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Notes

Alkylaluminum Derivatives of 2-Thiophenemethanol and 2-Furanmethanol. Molecular Structure of a Novel Organoaluminum Compound, $\{[(Me_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3S)_6]Al\}$, Containing Four- and Six-Coordinate Aluminum Centers

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Summary: The reaction of trialkylaluminum derivatives, R_3Al *(R = Me or Et), with alcohols such as 2-thiophenemethanol or 2-furanmethanol yields* $\{[(R_2M)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3E)_6]M\}$ *(M = Al; E = S, R = Me (**1a**), Et (**1b**); E = O, R = Me (**2**) and the corresponding alkane, RH, in high yields. The resulting complex metal alkoxides have been characterized by* ^1H *and* ^{13}C *NMR spectroscopy. The structure of **1a** was determined by single crystal X-ray diffraction techniques. **1a** was assigned to the orthorhombic cell system, space group Pbcn (No. 60), with cell constants* $a = 18.153(2)$ Å, $b = 11.176(2)$ Å, $c = 22.820(2)$ Å, *and* $Z = 4$. *The structure was refined to a final* $R = 5.99\%$ ($R_w = 5.39\%$) *based on 1422* ($I_o \geq 2.5\sigma(I)$) *observed reflections. The central core of* $\{[(Me_2Al)_3(\mu\text{-}OCH_2\text{-}C_4H_3S)_6]Al\}$ *contains an octahedral aluminum (III) bound through six bridging alkoxide units to three organoaluminum* Me_2Al- *moieties. In solution, the methylene protons of the 2-thiophenemethoxide ligand in **1a** and the 2-furanmethoxide ligand in **2** are diastereotopic, and the full spectrum is consistent with the solid state structure. The room temperature* ^1H *NMR spectra of compound **1b** is also consistent with this structure but show the additional feature of diastereotopic* CH_2 *groups in the ethyl moiety.*

Introduction

Applications of aluminum complexes in organic synthesis are well documented, and a number of organoaluminum complexes containing aryl, alkyl, alkoxy, amido, or thiolato ligands have been proposed as intermediates in regio- and stereoselective organic synthesis.[1-4] Further interest in these complexes is derived from the fact that they have the potential to serve as precursors for ceramic materials and as models for aluminum oxide catalysts. Results from our laboratory have established that potentially ambidentate ligands such as 2-mercaptopyridine and *l*-ephedrine react with simple alkylaluminum compounds to give a unique complex, $(R_2AlSPy)_2$, with a head-to-head bridged 2-pyridinethiolato ligand[5] and a dimeric complex, $(R_2Al\text{-}l\text{-ephedrine})_2$, with a five-coordinate aluminum.[6] Earlier several groups explored aluminum alkoxides and established that these species give a variety of structural types varying from monomeric derivatives when very bulky substituents are present[7-10] to tetrameric species with six-coordinate aluminum.[11-13] We now report the synthesis and characterization of dialkylaluminum complexes derived from 2-thiophenemethanol and 2-furanmethanol. The molecular structure of a novel organoaluminum compound, $\{[(Me_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3S)_6]Al\}$, containing both four- and six-coordinate aluminum centers as determined by single crystal X-ray diffraction techniques, is reported.

Experimental Section

General Data. All solvents were purified and dried by standard techniques.[14] Argon gas was purified by passing it through a series of columns containing Deox catalyst (Alfa), phosphorus pentoxide, and calcium sulfate. The trialkylaluminum derivatives (Me_3Al, 2 M solution in toluene (Aldrich); Et_3Al, 1.9 M solution in toluene (Aldrich); 2-thiophenemethanol (Aldrich), and 2-furanmethanol (Aldrich)) were used as received. All glassware used in the synthetic work was oven dried. The aluminum derivatives are both oxygen and water sensitive, so standard Schlenk line techniques were employed. ^1H and ^{13}C NMR spectra were recorded on either a QE-300 NMR or a GN-300 NMR General Electric spectrometer. The ^1H and ^{13}C chemical shifts were referenced to benzene peaks ($\delta = 7.15$ ppm for ^1H and $\delta = 128.00$ ppm for ^{13}C) while ^{27}Al chemical shifts were

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referenced to an external 1 M solution of $Al(NO_3)_3$ in D_2O. Variable temperature ^1H NMR spectra were recorded on a GN-300 NMR spectrometer in toluene-d_8 solutions of the respective compounds and were referenced to the residual CH_3 peak of toluene (^1H, δ = 2.09 ppm). Elemental analysis on selected compounds was performed by Galbraith Laboratories, Knoxville, TN.

