Syntheses and Structures of Alkylaluminum Complexes with a Tridentate Amido Ligand, Al(CH3)2(Et2NCH2CH2NCH2CH2NEt2) and Al3(CH3)8(Et2NCH2CH2NCH2CH2NEt2)

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Syntheses and Structures of Alkylaluminum Complexes with a Tridentate Amido Ligand, $Al(CH_3)_2(Et_2NCH_2CH_2NCH_2CH_2NEt_2)$ and $Al_3(CH_3)_8(Et_2NCH_2CH_2NCH_2CH_2NEt_2)$

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The reactions of $Al(CH_3)_3$ with the tridentate amine ligand $Et_2NCH_2CH_2NHCH_2CH_2NEt_2$ (tetraethyldiethylenetriamine, tedtaH) have been investigated. Depending on the ratio of the $Al(CH_3)_3$ complex and the tedtaH ligand, two new aluminum amido complexes were obtained. Compound 1 is a mononuclear complex with the composition $Al(CH_3)_2$(tedta) and a trigonal bipyramidal geometry, while compound 2 is a trinuclear complex with the composition $Al_3(CH_3)_8$(tedta) and an asymmetric open structure. The structures of these two compounds have been determined by X-ray diffraction analysis. Crystal data for 1: $C_{14}H_{34}AlN_3$, monoclinic, space group $P2_1/c$, $a = 8.155(2)$ Å, $b = 7.642(2)$ Å, $c = 14.158(2)$ Å, $\beta = 93.78(2)°$, $V = 880.4(3)$ Å^3, $d_{calc} = 1.024$ g cm^{-3}, $Z = 2$. For 2: $C_{20}H_{52}Al_3N_3$, monoclinic, space group $P2_1/n$, $a = 7.630(2)$ Å, $b = 25.415(7)$ Å, $c = 14.508(3)$ Å, $\beta = 97.46(2)°$, $V = 2789(1)$ Å^3, $d_{calc} = 0.989$ g cm^{-3}, $Z = 4$.

Introduction

The chemistry of alkylaluminum amido and imido complexes has attracted much attention recently due to the rich structural chemistry of this class of complexes and their possible applications in ceramic materials.[1-3] Most of the known alkylaluminum amido or imido complexes involve only monodentate amido or imido ligands.[1,2] A few aluminum complexes with bidentate amido or imido ligands have been reported recently.[3] Alkylaluminum complexes with tridentate amido and imido ligands remain poorly explored. Monodentate amido and imido aluminum complexes have been known to display versatile thermal properties and structural features such as cages and rings.[1-3] Polydentate amido and imido ligands not only can offer additional coordination sites but also may provide the aluminum complexes with additional stability, unusual reactivities, and structural features which may not be achieved in monodentate amido and imido systems. For these reasons, we have been interested in the reactions of trialkylaluminum complexes with polydentate primary and secondary amines. In this report, the syntheses and structures of two aluminum complexes with the tridentate amido ligand $Et_2NCH_2CH_2NCH_2CH_2NEt_2^-$ (tetraethyldiethylenetriamine, tedta) are described.

Experimental Section

All reactions were carried out under a nitrogen atmosphere by using a standard vacuum line or an inert atmosphere drybox. All solvents were freshly dried and distilled prior to use. The tetraethyldiethylenetriamine (tedtaH) ligand was prepared according to the published procedures.[4] Trimethylaluminum was purchased from Aldrich Chemical Co. NMR spectra were recorded on a Brüker AC-300 spectrometer. The elemental analyses were performed at Desert Analytics, Tucson, AZ, and Canadian Microanalytical Service, Delta, British Columbia. Several repeated elemental analyses were performed for both samples. However, the carbon contents in both samples were consistently lower than the calculated values. The poor accuracy of the elemental analytical results in aluminum amide complexes has been frequently observed before and was attributed to the incomplete combustion of the samples.[1e,2b] The best results obtained from the repeated elemental analyses are reported here.

