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Synthesis and Structures of Aluminum Alkanethiolate Complexes

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The homoleptic aluminum thiolate complex $[Al(\mu\text{-}S\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)_2]_2$ was prepared by reacting $AlBr_3$ with NaS-*t*-Bu while the analogous 2-propanethiolate complex $[Al(\mu\text{-}S\text{-}i\text{-}Pr)(S\text{-}i\text{-}Pr)_2]_2$ was synthesized by reacting $AlH_3(OEt_2)$ with *i*-PrSH. In the solid state, the dimers have tetrahedral Al atoms and *anti*-$Al(\mu\text{-}SR)_2Al$ four-member rings. The attempted synthesis of $[Al(\mu\text{-}S\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)_2]_2$ by reacting $Al(N\text{-}i\text{-}Pr_2)_3$ with *t*-BuSH in THF solvent yielded the thermally stable THF adduct $Al(S\text{-}t\text{-}Bu)_3(THF)$. The same reaction in diethyl ether solvent produced a mixture of $[Al(\mu\text{-}S\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)_2]_2$ and the salt $[i\text{-}Pr_2NH_2][Al(S\text{-}t\text{-}Bu)_4]$. In the solid-state structure of the salt, the anion $[Al(S\text{-}t\text{-}Bu)_4]^-$ has a distorted tetrahedral geometry. Reactions of $[Al(NMe_2)_3]_2$ and $AlH_3(NMe_2Et)$ with the alkanethiols yielded stable amine adducts $Al(SR)_3(R'NMe_2)$ (R = *i*-Pr or *t*-Bu; R′ = H or Et). The ligand adducts $Al(S\text{-}i\text{-}Pr)_3(HNMe_2)$ and $Al(S\text{-}t\text{-}Bu)_3(THF)$ have distorted trigonal pyramidal geometries in the solid state. Three of the new compounds, $[Al(\mu\text{-}S\text{-}i\text{-}Pr)(S\text{-}i\text{-}Pr)_2]_2$ and $Al(SR)_3(HNMe_2)$ (R = *i*-Pr or *t*-Bu), are viable precursor candidates for the chemical vapor deposition of aluminum sulfide films because they are thermally stable, volatile liquids at moderate temperatures.

We recently reported the synthesis of the homoleptic gallium alkanethiolate complexes $[Ga(\mu\text{-}SR)(SR)_2]_2$ (R = *i*-Pr or *t*-Bu) and the amine adduct $Ga(S\text{-}t\text{-}Bu)_3(HNMe_2)$.[1] The 2-propanethiolate dimer proved to be an excellent chemical vapor deposition precursor to Ga_2S_3 films because of its favorable physical properties and easy synthesis.[2] With these results in mind, we turned our attention to the synthesis of analogous aluminum alkanethiolate complexes for possible use as precursors to aluminum sulfide films and to complete the $M(SR)_3$ (R = alkyl) series of compounds for M = Al, Ga,[1] and In.[3] The synthesis of homoleptic aluminum alkanethiolate complexes has not been reported nor have there been any reports concerning the preparation of aluminum sulfide films. Power et al. have described, however, the synthesis and structures of the sterically bulky monomeric *arene*thiolate complexes $Al(S\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)_3$ and $Al(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3(THF)$,[4,5] and a large number of dialkylaluminum alkanethiolate and arenethiolate complexes are also known.[5,6−11] More recently, the syntheses of the interesting alkanethiolate alanes $Al(SR)H_2(NMe_3)$ (R = Et, *i*-Pr, or *t*-Bu), $Al(S\text{-}t\text{-}Bu)_2H(NMe_3)$, and $Al(S\text{-}t\text{-}Bu)H_2$ have been described.[12]

In this paper, we report on the synthesis and characterization of homoleptic aluminum alkanethiolate complexes and amine adducts of aluminum alkanethiolates.

Experimental Section

General Procedures and Reagents. All manipulations were carried out in a glovebox or by using Schlenk techniques. The solvents were purified according to standard methods and stored in the glovebox over molecular sieves. The thiols were purchased from Aldrich and degassed before use. $NaSCMe_3$ was obtained from Aldrich and washed with ether before use. $AlBr_3$, $AlCl_3$, and

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$AlH_3(NMe_2Et)$ were obtained from Aldrich and used as received. Nuclear magnetic resonance spectra were recorded on a 300-MHz instrument. The $^3J_{HH}$ coupling constants for the $CHMe_2$ and Et groups in the molecules were within the ranges 6.2−6.6 and 7.3−7.4 Hz, respectively. The ^{13}C resonances for **7** and **8** were assigned by using standard APT and DEPT NMR experiments. Aluminum-27 NMR spectra were referenced externally to $[Al(H_2O)_6]^{3+}$. $[Al(NMe_2)_3]_2$ and $Al(N\text{-}i\text{-}Pr_2)_3$ were prepared by following literature procedures.[13,14] The in situ preparation of $AlH_3(OEt_2)$ was based on a literature procedure.[15] Chemical analyses were performed by Galbraith Laboratories, Knoxville, TN; Midwest Microlab, LLC, Indianapolis, IN; and Oneida Research Services, Whitesboro, NY.

$[Al(\mu\text{-}S\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)_2]_2$ (1). $NaSCMe_3$ (0.39 g, 3.5 mmol) was added slowly to a solution of $AlBr_3$ (0.30 g, 1.1 mmol) in ether (20 mL). The mixture was stirred for 12 h after the addition was completed. The volatile components were removed under vacuum from the reaction mixture to yield a white solid. The solid was extracted with hexanes (2 × 15 mL), and the extracts were filtered over Celite. The volatile components were removed under vacuum from the filtrate to yield a white solid (yield 0.29 g, 0.49 mmol, 88%). Proton NMR spectra indicated the product is pure at this point. If desired, further purification can be accomplished by crystallizing the compound from hexanes at low temperature (−35 °C). The compound is thermally unstable (see Results and Discussion), which caused difficulty in obtaining a satisfactory analysis. Anal. Calcd for $C_{24}H_{54}S_6Al_2$: C, 48.94; H, 9.24. Found: C, 47.65; H, 8.69. ^1H NMR (C_6D_6): δ 1.75 (s, 36, $SCMe_3$), 1.69 (s, 18, μ-$SCMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 58.2 (s, μ-$SCMe_3$), 46.5 (s, $SCMe_3$), 37.1 (s, $SCMe_3$), 34.9 (s, μ-$SCMe_3$). ^{27}Al NMR (C_6D_6): δ 122 ($W_{1/2} = 2111$ Hz). IR (Nujol, NaCl, cm^{-1}): 1214 m, 1153 s, 995 m, 952 m, 850 m, 819 m, 765 m.