Reaction of Me_3Al with 2-Thiophenemethanol To Give 1a. 2-Thiophenemethanol (1.0 mL, 7.95 mmol) was suspended in pentane (60 mL), and Me_3Al solution (3.98 mL, 7.95 mmol) was syringed in as quickly (ca. 5 min) as permitted by the evolution of methane gas. The reaction was rapid and vigorous, as evidenced by gas evolution and the precipitation of the product. To ensure its completion the reaction mixture was stirred for 2 h. The solution was decanted, and the white precipitate was washed with 10–15 mL of pentane and dried under vacuum. The product was recrystallized from 10 mL of toluene at room temperature. This solid was identified as $\{[(Me_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3S)_6]Al\}$. Yield: 90%. Anal. Calcd for $C_{36}H_{48}O_6S_6Al_4$: C, 49.30; H, 5.52. Found: C, 49.18; H, 5.52. ^1H NMR (C_6D_6; δ, ppm): −0.68 (s, 3H, Al–Me); 5.39 (d, ^2J = 13 Hz, 1H), 5.28 (d, ^2J = 13 Hz, 1H) (OCH_2); 7.08 (m, 1H), 6.79 (m, 1H), 6.61 (m, 1H) (2-C_4H_3S). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): −8.5 (Al–Me); 60.5 (OCH_2); 127.3, 129.6, 140.4 (2-C_4H_3S).

Reaction of Et_3Al with 2-Thiophenemethanol To Give 1b. The procedure for this reaction is the same as described for **1a**, using 2-thiophenemethanol (1.0 mL, 7.95 mmol) and Et_3Al solution (4.18 mL, 7.95 mmol). The solid was isolated and purified as described for **1a**. This solid was identified as $\{[(Et_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3S)_6]Al\}$. Yield: 60%. Anal. Calcd for $C_{42}H_{60}O_6S_6Al_4$: C, 52.48; H, 6.29. Found: C, 51.77; H, 6.33. ^1H NMR (C_6D_6; δ, ppm): −0.00 (m, 1H), 0.23 (m, 1H) (Al–CH_2); 1.04 (t, 3H, ^3J = 8 Hz, Al–CH_2*Me*); 5.45 (d, ^2J = 13 Hz, 1H), 5.25 (d, ^2J = 13 Hz, 1H) (OCH_2); 7.14 (m, 1H), 6.82 (m, 1H), 6.66 (m, 1H) (2-C_4H_3S). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 1.8 (Al–CH_2); 9.3 (Al–CH_2*Me*); 60.6 (OCH_2); 127.5, 129.6, 140.7 (2-C_4H_3S).

Reaction of Me_3Al with 2-Furanmethanol To Give 2. To a stirred solution of 0.86 mL of 2-furanmethanol (0.98 g, 9.95 mmol) in 20 mL of diethyl ether, a dropwise addition of Me_3Al (5.0 mL, 9.95 mmol) was made over a period of ca. 5 min. Upon addition of Me_3Al, a vigorous evolution of gas was observed. The resulting solution was stirred for a period of an additional 1.5 h. Removal of volatiles under vacuum resulted in a white solid. The product was recrystallized by dissolving it in 12 mL of a pentane/diethyl ether (5:1) solution and then cooled to −20 °C to recrystallize the product. The solid was collected, washed with 10–15 mL of cold pentane, and dried under vacuum. This solid was identified as $\{[(Me_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3O)_6]Al\}$. Yield: 74%. Anal. Calcd for $C_{36}H_{48}O_{12}Al_4$: C, 55.38; H, 6.20. Found: C, 54.84; H, 6.12. ^1H NMR (C_6D_6; δ, ppm): −0.64 (s, 3H, Al–Me); 5.11 (d, ^2J = 13 Hz, 1H), 4.94 (d, ^2J = 13 Hz, 1H) (OCH_2); 6.99 (m, 1H), 6.25 (m, 1H), 5.94 (m, 1H) (2-C_4H_3O). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): −10.4 (Al–Me); 57.8 (OCH_2); 110.6, 110.8, 143.2, 152.6 (2-C_4H_3O).