Synthesis of $Al(CH_3)_2$(tedta) (1). A 1.0-mL aliquot of a 2.0 M solution of $Al(CH_3)_3$ (2.00 mmol) in toluene was added to a 5.0-mL toluene solution containing 0.43 g (2.00 mmol) of tedtaH at 23 °C. The solution became slightly yellow after stirring for 1 h. Upon concentration of the solution, colorless crystals of 1 formed (0.48 g, 1.77 mmol, 88% yield). Anal. Calcd for $C_{14}H_{34}AlN_3$: C, 61.95; H, 12.63; N, 15.48. Found: C, 60.51; H, 12.28; N, 15.01. ^1H NMR (δ, ppm, 298 K, toluene-d_8): −0.63 (s, 6H, Al–CH_3), 0.81 (t, 12H, $^3J = 7.2$ Hz, CH_3 of the ethyl group), 2.47 (t, 4H, $^3J = 6.0$ Hz, CH_2), 2.55 (qua, 8H, $^3J = 7.2$ Hz, CH_2 of the ethyl group), 2.88 (t, 4H, $^3J = 6.0$ Hz, CH_2). ^{13}C NMR (δ, ppm, 298 K benzene-d_6): 7.82 (CH_3 of the ethyl group); 42.66, 48.45, 52.59 (CH_2).

Synthesis of $Al_3(CH_3)_8$(tedta) (2). A 7.0-mL aliquot of a 2.0 M solution of $Al(CH_3)_3$ (14.0 mmol) in toluene was added to a 5.0-mL toluene solution containing 0.86 g (4.00 mmol) of tedtaH.

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1994.

(1) (a) *The Chemistry of Inorganic Homo and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vol. I. (b) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385. (c) Hitchcock, P. B.; Smith, J. D.; Thomas, K. M. *J. Chem. Soc.* **1976**, 1433. (d) Schauer, S. J.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1992**, *11*, 3287. (e) Choquette, D. M.; Timm, M. J.; Hobbs, J. L.; Rahim, M. M.; Ahmed, K. J.; Planalp, R. P. *Organometallics* **1992**, *11*, 529. (f) Davidson, M. G.; Elilio, D.; Less, S. L.; Martin, A.; Raithby, P. R.; Snaith, R.; Wright, D. S. *Organometallics* **1993**, *12*, 1. (g) Piero, G. D.; Cucinella, S.; Cesari, M. *J. Organomet. Chem.* **1979**, *173*, 263.

(2) (a) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1988**, *27*, 4335. (b) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1987**, *26*, 4341. (c) Jiang, Z.; Interrante, L. V. *Chem. Mater.* **1990**, *2*, 439. (d) Jiang, Z.; Interrante, L. V.; Kwon, D.; Tham, F. S.; Kullnig, R. *Inorg. Chem.* **1991**, *30*, 995.

(3) (a) Beachley, O. T., Jr.; Racette, K. C. *Inorg. Chem.* **1976**, *15*, 2110. (b) Beachley, O. T., Jr.; Racette, K. C. *Inorg. Chem.* **1975**, *14*, 2534. (c) Perego, G.; Dozzi, G. *J. Organomet. Chem.* **1981**, *205*, 21. (d) Dozzi, G.; Busetto, C.; Salvatori, T.; Cucinella, S. *J. Organomet. Chem.* **1980**, *192*, 17. (e) Leman, J. T.; Braddock-Wilking, J.; Coolong, A. J.; Barron, A. R. *Inorg. Chem.* **1993**, *32*, 4324. (f) Leman, J. T.; Barron, A. R. *Organometallics* **1989**, *8*, 1828.

(4) Sacco, L. J., Jr.; Anthony, P. Z.; Borgen, D. R.; Ginger, L. G. *J. Am. Chem. Soc.* **1954**, *76*, 303.

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The solution was stirred for 1 h. Upon concentration of the solution compound **2** precipitated (1.60 g, 3.80 mmol, 96% yield). Anal. Calcd for $C_{20}H_{52}Al_3N_3$: C, 57.84; H, 12.62; N, 10.12. Found: C, 57.26; H, 12.25; N, 9.87. ^{1}H NMR (δ, ppm, 298 K, benzene-d_6): −0.46 (s, 3H, Al–CH_3), −0.39 (s, 9H, Al–CH_3), −0.30 (s, 9H, Al–CH_3), −0.26 (s, 3H, Al–CH_3), 0.26 (m, 6H, CH_3 of the ethyl group), 0.74 (m, 3H, CH_3 of the ethyl group), 0.91 (t, 3H, CH_3 of the ethyl group), 2.00–3.30 (m, 12H, CH_2). ^{13}C NMR (δ, ppm, 298 K, toluene-d_8): −9.00 to −6.00 (broad, Al–CH_3); −5.02 (Al–CH_3); 7.35, 7.84, 8.47, 9.20 (CH_3 of the ethyl group); 42.67, 45.66, 46.20, 47.21, 48.47, 51.93, 52.63, 53.04 (CH_2).