$[Al(\mu\text{-}S\text{-}i\text{-}Pr)(S\text{-}i\text{-}Pr)_2]_2$ (2). A solution of $AlCl_3$ (0.30 g, 2.3 mmol) in ether (15 mL) was added to a solution of $LiAlH_4$ (0.26 g, 6.9 mmol) in ether (40 mL) at 0 °C. The solution turned cloudy immediately after the addition began. After the reaction mixture was stirred for 6 h, *i*-PrSH (2.6 mL, 2.1 g, 27 mmol) was added slowly via syringe. The reaction mixture was allowed to stir for 10 h before it was taken to dryness under vacuum to yield a white solid. The solid was extracted with hexanes (2 × 15 mL), and the extracts were filtered over Celite. The hexanes solvent was removed under vacuum from the filtrate to yield a thick pale yellow liquid. The liquid was dissolved in hexanes (5 mL), and the flask was placed in the freezer (−35 °C). After 12 h, colorless crystalline needles formed, which were isolated and dried under vacuum. The crystals were loaded in a sublimation apparatus and heated under vacuum (110−115 °C, 0.05 mmHg), which yielded a white solid on the coldfinger (yield 1.2 g, 2.4 mmol, 53%). Anal. Calcd for $C_{18}H_{42}S_6Al_2$: C, 42.82; H, 8.39. Found: C, 42.72; H, 8.23. ^1H NMR (−60 °C, C_7D_8): δ 3.92 (septet, 2, μ-$SCHMe_2$), 3.55 (septet, 4, $SCHMe_2$), 1.49 (d, 24, μ-$SCHMe_2$), 1.29 (d, 12, $SCHMe_2$).$^{13}C\{^1H\}$ NMR (−30 °C, $CDCl_3$): δ 41.0 (s, μ-$SCHMe_2$), 32.7 (s, $SCHMe_2$), 29.0 (s, $SCHMe_2$), 26.3 (s, μ-$SCHMe_2$). IR (Nujol, NaCl, cm^{-1}): 1365 s, 1307 m, 1246 s, 1153 s, 1112 m, 1051 s, 950 w, 931 s, 883 s.

$Al(\mu\text{-}t\text{-}Bu)_3(THF)$ (3). Method A. *t*-BuSH (0.53 mL, 0.42 g, 4.7 mmol) was added slowly to a solution of $Al(N\text{-}i\text{-}Pr_2)_3$ (0.31 g, 0.93 mmol) in THF (20 mL). The solution remained clear throughout the addition and subsequent 15 h of stirring. The reaction mixture was taken to dryness under vacuum to yield a white solid. The solid was dissolved in hexanes (10 mL), and the solution was filtered. The filtrate was concentrated under vacuum to 4 mL, and the flask was placed in the freezer (−35 °C). After 20 h colorless crystalline blocks had formed, which were isolated and dried under vacuum (yield 0.24 g, 0.65 mmol, 70%).

Method B. $[Al(\mu\text{-}S\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)_2]_2$ (0.10 g, 0.17 mmol) was dissolved in THF (20 mL) and stirred for 12 h. The reaction mixture was taken to dryness under vacuum to yield a white solid, which was identified as the THF adduct by using ^1H NMR. Anal. Calcd for $C_{16}H_{35}OS_3Al$: C, 52.41; H, 9.62. Found: C, 52.14; H, 9.32. ^1H NMR (C_6D_6): δ 4.00 (t, 4, THF), 1.75 (s, 27, $SCMe_3$), 1.04 (t, 4, THF). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 72.7 (s, THF), 44.4 (s, $SCMe_3$), 37.1 (s, $SCMe_3$), 24.7 (s, THF). ^{27}Al NMR (C_6D_6): δ 133 ($W_{1/2} =$ 1835 Hz). IR (Nujol, NaCl, cm^{-1}): 1213 w, 1163 s, 1041w, 995 s, 923 w, 844 s, 676 m.

$[i\text{-}Pr_2NH_2][Al(S\text{-}t\text{-}Bu)_4]$ (4). *t*-BuSH (1.2 mL, 0.99 g, 11 mmol) was added slowly to a solution of $Al(N\text{-}i\text{-}Pr_2)_3$ (0.70 g, 2.2 mmol) in ether (15 mL). The mixture was stirred for 14 h after the addition was completed. The volatile components were removed under vacuum from the reaction mixture to yield a white solid. The solid was extracted in toluene (10 mL), and the extract was filtered. The filtrate was concentrated under vacuum to 5 mL, and the flask was placed in the freezer (−35 °C). After 12 h colorless crystalline needles had formed, which were isolated and dried under vacuum (yield 0.99 g). A ^1H NMR spectrum of a C_6D_6 solution of the crystalline solid showed that it consisted approximately of a 2:1 mixture of $[i\text{-}Pr_2NH_2][Al(S\text{-}t\text{-}Bu)_4]$ and $[Al(\mu\text{-}S\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)_2]_2$. The spectrum also had resonances arising from *t*-BuSH and HN-*i*-Pr_2, as well as unidentified peaks. ^1H NMR (CD_3CN) of the salt: δ 1.45 (s, $SCMe_3$).

$Al(S\text{-}i\text{-}Pr)_3(HNMe_2)$ (5). Method A. *i*-PrSH (0.20 mL, 0.16 g, 2.1 mmol) was added slowly to a solution of $[Al(NMe_2)_3]_2$ (0.11 g, 0.34 mmol) in ether (20 mL). The solution remained clear throughout the addition and subsequent 12 h of stirring. The reaction was taken to dryness under vacuum to yield a white solid. The solid was dissolved in hexanes (15 mL), and the solution was filtered. The filtrate was concentrated under vacuum to 2 mL. The flask was placed in the freezer (−35 °C), and after 8 h, colorless crystalline needles had formed, which were isolated and dried under vacuum (yield 0.17 g, 0.57 mmol, 83%).