X-ray Structure Determination of $\{[(Me_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3S)_6]Al\}$, 1a. Crystals of **1a** were grown from a toluene solution at 20 °C. A crystal suitable for X-ray diffraction studies was mounted in a thin walled capillary tube in a drybox, plugged with grease, removed from the dry box, flame sealed, mounted on a goniometer head, and placed on a Nicolet P3/V diffractometer for data collection. Parameters from the crystal structure determination are presented in Table 1.

Table 1. Experimental Parameters for the X-ray Diffraction Study of $\{[(Me_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3S)_6]Al\}$, 1a

compd	$\{[(Me_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3S)_6]Al\}$
formula	$C_{36}H_{48}O_6S_6Al_4$
mol wt	877.09
cryst prep	recrystallized from toluene 20 °C
cryst color	colorless crystals
cryst syst	orthorhombic
space group	*Pbcn* (No. 60)
Z	4 (tetramers)
cell constants	determined from 25 high angle reflections in the 2θ range 40–80°
a (Å)	18.153(2)
b (Å)	11.176(2)
c (Å)	22.820(2)
vol (Å^3)	4629.6(9)
dens (calc) (g cm^{-3})	1.258
radiation type	Cu K$\bar{\alpha}$, λ = 1.541 84 Å with a Ni filter
temp (°C)	(room temperature) 20
type of data collcn	$\theta/2\theta$ scan
2θ scan range (deg)	8–100
octants used	*hkl*: *h*, 0–20; *k*, 0–12; *l*, 0–25
scan rate (deg min^{-1})	variable, 3–8
std reflns	3 measured per every 100 reflections, maximum deviation from the standard observed was 9%
no. of data collcd	2699
scan width	1.00–1.20
background/scan ratio	0.50
no. of unique reflns	2090
no. of obsd reflns	1422 with $(I_o) \geq 2.5\,\sigma(I)$
linear absn coeff (μ) (cm^{-1})	39.37
F(000) (electrons)	2304
abs corr	empirical, ψ scans
no. of params refined	250
obsd/param ratio	5.7:1
$R = \sum(\|F_o\| - \|F_c\|/\sum\|F_o\|$ (%)	5.99
$R_w = [\sum(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$ (%)	5.39
overall shift/esd	0.000
max shift/esd	0.001
residual electron dens (e Å^{-3})	0.34, 1.29 Å from C9

The crystal of **1a** was found to be in the orthorhombic cell system. Lattice constants were verified by axial photographs, and the crystal was assigned to the space group *Pbcn* (No. 60) which was later confirmed by successful refinement of the structure. Unit cell parameters were obtained from the least squares fit of the angular settings of the 25 high angle reflections with 40° < 2Θ < 80°. Data reduction was carried out using the SHELXTL program.[15] The direct methods routine produced an acceptable solution for the **1a** structure. Full-matrix least-squares refinement was carried out using SHELX-76.[16] The data were corrected for Lorentz and polarization effects, and scattering factors for neutral carbon, oxygen, sulfur, and aluminum atoms were used.[17] An empirical absorption correction was applied. Atomic coordinates and isotropic thermal parameters are listed in Table 2. Selected bond distances and angles are given in Table 3.

Results and Discussion

Synthesis. The hydroxyl proton in 2-thiophenemethanol and 2-furanmethanol reacts rapidly at room temperature with trialkylaluminum derivatives in a 1:1 stoichiometry, liberating the alkane and affording the corresponding organometallic alkoxides, $\{[(R_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3E)_6]Al\}$ (E = O, S), in high yield according to the general reaction shown in Scheme 1.

