum amide species have been formed either by metalation, reduction, or hydrometalation reactions or by a combination of these reaction pathways depending on the functionalities of the reactive nitrogen ligand, the source of aluminum hydride, and the reaction conditions.

Herein we report the syntheses and structural characterizations of a number of lithium aluminum tetraamide complexes isolated from the reaction of the aluminum triamide $[\{HN(t\text{-}Bu)CH_2CH_2N\text{-}t\text{-}Bu\}Al\{N(t\text{-}Bu)CH_2\}_2]$ (**1**) with *n*-BuLi in various solvents. The preparations of the monomeric solvent-free compound $[Li\{N(t\text{-}Bu)CH_2CH_2N\text{-}t\text{-}Bu\}_2Al]$ (**2**) and the diethyl ether adduct $[Et_2O{\cdot}Li\{N(t\text{-}Bu)CH_2CH_2N\text{-}t\text{-}Bu\}_2Al]$ (**3**) by lithiation in hexane and diethyl ether, respectively, are described. The reaction of the diethyl ether adduct **3** with 2 equiv of the chelating nitrogen Lewis bases TMEDA and *t*-Bu$_2$DAB in diethyl ether affords the ionic complex $[Li(TMEDA)_2][Al\{[N(t\text{-}Bu)CH_2]_2\}_2]$ (**4**) and a mixture of the paramagnetic species $[Li(t\text{-}Bu_2DAB)_2]$ and $[Al\{[N(t\text{-}Bu)CH_2]_2\}_2]$ (**5**), respectively. The neutral paramagnetic aluminum tetraamide species $[Al\{[N(t\text{-}Bu)CH_2]_2\}_2]$ (**6**) is formed from the oxidation of the anion $[Al\{[N(t\text{-}Bu)CH_2]_2\}_2]^-$ in the reaction of the diethyl ether adduct **3** with 0.5 equiv of HgCl$_2$.

Experimental Section

Syntheses. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon or nitrogen. Solvents were dried and then freeze/thaw-degassed prior to use. The aluminum triamide $[\{HN(t\text{-}Bu)CH_2CH_2N\text{-}t\text{-}Bu\}Al\{N(t\text{-}Bu)CH_2\}_2]$ (**1**) was prepared according to our literature procedure.[4,7] *n*-BuLi was obtained from Metallgesellschaft (AG) as a 1.60 M solution in hexane and was standardized prior to use. All other reagents were obtained from Aldrich. ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer in deuterated benzene or toluene and referenced to the residual ^{1}H resonances of the solvent (δ 7.15 or

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6.98). ^{13}C NMR spectra were recorded in deuterated benzene or toluene on a Bruker AC-200 spectrometer operating at 50 MHz using broad-band proton decoupling and were referenced to the ^{13}C resonances of the deuterated solvent (δ 128.0 or 20.4). Elemental analyses were performed by the Chemical and MicroAnalytical Services Pty. Ltd., Melbourne, Australia. Melting points were determined in sealed glass capillaries under argon and are uncorrected. IR spectra were recorded as Nujol mulls on NaCl plates using a Perkin-Elmer 1725X Fourier-transformed infrared spectrometer. EPR spectra were recorded on either a Varian E-12 or a Bruker pulsed ESR 380e FT/CW spectrometer. EPR spectral simulations were performed using the Bruker WIN-EPR Sim Fonia program (V1.2).

(a) Synthesis of [Li{N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}$_2$Al] (2). To a solution of [{HN(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}Al{N(*t*-Bu)CH$_2$}$_2$] **1** (1.00 g, 2.71 mmol) in hexane (20 mL) at 0 °C was added a solution of *n*-BuLi (1.70 mL, 1.60 M, 2.72 mmol) in hexane dropwise over 5 min. The colorless solution was allowed to warm to room temperature and was stirred for 1 h before concentrating *in vacuo* and cooling to −30 °C, whereupon large colorless crystals of **2** deposited overnight. Subsequent cropping of the crystals yielded more product (0.84 g, 83% yield): mp 117−119 °C; ^{1}H NMR (200 MHz, C_6D_6) δ 1.30 (4 × 18H, s, C*Me$_3$*), 2.94 (8H, s, NC*H$_2$*); ^{13}C NMR (50 MHz, C_6D_6) δ 30.9 (C*Me$_3$*), 46.1 (N*C*H$_2$), 51.9 (N*C*Me$_3$). Anal. Calcd for $C_{20}H_{44}N_4AlLi$: C, 64.14; H, 11.84; N, 14.96. Found: C, 64.15; H, 12.37; N, 15.41.

(b) Synthesis of [Et$_2$O·Li{N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}$_2$Al] (3). To a solution of [{HN(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}Al{N(*t*-Bu)CH$_2$}$_2$] (**1**) (1.00 g, 2.71 mmol) in diethyl ether (20 mL) at 0 °C was added a solution of *n*-BuLi (1.70 mL, 1.60 M, 2.72 mmol) in hexane dropwise over 5 min. The pale yellow solution was allowed to warm to room temperature and was stirred for 30 min before concentrating *in vacuo* and cooling to −30 °C, whereupon large colorless crystals of **3** deposited overnight. Subsequent cropping of the crystals yielded more product (1.11 g, 91% yield): mp 142−145 °C; ^{1}H NMR (200 MHz, C_6D_6) δ 0.81 (6H, t, $^{3}J_{H-H} = 7.1$ Hz, CH$_2$C*H$_2$*), 1.45 (4 × 18H, s, C*Me$_3$*), 2.97 (4H, q, $^{3}J_{H-H} = 7.1$ Hz, OC*H$_2$*), 3.05 (8H, s, NC*H$_2$*); ^{13}C NMR (50 MHz, C_6D_6) δ 14.2 (CH$_2$*C*H$_3$), 31.1 (C*Me$_3$*), 47.1 (N*C*H$_2$), 52.3 (N*C*Me$_3$), 65.9 (O*C*H$_2$). Anal. Calcd for $C_{24}H_{54}N_4AlLiO$: C, 64.25; H, 12.13; N, 12.49. Found: C, 64.55; H, 13.20; N, 13.82.

(c) Synthesis of [Li(TMEDA)$_2$][Al{[N(*t*-Bu)CH$_2$]$_2$}$_2$] (4). To a solution of [Et$_2$O·Li{N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}$_2$Al] (**3**) (0.74 g, 1.65 mmol) in diethyl ether (100 mL) at 0 °C was added neat TMEDA (0.50 g, 4.30 mmol) dropwise over 5 min. The colorless solution was allowed to warm to room temperature and filtered. The filtrate was concentrated *in vacuo* and cooled to −30 °C, whereupon colorless crystals of **4** deposited overnight. Subsequent cropping of the crystals yielded more product (0.95 g, 94% yield): mp 179−183 °C; ^{1}H NMR (200 MHz, C_7D_8) δ 1.48 (4 × 18H, s, C*Me$_3$*), 1.99 (12H, s, N*Me*), 2.02 (8H, s, NC*H$_2$*), 3.02 (8H, s, NC*H$_2$*); ^{13}C NMR (50 MHz, C_7D_8) δ 31.5 (C*Me$_3$*), 46.3 (N*C*H$_2$), 47.4 (N*C*H$_2$), 52.2 (N*C*Me$_3$), 57.8 (N*Me*). Anal. Calcd for $C_{32}H_{76}N_8AlLi$: C, 63.33; H, 12.62; N, 18.46. Found: C, 63.29; H, 12.68; N, 18.58.

(d) Synthesis of [Li(*t*-Bu$_2$DAB)$_2$][Al{[N(*t*-Bu)CH$_2$]$_2$}$_2$] (5). To a solution of [Et$_2$O·Li{N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}$_2$Al] (**3**) (0.57 g, 1.27 mmol) in diethyl ether (50 mL) at 0 °C was added a solution of *t*-Bu$_2$-DAB (0.45 g, 2.67 mmol) in diethyl ether (10 mL) dropwise over 5 min. The yellow solution was allowed to warm to room temperature and filtered. The filtrate was concentrated *in vacuo* and cooled to −30 °C, whereupon large deep green crystals of **5** deposited overnight from the brown solution. Subsequent cropping of the crystals yielded more product with difficulty (0.59 g, 65% yield): mp 80 °C dec; $g_{av} = 1.9443$ (diethyl ether). Anal. Calcd for $C_{40}H_{84}N_8AlLi$: C, 67.56; H, 11.91; N, 15.76. Found: C, 67.46; H, 12.12; N, 15.81.