Method B. $HNMe_2$ (0.01 g, 0.26 mmol) was added to a solution of $[Al(\mu\text{-}S\text{-}i\text{-}Pr)(S\text{-}i\text{-}Pr)_2]_2$ (0.06 g, 0.12 mmol) in toluene (15 mL). The solution remained clear throughout the addition and subsequent 12 h of stirring. The reaction mixture was taken to dryness under vacuum to yield a white solid that was identified as the amine adduct by using ^1H NMR. Anal. Calcd for $C_{11}H_{28}NS_3Al$: C, 44.39; H, 9.50; N, 4.71. Found: C, 44.24; H, 9.27; N, 4.59. ^1H NMR (C_6D_6): δ 3.59 (septet, 3, $SCHMe_2$), 2.2 (br, 1, $HNMe_2$), 1.92 (d, $J = 6$ Hz, 6, $HNMe_2$), 1.53 (d, 18, $SCHMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 37.0 (s, 2, $HNMe_2$), 31.8 (s, 3, $SCHMe_2$), 29.4 (s, 6, $SCHMe_2$). IR (Nujol, NaCl, cm^{-1}): ν(NH) 3083 s, 2568 w, 2472 w, 2429 w, 2244 w, 2121 w, 1403m, 1361 s, 1288 s, 1253 s, 1151 s, 1108 s, 1062 s, 1049 s, 1014 s, 923 w, 885 s, 622 s.

$Al(S\text{-}t\text{-}Bu)_3(HNMe_2)$ (6). *t*-BuSH (0.20 mL, 0.16 g, 1.8 mmol) was added slowly to a solution of $[Al(NMe_2)_3]_2$ (0.09 g, 0.28 mmol) in ether (20 mL). The solution remained clear throughout the addition and subsequent 15 h of stirring. The reaction mixture was taken to dryness under vacuum to yield a white solid. The solid was dissolved in hexanes (15 mL), and the solution was filtered. The filtrate was concentrated under vacuum to 2 mL. The flask was placed in the freezer (−35 °C), and after 8 h, colorless

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Table 1. Crystal Data for [Al(*μ*-S-*t*-Bu)(S-*t*-Bu)$_2$]$_2$ (**1**), [Al(*μ*-S-*i*-Pr)(S-*i*-Pr)$_2$]$_2$ (**2**), Al(S-*t*-Bu)$_3$(THF) (**3**), [*i*-Pr$_2$NH$_2$][Al(S-*t*-Bu)$_4$] (**4**), and Al(S-*i*-Pr)$_3$(HNMe$_2$) (**5**)

param	[Al(*μ*-S-*t*-Bu)(S-*t*-Bu)$_2$]$_2$ (**1**)	[Al(*μ*-S-*i*-Pr)(S-*i*-Pr)$_2$]$_2$ (**2**)	Al(S-*t*-Bu)$_3$(THF) (**3**)	[*i*-Pr$_2$NH$_2$][Al(S-*t*-Bu)$_4$] (**4**)	Al(S-*i*-Pr)$_3$(HNMe$_2$) (**5**)
chem formula	$C_{24}H_{54}S_6Al_2$	$C_{18}H_{42}S_6Al_2$	$C_{16}H_{35}OS_3Al$	$C_{22}H_{52}NS_4Al$	$C_{11}H_{28}NS_3Al$
fw	588.99	504.84	366.60	485.87	297.50
cryst dim., mm	0.40 × 0.15 × 0.10	0.40 × 0.35 × 0.35	0.28 × 0.20 × 0.20	0.40 × 0.25 × 0.15	0.32 × 0.20 × 0.04
space group	$P\bar{1}$ (triclinic)	$P\bar{1}$ (triclinic)	$P2_1/c$ (monoclinic)	$P2_1/n$ (monoclinic)	$P\bar{1}$ (triclinic)
a, Å	9.8289(9)	9.214 7(6)	11.98 97(8)	11.5805(6)	9.1283(14)
b, Å	9.9282(9)	9.495 2(6)	10.46 90(7)	16.6422(9)	9.5458(15)
c, Å	10.1097(9)	10.33 21(7)	17.26 06(11)	16.2986(9)	10.7303(16)
α, deg	83.565(2)	69.21 5(1)	90	90	106.226(3)
β, deg	62.227(1)	89.28 6(1)	99.00 8(1)	94.008(1)	95.045(3)
γ, deg	74.623(1)	61.62 6(1)	90	90	93.103(3)
temp, °C	−50(2)	−50(2)	−50(2)	−50(2)	−50(2)
Z	1	1	4	4	2
V, Å^3	841.57(13)	730.1 2(8)	2139. 8(2)	3133.5(3)	891.3(2)
D_{calcd}, g/cm^3	1.162	1.148	1.138	1.030	1.109
μ, mm^{-1}	0.471	0.532	0.386	0.340	0.446
R, R_w[a]	0.0456, 0.138[b]	0.0324, 0.0833[d]	0.0365, 0.0859[e]	0.0288, 0.0707[c]	0.0460, 0.1179[f]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [b] $w = [\sigma^2(F_o^2) + (0.0107P)^2 + (3.4463P)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. [c] $w = [\sigma^2(F_o^2) + (0.0256P)^2 + (1.7956P)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. [d] $w = [\sigma^2(F_o^2) + (0.0402P)^2 + (0.5617P)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. [e] $w = [\sigma^2(F_o^2) + (0.0265P)^2 + (3.0878P)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. [f] $w = [\sigma^2(F_o^2) + (0.0900P)^2 + (0.3761P)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

crystalline needles had formed, which were dried under vacuum (yield 0.17 g, 0.50 mmol, 88%). A satisfactory carbon analysis was not obtained in two attempts. Anal. Calcd for $C_{14}H_{34}NS_3Al$: C, 49.51; H, 10.09; N, 4.12. Found (average of two attempts): C, 48.63; H, 9.74; N, 4.03. ^{1}H NMR (C_6D_6): δ 2.05 (d, J = 6 Hz, 6, HN*Me*$_2$), 1.74 (s, 27, SC*Me*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 44.6 (s, S*C*Me$_3$), 37.5 (s, HN*Me*$_2$), 37.1 (s, SC*Me*$_3$). IR (Nujol, NaCl, cm^{-1}): ν(NH) 3176 s, 1363 s, 1282 m, 1213 m, 1157 s, 1108 m, 1056 s, 1012 s, 883 s, 819 m.