Reaction of $Al(CH_3)_3$ with tedtaH in a 2:1 Ratio. A 0.43-g (2.0-mmol) quantity of tedtaH and 2.0 mL of a 2.0 M solution of $Al(CH_3)_3$ (4.0 mmol) in toluene were mixed at 23 °C, and the mixture was stirred for 0.5 h. After the removal of the solvent, the content of the residue was examined by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of this mixture matches those of compound **1** and compound **2** with a 1:1 ratio.

X-ray Crystallographic Analysis. The colorless crystals of compound **1** were obtained from a concentrated toluene solution, and the colorless crystals of compound **2** were obtained from a concentrated THF solution. Both crystals were mounted in 0.5-mm capillaries and sealed with epoxy glue. Data were collected at 23 °C over the range $2 < 2\theta < 47°$ for **1** and $2 < 2\theta < 40°$ for **2** on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation operated at 50 kV and 35 mA. The cell constants and an orientation matrix for data collection were obtained from 18 reflections in the range $20 < 2\theta < 27°$ for **1** and from 20 reflections in the range $8 < 2\theta < 20°$ for **2**. Three standard reflections were measured every 147 reflections. No significant decay was observed in both crystals. The total number of reflections collected is 1532 for **1** and 2241 for **2**. The number of unique reflections is 1421 (R_{merg} = 10.68) for **1** and 1984 (R_{merg} = 6.79) for **2**. Data were processed on a Silica Graphic computer using the TEXSAN crystallographic package and corrected for Lorentz polarization effects. Neutral-atom scattering factors were taken from Cromer and Waber.[5]

The crystals of compounds **1** and **2** belong to the monoclinic crystal system with the space groups being $P2_1/c$ and $P2_1/n$, respectively. Both structures were solved by direct methods. Full-matrix least squares refinements were applied. All non-hydrogen atoms in **1** were refined anisotropically. Due to the low ratio of data/variables, only the metal atoms, N(1), N(3), and C(13)–C(20) atoms in **2** were refined anisotropically. The positions of hydrogen atoms in both compounds were calculated, and their contributions in the structure factor calculations were included. The high *R* factor of **1** may be attributed to the quality of the crystal. The data of crystallographic analysis are given in Table 1. The details can be found in the supplementary material.

Table 1. Crystallographic Data

compd	**1**	**2**
formula	$C_{14}H_{34}AlN_3$	$C_{20}H_{52}Al_3N_3$
fw	271.4	415.6
space group	$P2_1/c$	$P2_1/n$
a, Å	8.155(2)	7.630(2)
b, Å	7.642(2)	25.415(7)
c, Å	14.158(2)	14.508(3)
α, deg	90	90
β, deg	93.78(2)	97.46(2)
γ, deg	90	90
V, Å^3	880.4(3)	2789(1)
Z	2	4
d_{calcd}, g cm^{-3}	1.024	0.989
μ, cm^{-1}	1.07	1.45
λ(Mo Kα), Å	0.71069	
T, °C	23	
R^a	0.103	0.060
$R_w{}^b$	0.094	0.054

^{a} $R = [\sum_{i=1}^n(|F_o|_i - |F_c|_i)]/\sum_{i=1}^n|F_o|_i$. ^{b} $R_w = ([\sum_{i=1}^n w_i(|F_o|_i - |F_c|_i)^2]/\sum_{i=1}^n w_i|F_o|_i^2)^{1/2}$, $w = 1/\sigma^2(F_o)$.

Table 2. Positional and Thermal Parameters for 1

atom	*x*	*y*	*z*	*B*(eq),^{a} Å^2
Al(1)	$^1/_2$	0.2714(6)	$^1/_4$	2.1(2)
N(1)	$^1/_2$	0.030(2)	$^1/_4$	2.7(7)
N(2)	0.721(1)	0.210(1)	0.3603(5)	2.5(4)
C(1)	0.631(1)	0.410(2)	0.1628(7)	3.5(6)
C(2)	0.633(2)	−0.073(2)	0.2918(9)	3.9(7)
C(3)	0.777(1)	0.048(2)	0.3156(7)	3.5(6)
C(4)	0.655(1)	0.177(1)	0.4534(7)	3.2(6)
C(5)	0.773(2)	0.088(2)	0.5278(8)	4.8(7)
C(6)	0.861(1)	0.335(2)	0.3686(7)	3.3(6)
C(7)	0.821(2)	0.514(2)	0.4057(8)	4.6(7)