(e) Synthesis of [Al{[N(*t*-Bu)CH$_2$]$_2$}$_2$] (6). To a solution of [Et$_2$O·Li{N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}$_2$Al] (**3**) (0.15 g, 0.33 mmol) in diethyl ether (20 mL) at 0 °C was added solid HgCl$_2$ (0.05 g, 0.18 mmol) portionwise over 10 min. Mercury metal deposited instantly, giving a yellow/orange solution with a gray precipitate. The solution was allowed to warm to room temperature, stirred overnight, and filtered. The volatiles were removed *in vacuo* from the resultant yellow solution, giving a brown powder, which was sublimed *in vacuo* (140 °C, 10^{-1} mmHg), yielding large yellow/orange crystals of **6** (0.09 g, 71% yield): mp 177−178 °C; $g_{av} = 1.9948$ (hexane). Anal. Calcd for $C_{20}H_{44}N_4Al$: C, 65.35; H, 12.07; N, 15.24. Found: C, 61.89; H, 10.65; N, 15.50.

Table 1. Crystallographic Data for Compounds **2**−**6**

Compound **2**	
$C_{20}H_{44}N_4AlLi$	fw 374.52
$a = 15.894(5)$ Å	space group $P\bar{1}$ (No. 2)
$b = 15.473(5)$ Å	$T = 25$ °C
$c = 9.975(3)$ Å	$\lambda = 0.710\ 69$ Å
$\alpha = 93.74(2)°$	$\rho_{calcd} = 1.040$ g cm^{-3}
$\beta = 91.97(2)°$	$\mu = 0.9$ cm^{-1}
$\gamma = 102.07(3)°$	$R^a = 0.056$
$V = 2391(1)$ Å^3	$R_w{}^b = 0.053$
$Z = 4$	$N, N_o = 6641, 3412$
$2\theta_{max} = 46°$	
Compound **3**	
$C_{24}H_{54}N_4AlLiO$	space group $C2/c$ (No. 15)
$a = 15.835(5)$ Å	$T = 25$ °C
$b = 12.054(3)$ Å	$\lambda = 0.71069$ Å
$c = 16.456(5)$ Å	$\rho_{calcd} = 1.020$ g cm^{-3}
$\beta = 111.56(3)°$	$\mu = 0.9$ cm^{-1}
$V = 2921(1)$ Å^3	$R^a = 0.072$
$Z = 4$	$R_w{}^b = 0.081$
fw 448.64	$N, N_o = 2580, 1731$
$2\theta_{max} = 50°$	
Compound **4**	
$C_{32}H_{76}N_8AlLi$	space group $Pbca$ (No. 61)
$a = 19.349(4)$ Å	$T = 25$ °C
$b = 22.227(7)$ Å	$\lambda = 0.710\ 69$ Å
$c = 19.070(3)$ Å	$\rho_{calcd} = 0.983$ g cm^{-3}
$V = 8201(3)$ Å^3	$\mu = 0.8$ cm^{-1}
$Z = 8$	$R^a = 0.075$
fw 606.94	$R_w{}^b = 0.070$
$2\theta_{max} = 50°$	$N, N_o = 7219, 2222$
Compound **5**	
$C_{40}H_{84}N_8AlLi$	space group $Pmmn$ (No. 59)
$a = 13.874(4)$ Å	$T = 25$ °C
$b = 13.473(6)$ Å	$\lambda = 0.710\ 69$ Å
$c = 12.717(3)$ Å	$\rho_{calcd} = 0.993$ g cm^{-3}
$V = 2377(1)$ Å^3	$\mu = 0.8$ cm^{-1}
$Z = 2$	$R^a = 0.046$
fw 711.09	$R_w{}^b = 0.039$
$2\theta_{max} = 60°$	$N, N_o = 3724, 1549$
Compound **6**	
$C_{20}H_{44}N_4Al$	space group $C2/c$ (No. 15)
$a = 16.721(4)$ Å	$T = 25$ °C
$b = 9.454(4)$ Å	$\lambda = 0.710\ 69$ Å
$c = 16.460(8)$ Å	$\rho_{calcd} = 1.021$ g cm^{-3}
$\beta = 113.27(3)°$	$\mu = 0.9$ cm^{-1}
$V = 2390(2)$ Å^3	$R^a = 0.062$
$Z = 4$	$R_w{}^b = 0.071$
fw 367.58	$N, N_o = 2100, 1129$
$2\theta_{max} = 50°$	

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

Crystal Structure Determinations. Crystals of compound **2** suitable for X-ray structure determination were grown from hexane solutions at −30 °C and were mounted in sealed capillaries under an argon atmosphere. Crystals of compounds **3**−**5** suitable for X-ray structure determination were grown from diethyl ether solutions at −30 °C and were mounted in sealed capillaries under an argon atmosphere. Crystals of compound **6** suitable for X-ray structure determination were grown by sublimation *in vacuo* at −140 °C (10^{-1} mmHg) and were mounted in sealed capillaries under an argon atmosphere. Unique diffractometer data sets (N independent reflections) were measured using an Enraf-Nonius CAD4 diffractometer. Reflections with $I > 3.0\sigma(I)$ for were considered "observed" N_o and used in the full-matrix least-squares refinements, minimizing $\sum w\Delta^2$ after solution of the structures by direct methods. Conventional residuals on $|F|$ at convergence are quoted. No extensive, significant extinction effects were found. Neutral-atom complex scattering factors were employed.[16] Computation used the XTAL 3.0 program system.[17] A summary of crystal and solution and refinement data is given in Table 1. Non-hydrogen and

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(16) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. 4.

Table 2. Non-Hydrogen Atom Coordinates and Isotropic Equivalent Thermal Parameters for **2**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}, Å^2
Al1	1.22424(9)	0.30520(10)	1.01690(14)	0.0402(9)
N11	1.1214(2)	0.3362(3)	1.0852(4)	0.048(2)
C111	1.0520(3)	0.2807(4)	1.1580(6)	0.059(3)
C112	0.9854(4)	0.3326(4)	1.2045(6)	0.093(4)
C113	1.0048(4)	0.1992(4)	1.0739(6)	0.087(4)
C114	1.0924(4)	0.2520(5)	1.2818(6)	0.102(5)
C11	1.0871(3)	0.3788(4)	0.9751(6)	0.068(4)
C12	1.1591(4)	0.4272(4)	0.8972(6)	0.070(4)
N12	1.2214(2)	0.3714(3)	0.8732(4)	0.049(2)
C121	1.2677(3)	0.3866(4)	0.7488(5)	0.057(3)
C122	1.3412(4)	0.3398(4)	0.7503(5)	0.084(4)
C123	1.3046(4)	0.4857(4)	0.7352(6)	0.081(4)
C124	1.2073(4)	0.3516(4)	0.6233(6)	0.091(4)
N13	1.3014(2)	0.3454(3)	1.1721(4)	0.041(2)
C131	1.3790(3)	0.4178(3)	1.1865(5)	0.047(3)
C132	1.4076(3)	0.4432(3)	1.3348(5)	0.065(4)
C133	1.3566(3)	0.4983(3)	1.1269(5)	0.060(3)
C134	1.4559(3)	0.3945(4)	1.1143(6)	0.070(4)
C13	1.3173(3)	0.2624(4)	1.2226(5)	0.057(3)
C14	1.3146(4)	0.1909(3)	1.1106(6)	0.067(4)
N14	1.2445(3)	0.1933(3)	1.0128(4)	0.048(2)
C141	1.2195(4)	0.1139(4)	0.9221(6)	0.062(4)
C142	1.1551(4)	0.1297(4)	0.8143(6)	0.081(4)
C143	1.2962(4)	0.0890(4)	0.8501(6)	0.089(4)
C144	1.1759(4)	0.0344(4)	0.9971(6)	0.082(4)
Li1	1.2047(6)	0.3966(6)	1.2332(9)	0.066(6)
Al2	0.72917(10)	0.20650(10)	0.67575(15)	0.0431(9)
N21	0.7636(3)	0.0957(3)	0.6326(4)	0.050(3)
C211	0.8476(3)	0.0778(3)	0.5937(5)	0.053(3)
C212	0.8494(4)	−0.0211(4)	0.5972(6)	0.080(4)
C213	0.8724(4)	0.1066(4)	0.4549(6)	0.089(4)
C214	0.9151(4)	0.1290(4)	0.6968(7)	0.090(4)
C21	0.6922(4)	0.0438(4)	0.5489(8)	0.106(5)
C22	0.6313(4)	0.0914(4)	0.4941(7)	0.091(5)
N22	0.6338(2)	0.1758(3)	0.5655(4)	0.051(3)
C221	0.5636(3)	0.2185(4)	0.5292(6)	0.058(4)
C222	0.5807(3)	0.3115(4)	0.5994(6)	0.069(4)
C223	0.4764(4)	0.1681(4)	0.5706(7)	0.107(5)
C224	0.5566(4)	0.2291(5)	0.3772(7)	0.104(5)
N23	0.7274(3)	0.2051(3)	0.8683(4)	0.054(3)
C231	0.6551(4)	0.1700(4)	0.9542(6)	0.079(4)
C232	0.6892(5)	0.1564(5)	1.0951(7)	0.116(6)
C233	0.6094(4)	0.0814(5)	0.8892(7)	0.105(5)
C234	0.5870(4)	0.2283(5)	0.9659(7)	0.123(6)
C23	0.7739(4)	0.2929(4)	0.9221(5)	0.080(4)
C24	0.8398(4)	0.3312(3)	0.8278(6)	0.065(4)
N24	0.8059(2)	0.3125(2)	0.6889(4)	0.044(2)
C241	0.8481(3)	0.3728(3)	0.5929(5)	0.049(3)
C242	0.8098(3)	0.3399(3)	0.4524(5)	0.060(3)
C243	0.8327(3)	0.4665(3)	0.6252(6)	0.071(4)
C244	0.9467(3)	0.3800(4)	0.5955(6)	0.078(4)
Li2	0.7741(8)	0.0982(7)	0.8329(11)	0.094(8)