Al(S-*i*-Pr)$_3$(NMe$_2$Et) (7). $AlCl_3$ (0.27 g, 2.0 mmol) in ether (10 mL) was added to $LiAlH_4$ (0.24 g, 6.3 mmol) in ether (25 mL) at 0 °C. The solution turned cloudy immediately. After 6 h of stirring, EtNMe$_2$ (0.97 mL, 0.66 g, 9.0 mmol) and *i*-PrSH (2.4 mL, 1.9 g, 25 mmol) were added sequentially to the mixture. After 10 h of stirring, the reaction mixture was taken to dryness in vacuo to yield a white solid. The solid was dissolved in hexanes (15 mL), and the solution was filtered. The filtrate was collected and concentrated in vacuo to 5 mL. The flask was placed in the freezer (−35 °C), and after 10 h, colorless crystalline blocks had formed, which were isolated and dried in vacuo (yield 1.9 g, 5.9 mmol, 73%). A satisfactory carbon analysis was not obtained. Anal. Calcd for $C_{13}H_{32}NS_3Al$: C, 47.97; H, 9.91; N, 4.30. Found: C, 48.56; H, 9.77; N, 4.36. ^{1}H NMR (C_6D_6): δ 3.69 (septet, 3, SC*H*Me$_2$), 2.74 (q, 2, NMe$_2$C*H*$_2$CH$_3$), 2.03 (s, 6, N*Me*$_2$CH$_2$CH$_3$), 1.57 (d, 18, SCH*Me*$_2$), 0.41 (t, 3, NMe$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 51.8 (s, NMe$_2$*C*H$_2$CH$_3$), 42.0 (s, S*C*HMe$_2$), 32.6 (s, N*Me*$_2$CH$_2$CH$_3$), 29.7 (s, SCH*Me*$_2$), 6.3 (s, NMe$_2$CH$_2$*C*H$_3$). ^{27}Al NMR (C_6D_6): δ 151 ($W_{1/2}$ = 610 Hz). IR (Nujol, NaCl, cm^{-1}): 1475 m, 1448 m, 1427 m, 1398 w, 1326 w, 1309 w, 1251 s, 1199 s, 1151 s, 1081 s, 1051 s, 1020 s, 995 s, 916 s, 887 s, 806 w, 765 s, 622 m, 588 m.

Al(S-*t*-Bu)$_3$(NMe$_2$Et) (8). *t*-BuSH (1.7 mL, 1.4 g, 15 mmol) was added slowly to a toluene (10 mL) solution of AlH$_3$(NMe$_2$Et) (0.50 g, 4.8 mmol) at 0 °C. The solution turned cloudy after the thiol was added. The reaction mixture gradually became clear while it was stirred for 12 h. The mixture was taken to dryness under vacuum to yield a white solid. The solid was dissolved in a hexanes−ether mixture (1:1; 15 mL), and the solution was filtered. The filtrate was concentrated under vacuum to 5 mL. The flask was placed in the freezer (−35 °C), and after 12 h, colorless crystalline blocks had formed, which were isolated and dried under vacuum (yield 1.2 g, 3.3 mmol, 69%). Anal. Calcd for $C_{16}H_{38}NS_3Al$: C, 52.28; H, 10.44; N, 3.81. Found: C, 52.15; H, 10.24; N, 3.89. ^{1}H NMR (C_6D_6): δ 3.03 (q, 2, NMe$_2$C*H*$_2$CH$_3$), 2.15 (s, 6, N*Me*$_2$CH$_2$CH$_3$), 1.81 (s, 27, SC*Me*$_3$), 0.40 (t, 3, NMe$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H}NMR (C_6D_6): δ 50.4 (s, NMe$_2$*C*H$_2$CH$_3$), 45.2 (s, S*C*Me$_3$), 41.2 (s, N*Me*$_2$CH$_2$CH$_3$), 37.0 (s, SC*Me*$_3$), 5.40 (s, NMe$_2$CH$_2$*C*H$_3$). IR (Nujol, NaCl, cm^{-1}): 1426 m, 1399 m, 1360 s, 1238 m, 1215 m, 1198 m, 1168 s, 1150 s, 1098 m, 1077 s, 1018 s, 999 s, 915 s, 819 s, 765 s, 581 s.

X-ray Crystallography. X-ray crystallographic data were collected for [Al(*μ*-S-*t*-Bu)(S-*t*-Bu)$_2$]$_2$ (colorless blocks), [Al(*μ*-S-*i*-Pr)(S-*i*-Pr)$_2$]$_2$ (colorless needles), [*i*-Pr$_2$NH$_2$][Al(S-*t*-Bu)$_4$] (colorless columns), Al(S-*t*-Bu)$_3$(THF) (colorless blocks), and Al(S-*i*-Pr)$_3$(HNMe$_2$) (colorless needles). The crystals of [Al(*μ*-S-*i*-Pr)(S-*i*-Pr)$_2$]$_2$, Al(S-*t*-Bu)$_3$(THF), and Al(S-*i*-Pr)$_3$(HNMe$_2$) were grown from cold (−35 °C) hexanes solutions. The crystals of [*i*-Pr$_2$NH$_2$][Al(S-*t*-Bu)$_4$] and [Al(*μ*-S-*t*-Bu)(S-*t*-Bu)$_2$]$_2$ were hand selected by their shape from a crystalline mixture of the two compounds that had been grown from a cold (−35 °C) toluene solution. Crystal data are presented in Table 1.

Some details concerning the crystallographic studies are as follows:

1: The Laue symmetry was determined to be $\bar{1}$, and the space group was shown to be either $P1$ or $P\bar{1}$. Space group $P\bar{1}$ was established by refinement. The molecule lies on a crystallographic inversion center, with 1/2 molecule per asymmetric unit. One of the three independent *tert*-butyl groups is disordered 50:50 over two different orientations.