^{a} $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(bb^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

Table 3. Bond Lengths (Å) and Angles (deg) for 1

Distances			
Al1–N1	1.84(1)	N2–C3	1.48(1)
Al1–N2	2.350(8)	N2–C4	1.48(1)
Al1–C1	1.99(1)	N2–C6	1.49(1)
C2–C3	1.52(2)	C4–C5	1.54(1)
N1–C2	1.44(1)	C6–C7	1.51(2)
Angles			
N1–Al1–N2	78.5(2)	Al1–N2–C3	97.4(6)
N1–Al1–C1	122.1(4)	Al1–N2–C4	108.8(6)
Al1–N2–C6	118.3(6)	C2–N1–C2′	114(1)
N2–Al1–N2′	157.0(5)	C3–N2–C4	112.3(9)
N2–Al1–C1	95.7(4)	C3–N2–C6	108.2(9)
N2–Al1–C1′	96.4(4)	C4–N2–C6	111.1(8)
C1–Al1–C1′	115.9(8)	N1–C2–C3	108(1)
Al1–N1–C2	123.2(7)	N2–C3–C2	110(1)
N2–C4–C5	116.4(9)	N2–C6–C7	115(1)

Results and Discussion

Synthesis and Structure of $Al(CH_3)_2(tedta)$ (1). Compound **1** was obtained readily from the reaction of $Al(CH_3)_3$ with 1 equiv of tedtaH ligand in toluene at 23 °C. One of the methyl groups of the $Al(CH_3)_3$ complex was removed, presumably in the form of methane. The ^{1}H NMR spectrum of compound **1** displayed significant shifts in comparison with that of the free tedtaH ligand, indicative of the formation of the amide ligand. The structure of compound **1** in the solid state has been determined by single-crystal X-ray diffraction analysis. Positional and thermal parameters are given in Table 2. Bond lengths and angles are listed in Table 3. As shown in Figure 1, the molecule of **1** possesses a 2-fold rotation axis on which the Al(1) and N(1) atoms lie. The N(1) atom has an essentially trigonal planar geometry, as indicated by the bond angles C(2)–N(1)–C(2′) = 114(1) and Al(1)–N(1)–C(2) = 123.2(7)°. The coordination geometry of the aluminum atom is approximately trigonal bipyramidal with N(2) and N(2′) occupying the axial positions, N(2)–Al(1)–N(2′) = 157.0(5)°. The aluminum–ligand bonds on the equatorial plane are significantly shorter than the axial Al–N distance, Al(1)–C(1) = 1.99(1), Al(1)–N(1) = 1.84(1), and Al(1)–N(2) = 2.350(8) Å. Five-coordinate aluminum complexes with a trigonal bipyramidal geometry are not very common, but have been reported previously.[6] Although the N(1) atom has a trigonal planar geometry, the five-membered chelate ring is not planar. As a result, the two hydrogen atoms on C(2) are chemically nonequivalent, and so are the two hydrogen atoms on C(3). The chemical environments of the two ethyl groups bonded to the N(2) center are also different

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(5) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2-2A.

(6) Müller, G.; Krüger, C. *Acta Crystallorg.* **1984**, *C40*, 628.

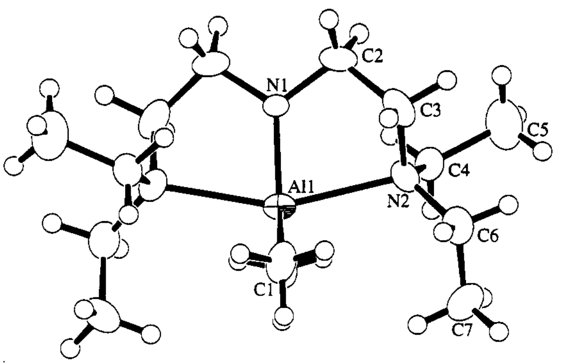

Figure 1. ORTEP diagram for compound 1 with the labeling scheme and 50% thermal ellipsoids.

