

Toward Unusual Al-O Compounds. Synthesis and Molecular Structure of $[Al_4O(OCH_2CF_3)_{11}]^-$: Structural Characterization of a Novel Al_4O_{12} Cluster

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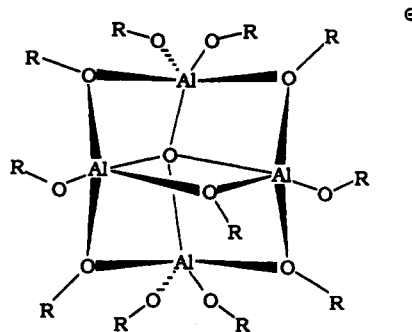
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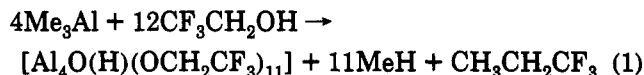
Summary: Reaction of Me_3Al with CF_3CH_2OH in hexane at $-78^\circ C$ affords the novel crystalline complex $[Al_4O(H)(OCH_2CF_3)_{11}]^-$ in high yield. The title compound crystallizes in the orthorhombic space group $Pna2_1$, with unit cell parameters $a = 16.875(8) \text{ \AA}$, $b = 13.575(5) \text{ \AA}$, $c = 19.423(8) \text{ \AA}$, $V = 4449 \text{ \AA}^3$, $Z = 4$, and $D_{calc} = 1.82 \text{ g cm}^{-3}$. Refinement converged at $R = 0.072$, $R_w = 0.083$ for 2837 observed reflections ($I > 2.5 \sigma(I)$). While the exterior is dominated by CF_3CH_2- groups, the core of the molecule consists of an interesting, high-oxygen content Al_4O_{12} cluster. Furthermore, it is significant that the coordination sphere of the four core aluminum atoms is constituted solely by oxygen atoms, each metal atom being five-coordinate and residing in distorted trigonal bipyramidal environments.

The fact that Al-O compounds are ubiquitous in Nature begs the point that aluminum forms more compounds with oxygen than with any other element. Indeed, the organoaluminum chemistry of oxygen-containing compounds is as rich as it is varied. While contemporary studies with simple ethers initially concerned addition products such as bis(trimethylaluminum)-dioxane, $(Me_3Al)_2 \cdot C_4H_8O_2$,¹ organoaluminum complexes have also been prepared with crown ethers such as dibenzo-18-crown-6 and 15-crown-5.² These organoaluminum-crown ether compounds demonstrated that the Al-O interaction is sufficiently substantial so as to essentially turn the crown ether *inside out*. Such studies notwithstanding, the organoaluminum chemistry of oxygen-containing compounds is presently experiencing perhaps its most prolific period. This renaissance is due, arguably in large measure, to a class of high-oxygen content Al-O compounds which were brought to the fore principally in the last decade—namely *aluminoxanes*. Aluminoxanes, classically defined as intermediates in the hydrolysis of organoaluminum compounds toward aluminum hydroxides, necessarily contain Al-O-Al fragments. An elegant review of these substances has recently been published.³ Although aluminoxanes have demonstrated astounding activity in certain polymerization systems, most notably as cocatalysts in Ziegler-Natta systems,⁴⁻⁸ rarely has a group of compounds generated such widespread interest and yet relatively so

little be known about their constitution and structure. The associated complications of preparing and isolating discrete molecular complexes of high-oxygen content organoaluminum compounds are legion. Consequently, such difficulties have hindered the development of this area. Herein we report the synthesis and molecular structure of the novel crystalline complex $[Al_4O(H)(OCH_2CF_3)_{11}]^-$ ($R = CF_3CH_2-$),



isolated from reaction of trimethylaluminum, Me_3Al , with trifluoroethanol, CF_3CH_2OH , in hexane.⁹ While the mechanism which affords $[Al_4O(H)(OCH_2CF_3)_{11}]^-$ is unclear, mass balance suggests eq 1. The title compound



represents a structural characterization of an interesting high-oxygen content Al-O compound. Moreover, the $[Al_4O(OCH_2CF_3)_{11}]^-$ molecular core consists of an intriguing Al_4O_{12} cluster.