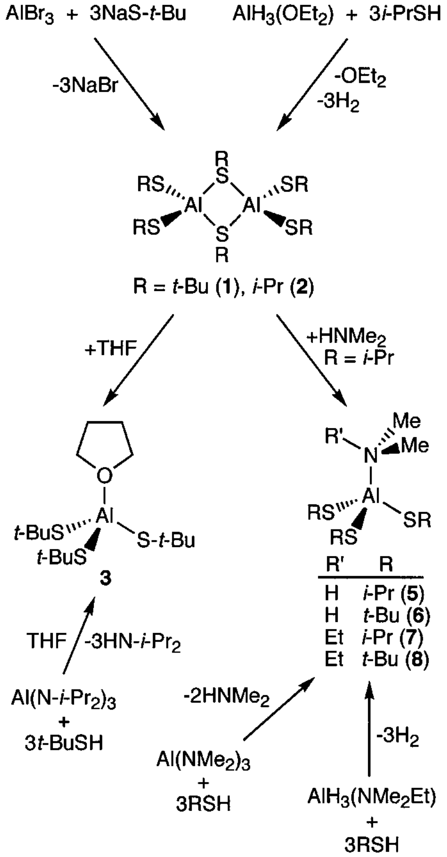
2: The Laue symmetry was determined to be $\bar{1}$, and the space group was shown to be either $P1$ or $P\bar{1}$. Space group $P\bar{1}$ was established by refinement. The asymmetric unit consists of one-half molecule situated about an inversion center. One of the thiolate ligands was found to be disordered 65:35 over two slightly different orientations.

3: The Laue symmetry was determined to be $2/m$, and from the systematic absences noted the space group was shown unambiguously to be $P2_1/c$. The THF ligand is disordered 50:50 over two slightly different positions.

4: The Laue symmetry was determined to be $2/m$, and from the systematic absences noted the space group was shown unambiguously to be $P2_1/n$.

5: The Laue symmetry was determined to be $\bar{1}$, and the space group was shown to be either $P1$ or $P\bar{1}$. Space group $P\bar{1}$ was established by refinement. One of the isopropyl groups was found to be disordered approximately 50:50 over two slightly different

Scheme 1



orientations, and this was modeled using rigid bodies based on one of the ordered ligands.

Results and Discussion

Synthesis. Scheme 1 is a summary of the synthetic results. The reaction of $AlBr_3$ with NaS-*t*-Bu in ether produced [Al(μ-S-*t*-Bu)(S-*t*-Bu)$_2$]$_2$ (**1**) in high yield (Scheme 1). The analogous reactions using $AlCl_3$ in place of $AlBr_3$ failed to produce **1** or other tractable products, presumably because of the formation of sodium salt compounds (i.e., Na[Al(SR)$_{4-n}$Cl$_n$]). Surprisingly, the reaction of $AlBr_3$ with NaS-*i*-Pr did not yield [Al(μ-S-*i*-Pr)(S-*i*-Pr)$_2$]$_2$ (**2**), the 2-propanethiolate analogue of **1**. It is not clear why this reaction failed, but it is possible the smaller 2-propanethiolate ligand also permitted the formation of undesirable salt compounds (i.e., Na[Al(SR)$_{4-n}$Br$_n$]). Compound **2** was finally prepared (Scheme 1) by reacting 2-propanethiol with $AlH_3(OEt_2)$, which had been prepared in situ.[15] A problem with this preparation was the presence of a persistent unidentified impurity that necessitated the use of a two-step purification process to obtain pure **2**. The yield of **2** after the two purification steps was around 50%.

Compound **1** decomposed slowly at room temperature in the glovebox (a few percent/day), rapidly in boiling hexane, and rapidly at approximately 90 °C during an attempted sublimation. Compound **2** was more stable. In a sublimation apparatus it melted at approximately 95 °C and distilled at 110−115 °C/0.05 mmHg, condensing on the coldfinger (−78 °C) as a solid.

In the analogous gallium thiolate chemistry, the syntheses of [Ga(μ-SR)(SR)$_2$]$_2$ (R = *i*-Pr or *t*-Bu) and the amine adduct Ga(S-*t*-Bu)$_3$(HNMe$_2$) were accomplished by reacting the amides Ga(N-*i*-Pr$_2$)$_3$ and Ga(NMe$_2$)$_3$, respectively, with the alkanethiols.[1] In the reaction involving Ga(N-*i*-Pr$_2$)$_3$ and *i*-PrSH, the salt intermediate [*i*-Pr$_2$NH$_2$][Ga(S-*i*-Pr)$_4$] was isolated, which was converted thermally to [Ga(μ-S-*i*-Pr)(S-*i*-Pr)$_2$]$_2$. In an effort to mimic the gallium chemistry, we attempted the synthesis of **1** by reacting Al(N-*i*-Pr$_2$)$_3$ with *t*-BuSH. When the reaction was carried out in THF solvent, the THF adduct Al(S-*t*-Bu)$_3$(THF) (**3**) was isolated (Scheme 1). Compound **3** was prepared more directly and in essentially quantitative yield by simply adding THF to **1**. Heating solid samples or toluene solutions of **3** under vacuum failed to remove THF from **3** and convert it to **1**.

Reactions of Al(N-*i*-Pr$_2$)$_3$ with *t*-BuSH in diethyl ether produced, after workup, a crystalline mixture containing **1** and [*i*-Pr$_2$NH$_2$][Al(S-*t*-Bu)$_4$] (**4**) (both identified by X-ray crystallography). Proton NMR spectra of both the crude mixture obtained from the synthesis after solvent removal and the crystalline mixture obtained after the workup showed resonances consistent with **1**, **4**, HN-*i*-Pr$_2$, and *t*-BuSH, as well as other unidentified peaks. Unlike the smooth thermal conversion of [*i*-Pr$_2$NH$_2$][Ga(S-*i*-Pr)$_4$] to [Ga(μ-S-*i*-Pr)(S-*i*-Pr)$_2$]$_2$,[1] the attempted thermal conversion of **4** to **1** in the solid state or in solution resulted in decomposition. Exhaustive extractions with hexanes or Soxhlet extraction using pentane from the crude product mixture permitted the isolation of **1**, but **4** was not separated completely from **1** by the extraction procedure or fractional crystallization. The attempted direct synthesis of **4** by reacting **1** with *t*-BuSH and HN-*i*-Pr$_2$ in hexanes or ether produced, according to NMR spectra, a crude product mixture containing, again, **1**, **4**, HN-*i*-Pr$_2$, and *t*-BuSH. These observations suggested that **1**, **4**, HN-*i*-Pr$_2$, and *t*-BuSH were in equilibrium and that attempts to obtain spectra of **4** free of **1**, HN-*i*-Pr$_2$, and *t*-BuSH would not be possible.