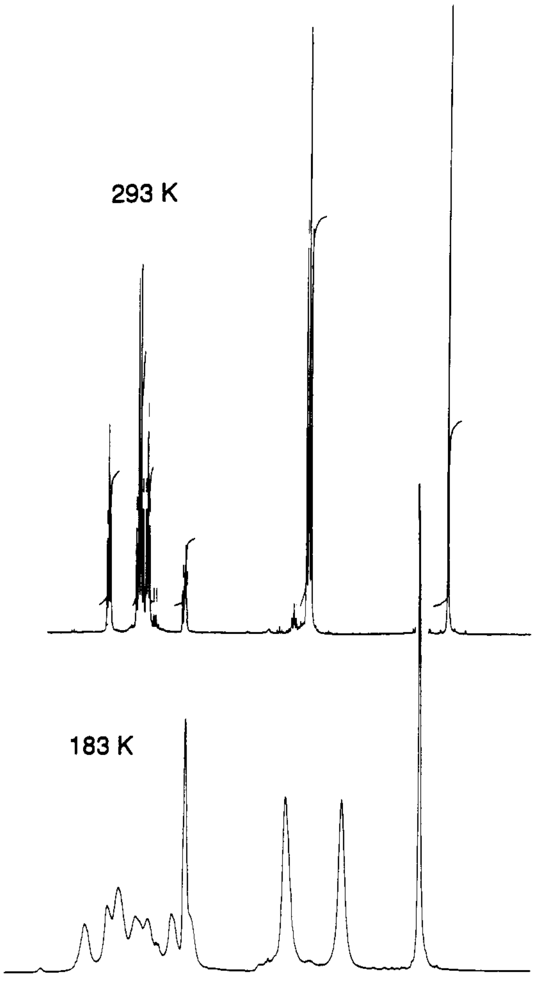

Figure 2. ^1H NMR spectra of compound 1 in toluene-d_8.

due to the relative orientation of the ethyl groups in the solid state. If the structure of this compound in solution is the same as that in the solid state, two distinct methyl signals should be observed in the ^1H NMR spectrum of this compound. However, at 293 K, a well resolved ^1H NMR spectrum was obtained (Figure 2), where only one chemical shift due to the methyl groups and one chemical shift due to the C(4) and C(6) methylene groups were observed, suggesting that the two ethyl groups have the same chemical environments in solution. The chemical shifts corresponding to the hydrogen atoms on C(2) and C(3) are two well resolved triplets, an indication that the two hydrogen atoms on C(2) or C(3) are also chemically equivalent in solution. The ^{13}C NMR spectrum of this compound shows four well resolved signals in the aliphatic region, corresponding to the methyl, the C(4) and C(6) methylene groups, the C(2) methylene group, and the C(3) methylene group, which is consistent with the ^1H NMR results. When the temperature was decreased, the ^1H NMR spectrum became more complex. The variable temperature ^1H NMR spectra of this compound illustrated clearly that there is a dynamic process occurring in solution. At 183 K, two distinct methyl signals were observed and the methylene chemical shift region displayed multiple signals and complicated coupling patterns (Figure 2), which is consistent with the observed solid state structure. These results lead us to believe that (a) the N(1) atom retains the trigonal planar geometry and (b) the N(2) and N(2′) atoms are either very weakly associated with the aluminum center or dissociated from the aluminum center so that the five-membered ring strain is released and a mirror plane containing all three nitrogen atoms and the C(2) and C(3) atoms is produced. As a result, the two hydrogen atoms on the C(2) and C(3) methylene groups have identical chemical environments and all the methyl groups of the tedta ligand are equivalent. A possible dynamic process responsible for the observed solution behavior is illustrated in Scheme 1. The origin of this dynamic process could be attributed to the weak axial aluminum–nitrogen bonds in this complex.

The structure of compound 1 has a striking resemblance to those of $VCl_2(tedta)_3$ and $VPh_2(tedta)_3$ reported earlier by Edwards and co-workers[7] where the two ethyl groups on the nitrogen center have the same orientation as that in 1. In addition, the vanadium complexes display similar metal–ligand bond length variations and the vanadium center has the same trigonal bipyramidal coordination geometry as observed in compound 1. Thus, we believe that the tedta ligand and steric factors dictate the structures observed in these complexes and have caused the similarity of these structures.

It is conceivable that the tedta ligand in compound 1 could accommodate additional aluminum centers, since the two amino groups are only weakly bonded. We therefore investigated the reaction of the tedtaH ligand with excess trimethylaluminum.