X-ray intensity data were collected on a Enraf-Nonius CAD-4 diffractometer using an ω - 2θ scan technique with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $20^\circ C$. The title compound crystallizes in the orthorhombic space group $Pna2_1$ with unit cell dimensions $a = 16.875(8) \text{ \AA}$, $b = 13.575(5) \text{ \AA}$, $c = 19.423(8) \text{ \AA}$, $V = 4449 \text{ \AA}^3$, $Z = 4$, and $D_{calc} = 1.81 \text{ g cm}^{-3}$. The structure was solved by direct methods

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(9) Inside the drybox a reaction vessel was charged with hexane (20 mL) and Me_3Al (Ethyl Corp.) (1.0 mL, 10 mmol). To the cooled reaction vessel ($-78^\circ C$) was added CF_3CH_2OH (Alfa, 99%+) (2.4 mL, 33 mmol). The system was allowed to slowly warm to room temperature. Upon reaching room temperature, the system was heated to $80^\circ C$ for 6 h. X-ray quality crystals of $[Al_4O(H)(OCH_2CF_3)_{11}]^-$ were isolated (0.27 g, 90% yield, based on Me_3Al) upon cooling for several days in the freezer.

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using SHELXS¹⁰ and refined, based on 2837 observed reflections ($I > 2.5\sigma(I)$), using SHELX76.¹¹ Refinement, which was hindered by substantial thermal motion of the CF₃ groups (the two most prominent being C(12), F(16)–F(18) and C(16), F(22)–F(24)), converged at $R = 0.072$ and $R_w = 0.083$. Analysis of crystal packing revealed that one of the CF₃CH₂– groups (O(4), C(5), C(6) and F(7)–F(9)) is oriented toward the negative end of the *c*-axis for all molecules in the crystal. This verification of a polar axis in the crystal confirms the choice of space group $Pna2_1$ over the alternative centrosymmetric space group, $Pnma$. The X-ray crystal structure of [Al₄O(OCH₂CF₃)₁₁][–] is given in Figure 1a while Figure 1b provides a more uncluttered view of the Al₄O₁₂ molecular core, as the CF₃CH₂– groups have been omitted.

Under the assumption that O(1) is an oxide (*vide infra*), one H⁺ ion is necessary for charge balance. The most likely atoms to which the H⁺ ion may be affiliated are the six terminal oxygen atoms, namely O(2), O(6), O(7), O(9), O(11), or O(12). Of the six, O(6) and O(11) are most notable. Instead of short Al–O distances (as is found with the other four oxygen atoms), relatively long interactions of 1.833(8) and 1.802(8) Å are observed for Al(2)–O(6) and Al(4)–O(11), respectively. In addition, instead of wide (ca. 160°) Al–O–C angles, as is found with the other four terminal alkoxides, the Al–O(6,11)–C angles are much sharper: 126.5(8) and 128.4(7)°, respectively. Collectively, these points suggest two main possibilities: (1) The central oxygen atom, O(1), is actually a hydroxide, OH[–]; (2) The H⁺ ion is localized on either O(6) or O(11), or is disordered over these two possible sites, thus making one of these groups ROH. Relative to the former, a hydroxide ion suggests the presence of water in the system. As it is difficult to ascertain whether water was present, this explanation cannot be ruled out. However, as this model necessitates a five-coordinate oxygen atom, it appears unlikely. Relative to the latter, the extremely short intramolecular O(6)···O(11) contact of 2.40(1) Å and the geometry of this interaction about the two oxygen atoms (Al(2)–O(6)···O(11), 108.4(6)°; C(9)–O(6)···O(11), 120.2(8)°; Al(4)–O(11)···O(6), 110.4(6)°; C(19)–O(11)···O(6), 118.2(8)°) suggest strong hydrogen bonding between these groups. Indeed, this situation is similar to that found in the H₃O₂[–] anion which behaves as a bridging ligand in metal complexes which were originally thought to be hydroxo/aquo complexes.¹² These observations are consistent with the latter explanation. However, the high thermal motion of the CF₃ groups coupled with the disorder present in the molecule make it virtually impossible to locate the H⁺ ion to verify either of these possibilities.