Table 3. Non-Hydrogen Atom Coordinates and Isotropic Equivalent Thermal Parameters for **3**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}, Å^2
Al	0.00000	0.32476(13)	0.25000	0.0406(8)
N1	0.0969(2)	0.4278(3)	0.2634(2)	0.0553(17)
C11	0.1426(3)	0.4567(3)	0.2023(3)	0.067(3)
C12	0.1970(3)	0.5654(4)	0.2298(4)	0.098(3)
C13	0.2079(4)	0.3676(5)	0.1967(7)	0.186(7)
C14	0.0705(4)	0.4751(5)	0.1143(3)	0.098(4)
C1	0.1602(4)	0.4061(6)	0.3525(4)	0.166(5)
C2	0.1480(3)	0.3130(4)	0.3950(3)	0.082(3)
N2	0.0624(2)	0.2567(2)	0.35320(19)	0.0485(16)
C21	0.0491(3)	0.1591(3)	0.4006(2)	0.059(2)
C22	−0.0426(3)	0.1081(4)	0.3484(3)	0.081(3)
C23	0.1225(3)	0.0711(4)	0.4129(3)	0.079(3)
C24	0.0513(4)	0.1898(4)	0.4922(3)	0.097(3)
Li	0.00000	0.5457(8)	0.25000	0.086(7)
O	0.00000	0.7058(5)	0.25000	0.224(8)
C101	−0.0479(12)	0.7763(8)	0.1844(12)	0.274(19)
C102	−0.1123(12)	0.7110(13)	0.1071(8)	0.263(15)

Table 4. Non-Hydrogen Atom Coordinates and Isotropic Equivalent Thermal Parameters for **4**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}, Å^2
Al	0.70627(11)	0.50674(11)	0.25487(13)	0.0403(8)
N11	0.6111(3)	0.5118(3)	0.2444(4)	0.044(2)
C111	0.5659(4)	0.5088(4)	0.1828(5)	0.054(4)
C112	0.5153(5)	0.5619(4)	0.1813(5)	0.083(5)
C113	0.5250(5)	0.4508(4)	0.1801(6)	0.105(6)
C114	0.6116(5)	0.5131(4)	0.1168(5)	0.082(4)
C11	0.5784(4)	0.5018(4)	0.3112(5)	0.066(4)
C12	0.6259(5)	0.5211(4)	0.3694(4)	0.060(4)
N12	0.6957(3)	0.5058(3)	0.3519(3)	0.046(2)
C121	0.7461(4)	0.5065(4)	0.4091(4)	0.056(3)
C122	0.8175(4)	0.4958(5)	0.3777(4)	0.080(4)
C123	0.7460(5)	0.5657(4)	0.4495(5)	0.092(5)
C124	0.7324(5)	0.4550(5)	0.4609(5)	0.086(5)
N13	0.7600(3)	0.5646(3)	0.2112(4)	0.045(3)
C131	0.7620(5)	0.6292(3)	0.2147(5)	0.049(4)
C132	0.7666(5)	0.6577(4)	0.1417(5)	0.085(5)
C133	0.8220(5)	0.6529(4)	0.2602(5)	0.086(5)
C134	0.6947(5)	0.6504(4)	0.2490(6)	0.106(5)
C13	0.8202(5)	0.5361(4)	0.1795(5)	0.074(5)
C14	0.8058(5)	0.4723(4)	0.1659(5)	0.071(4)
N14	0.7575(3)	0.4463(3)	0.2147(3)	0.041(3)
C141	0.7517(5)	0.3818(4)	0.2139(5)	0.058(4)
C142	0.6960(5)	0.3626(3)	0.2676(5)	0.076(4)
C143	0.8195(5)	0.3501(4)	0.2350(5)	0.088(5)
C144	0.7295(5)	0.3575(4)	0.1415(5)	0.074(4)
Li	0.5070(7)	0.7272(7)	0.4773(7)	0.058(6)
N21	0.6066(4)	0.7685(4)	0.4761(5)	0.085(4)
C211	0.6604(6)	0.7398(7)	0.5149(7)	0.149(7)
C212	0.6042(7)	0.8303(6)	0.5008(8)	0.174(9)
C21	0.6223(6)	0.7644(8)	0.4006(7)	0.174(9)
C22	0.5664(6)	0.7763(6)	0.3535(6)	0.140(7)
N22	0.5062(4)	0.7378(3)	0.3654(4)	0.062(3)
C221	0.4463(5)	0.7694(5)	0.3383(5)	0.101(5)
C222	0.5116(6)	0.6817(5)	0.3269(6)	0.118(6)
N23	0.4914(4)	0.6404(4)	0.5238(4)	0.079(4)
C231	0.4627(6)	0.5984(5)	0.4717(7)	0.126(7)
C232	0.5494(6)	0.6116(6)	0.5580(7)	0.159(8)
C23	0.4365(7)	0.6535(6)	0.5745(7)	0.133(7)
C24	0.3983(8)	0.7059(8)	0.5661(9)	0.215(10)
N24	0.4274(4)	0.7595(4)	0.5419(4)	0.080(4)
C241	0.3735(7)	0.7944(7)	0.5113(7)	0.185(9)
C242	0.4550(8)	0.7923(10)	0.5998(8)	0.26(1)

important hydrogen atom coordinates are given in Tables 2−6. Molecular projections showing numbering schemes are given in Figures 1−8. Important molecular geometries are given in Table 7. Thermal ellipsoids are drawn at the 20% probability level. For clarity, only the vinylic hydrogen atoms of the cation of compound **5** are shown as spheres of arbitrary radii in Figure 7; all other methylene and methyl hydrogen atoms are omitted. Anisotropic thermal parameters were refined for all non-hydrogen atoms in each structure. All hydrogen atoms were calculated in idealized positions and constrained in x, y, z, and U_{iso} for all five structures with the exception of compound **5**, for which all hydrogen atoms were refined in x, y, z, and U_{iso}. Temperature factors for methyl and methylene hydrogen atoms were estimated at 1.5 × U_{ii}(average) of the attached carbon atom.

Results

Synthesis. The monomeric unsolvated and diethyl ether coordinated lithium aluminum tetraamides [Li{N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}$_2$Al] (**2**) and [Et$_2$O·Li{N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}$_2$Al] (**3**) were prepared *via* lithiation of the secondary amine functionality of the aluminum triamide [{HN(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}Al{N(*t*-Bu)CH$_2$}$_2$] (**1**) with *n*-BuLi in hexane and diethyl ether, respectively, according to Scheme 1. The reaction of the diethyl ether adduct **3** with 2 equiv of the chelating nitrogen Lewis bases TMEDA and *t*-Bu$_2$DAB in diethyl ether afford the ionic complex [Li(TMEDA)$_2$][Al{[N(*t*-Bu)CH$_2$]$_2$}$_2$] and [Li(*t*-BuDAB)$_2$][Al{[N(*t*-Bu)CH$_2$]$_2$}$_2$]. The reaction of the diethyl

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(17) *XTAL User's Manual*, Version 3.0; Hall, S. R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland: Nedlands, Australia, and College Park, MD, 1990.