Synthesis and Structure of $Al_3(CH_3)_8(tedta)$ (2). As anticipated, the reactions of excess trimethylaluminum with the tedtaH ligand indeed produced new species. The reaction of $Al(CH_3)_3$ with tedtaH in a 3:1 ratio in toluene at 23 °C produced a new trinuclear compound with the composition $Al_3(CH_3)_8(tedta)$ (2) in nearly quantitative yield (eq 2). The reaction of $Al(CH_3)_3$ with tedtaH in a 2:1

$$Al(CH_3)_3 + tedtaH \rightarrow Al(CH_3)_2(tedta) + CH_4 \quad (1)$$

$$3Al(CH_3)_3 + tedtaH \rightarrow Al_3(CH_3)_8(tedta) + CH_4 \quad (2)$$

$$4Al(CH_3)_3 + 2tedtaH \rightarrow Al(CH_3)_2(tedta) + Al_3(CH_3)_8(tedta) + 2CH_4 \quad (3)$$

ratio produced a 1:1 mixture of compound 1 and compound 2 (eq 3), as indicated by ^1H NMR spectra. The absence of the dinuclear complex with a 2:1 ratio of Al:tedta could be because of its thermodynamic instability.

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[7] (a) Wills, A. R.; Edwards, P. G.; Short, R. L.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* 1988, 115. (b) Wills, A. R.; Edwards, P. G.; Harman, M.; Hursthouse, M. B. *Polyhedron* 1989, *8*, 1457.

Scheme 1

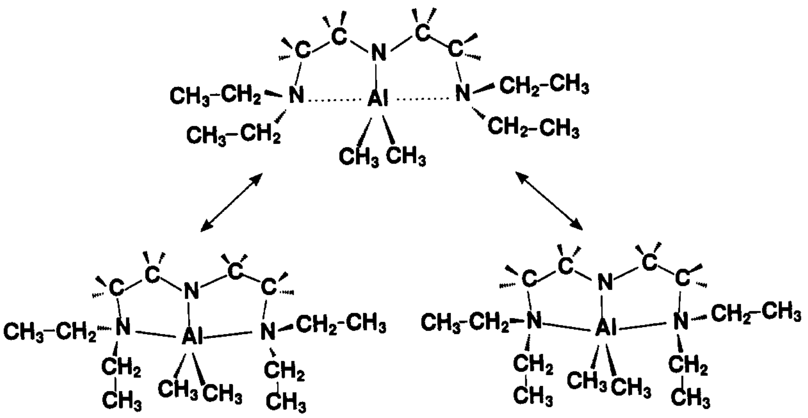


Table 4. Positional and Thermal Parameters for 2

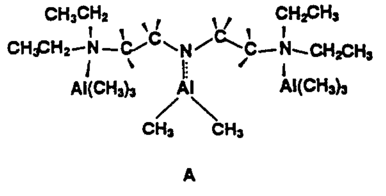
atom	*x*	*y*	*z*	*B*(eq),[a] Å^2
Al(1)	0.1039(5)	0.7384(2)	0.1651(3)	3.3(2)
Al(2)	0.0353(6)	0.6540(2)	–0.0150(3)	4.3(3)
Al(3)	–0.2423(6)	–0.5743(2)	0.3400(3)	4.7(3)
N(1)	–0.083(1)	0.7916(4)	0.1159(7)	2.6(6)
N(2)	–0.040(1)	0.6806(3)	0.1069(6)	2.2(2)
N(3)	–0.127(2)	0.5476(4)	0.2247(7)	3.4(7)
C(1)	0.330(2)	0.7482(5)	0.1212(9)	5.4(4)
C(2)	0.118(2)	0.7369(5)	0.3007(8)	4.7(4)
C(3)	0.102(2)	0.7126(5)	–0.0928(9)	5.4(4)
C(4)	–0.167(2)	0.6162(6)	–0.085(1)	6.4(4)
C(5)	0.244(2)	0.6082(5)	0.021(1)	6.1(4)
C(6)	–0.341(2)	0.5112(5)	0.398(1)	6.4(4)
C(7)	–0.049(2)	0.6077(6)	0.424(1)	6.4(4)
C(8)	–0.433(2)	0.6246(5)	0.2949(9)	5.4(4)
C(9)	–0.213(2)	0.7584(5)	0.0535(8)	3.4(3)
C(10)	–0.221(2)	0.7028(5)	0.0929(8)	3.2(3)
C(11)	–0.028(2)	0.6380(5)	0.1778(8)	3.4(3)
C(12)	–0.133(2)	0.5882(5)	0.1481(8)	3.3(3)
C(13)	–0.173(2)	0.8136(5)	0.1929(9)	3.3(8)
C(14)	–0.308(2)	0.8556(5)	0.171(1)	5.3(9)
C(15)	–0.015(2)	0.8351(6)	0.060(1)	4.5(9)
C(16)	0.110(2)	0.8714(5)	0.118(1)	6(1)
C(17)	0.064(2)	0.5310(6)	0.249(1)	5(1)
C(18)	0.096(2)	0.4872(6)	0.317(1)	8(1)
C(19)	–0.229(2)	0.5000(5)	0.181(1)	5(1)
C(20)	–0.415(2)	0.5084(5)	0.141(1)	6(1)