In contrast to the results obtained using Al(N-*i*-Pr$_2$)$_3$ as a reagent, reactions of [Al(NMe$_2$)$_3$]$_2$ with the alkanethiols produced the stable amine adducts Al(SR)$_3$(HNMe$_2$) (R = *i*-Pr (**5**) or *t*-Bu (**6**)). Compound **5** was also prepared in essentially quantitative yield by reacting **2** with HNMe$_2$. Similarly, AlH$_3$(NMe$_2$Et) reacted with RSH to yield Al(SR)$_3$(NMe$_2$Et) (R = *i*-Pr (**7**) or *t*-Bu (**8**)). A problem with an unidentified impurity was encountered when commercially obtained AlH$_3$(NMe$_2$Et) was used to prepare **7**, although an analogous impurity was not observed in the preparation of **8**. Attempts to separate the impurity from **7** by using sublimation or fractional crystallization failed. Pure samples of **7** were finally synthesized by using freshly prepared AlH$_3$(NMe$_2$Et) as the starting material.

During attempts to sublime **5** and **6**, the compounds melted and, upon further heating, they condensed on the coldfingers (−78 °C) as solids (at 85−90 °C/0.05 mmHg and 90−95 °C/0.05 mmHg, respectively). Compounds **7** and **8** sublimed cleanly under vacuum at 125 and 95 °C, respectively.

X-ray Crystallographic Studies. The X-ray crystal structures of [Al(μ-S-*t*-Bu)(S-*t*-Bu)$_2$]$_2$ (**1**), [Al(μ-S-*i*-Pr)(S-

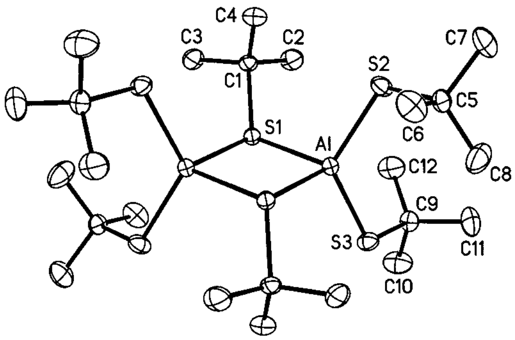


Figure 1. View of the $[Al(\mu\text{-}S\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)_2]_2$ (**1**) molecule, showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogen atoms omitted.

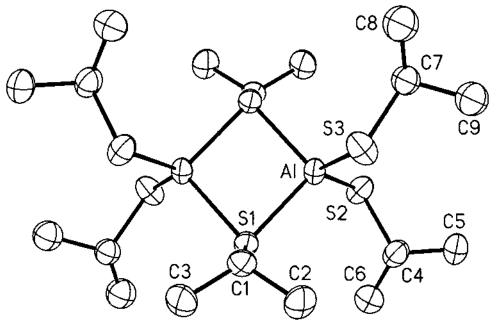


Figure 2. View of $[Al(\mu\text{-}S\text{-}i\text{-}Pr)(S\text{-}i\text{-}Pr)_2]_2$ (**2**), showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogen atoms omitted.

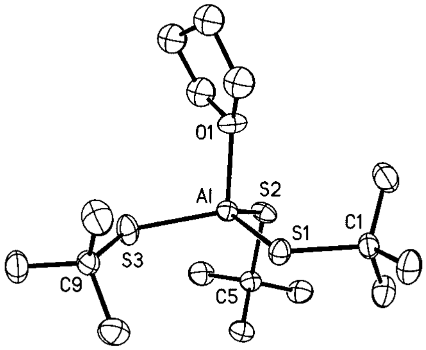


Figure 3. View of the $Al(S\text{-}t\text{-}Bu)_3(THF)$ (**3**) molecule, showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogen atoms omitted.

i-Pr)$_2$]$_2$ (**2**), $Al(S\text{-}t\text{-}Bu)_3(THF)$ (**3**), $[i\text{-}Pr_2NH_2][Al(S\text{-}t\text{-}Bu)_4]$ (**4**), and $Al(S\text{-}i\text{-}Pr)_3(HNMe_2)$ (**5**) were determined (Figures 1−5, respectively). The molecules of **1** and **2** lie on crystallographic inversion centers, with 1/2 molecule per asymmetric unit. Selected bond distances and angles for **1**−**5** and two closely related gallium molecules are presented in Table 2.

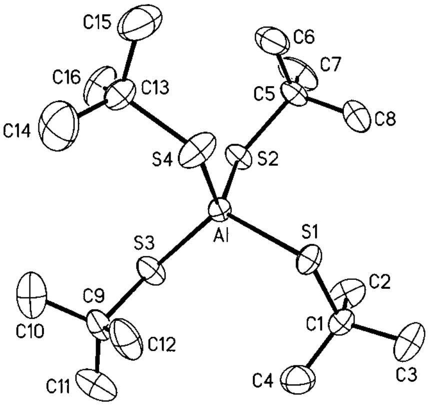


Figure 4. View of the anion in $[i\text{-}Pr_2NH_2][Al(S\text{-}t\text{-}Bu)_4]$ (**4**), showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogen atoms omitted.

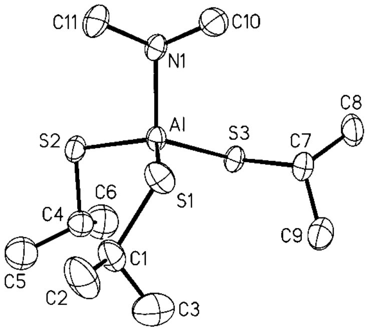


Figure 5. View of the $Al(S\text{-}i\text{-}Pr)_3(HNMe_2)$ (**5**) molecule, showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogen atoms omitted.