Table 5. Non-Hydrogen Atom Coordinates and Isotropic Equivalent Thermal Parameters for **5**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}, Å^2
Al1	0.25000	0.25000	0.88668(9)	0.0434(4)
C11[a]	0.265(3)	0.3037(3)	1.0893(3)	0.065(7)
N11	0.25000	0.34736(16)	0.98832(17)	0.0496(9)
C111	0.25000	0.4548(2)	0.9828(3)	0.063(1)
C112	0.25000	0.4845(3)	0.8673(4)	0.086(2)
C113	0.1600(3)	0.4999(2)	1.0342(3)	0.101(2)
C12[a]	0.3014(3)	0.2671(19)	0.6833(3)	0.070(6)
N12	0.34428(16)	0.25000	0.78459(18)	0.0545(9)
C121	0.4488(2)	0.25000	0.7898(3)	0.065(1)
C122	0.4789(3)	0.25000	0.9043(4)	0.088(2)
C123	0.4922(3)	0.3422(3)	0.7370(4)	0.110(2)
Li2	0.25000	0.75000	0.5793(5)	0.059(3)
C21	0.3033(2)	0.75000	0.7858(3)	0.061(1)
N21	0.34998(17)	0.75000	0.7015(2)	0.0525(9)
C211	0.4573(2)	0.75000	0.7054(3)	0.064(1)
C212	0.4903(3)	0.75000	0.5914(4)	0.094(2)
C213	0.4919(3)	0.6560(3)	0.7601(4)	0.106(2)
C22	0.25000	0.6954(2)	0.3711(3)	0.0559(10)
N22	0.25000	0.64832(18)	0.45641(19)	0.0547(9)
C221	0.25000	0.5382(2)	0.4580(3)	0.065(1)
C222	0.25000	0.4907(4)	0.3466(4)	0.126(3)
C223	0.3415(4)	0.5087(3)	0.5131(5)	0.138(2)

[a] Site occupancy 0.5.

Table 6. Non-Hydrogen Atom Coordinates and Isotropic Equivalent Thermal Parameters for **6**

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}, Å^2
Al	0.50000	0.42557(18)	0.25000	0.0554(9)
N11	0.4015(2)	0.5244(4)	0.2415(2)	0.0667(19)
C111	0.3488(3)	0.6346(5)	0.1812(3)	0.080(2)
C112	0.3885(4)	0.6642(7)	0.1137(3)	0.139(4)
C113	0.2550(3)	0.5822(7)	0.1308(3)	0.138(4)
C114	0.3488(5)	0.7702(7)	0.2281(4)	0.150(4)
C11	0.3750(3)	0.4813(7)	0.3071(3)	0.100(3)
C12	0.4309(4)	0.3744(7)	0.3677(3)	0.106(3)
N12	0.5005(2)	0.3275(4)	0.34715(19)	0.0662(19)
C121	0.5551(3)	0.2162(5)	0.4025(2)	0.075(3)
C122	0.6307(3)	0.1894(6)	0.3742(3)	0.110(3)
C123	0.5046(4)	0.0772(6)	0.3895(4)	0.130(4)
C124	0.5932(5)	0.2595(8)	0.4991(3)	0.162(5)

ether adduct **3** with 0.5 equiv of $HgCl_2$ leads to oxidation of the tetraamidoaluminate, giving the neutral paramagnetic species **6**. Compounds **2**−**6** were isolated as air- and moisture-sensitive crystalline solids and were characterized using ^1H and ^{13}C NMR spectroscopy, infrared spectroscopy, microanalysis, and X-ray structure determinations. Compounds **5** and **6** were also characterized by EPR spectroscopy.

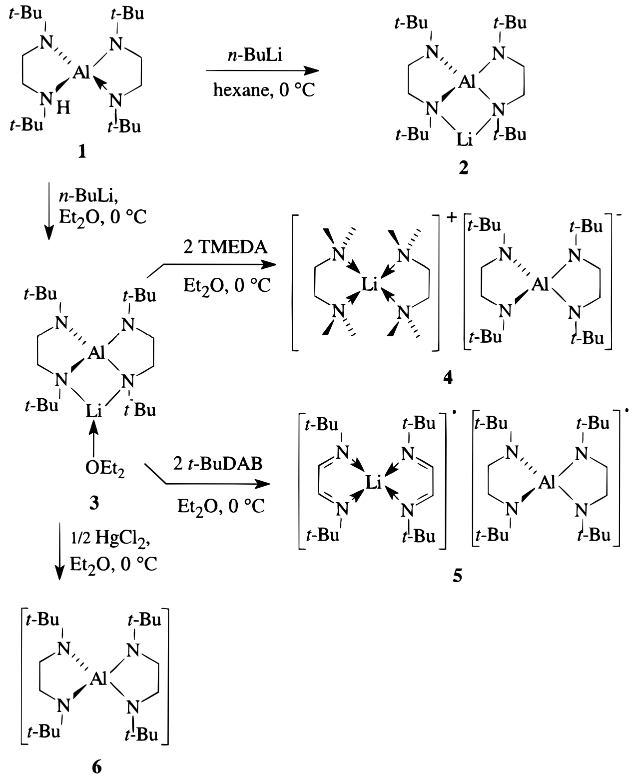
The formation of either uncoordinated monomeric or coordinated monomeric and ionic lithium aluminum tetraamides **2**−**4** is consistent with the ability of multidentate Lewis bases to more effectively solvate lithium centers than their monodentate counterparts. In this case, the bidentate Lewis base TMEDA is effective in removing the lithium center from the coordination sphere of the aluminum tetraamide. Presumably, the lithium center can achieve a maximum coordination number of 3 when remaining coordinated to the aluminum tetraamide, as in the diethyl ether adduct **3**, and so preferably attains a coordination number of 4 by coordinating to two chelating TMEDA molecules giving, the separated cation and anion pair $[Li(TMEDA)_2]^+$, $[Al\{[N(t\text{-}Bu)CH_2]_2\}_2]^-$. The coordination number of the lithium center being restricted to 3 when coordinating to the aluminum tetraamide presumably also accounts for the unsolvated lithium aluminum tetraamide **2** not associating further to give a linear polymeric complex by utilizing the bridging ability of the remaining three-coordinate nitrogen centers. Instead, the unsolvated monomeric species is found, for which the unusually low coordination number of 2 is observed for the lithium center.

Table 7. Selected Structural Parameters (Distances, Å; Angles, deg)[a]

Compound 2			
Bond Distances			
Molecule 1			
Al1−N11	1.930(4)	Al1−N14	1.825(5)
Al1−N12	1.820(4)	N11−Li1	1.993(9)
Al1−N13	1.927(4)	N13−Li1	1.97(1)
Molecule 2			
Al2−N21	1.933(5)	Al2−N24	1.823(4)
Al2−N22	1.802(4)	N21−Li2	2.00(1)
Al2−N23	1.924(4)	N23−Li2	1.97(1)
Contact Distances			
Al1−Li1	2.57(1)	Al2−Li2	2.56(1)
Bond Angles			
Molecule 1			
N11−Al1−N12	92.2(2)	N12−Al1−N14	126.1(2)
N11−Al1−N13	99.0(2)	N13−Al1−N14	93.0(2)
N11−Al1−N14	123.4(2)	N11−Li1−N13	95.5(4)
N12−Al1−N13	122.3(2)		
Molecule 2			
N21−Al2−N22	92.8(2)	N22−Al2−N24	126.6(2)
N21−Al2−N23	99.8(2)	N23−Al2−N24	91.5(2)
N21−Al2−N24	122.1(2)	N21−Li2−N23	96.3(6)
N22−Al2−N23	123.5(2)		
Compound 3			
Bond Distances			
Al−N1	1.922(3)	N1−Li	2.043(8)
Al−N2	1.817(3)	Li−O	1.93(1)
Contact Distances			
Al−Li	2.663(10)		
Bond Angles			
N1−Al−N2	92.8(1)	N2−Al−N2^{i}	126.3(2)
N1−Al−N1^{i}	99.5(2)	N1−Li−O	134.1(2)
N1−Al−N2^{i}	122.4(2)	N1−Li−N1^{i}	91.8(4)
Compound 4			
Bond Distances			
Cation			
Li−N21	2.14(2)	Li−N23	2.14(2)
Li−N22	2.15(2)	Li−N24	2.10(2)
Anion			
Al−N11	1.856(6)	Al−N13	1.851(7)
Al−N12	1.861(6)	Al−N14	1.837(7)
Bond Angles			
Cation			
N21−Li−N22	87.1(6)	N22−Li−N23	120.5(7)
N21−Li−N23	121.2(7)	N22−Li−N24	122.7(7)
N21−Li−N24	121.4(8)	N23−Li−N24	87.8(6)
Anion			
N11−Al−N12	89.9(3)	N12−Al−N13	121.1(3)
N11−Al−N13	117.9(3)	N12−Al−N14	117.7(3)
N11−Al−N14	122.3(3)	N13−Al−N14	91.0(3)
Compound 5			
Bond Distances			
Lithium Species			
Li2−N21	2.083(5)	Li2−N22	2.078(5)
Aluminum Species			
Al1−N11	1.842(2)	Al1−N12	1.843(2)
Bond Angles			
Lithium Species			
N21−Li2−N22	124.13(6)	N22−Li2−N22^{iii}	82.5(3)
N21−Li2−N21^{iii}	83.5(3)		
Aluminum Species			
N11−Al1−N12	119.63(6)	N12−Al1−N12^{ii}	90.4(1)
N11−Al1−N11^{ii}	90.8(1)		
Compound 6			
Bond Distances			
Al−N11	1.850(4)	Al−N12	1.845(4)
Bond Angles			
N11−Al−N12	91.1(2)	N11−Al−N12^{iv}	119.3(1)
N11−Al−N11^{iv}	119.3(2)	N12−Al−N12^{iv}	119.7(2)