The thermodynamic driving force in much of the organometallic chemistry of aluminum is traced to the substantial affinity which exists between aluminum and oxygen. Indeed, such is largely responsible for the violent nature of the reaction of aluminum alkyls with water. Clearly, the ability to control the interaction of aluminum alkyls with compounds containing regnant oxygen atoms is paramount if high-oxygen content organoaluminum compounds are to be facilely prepared and studied. Indeed, the fact that the literature reveals a paucity of structural studies of such compounds is evidence of the

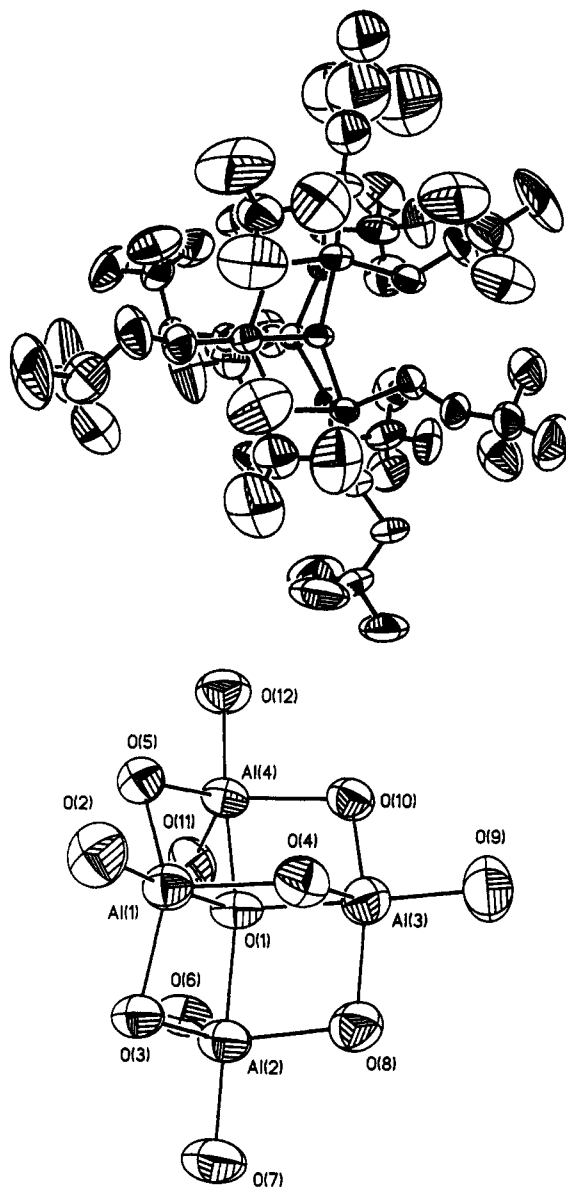


Figure 1. (a, top) Molecular structure of the [Al₄O(OCH₂CF₃)₁₁][–] anion. (b, bottom) Molecular structure of the [Al₄O(OCH₂CF₃)₁₁][–] core (omitting CF₃CH₂ groups). Selected bond distances (Å) and angles (deg): Al(1)–O(1) 1.887(7), Al(1)–O(2) 1.687(8), Al(1)–O(3) 1.839(7), Al(1)–O(4) 1.849(7), Al(1)–O(5) 1.841(7), Al(2)–O(1) 1.897(8), Al(2)–O(3) 1.867(8), Al(2)–O(6) 1.833(8), Al(2)–O(7) 1.695(9), Al(2)–O(8) 1.894(9), Al(3)–O(1) 1.902(8), Al(3)–O(4) 1.825(8), Al(3)–O(8) 1.844(8), Al(3)–O(9) 1.72(1), Al(3)–O(10) 1.833(8), Al(4)–O(1) 1.871(8), Al(4)–O(5) 1.891(7), Al(4)–O(10) 1.865(8), Al(4)–O(11) 1.802(8), Al(4)–O(12) 1.715(9); O(1)–Al(1)–O(2) 175.9(4), O(1)–Al(1)–O(3) 77.6(3), O(2)–Al(1)–O(3) 106.0(3), O(1)–Al(1)–O(4) 78.6(3), O(2)–Al(1)–O(4) 101.7(4), O(3)–Al(1)–O(4) 108.2(3), O(1)–Al(1)–O(5) 77.0(3), O(2)–Al(1)–O(5) 99.1(4), O(3)–Al(1)–O(5) 127.6(3), O(4)–Al(1)–O(5) 110.6(3), O(1)–Al(2)–O(3) 76.7(3), O(1)–Al(2)–O(6) 87.4(4), O(3)–Al(2)–O(6) 116.3(4), O(1)–Al(2)–O(7) 169.1(4), O(3)–Al(2)–O(7) 95.3(4), O(6)–Al(2)–O(7) 102.8(4), O(1)–Al(2)–O(8) 77.2(3), O(3)–Al(2)–O(8) 116.8(4), O(6)–Al(2)–O(8) 118.7(4), O(7)–Al(2)–O(8) 100.5(4), O(1)–Al(3)–O(4) 78.8(3), O(1)–Al(3)–O(8) 78.3(4), O(4)–Al(3)–O(8) 107.7(4), O(1)–Al(3)–O(9) 178.2(4), O(4)–Al(3)–O(9) 101.8(4), O(8)–Al(3)–O(9) 103.1(4), O(1)–Al(3)–O(10) 77.3(3), O(4)–Al(3)–O(10) 110.2(4), O(8)–Al(3)–O(10) 129.3(4), O(9)–Al(3)–O(10) 100.9(4), O(1)–Al(4)–O(5) 76.2(3), O(1)–Al(4)–O(10) 77.3(3), O(5)–Al(4)–O(10) 114.4(3), O(1)–Al(4)–O(11) 87.3(4), O(5)–Al(4)–O(11) 120.4(4), O(10)–Al(4)–O(11) 116.8(4), O(1)–Al(4)–O(12) 169.7(4), O(5)–Al(4)–O(12) 99.5(4), O(10)–Al(4)–O(12) 96.5(4), O(11)–Al(4)–O(12) 102.8(4).