The most common path for the reaction of an alcohol with a trialkylmetal derivative yields a simple bridged dimer or trimer and is almost certainly the first step in the

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Table 2. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms in {[Me$_2$Al)$_3$(μ-OCH$_2$-2-C$_4$H$_3$S)$_6$]Al}, 1a

atom	x	y	z	U_{eq}[a] (Å^2)
Al1	0.00000	0.0424(3)	0.75000	0.038(1)
Al2	0.1396(1)	−0.0882(2)	0.7497(1)	0.0507(8)
Al3	0.00000	0.3023(3)	0.75000	0.057(1)
S1	0.1062(2)	−0.1094(3)	0.5662(1)	0.105(1)
S2	0.1214(2)	−0.0536(3)	0.9312(1)	0.107(1)
S3	0.0205(2)	0.2122(3)	0.5584(1)	0.107(1)
O1	0.0548(2)	−0.0738(4)	0.7066(2)	0.042(2)
O2	0.0896(2)	0.0237(4)	0.7930(2)	0.042(2)
O3	0.0337(2)	0.1764(4)	0.7053(2)	0.044(2)
C1	0.2280(4)	−0.0249(8)	0.7101(4)	0.078(4)
C2	0.1519(4)	−0.2442(7)	0.7876(4)	0.079(4)
C3	0.0791(5)	0.3972(7)	0.7867(4)	0.096(4)
C4	0.0305(4)	−0.1650(7)	0.6676(4)	0.067(4)
C5	0.0888(5)	−0.1998(8)	0.6242(3)	0.059(4)
C6	0.1349(5)	−0.2964(8)	0.6280(4)	0.064(4)
C7	0.1865(6)	−0.290(1)	0.5795(5)	0.109(6)
C8	0.1769(6)	−0.196(1)	0.5447(5)	0.108(5)
C9	0.1255(4)	0.0977(8)	0.8353(3)	0.060(3)
C10	0.1673(5)	0.0264(8)	0.8791(3)	0.062(4)
C11	0.2458(4)	0.0072(8)	0.8795(3)	0.055(3)
C12	0.2594(6)	−0.073(1)	0.9264(6)	0.127(7)
C13	0.1989(6)	−0.112(1)	0.9563(5)	0.109(6)
C14	0.0939(4)	0.1833(7)	0.6648(3)	0.059(3)
C15	0.0784(4)	0.2608(8)	0.6120(3)	0.061(4)
C16	0.1079(5)	0.3747(8)	0.6003(4)	0.074(4)
C17	0.0830(8)	0.408(1)	0.5439(7)	0.142(8)
C18	0.0358(7)	0.335(1)	0.5174(5)	0.117(6)

[a] $U_{eq} = {}^1/_3 \sum_i \sum_j U_{ij} a_i^* \cdot a_j \bar{a}_i \cdot \bar{a}_j$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for {[(Me$_2$Al)$_3$(μ-OCH$_2$-2-C$_4$H$_3$S)$_6$]Al}, 1a[a]

Al1–O1	1.912(5)	Al1–O1–Al2	102.6(2)
Al1–O2	1.911(4)	Al1–O2–Al2	102.6(2)
Al1–O3	1.912(5)	Al1–O3–Al3	101.4(2)
Al2–O1	1.833(5)	O1–Al1–O2	75.5(2)
Al2–O2	1.834(5)	O1–Al1–O3′	167.0(2)
Al2–C1	1.973(8)	O1–Al2–O2	79.3(2)
Al2–C2	1.960(9)	O2–Al1–O2′	167.5(3)
Al3–O3	1.843(5)	O3–Al1–O3′	76.9(2)
Al3–C3	1.971(9)	O3–Al3–O3′	80.4(2)
		C1–Al2–C2	115.4(3)
		C3–Al3–C3′	114.9(4)

[a] Prime indicates $-x$, y, $-z + {}^1/_2$ symmetry operation.