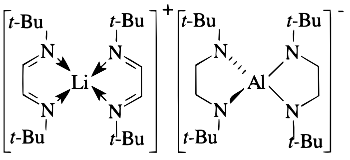
[a] Symmetry operations: (i) −*x*, *y*, 0.5 − *z*; (ii) 0.5 − *x*, 0.5 − *y*, *z*; (iii) 0.5 − *x*, 1.5 − *y*, *z*; (iv) 2 − *x*, *y*, 0.5 − *z*.

Scheme 1

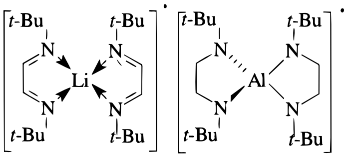


The monomeric complexes **2** and **3** are apparently fluxional in solution. At room temperature, the ^{1}H NMR spectra of the complexes exhibit single sharp resonances for the *tert*-butyl and methylene protons in benzene-d_6, indicating that the lithium centers are migrating among the amide nitrogen centers. Variable-temperature ^{1}H NMR studies in toluene-d_8 were undertaken to attempt to freeze out the fluxional process, but at low temperature the spectra were not significantly altered and single resonances were observed for each of the *tert*-butyl and methylene protons down to −80 °C. Similarly, the ionic complex **4** did not display significant temperature effects in its ^{1}H NMR spectrum. The compound is insoluble in hexane and has good solubility in benzene and diethyl ether, though it is difficult to dissolve.

Interestingly, the *t*-Bu$_2$DAB complex **5** appears to be best formulated as a mixture of the neutral paramagnetic species [Li(*t*-Bu$_2$DAB)$_2$][18] and **6** (**II**) and not the ionic complex (**I**) analogous to the TMEDA adduct **4**. The ^{1}H NMR spectrum of the complex exhibits no sharp resonances at any temperature range studied except for small resonances assignable to hydrolyzed species including **1**. The compound is insoluble in hexane and has good solubility in benzene and diethyl ether, though it is difficult to dissolve. The EPR spectrum recorded in diethyl ether solution at room temperature appears to be a combination of signals from [Li(*t*-Bu$_2$DAB)$_2$][18] and the aluminum radical [Al{[N(*t*-Bu)CH$_2$]$_2$}$_2$]$^•$ (see below). The complex is also EPR active in the solid state, exhibiting a broad signal at the field of the [Li(*t*-Bu$_2$DAB)$_2$] signal in the solution spectrum. However, the crystal structure of the complex (*vide infra*) is most consistent with the ionic formulation **I**.



I



II

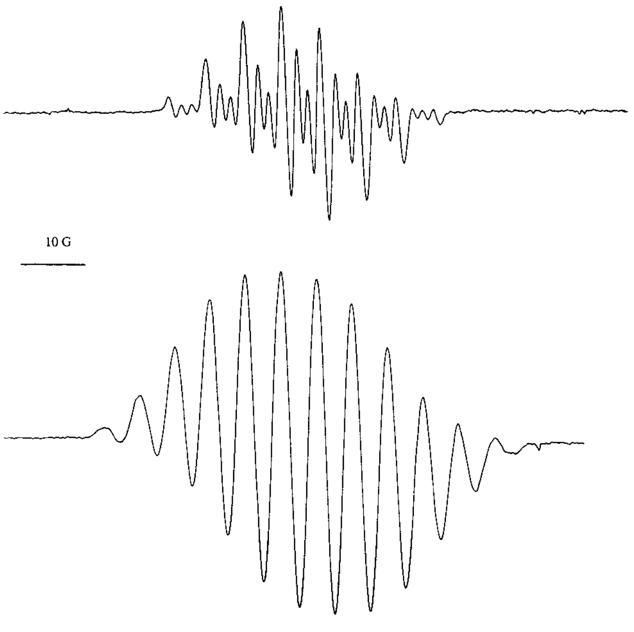


Figure 1. Room-temperature EPR spectra of [Li(*t*-Bu$_2$DAB)$_2$][Al{[N(*t*-Bu)CH$_2$]$_2$}$_2$] (**5**) (above; ether solution) and [Al{[N(*t*-Bu)CH$_2$]$_2$}$_2$] (**6**) (below; hexane solution).

The ^{1}H NMR spectrum of the neutral paramagnetic aluminum tetraamide **6** also exhibits no sharp resonances in any temperature range studied, except for small resonances assignable to hydrolyzed species including **1**. The EPR spectrum recorded in hexane solution at room temperature is quite well resolved, exhibiting 12 lines ($g = 2.0061$), Figure 1. At low temperature, the spectrum broadens slightly without becoming simplified. Simulation of the spectrum is possibly assuming an N-centered radical with coupling of the unpaired electron to one N center (a_N = 11.0 G), the metal center (a_{Al} = 5.4 G), and two methylene protons (a_H = 5.4 G). Thus, on the EPR time scale, the spin density is localized on one ligand nitrogen. This however is not apparent in the solid state structure.

X-ray Structure Commentary. (a) Structure of 2. Complex **2** crystallizes as prismatic crystals in the triclinic space group $P\bar{1}$ with four molecules in the unit cell, the asymmetric unit comprising two discrete monomeric molecules with no significant differences between the two molecules, Figures 2 and 3. The dimetalated ethylenediamide ligands act as bidentate ligands, chelating the aluminum atoms, with one nitrogen center of each ligand binding to a lithium center. Four-fold coordination for the aluminum atoms is achieved, and they exhibit distorted tetrahedral N(amido)$_2${μ-N(amido)$_2$} coordination environments. The lithium centers are two-coordinate, having N{μ-N(amido)$_2$} bent coordination environments. The molecules possess noncrystallographic C_2 symmetry, broken by the C(*n*1)−C(*n*2) torsions.

Selected geometrical parameters are given in Table 7. The Al−N(amido) distances to the three- and four-coordinate nitrogen centers of **2**, 1.802(4)−1.825(5) and 1.924(4)−1.933(5) Å, are typical for aluminum amides. The distances are consistent with the change in coordination number of the nitrogen centers and the coordination geometries of the nitrogen

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[18] Gardiner, M. G.; Hanson, G. R.; Henderson, M. J.; Lee, F.-C.; Raston, C. L. *Inorg. Chem.* **1994**, *33*, 2456.

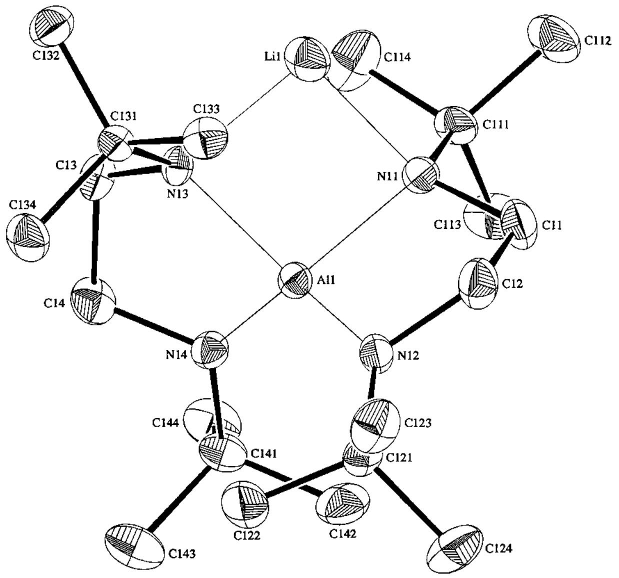


Figure 2. Molecular projection of [Li{N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}$_2$Al] (**2**) (molecule 1) showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity, hydrogen atoms are omitted.