Compounds **1** and **2** are dimeric with two bridging thiolate ligands. The coordination geometries at the aluminum atoms can be described as distorted tetrahedral. The central cores of the molecules have *anti*-$Al(\mu\text{-}SR)_2Al$ four-member rings. The four-member ring in **1** is a near perfect square while in **2** it is a rhombus with internal angles 84 and 96°. An *anti*-$Al(\mu\text{-}SR)_2Al$ four-member ring was also found in the aluminum alkyl and aryl complexes $[R_2Al(\mu\text{-}SR')]_2$ ($R = Me$, $R' = Me$,[9] $SiPh_3$,[10] C_6F_5;[8] $R = Mes$, $R' = CH_2Ph$ or Ph;[10] $R = R' = CH_2\text{-}t\text{-}Bu$)[11] and $[Ga(\mu\text{-}S\text{-}i\text{-}Pr)(S\text{-}i\text{-}Pr)_2]_2$.[1] The three-coordinate bridging sulfur atom in **1** is significantly flattened compared to that of **2** ($\Sigma(X{-}S1{-}Y) = 329°$ vs 302°, respectively) and $[Ga(\mu\text{-}S\text{-}i\text{-}Pr)(S\text{-}i\text{-}Pr)_2]_2$ ($\Sigma(X{-}S1{-}Y) = 301°$).[1] The difference in planarity at sulfur is related to the bulk of the sulfur substituent with the bulkier t-Bu group causing a greater flattening than the smaller i-Pr group. Another consequence of the steric bulk of the substituents is manifested in the Al−S bond distances, which are longer by 0.01−0.02 Å in **1** than in **2**. The Al−S1 and Al−S1′ distances within the four-member rings of both **1** and **2** differ only slightly. The Al−S distances in **2** are shorter than the corresponding distances in $[Ga(\mu\text{-}S\text{-}i\text{-}Pr)(S\text{-}i\text{-}Pr)_2]_2$,[1] which reflects the difference in M^{3+} radii (Al^{3+} 0.57 Å vs Ga^{3+} 0.62 Å).[16]

The structures of the ligand adducts **3** and **5** resemble those of $AlH(S\text{-}t\text{-}Bu)_2(NMe_3)$,[12] $Al(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3(THF)$,[5] $Ga(S\text{-}t\text{-}Bu)_3(HNMe_2)$,[1] and $In(S\text{-}t\text{-}Bu)_3(py)$.[3] Molecules of **3** and **5** can be described as having distorted trigonal pyramidal geometries with THF and $HNMe_2$, respectively, occupying the apical positions. The aluminum and three sulfur atoms in **3** and **5** approach planarity ($\Sigma(S{-}M{-}S) = 348°$ (**3**) and 345° (**5**)) with the Al atoms lying 0.44 and 0.51 Å, respectively, out of the planes defined by the sulfur atoms. In $Al(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3(THF)$,[5] $Ga(S\text{-}t\text{-}Bu)_3(HNMe_2)$,[1] and

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(16) Emsley, J. *The Elements*; Clarendon Press: Oxford, U.K., 1989.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Al(\mu\text{-S-}t\text{-Bu})(S\text{-}t\text{-Bu})_2]_2$ (**1**), $[Al(\mu\text{-S-}i\text{-Pr})(S\text{-}i\text{-Pr})_2]_2$ (**2**), $Al(S\text{-}t\text{-Bu})_3(THF)$ (**3**), $[i\text{-Pr}_2NH_2][Al(S\text{-}t\text{-Bu})_4]$ (**4**), $Al(S\text{-}i\text{-Pr})_3(HNMe_2)$ (**5**), and the Related Gallium Complexes $[Ga(\mu\text{-S-}i\text{-Pr})(S\text{-}i\text{-Pr})_2]_2$ and $Ga(S\text{-}t\text{-Bu})_3(HNMe_2)$

param	**1**	**2**	$[Ga(\mu\text{-S-}i\text{-Pr})(S\text{-}i\text{-Pr})_2]_2$	**3**	**4**	**5**	$Ga(S\text{-}t\text{-Bu})_3(HNMe_2)$
M−S1	2.3507(18)	2.3398(9)	2.3799(6)	2.2236(12)	2.2753(7)	2.2261(14)	2.2477(5)
M−S2	2.2096(18)	2.1804(9)	2.2106(7)	2.2207(12)	2.2719(7)	2.2150(14)	2.2402(5)
M−S3	2.2085(18)	2.1880(10)	2.2188(6)	2.2223(12)	2.2476(8)	2.2298(14)	2.2649(4)
M−S4					2.2402(8)		
M−S1′	2.3434(18)	2.3347(9)	2.3611(6)				
M−E1[a]				1.906(2)		1.967(3)	2.0758(14)
S1−M−S2	107.75(7)	111.57(4)	110.07(2)	122.31(5)	116.30(3)	120.39(6)	115.117(17)
S1−M−S3	110.99(7)	107.52(3)	108.47(2)	115.11(5)	118.23(3)	115.31(6)	113.393(18)
S1−M−S4					90.54(3)		
S2−M−S3	123.82(8)	120.97(4)	122.33(3)	110.98(5)	91.47(3)	109.18(6)	119.264(18)
S1−M−S1′	89.68(6)	96.44(3)	95.07(2)				
S2−M−S4					118.21(3)		
S2−M−S1′	112.68(7)	108.19(3)	108.33(2)				
S3−M−S4					124.62(4)		
S3−M−S1′	106.66(7)	109.37(4)	109.13(2)				
M−S−M	90.32(6)	83.56(3)	84.93(2)				
E1−M−S1				105.56(7)		100.68(10)	100.56(5)
E1−M−S2				94.49(8)		101.30(10)	107.88(4)
E1−M−S3				104.23(8)		107.82(10)	96.60(4)
$\Sigma(X-S_{bridge}-Y)$	329	302	301				

[a] E = N except for compound **3**, where E = O.

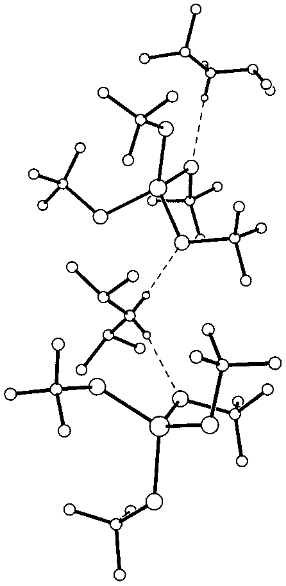

Figure 6. Ball-and-stick plot of $[i\text{-Pr}_2NH_2][Al(S\text{-}t\text{-Bu})_4]$ (**4**), showing the N−H···S interactions between $[(i\text{-Pr})_2NH_2]^+$ and $[Al(S\text{-}i\text{-Pr})_4]^-$.

$In(S\text{-}t\text{-Bu})_3(py)$,[3] for comparison, the three S−M−S angles sum to 341, 348, and 351°, respectively.