[a] $B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(bb^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

Table 5. Bond Lengths (Å) and Angles (deg) for 2

Distances			
Al(1)–N(1)	2.03(1)	Al(1)–N(2)	1.959(9)
Al(1)–C(1)	1.93(1)	Al(1)–C(2)	1.96(1)
Al(2)–N(2)	2.044(9)	Al(2)–C(3)	1.98(1)
Al(2)–C(4)	1.98(1)	Al(2)–C(5)	1.99(1)
Al(3)–N(3)	2.10(1)	Al(3)–C(6)	2.00(1)
Al(3)–C(7)	1.98(1)	Al(3)–C(8)	1.98(1)
N(1)–C(9)	1.51(1)	N(1)–C(13)	1.49(1)
N(1)–C(15)	1.51(1)	N(2)–C(10)	1.49(1)
N(2)–C(11)	1.49(1)	N(3)–C(12)	1.51(1)
N(3)–C(17)	1.51(2)	C(9)–C(10)	1.53(1)
N(3)–C(19)	1.53(2)	C(11)–C(12)	1.53(1)
C(13)–C(14)	1.49(2)	C(15)–C(16)	1.51(2)
C(17)–C(18)	1.48(2)	C(19)–C(20)	1.47(2)
Angles			
N(1)–Al(1)–N(2)	91.1(4)	C(9)–N(1)–C(15)	109(1)
N(1)–Al(1)–C(1)	114.7(5)	C(13)–N(1)–C(15)	110.8(9)
N(1)–Al(1)–C(2)	108.1(5)	Al(1)–N(2)–Al(2)	114.6(5)
N(2)–Al(1)–C(1)	115.4(5)	Al(1)–N(2)–C(10)	103.5(7)
N(2)–Al(1)–C(2)	111.8(5)	Al(1)–N(2)–C(11)	105.6(7)
C(1)–Al(1)–C(2)	113.6(5)	Al(2)–N(2)–C(10)	111.7(7)
N(2)–Al(2)–C(3)	111.6(5)	Al(2)–N(2)–C(11)	111.1(7)
N(2)–Al(2)–C(4)	108.4(5)	C(10)–N(2)–C(11)	110.0(9)
N(2)–Al(2)–C(5)	105.6(5)	Al(3)–N(3)–C(12)	112.8(8)
C(3)–Al(2)–C(4)	108.4(6)	Al(3)–N(3)–C(17)	113.1(8)
C(3)–Al(2)–C(5)	109.7(6)	Al(3)–N(3)–C(19)	110.1(8)
C(4)–Al(2)–C(5)	113.2(6)	C(12)–N(3)–C(17)	107(1)
N(3)–Al(3)–C(6)	107.3(5)	C(12)–N(3)–C(19)	105(1)
N(3)–Al(3)–C(7)	106.0(6)	C(17)–N(3)–C(19)	107(1)
N(3)–Al(3)–C(8)	108.1(6)	N(1)–C(9)–C(10)	110(1)
C(6)–Al(3)–C(7)	111.8(6)	N(2)–C(10)–C(9)	109(1)
C(6)–Al(3)–C(8)	110.9(6)	N(2)–C(11)–C(12)	115(1)
C(7)–Al(3)–C(8)	112.4(6)	N(3)–C(12)–C(11)	113(1)
Al(1)–N(1)–C(9)	102.5(7)	N(1)–C(13)–C(14)	119(1)
Al(1)–N(1)–C(13)	110.8(8)	N(1)–C(15)–C(16)	113(1)
Al(1)–N(1)–C(15)	113.6(8)	N(3)–C(17)–C(18)	116(1)
C(9)–N(1)–C(13)	109.4(9)	N(3)–C(19)–C(20)	117(1)