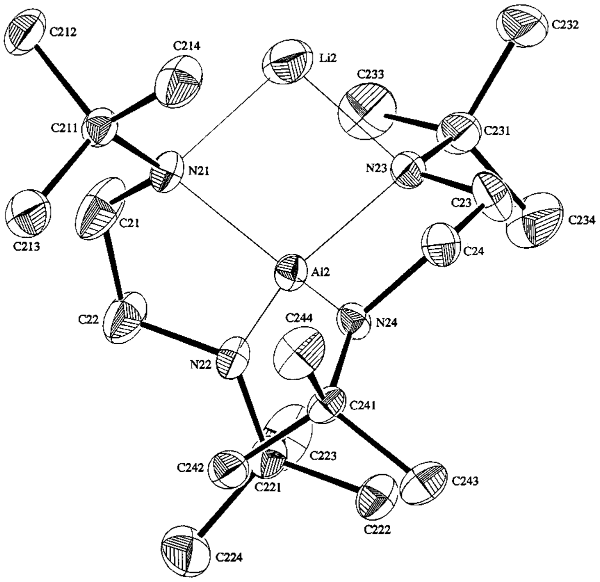


Figure 3. Molecular projection of [Li{N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}$_2$Al] (**2**) (molecule 2) showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity, hydrogen atoms are omitted.

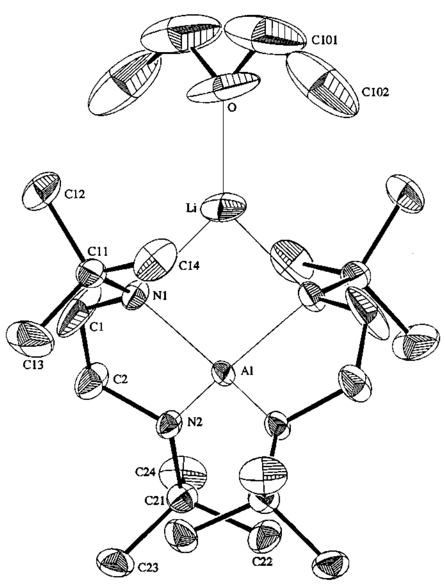
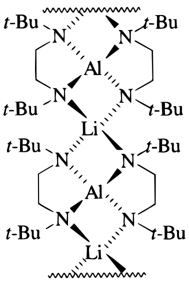
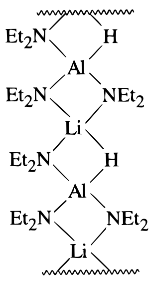


Figure 4. Molecular projection of [Et$_2$O·Li{N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}$_2$-Al] (**3**) showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 20% probability level, that of C1 being suggestive of unresolved disorder. For clarity, hydrogen atoms are omitted.

centers in the two instances, being planar ($\sum(\mathrm{C{-}N{-}Al,C}) > 358.8^\circ$) for the former and distorted tetrahedral ($\sum(\mathrm{C{-}N{-}Al,C}) = 344.9{-}347.3^\circ$) for the latter case. The Li−N distances range from 1.97(1) to 2.00(1) Å and are unexceptional for bridging amide ligands binding to lithium centers. The N−Al−N ligand bite angles (91.5(2)−93.0(2)°) represent the largest distortions from ideal tetrahedral coordination for the aluminum centers. The N−Al−N angles for the nitrogen centers involved in bonding to the lithium centers (99.0(2) and 99.8(2)°) are also acute; the converse also holds for those involving the nitrogens not binding lithium (126.1(2) and 126.6(2)°). The dihedral angles between the planes defined by the chelate rings (NCCN) are 77.3 and 79.9° in the two crystallographically independent molecules and are presumably made acute by the lithium centers bridging two of the amido nitrogen centers and distort the geometries from the ideal orthogonally disposed geometries. The geometries at the lithium centers are bent, the highly acute N−Li−N angles measuring 95.5(4) and 96.3(6)° for the two independent molecules, which leaves a large portion of the coordination sphere of the lithium centers devoid of any primary interactions and is a consequence of the inclusion of the lithium centers in the four-membered LiN$_2$Al rings. The Li···Al cross-ring distances measure 2.57(1) and 2.56(1) Å. In accordance with the low coordination number of 2 for the lithium centers, we estimate close Li···H agostic type interactions to the *tert*-butyl protons as close as 2.1 Å (Li···C distance of 2.63(1) Å), which compensate for the lack of electron density at the lithium centers. Presumably, the steric protection afforded to the lithium centers prevents further association of the molecules into a linear polymeric arrangement as in **IV**, as was found for the lithium triamidoaluminum hydride complex {(μ-NEt$_2$)$_2$Al(μ-NEt$_2$)(μ-H)Li}$_n$ **III**.[19] Other bond angles within the molecule are unexceptional and do not require comment.



III



IV

(b) Structure of 3. Complex **3** crystallizes as prismatic crystals in the monoclinic space group *C*2/*c* with four molecules in the unit cell, the asymmetric unit comprising half of a discrete monomeric molecule with crystallographic C_2 symmetry, Figure 4, with the diethyl ether oxygen and the lithium and aluminum centers lying on the C_2 axis. The dimetalated ethylenediamide moieties act as bidentate ligands, chelating the aluminum atom, with one nitrogen center of each ligand binding to the lithium center. Four-fold coordination for the aluminum atoms is achieved, and they also exhibit distorted tetrahedral N(amido)$_2$-{μ-N(amido)$_2$} coordination environments. The lithium centers are three-coordinate, having a N{μ-N(amido)$_2$}O(ether) distorted trigonal planar coordination environment.

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Selected geometrical parameters are given in Table 7. The Al−N(amido) distances to the three- and four-coordinate nitrogen centers of **3**, 1.817(3) and 1.922(3) Å, are not significantly different from those of the unsolvated compound **2** and are again consistent with the change in coordination number of the nitrogen centers and the coordination geometries of the nitrogen centers in the two instances, being planar (Σ(C−N−Al,C) = 360.0°) for the former and distorted tetrahedral (Σ(C−N−Al,C) = 346.2°) for the latter case. The Li−N distance measures 2.043(8) Å and has increased significantly relative to that of compound **2** in response to the coordinated diethyl ether molecule. The Li−O distance of 1.93(1) Å is typical for diethyl ether solvates of lithium amide species, comparable with the Li−O distances of 1.943(6) and 1.96(1) Å in the three-coordinate lithium amide dimers $[\{Et_2O{\cdot}Li[\mu\text{-}N(SiMe_3)_2]\}_2]$[20,21] and $[trans\text{-}\{Et_2O{\cdot}Li[\mu\text{-}N(H)B(2,4,6\text{-}Me_3\text{-}C_6H_2)_2]\}_2]$.[22] The Li−O distance in the substituted lithium anilide dimer $[trans\text{-}\{Et_2O{\cdot}Li[\mu\text{-}NH(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]\}_2]$ is significantly shorter at 1.906(5) Å,[23] while still having three-coordinate lithium atoms. The N−Al−N ligand bite angle of 92.8(1)° represents the largest distortion from ideal tetrahedral coordination for the aluminum center. The N−Al−N angle for the nitrogen centers involved in bonding to the lithium center (99.5(2)°) is also acute, the converse holding for those involving the nitrogens not binding lithium, 126.3(2)°. The dihedral angle between the planes defined by the chelate rings (NCCN) is 76.5° and is again presumably made acute by the influence of the lithium centers bridging two of the amido nitrogen centers. The geometry at the lithium centers is distorted trigonal planar, the highly acute N−Li−N angle measuring 91.8(4)°, and is a consequence of the inclusion of the lithium centers in the four-membered LiN_2Al rings, the sum of the angles about the lithium, Σ(N−Li−N,O), being 360.0°. The oxygen center of the diethyl ether molecule occupies the portion of the coordination sphere of the lithium center which is devoid of any primary interactions in the unsolvated compound **2** and accordingly the closest Li···H agostic type interactions with the *tert*-butyl protons are longer at 2.42 Å (Li···C distance of 2.859(7) Å). The Li···Al cross-ring distance measures 2.66(1) Å and is considerably increased relative to that in **2**. Other bond angles within the molecule are unexceptional.