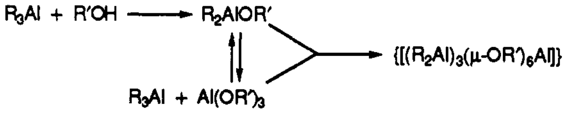
Scheme 1

$$4R_3Al + 6R'OH \longrightarrow \{[(R_2Al)_3(\mu\text{-}OR')_6Al]\} + 6RH$$

R = Me, (**1a**), Et (**1b**)
OR′ = 2-thiophenemethoxide
R = Me, **2**
OR′ = 2-furanmethoxide

current process. Following the initial formation of the (R$_2$MOR′)$_n$ moiety, some form of reorganization reaction must occur and elimination of an additional alkyl group must take place. The elimination proceeds most readily with trialkyls.[1] The reorganization process is well established in organoaluminum chemistry, and Bradley[18] has suggested that the preferred structure for alkoxides would contain a central six-coordinate aluminum atom. One possible path for this process is suggested in Scheme 2. Alternative paths are also possible, but no data are available to establish a specific mechanism for this reaction. Compounds **1a**, **1b**, and **2** have been isolated as colorless, transparent crystals. The complexes are both air and moisture sensitive, decomposing in the solid state and in solution on exposure to air. They have limited solubility in hydrocarbons such as pentane, benzene, and toluene and are very soluble in donor solvents such as diethyl ether and tetrahydrofuran.

Scheme 2



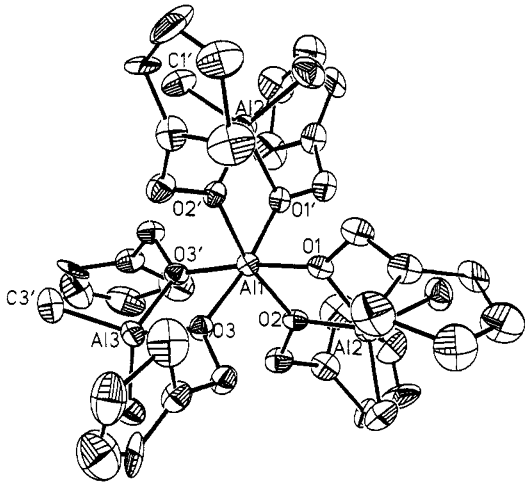


Figure 1. ORTEP diagram of {[(Me$_2$Al)$_3$(μ-OCH$_2$-2-C$_4$H$_3$S)$_6$]Al}, **1a**, showing the atom labeling scheme. Hydrogen atoms are omitted for clarity.

Molecular Geometry of {[(Me$_2$Al)$_3$(μ-OCH$_2$-2-C$_4$H$_3$S)$_5$]Al}, 1a. An ORTEP diagram of the molecular unit of **1a** is shown in Figure 1. Selected bond lengths and bond angles are listed in Table 3.

The molecular structure consists of a discrete unit with a central aluminum atom bridged to three Me$_2$Al moieties by six 2-thiophenemethoxide ligands. The Al$_4$O$_6$ core consists of one six-coordinate and three four-coordinate aluminum atoms. The central aluminum atom can be considered as a 3$^+$ cation surrounded by six oxygen atoms from three bidentate [R$_2$Al(OR′)$_2$]$^-$ groups in a distorted octahedral configuration. The bite angles of the bidentate [R$_2$Al(OR′)$_2$]$^-$ ligands are 75.5 and 76.9°. This geometry of the aluminum–oxygen framework is reminiscent of that found in aluminum isopropylate [Al(O-*i*-Pr)$_3$]$_4$,[11,12] {[(Me$_3$Si)$_2$Al(NH$_2$)$_2$]$_3$Al},[19] and [{N(CH$_2$CH$_2$O)$_3$}Al]$_4$.[13] The molecule has C_2 symmetry with a 2-fold axis passing through Al1 and Al3, thus requiring all four Al atoms to lie in the same plane. The Al1–O1–Al2–O2 ring makes a 57.53° angle and Al1–O3–Al3–O3′ makes a 58.82° angle with this plane. The O1 and O3′ pair and O2 and O2′ pair occupy the *trans* positions of the octahedron and their angles vary from the expected 180° for a perfect octahedron (O1–Al1–O3′ = O3–Al1–O1′ = 167.0°, O2–Al–O2′ = 167.5°). The average Al1–O distance of 1.911 Å falls into the range previously recorded.[20-22]

