

A Structurally Diverse Series of Aluminum Chloride Alkoxides $[\text{Cl}_x\text{Al}(\mu\text{-OR})_y]_n$ ($\text{R} = n\text{Bu}, {}^i\text{Hex}, \text{Ph}, 2,4\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3$)

Zdenek Moravec,[†] Radek Sluka,[†] Marek Necas,[†] Vojtech Jancik,[‡] and Jiri Pinkas^{*,†}

[†]Department of Chemistry, Masaryk University, Kotlarska 2, CZ-61137 Brno, Czech Republic, and [‡]Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510, México D.F., México

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A diverse series of aluminum chloride alkoxides, $[\text{Cl}_x\text{Al}(\mu\text{-OR})_y]_n$ ($\text{R} = n\text{Bu}, {}^i\text{Hex}, \text{Ph}, 2,4\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3$), was synthesized using the reactions of dichlorethylalane (EtAlCl_2) with cyclohexanol (${}^i\text{HexOH}$), n -butanol ($n\text{BuOH}$), and phenols (PhOH and $2,4\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3\text{OH}$). Eight molecular products were isolated and structurally characterized. The dimeric $[\text{Cl}_2\text{Al}(\mu\text{-O}^i\text{Hex})_2\text{AlCl}_2]$ (**1**) was the smallest oligomer isolated among the cyclohexanolate derivatives. The adduct of **1** with cyclohexanol is a dinuclear molecule $[\text{Cl}_2(\text{HO}^i\text{Hex})\text{Al}(\mu\text{-O}^i\text{Hex})_2\text{AlCl}_2]$ (**2**) which represents a possible intermediate in the conversion reaction leading to the formation of a trinuclear bicyclic $[\text{ClAl}\{(\mu\text{-O}^i\text{Hex})_2\text{AlCl}_2\}_2]$ (**3**). Two polymorphic forms of **3** were isolated. Further coordination of cyclohexanol to the Lewis acidic five-coordinate aluminum atom in **3** provided $[\text{Cl}(\text{HO}^i\text{Hex})\text{Al}\{(\mu\text{-O}^i\text{Hex})_2\text{AlCl}_2\}_2]$ (**4**) with octahedrally coordinated central aluminum. Compound **4** could be regarded as a precursor to the well-known Mitsubishi (tridiamond) tetranuclear species. The reactions of EtAlCl_2 with less sterically demanding $n\text{BuOH}$ yielded a cyclic trimer, $[\text{Cl}_2\text{Al}(\mu\text{-O}^n\text{Bu})]_3$ (**5**), and a unique trinuclear ionic species, $[\text{Cl}_2\text{Al}\{(\mu\text{-OH})(\mu\text{-O}^n\text{Bu})\text{AlCl}(\text{HO}^n\text{Bu})_3\}_2]\text{Cl}$ (**6**) with a linear $\text{Al}(\mu\text{-O})_2\text{Al}(\mu\text{-O})_2\text{Al}$ core. In the reactions with phenols, the aromatic groups preferentially stabilized dimeric structures of $[\text{Cl}_2\text{Al}(\mu\text{-OR})_2\text{AlCl}_2]$ ($\text{R} = \text{Ph}$, **7**; $2,4\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3$, **8**). Since these compounds could be considered as intermediates in the nonhydrolytic condensation reactions of metal halides with metal alkoxides, a mixture of EtAlCl_2 with ${}^i\text{HexOH}$ was used as a precursor for the nonaqueous synthesis of alumina by alkylhalide elimination.

Introduction

Aluminum chloride alkoxides $[\text{Cl}_x\text{Al}(\mu\text{-OR})_y]_n$ ($\text{R} = \text{alkyl}, \text{aryl}$) are molecules that possess reaction centers of a high Lewis acidity and therefore were studied as species important to catalysis in organic reactions of carbonyl compounds and also in ring-opening polymerizations.¹ The presence of both $\text{Al}-\text{Cl}$ and $\text{Al}-\text{OR}$ bonds that are capable of alkylhalide elimination and condensation to $\text{Al}-\text{O}-\text{Al}$ makes aluminum chloride alkoxides promising precursors for the nonaqueous synthesis of aluminum oxide. They were considered as intermediates in

the preparation of alumina materials by nonhydrolytic sol-gel,² thermolytic,³ and atomic layer deposition⁴ methods.

There are only two structurally characterized examples of monomeric aluminum chloride alkoxides, $\text{ROAlCl}_2(\text{OEt}_2)$ (Chart 1; **A**, $\text{R} = 2,6\text{-}^t\text{Bu}_2\text{-4-MeC}_6\text{H}_3$ ^{5a} and $2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2$ ^{5b}), that were sterically protected by bulky aryloxy groups and electronically stabilized by the coordination of Et_2O . Aluminum chloride alkoxides with smaller substituents undergo intermolecular coordination of alkoxide oxygens to the Lewis acidic Al atoms and are thus stabilized by the formation of oligomers. Dimeric⁶ and trimeric⁷ aluminum chloride alkoxides $[\text{ROAlCl}_2]_n$ (Chart 1; $n = 2$ (**B**), 3 (**C**)) are more common than monomers, and they were in some cases proposed to exist simultaneously in solution.^{6,8} ROAlCl_2 oligomers undergo

*To whom correspondence should be addressed. Phone: +420549496493. Fax: +420549492443. E-mail: jpinkas@chemi.muni.cz.