(c) Structure of 4. Complex **4** crystallizes as prismatic crystals in the orthorhombic space group *Pbca* with eight discrete ion pairs in the unit cell, the asymmetric unit comprising one ion pair, Figures 5 and 6. The complex is best described as an ionic lithium aluminum tetraamide. The lithium center of the cation is coordinatively saturated by two chelating TMEDA molecules, giving it a distorted tetrahedral coordination environment. The cation is devoid of crystallographic symmetry but approximates to D_2 symmetry. The aluminum center of the anion is surrounded by two dimetalated ethylenediamide ligands which act as bidentate ligands, chelating the metal center which is in a 4-fold, distorted tetrahedral coordination environment. The anion is devoid of crystallographic symmetry but approximates to D_2 symmetry.

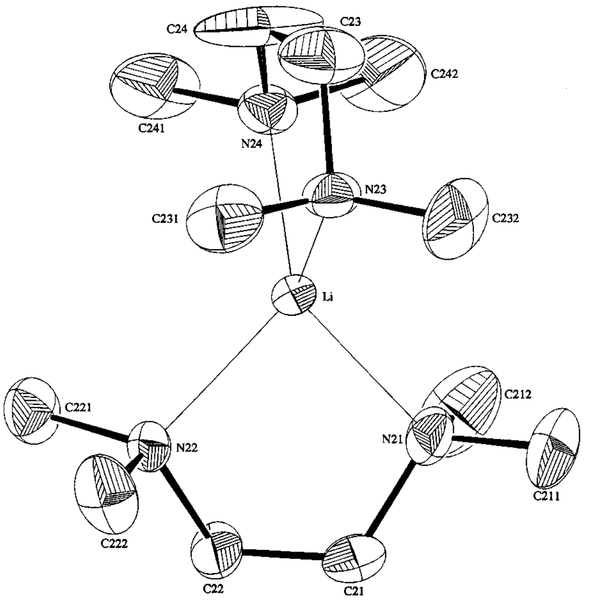

Figure 5. Molecular projection of the cation of $[Li(TMEDA)_2][Al\{[N(t\text{-}Bu)CH_2]_2\}_2]$ (**4**) showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity, hydrogen atoms are omitted.

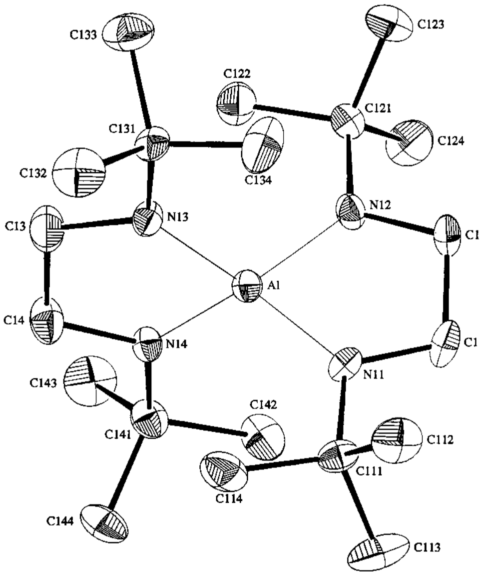

Figure 6. Molecular projection of the anion of $[Li(TMEDA)_2][Al\{[N(t\text{-}Bu)CH_2]_2\}_2]$ (**4**) showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity, hydrogen atoms are omitted.

Selected geometrical parameters are given in Table 7. The cation $[Li(TMEDA)_2]^+$ has been structurally authenticated on a number of occasions and will not be discussed at length here.[24] The Li−N distances range from 2.10(2) to 2.15(2) Å, the dihedral angle between the planes defined by the chelate rings (NCCN) is approximately orthogonal at 91.4°, and the N−Li−N bite angles of the TMEDA chelate measure 87.1(6) and 87.8(6)°.

The Al−N(amido) distances of the anion $[Al\{[N(t\text{-}Bu)\text{-}CH_2]_2\}_2]^-$, 1.837(7)−1.861(6) Å, are slightly longer than typically observed in neutral aluminum amide complexes with trigonal planar terminal amido nitrogen centers, for example, the aluminum amide complexes *cis*- and *trans*-[{[μ-N(*t*-Bu)-

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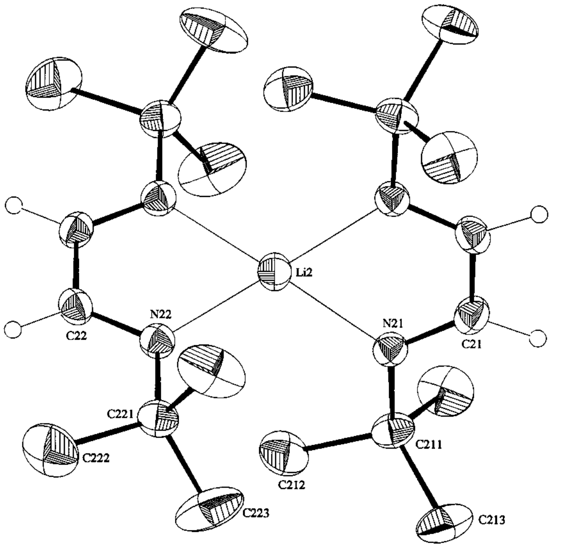

Figure 7. Molecular projection of the lithium species of [Li(t-Bu$_2$-DAB)$_2$][Al{[N(t-Bu)CH$_2$]$_2$}$_2$] (**5**) showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity, only the chelate ring hydrogen atoms are shown as spheres of arbitrary radii; all other hydrogen atoms are omitted.

CH$_2$CH$_2$N-t-Bu]AlH}$_2$][7] (1.756(9)−1.781(7) Å) and [HN(t-Bu)-CH$_2$CH$_2$N(t-Bu)AlHCl][4] (1.799(9) Å), which feature the same ethylenediamine ligand, and the well-ordered structure of the aluminum triamide [{HN(SiMe$_3$)CH$_2$CH$_2$NSiMe$_3$}Al{N(SiMe$_3$)-CH$_2$}$_2$] in which the Al−N(amido) distances are 1.812(6)−1.818(5) Å.[6] The increased Al−N distances in the anionic complex here are in accordance with the extra electron on the aluminum center. The amido nitrogen centers are approximately planar, Σ(C−N−Al,C) > 358.0°. The planes defined by the ethylenediamide chelate rings (NCCN) are approximately orthogonal, with their dihedral angle measuring 91.4°. The N−Al−N ligand bite angles of the chelate rings measure 89.9(3) and 91.0(3)°. Other bond angles within the molecule are unexceptional.

(d) Structure of 5. Complex **5** crystallizes as prismatic crystals in the orthorhombic space group *Pmmn* with two discrete lithium and aluminum species in the unit cell, the asymmetric unit comprising one quarter of each lithium and aluminum species, Figures 7 and 8. The lithium center is coordinatively saturated by two chelating t-Bu$_2$DAB molecules, giving it a distorted tetrahedral coordination environment. The lithium species has 2*mm* crystallographic symmetry, higher symmetry being lost due to the inequivalence of the t-Bu$_2$DAB ligands, *viz.* 180° rotation of the *tert*-butyl groups, which are otherwise chemically equivalent. The aluminum center is surrounded by two dimetalated ethylenediamide ligands that act as bidentate ligands, chelating the metal center, which is in a 4-fold, distorted tetrahedral coordination environment. The aluminum species has 2*mm* crystallographic symmetry, which necessitates a disorder in the ethylene linkage of the ethylenediamide ligands, being modeled by two carbon positions for the methylene carbon atoms and their associated protons.