One of the possible structures proposed for compound 2 is A where the central aluminum has trigonal planar geometry, as shown in the sketch. Such a geometry is uncommon, but has been observed previously in dialkylaluminum amides where the trigonal planar geometry of the aluminum was stablized by the bulky alkyl and amido ligands.[8] The ^1H NMR spectrum of compound 2 at 293 K has four chemical shifts due to the methyl groups bonded to the aluminum centers with a relative ratio of 1:3:3:1 and three chemical shifts due to the methyl groups of the tedta ligand with complex coupling patterns and a relative ratio of 1:1:2, indicative of the presence of an asymmetric structure. The ^{13}C NMR spectrum of this compound at 298 K revealed eight chemical shifts due to the carbon atoms of the tedta ligand which supports further the possible presence of an asymmetric structure of compound 2. The asymmetric structure of compound 2 was confirmed by single-crystal X-ray diffraction analysis. The molecular structure of 2 is shown in Figure 3. Positional and thermal parameters are given in Table 4. Selected bond distances and angles are listed in Table 5. There are three different aluminum centers in this complex, one $Al(CH_3)_2$ and two $Al(CH_3)_3$. Instead of the formation of a single Al–N bond, the $Al(CH_3)_2$ unit is attached to the amido nitrogen and one amino nitrogen with a typical tetrahedral geometry. The Al(1)–N(1) and Al(1)–N(2) distances are nearly identical. The Al(1)–N(2) distance (1.959(9) Å) is significantly longer than that of Al(1)–N(1) in 1 (1.84(1) Å), which can be attributed to the geometric difference of the amido nitrogen in these two complexes, tetrahedral versus trigonal planar. Instead of being coordinated to the amino



A

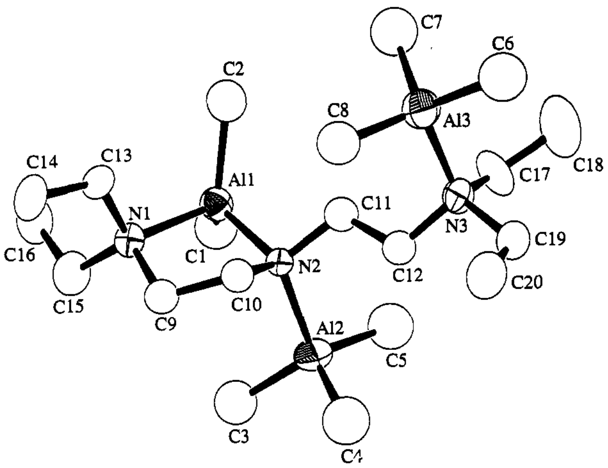


Figure 3. ORTEP diagram for compound **2** with the labeling scheme and 50% thermal ellipsoids.

nitrogen, the Al(2) atom is coordinated to the amido nitrogen, and consequently, the N(2) atom has a tetrahedral geometry. The Al(2)–N(2) bond length is essentially the same as the Al(1)–N(2) distance. In comparison with structure **A**, the observed asymmetric structure of **2** is probably thermodynamically favored because it not only makes the chelation possible but also maximizes the number of Al–N bonds. The bonding preference of the $Al(CH_3)_3$ unit to the amido site other than the amino site could also be explained by the relative higher nucleophilicity of the negatively charged amido nitrogen and the weak Al–N p–p π interaction[8] in **A**. Secondary amido ligands as a bridge for two aluminum centers have been frequently observed.[1-3] The third aluminum center Al(3) is bonded to the amino nitrogen N(3) with a normal bond length. The solid state structure is consistent with the ^{13}C NMR spectrum, where none of the carbon atoms of the tedta ligand have the same chemical environment. Although a few dozen polynuclear alkylaluminum complexes with amido or imido ligands have been reported previously, they are limited to monodentate or bidentate ligands. Compound **2** is one of the few rare examples[9] of polynuclear alkylaluminum complexes with tridentate amido ligands. The asymmetric open structure of this compound makes it even more interesting since most of the previously known polynuclear alkylaluminum complexes have symmetric and cyclic structures.[1-3] We believe that the asymmetric feature of this compound could find use in certain organic syntheses. Investigations on the reactivity of compounds **1** and **2** will be conducted in our laboratory.

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Supplementary Material Available: Tables of crystallographic data, positional and thermal parameters including hydrogen atoms, and anisotropic thermal parameters (12 pages). Ordering information is given on any current masthead page.

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[8] (a) Petrie, M. A.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 1135. (b) Waggoner, K. M.; Ruhlandt-Senge, K.; Wehmschulte, R. J.; He, X.; Olmstead, M. M.; Power, P. P. *Ibid.* **1993**, *32*, 2557.

[9] Wannagat, U.; Blumenthal, T.; Brauer, D. J.; Bürger, H. *J. Organomet. Chem.* **1983**, *249*, 33.