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associated difficulties present in these systems. These difficulties notwithstanding, some very promising results have recently been obtained resulting in the synthesis and structure of a number of intriguing aluminoxanes.¹³ Perhaps most prominent among these is the synthesis and structure of the [(*t*-Bu)Al-O]₆ hexamer isolated from the thermolysis of [(*t*-Bu)₂Al-(μ-OH)]₃.³ This novel aluminoxane may be considered the fusing of two Al₃O₃ six-membered rings such that each oxygen atom is three-coordinate and each aluminum atom is four-coordinate. Overall, this aluminoxane hexamer is structurally quite similar to a class of open-caged hexameric iminoalanes, [XAl-N(*i*-Pr)]₆ (X = H, Me, Cl).¹⁴ An insightful structural perspective may also be obtained from an examination of the [Al₇O₆Me₁₆]⁻ anion, which as reported by Atwood,¹⁵ may be prepared by reaction of Me₃Al with either KO₂ or Cs₂O. The [Al₇O₆Me₁₆]⁻ anion, which consists of an open Al₆O₆ skeleton capped by a seventh aluminum atom, significantly was postulated as a possible decomposition pathway, a *thermodynamic sink* of sorts, for high-oxygen content organoaluminum complexes. The core of the anion consisted of six aluminum atoms each bonding to two terminal methyl groups, while the unique aluminum atom was found to bond to only one methyl group. Furthermore, each oxygen atom in [Al₇O₆Me₁₆]⁻ is three-coordinate: Al-O bond distances ranging from 1.83(2) to 2.06(4) Å. The simpler, yet just as intriguing, superoxide-based [Me₃Al-O₂-AlMe₃]⁻ anion, prepared from reaction of Me₃Al with KO₂ in the presence of dibenzo-18-crown-6, is noteworthy as it contains an unusual μ²-O₂⁻ ion.¹⁶ The Al-O bond distances were found to be 1.852(9) and 1.868(9) Å, while the Al-O-Al bond angle was determined to be 128.3(7)°.