Selected geometrical parameters are given in Table 7. The geometry of the lithium species can be compared with that of the neutral species [Li(t-Bu$_2$DAB)$_2$][18] prepared by the reduction of the diazabutadiene with lithium metal in hexane. In that case it was found by solution EPR spectroscopy and crystallographic studies that the bis(σ,σ-diazabutadiene-N,N') complex contained one neutral chelating t-Bu$_2$DAB ligand and one singly reduced t-Bu$_2$DAB ligand, which was reflected in the Li−N, N−C, and C−C distances of the complex, measuring 2.134(7)−2.148(6), 1.236(5)−1.248(5), and 1.488(5) Å, respectively, for the neutral chelating ligand and 1.993(7)−1.996(8), 1.317(5)−1.317(6), and 1.399(7) Å, respectively, for the singly reduced chelating ligand in which the unpaired electron resides in the LUMO of the diazabutadiene which has carbon−carbon double-bond and nitrogen−carbon single-bond character. In the present case, the crystallographic parameters suggest that both of the chelating ligands are bound as neutral chelates, with N−C and C−C distances of 1.253(4)−1.257(4) and 1.470(4)−1.480(4) Å. These N−C and C−C distances are similar to those found in the uncoordinated diazabutadiene N,N'-dicyclohexyl-1,4-diazabuta-1,3-diene, which measure 1.25 and 1.48 Å,[25] and the coordination complex [Me$_2$Zn(t-Bu$_2$DAB)], 1.25(1) and 1.48(1) Å.[26] This is more consistent with the formulation of the complex as ionic, as depicted in structure **I**. However, on the EPR time scale, the presence of the paramagnetic complex depicted in structure **II** is implied. The Li−N distances in [Li(t-Bu$_2$DAB)$_2$][18] measured 2.134(7)−2.148(6) and 1.993(7)−1.996(8) Å for the neutral and singly reduced ligands. In the present case, the Li−N(imine) distances are between these ranges at 2.078(5) and 2.083(5) Å. The Li−N distances here are shorter than those in the four-coordinate (aryloxy)lithium complex [{LiO{4-Me-2,6-[N(i-Pr)CH]$_2$C$_6$H$_2$}}$_3$], 2.12 Å,[27] and are longer than those found in [*cis*-{Li[μ-N(t-Bu)CH(t-Bu)CHN-t-Bu]}$_2$], 1.977(6) Å,[28] and [*trans*-{Li[μ-N(SiMe$_3$)C(Ph)CHC-(Ph)NSiMe$_3$]}$_2$], 1.95(1) Å,[29] which is in accordance with the lithium centers being three-coordinate in these complexes. The planes defined by the diazabutadiene chelate rings (NCCN) are crystallographically constrained to be orthogonal. The N−Li−N ligand bite angles of the chelate rings measure 82.5(3) and 83.5(3)°.

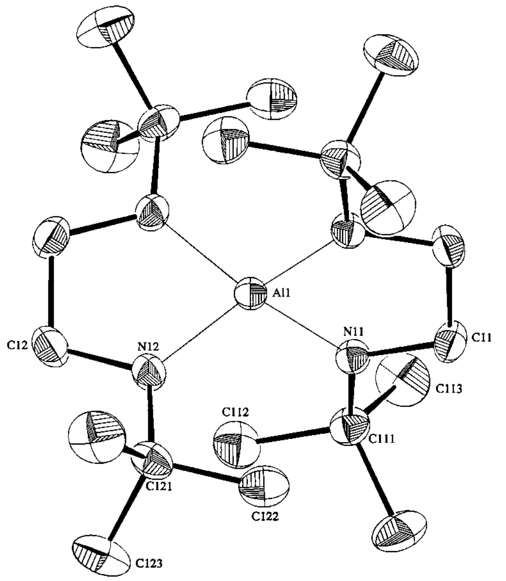

Figure 8. Molecular projection of the aluminum species of [Li(t-Bu$_2$-DAB)$_2$][Al{[N(t-Bu)CH$_2$]$_2$}$_2$] (**5**) showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity, hydrogen atoms are omitted.

The geometrical parameters for the aluminum species in compound **5** will not be discussed in detail owing to their similarity to those found in compound **4**. The Al−N(amido) distances measure 1.842(2)−1.843(2) Å, the amido nitrogen

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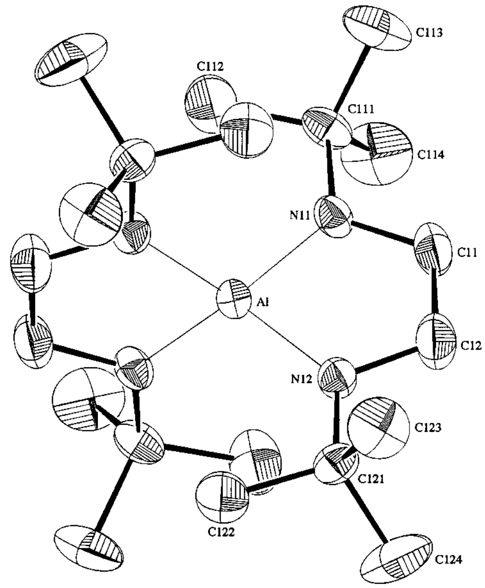
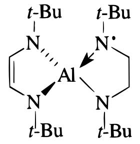


Figure 9. Molecular projection of [Al{[N(*t*-Bu)CH$_2$]$_2$}$_2$] (**6**) showing the atom-labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity, hydrogen atoms are omitted.

centers being approximately planar, ∑(C−N−Al,C) > 359.3°. The planes defined by the ethylenediamide chelate rings (NCCN) are crystallographically constrained to be orthogonal. The N−Al−N ligand bite angles of the chelate rings measure 90.8(1) and 90.4(1)°. Other bond angles within the molecule are unexceptional.

(e) Structure of 6. Complex **6** crystallizes as prismatic crystals in the triclinic space group *C*2/*c* with four molecules in the unit cell, the asymmetric unit comprising half of a discrete molecule with crystallographic C_2 symmetry, Figure 9. The aluminum tetraamide complex contains two chelating dimetalated ethylenediamide ligands. The aluminum center is in a distorted tetrahedral coordination environment.

Selected geometrical parameters are given in Table 7. Compound **6** is isostructural with its percursor, [{HN(*t*-Bu)-CH$_2$CH$_2$N-*t*-Bu}Al{N(*t*-Bu)CH$_2$}$_2$] (**1**), in which the unique secondary amine center was disordered over each possible nitrogen site.[7] Geometrical parameters worthy of note for the structure of **6** include the Al−N distances from the amide nitrogen centers to the aluminum center, which range from 1.845(4) to 1.850(4) Å. Each of the nitrogen centers has an approximately planar coordination geometry (∑(C−N−Al,C) > 359.9°). The Al−N distances here compare with those of the uncoordinated anions in the structures of compounds **4** and **5**, which range from 1.837(7) to 1.861(6) Å, and the disordered aluminum triamide **1**, 1.850(5) and 1.870(5) Å. The Al−N distances can also be compared to those in the related aluminum tetraamide [{(CH$_2$N-*t*-Bu)$_2$}Al{N(*t*-Bu)CH}$_2$], **V**, in which the unpaired electron is believed to reside on one nitrogen center of the ethylenediamide ligand, giving it distinct short (1.813(3) Å) and long (2.057(4) Å) Al−N distances to the planar and pyramidal nitrogen centers, the unpaired electron residing on the latter nitrogen center.[8,30] The present structure of **6** then suggests that the unpaired electron lies in a molecular orbital which extends over all four nitrogen centers and the aluminum center or that there is a packing disorder for the molecules in the crystal lattice.



V

Conclusion

We have been able to identify and structurally characterize four products obtained from the lithiation reactions of the aluminum triamide [{HN(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}Al{N(*t*-Bu)-CH$_2$}$_2$] with *n*-BuLi in hexane and diethyl ether. The resulting lithium aluminum tetraamides have been isolated as the monomeric solvent-free complex and diethyl ether adduct [Li{N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}$_2$Al] (**2**) and [Et$_2$O•Li{N(*t*-Bu)CH$_2$CH$_2$N-*t*-Bu}$_2$Al]. The ionic species [Li(TMEDA)$_2$][Al{[N(*t*-Bu)CH$_2$]$_2$}$_2$] and paramagnetic species [Li{[N(*t*-BuDAB)$_2$][Al{[N(*t*-Bu)-CH$_2$]$_2$}$_2$] could be prepared by the respective reactions of the diethyl ether adduct with 2 equiv of the chelating nitrogen Lewis bases TMEDA and *t*-Bu$_2$DAB in diethyl ether. Oxidation of the anion [Al{[N(*t*-Bu)CH$_2$]$_2$}$_2$]$^-$ by HgCl$_2$ affords the neutral paramagnetic species [Al{[N(*t*-Bu)CH$_2$]$_2$}$_2$]. We are currently studying the chemistry of these lithium aluminate species in the preparation of other main group derivatives and are investigating the redox chemistry of the neutral aluminum species in transition metal chemistry.

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Supporting Information Available: Lists of complete atomic coordinates, U_{ij} values, bond distances and angles, and X-ray diffraction experimental details for compounds **2**−**6** (24 pages). Ordering information is given on any current masthead page.

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