The coordination geometries about three peripheral atoms, Al2, Al2′, and Al3, are distorted tetrahedral. The critical angles are given in Table 3, and all are within the normal range for organoaluminum complexes. On the whole, the (AlO)$_2$ rings are virtually planar. The average

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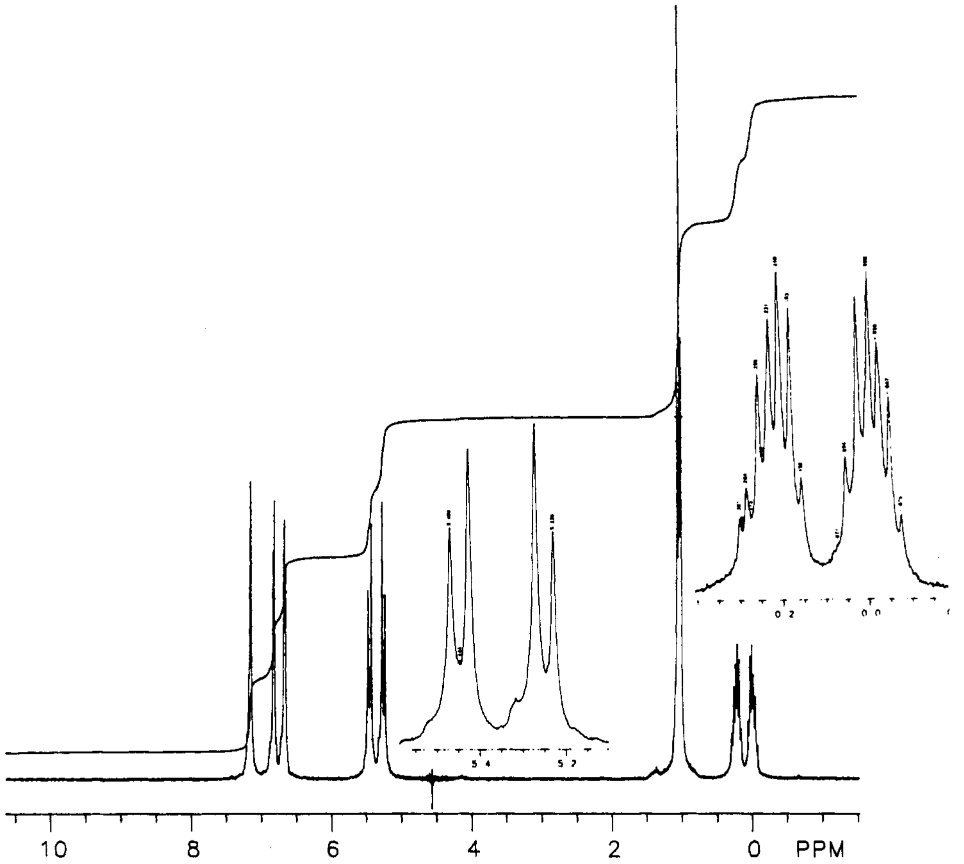

Figure 2. ^1H NMR spectrum of $\{[(Et_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3S)_6]Al\}$, **1b**. The insets show the OCH_2 and CH_2CH_3 regions.

Al–C bond distance of 1.968 Å is normal by comparison with the many examples in the literature.[20-22] However the average Al–O bond distance of 1.829 Å is shorter than that found in octahedral Al1–O bond distances but compares favorably with the Al–O distances observed for bridge bonds between four-coordinate aluminum atoms.[20-22]

The 2-thiophenemethoxide ligands have two potential coordination sites, oxygen and sulfur, similar to the tetrahydrofurfural methoxide ligand which uses both sites to give dinuclear five-coordinate organoaluminum complexes,[23] but in this case the second donor atom, sulfur, is beyond bonding distance to any metal center. The thiophene rings lie above and below the corresponding $(AlO)_2$ plane and are nearly parallel to it. The average Al–S distance is 4.304 Å, which is more than the sum of the van der Waals radii of 3.86 Å, precluding any Al–S bonding.[24] The molecular packing indicates that there are no significant intermolecular interactions.