A number of points are worthy of discussion concerning structure and bonding in [Al₄O(OCH₂CF₃)₁₁]⁻. It is particularly interesting that the methyl groups have been completely displaced even as the coordination sphere of each aluminum atom has been substantially expanded—resulting in a purely inorganic, Al₄O₁₂ molecular core. Furthermore, the Al₄O₁₂ core contains five conterminous Al₂O₂ four-membered rings, the -Al(1)-O(1)-Al(3)-O(4)- ring being roughly orthogonal to the remaining

four Al₂O₂ fragments. The four aluminum atoms are bridged by CF₃CH₂O- groups to form an eight-membered Al₄O₄ ring. An additional CF₃CH₂O- group bridges two cross-ring aluminum atoms (Al(1) and Al(3)); these two aluminum atoms each have one additional terminal CF₃CH₂O- group, while the other two (Al(2) and Al(4)) each have two terminal CF₃CH₂O- groups. A unique oxygen atom, O(1), lying in a position roughly opposite that of the cross-ring bridging CF₃CH₂O(4)- group, coordinates to all four of the aluminum atoms in a severely distorted tetrahedral, or perhaps a *seesaw*, geometry and completes a distorted trigonal bipyramidal coordination sphere about each aluminum atom (O_{ax}-Al-O_{ax} range, 169.1(4)-178.2(4)°; O_{eq}-Al-O_{eq} range, 107.7(4)-129.3(4)°; O_{ax}-Al-O_{eq} range, 76.2(3)-106.0(3)°). Furthermore, this four-coordinate oxygen atom occupies an axial position of the coordination sphere of each aluminum atom, with Al-O bonds ranging from 1.871(8) to 1.902(8) Å. The terminal CF₃CH₂O- groups at the opposite axial positions have quite short Al-O bonds of 1.687(8)-1.72(1) Å while the bridging CF₃CH₂O- groups occupy equatorial positions and have longer Al-O bonds of 1.802(8)-1.894(9) Å. Indeed, [Al₄O(OCH₂CF₃)₁₁]⁻ contains two-, three-, and four-coordinate oxygen atoms. The Al₄O₄ (O(3)-O(5)-O(8)-O(10)) molecular skeleton of the title compound bears a striking resemblance to the Ti₄O₄ core of the recently reported [(TiCl)₂(μ₂-O){μ₂-η⁵-η⁵-(C₅H₄)₂SiMe₂}]₂(μ-O)₂ compound, as in both cases the four oxygen atoms constitute a plane.¹⁷

The isolation of a compound such as [Al₄O(H)(OCH₂CF₃)₁₁] from reaction of Me₃Al with CF₃CH₂OH is as unexpected as it is interesting. This study will serve as a benchmark, as additional methods may be considered for the preparation for high-oxygen content organoaluminum compounds.

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Supplementary Material Available: A packing diagram, a textual summary of data collection and refinement, and tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (11 pages). Ordering information is given on any current masthead page.

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