The anion in the salt **4** has a distorted tetrahedral geometry resembling the anions in $[(i\text{-Pr})_2NH_2][Ga(S\text{-}i\text{-Pr})_4]$,[1] $[i\text{-Pr}_4N][Ga(SEt)_4]$, and $[Et_4N][Ga(SPh)_4]$.[17] In the AlS_4 core, the S−Al−S angles vary over the wide range of 90−125°. The S−Ga−S angles in $[Ga(S\text{-}i\text{-Pr})_4]^-$ and $[Ga(SPh)_4]^-$ are in the ranges 97−118 and 100−115°, respectively, while those in the less sterically crowded anion $[Ga(SEt)_4]^-$ are all ≈109°.[17] In the solid, the cation $[(i\text{-Pr})_2NH_2]^+$ is associated with the $[Al(S\text{-}i\text{-Pr})_4]^-$ anions via weak N−H···S1 and N−H···S2 hydrogen bonding (Figure 6). The hydrogen bonding (average N···S = 3.38 Å) makes the Al−S bonds (S1 and S2) slightly longer (by <0.035 Å) than the other two Al−S bonds.

The terminal Al−S distances in **1**−**5** range from 2.18 to 2.28 Å, with the shortest distances found in the 2-propanethiolate dimer **2** and, as expected, the longest in the sterically congested anion **4**. These distances are within the range of terminal distances found in $Al(S\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)_3$ (average 2.185(2) Å),[4] $n\text{-}BuAl(S\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2$ (average 2.191(2) Å), $t\text{-}BuAl(S\text{-}2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2$ (average 2.195(2) Å), $Al(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3(THF)$ (average 2.227(2) Å),[5] and $AlH(S\text{-}t\text{-Bu})_2(NMe_3)$ (average 2.2396(5) Å).[12] The $Al-S_{bridge}$ bond distances (2.3347(9)−2.3507(18) Å) in **1** and **2** are slightly shorter than the $Al-S_{bridge}$ distances reported for $[R_2Al(\mu\text{-}SR')]_2$ compounds, where R = Mes and R′ = CH_2Ph or Ph,[10] R = Me and R′ = $SiPh_3$ or C_6F_5,[8,10] R = R′ = $CH_2\text{-}t\text{-Bu}$,[11] and R = t-Bu and R′ = $2,4,6\text{-}i\text{-}Pr_3C_6H_2$ (2.353(2)−2.424(4) Å).[5] The Al−O distance in **3** (1.906(2) Å) is slightly longer than the Al−O distance in $Al(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3(THF)$ (1.859(4) Å),[5] and the Al−N distance in **5** (1.967(3) Å) is shorter than the Al−N distance in $AlH(S\text{-}t\text{-Bu})_2(NMe_3)$ (2.020(1) Å).[12]

NMR Studies. In the ^1H NMR spectrum of **1**, two singlets in a 2:1 ratio corresponding to the terminal and bridge thiolate ligands, respectively, were observed, which is consistent with the solid-state structure. On the basis of the solid-state structure of **2**, the ^1H NMR spectrum would be expected to consist of three doublets of equal intensity in the methyl region, but in fact, spectra for **2** were temperature dependent. The room-temperature ^1H NMR spectrum in toluene-d_8 consisted of two broad resonances in a 2:1 integral ratio in the isopropyl methine region and a single broad resonance in the isopropyl methyl region. As the temperature of the probe was lowered to −40 °C, the two methine resonances sharpened into septets and the broad signal in the methyl region separated into two doublets in a 2:1 integral ratio. The same spectrum was observed at −90 °C, the lowest temperature examined. The low-temperature spectra are consistent with the dimer structure observed in the solid state for **2** only if there is another low-energy fluxional process

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(17) Maelia, L. E.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1896.

occurring that would make the four terminal isopropyl methyl groups equivalent. A fluxional process involving an umbrella-like inversion at the 3-coordinate bridging sulfur atom coupled with rapid S−C bond rotation is a possible explanation for the observations.[1]

The ^{1}H and ^{13}C NMR spectra of **3** and **5**−**8** are consistent with the structures shown in Scheme 1 and the solid-state structures. In the ^{1}H NMR spectrum of **5**, a very broad peak was observed for N*H*, but in **6,** the analogous resonance was not located. In both **5** and **6**, the amine methyl groups appear as doublets due to coupling with N*H*.

Aluminum-27 NMR spectra for **1**, **3**, and **7** showed chemical shifts of 122, 133, and 151 ppm, respectively, which are within the range of previously observed values.[18,19]

Conclusion

The aluminum alkanethiolate complexes $[Al(\mu\text{-}SR)(SR)_2]_2$ (R = *t*-Bu and *i*-Pr) and the amine adducts $Al(SR)_3(R'NMe_2)$ (R = *i*-Pr, R′ = H or Et; R = *t*-Bu, R′ = H or Et) were synthesized. The synthesis of $Al(S\text{-}i\text{-}Pr)_3$ and $Al(S\text{-}t\text{-}Bu)_3$ completes the series of $M(SR)_3$ compounds, where M = Al, Ga, or In and R = *i*-Pr or *t*-Bu.[1,3] $[Al(\mu\text{-}S\text{-}i\text{-}Pr)(S\text{-}i\text{-}Pr)_2]_2$ and $[Al(\mu\text{-}S\text{-}t\text{-}Bu)(S\text{-}t\text{-}Bu)_2]_2$ are the first structurally characterized examples of homoleptic aluminum *alkane*thiolate complexes.

The motivation for this synthetic study was the possible use of the aluminum alkanethiolate compounds as chemical vapor deposition precursors to aluminum sulfide films. The new compounds $[Al(\mu\text{-}S\text{-}i\text{-}Pr)(S\text{-}i\text{-}Pr)_2]_2$ and $Al(SR)_3(HNMe_2)$ (R = *i*-Pr or *t*-Bu) have the most favorable physical properties for use as precursors because they are liquids at moderate temperatures and distill without decomposition. Studies using these complexes as precursors in a low-pressure chemical vapor deposition process are in progress. Preliminary results suggest that the prepared films are highly air sensitive,[20] which has complicated their characterization.

Acknowledgment. Dr. James Korp provided technical assistance with the crystal structure determinations. This work was supported in part by the Robert A. Welch Foundation, the MRSEC Program of the National Science Foundation under Award No. DMR-9632667, and the State of Texas through the Texas Center for Superconductivity at the University of Houston.

Supporting Information Available: Five X-ray crystallographic files in CIF format for **1**−**5.** This material is available free of charge via the Internet at http://pubs.acs.org.

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