NMR Studies. In the ^1H NMR spectrum of $\{[(R_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3E)_6]Al\}$ the absence of the –OH resonance of 2-thiophenemethanol and 2-furanmethanol, the presence of a sharp upfield resonace for the α protons of the alkyl group attached to the group 13 element, and the resonances associated with the alkoxy groups in the appropriate ratio provide good evidence for $-MR_2$ coordination at the alkoxy oxygen by comparison with chemical shifts of similar groups in the starting materials.

The ^1H NMR resonance of the methylene group bound to the bridging oxygen atom in all of the compounds appears as an AB quartet with J_{AB} varying from 10 to 13 Hz. Examination of the structure reveals that the molecule has idealized D_3 symmetry since a central Al^{3+} is coordinated by three Me_2AlO_2 units, each of which functions as a bidentate ligand. In the D_3 symmetry, the molecule has a C_3 axis, making all of the groups equivalent, and three C_2 axes, each passing through one four-coordinate aluminum and the six-coordinate aluminum. These structural results suggest that there is only one type of μ-OR and one type of peripheral Me_2Al group. However, in **1a**, each bridging oxygen atom is dissymmetric since it has attached to it three different substituents: Me_2Al, six-coordinate Al^{3+}, $CH_2\text{-}2\text{-}C_4H_3S$, and a lone pair. The presence of such a pyramidal atom in the structure guarantees that there will be no element of symmetry. Under these conditions, the methylene protons of the $\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3S$ group are diastereotopic. As expected, the AB pattern is retained even under conditions of fast rotation (76 °C). **2** shows identical results at room temperature. In the case of the ethyl derivative, **1b**, the OCH_2 protons show a similar pattern, but the spectrum becomes much more complex because the CH_2 protons of the ethyl group are also diastereotopic, and additional coupling is observed. A spectrum of **1b** is shown in Figure 2. The multiplicity of the methylene protons arises due to a combination of geminal and vicinal coupling, thereby giving the methylene resonance a complex sixteen line pattern. These results suggest that in solution all three compounds have the same general structure as **1a**. In addition, the temperature independence of the ^1H NMR spectrum of **1a** shows that this compound does not undergo rapid reorganization or dissociation in solution up to 75 °C. This is consistent with the stable Al-O-Al bridge bonds present in the molecule and indicates the robust character of the central core of this complex.

The ^{13}C NMR spectra of **1a**, **1b**, and **2** show the lines

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(23) Sierra, M. L.; de Mel, V. S. J.; Oliver, J. P. Unpublished results.

(24) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, New York, 1960.

anticipated for the observed structure. The assignment of the resonances are as follows: The signals at 8–10 ppm are those of the methylene of the Et_2Al–moiety; the resonances between 57 and 60 ppm are associated with the $-OCH_2$ unit; the ring carbons 3 and 4 are at 120–130 ppm with identical chemical shifts, carbon 5 in the 130–140 ppm in the furan derivatives.

In the ^{27}Al NMR spectra, the resonances associated with the aluminum atoms of the $-AlR_2$ moiety were not observed. However, the central aluminum atom in an octahedral environment of the $\{[(R_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3E)_6]Al\}$ complex shows a resonance with $\delta = 9.0$ ppm for **1a** and 10.0 ppm for **1b**. These shifts are typical of aluminum complexes containing a six-coordinate aluminum atom.[25-27]

The study provides further evidence for the unusual properties and structures of the organoaluminum derivatives prepared with multifunctional groups. In this instance both four- and six-coordinate aluminum atoms are present in the same molecule. Further, the asymmetry at the bridging oxygen atom gives rise to the nonequivalence of methylene protons.

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Supplementary Material Available: Listings of bond lengths and angles, anisotropic thermal parameters for the nonhydrogen atoms, and coordinates and isotopic thermal parameters for the hydrogen atoms (6 pages). Ordering information is given on any current masthead page.

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