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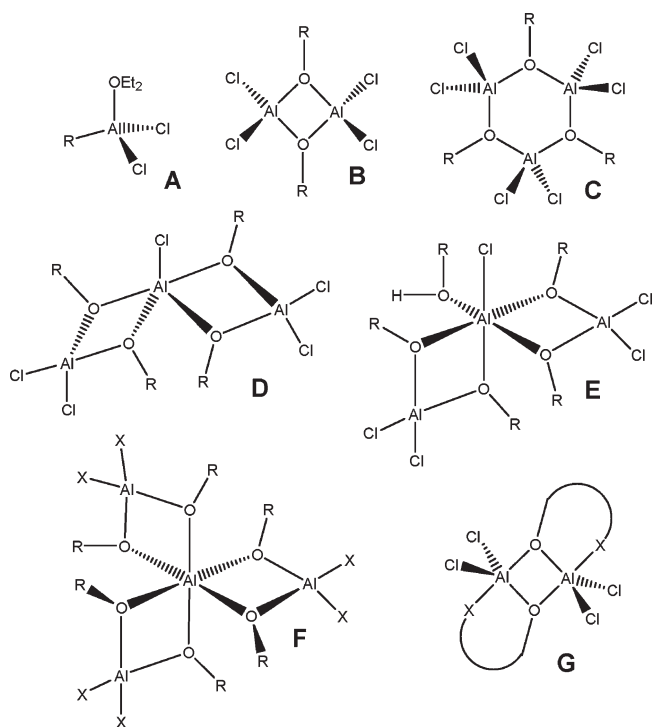
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Chart 1



redistribution reactions in solution⁹ and on crystallization provide neutral or ionic polynuclear complexes with Al/OR/Cl stoichiometry different from the starting ratio 1:1:2. One type of these oligomers is the trinuclear bicyclic molecules $[\text{ClAl}\{(\mu\text{-OR})_2\text{AlCl}_2\}_2]$ (Chart 1; **D**, R = Et, ⁶nBu, ⁶iBu, ⁶Pr, ^{6,10}CH₂⁶Bu⁶) with one five- and two four-coordinate Al atoms. The transformation of ROAlCl₂ to $[\text{ClAl}\{(\mu\text{-OR})_2\text{AlCl}_2\}_2]$ probably involves a Cl/OR ligand redistribution or replacement of Cl in the reaction with ROH since a third of the ROAlCl₂ molecules must be converted to (RO)₂AlCl to finally form $[\text{ClAl}\{(\mu\text{-OR})_2\text{AlCl}_2\}_2]$. The mechanism of this reaction has not been completely elucidated. The compounds of this type were also prepared by the scrambling reactions of AlCl₃ and Al(OR)₃¹⁰ or by the reactions of the stoichiometry-optimized mixtures of MeOAlCl₂ and (MeO)₂AlCl with bifunctional alcohols.¹¹ The structural motif **D** is also known in other families of compounds, such as homoleptic trimeric aluminum alkoxide [⁶HexOAl{ $(\mu\text{-O}^{\text{c}}\text{Hex})_2\text{Al}(\text{O}^{\text{c}}\text{Hex})_2$ }]₃¹² and alkyl alkoxides $[\text{RAl}\{(\mu\text{-OR})_2\text{AlR}_2\}_2]$.¹³

A molecule that can be regarded as being derived from these $[\text{ClAl}\{(\mu\text{-OR})_2\text{AlCl}_2\}_2]$ trinuclear species by the coordination of an alcohol to the central Al atom was structurally characterized for ⁶PrOH and features a six-coordinate Al center (Chart 1; **E**, R = ⁶Pr).¹⁴ It was obtained from the reaction of MeAlCl₂ with ⁶PrOH in a 1:2 stoichiometric ratio.

Tetranuclear tricyclic molecules of a specific structure resembling the Mitsubishi logo (Chart 1; **F**)¹⁵ were observed in several classes of aluminum compounds, such as homoleptic alkoxide tetramers $[\text{Al}(\text{OR})_3]_4$,¹⁵ alkyl alkoxides $[\text{Al}\{(\mu\text{-OR})_2\text{MR}_2\}_3]$, and heterometallic alkoxides $[\text{M}\{(\mu\text{-OR})_2\text{Al}(\text{OR})_2\}_3]$.¹⁶ These molecules proved to be attractive stoichiometric precursors to oxide materials, such as Al₂O₃ or mixed metal oxides.¹⁷ The thermolysis reactions of aluminum chloride alkoxides with aluminum alkyl alkoxides could also lead to the formation of Al–O–Al moieties and alumoxane materials.¹⁸

Interestingly, also several aluminum chloride alkoxides $[\text{Al}\{(\mu\text{-OR})_2\text{AlCl}_2\}_3]$ (Chart 1; **F**, R = Et, ⁶nBu,^{6,19}) were shown to possess the Mitsubishi structure. They were formed by different routes, such as alcoholysis of RAlCl₂ followed by a conversion reaction of an unknown mechanism, or by ligand-scrambling reactions between EtAlCl₂ and Al(OR)₃.

We are interested in the synthesis of molecular precursors for aluminum oxide and phosphate materials.²⁰ Aluminum chloride alkoxides emerge as suitable starting reagents for the fabrication of alumina and aluminophosphates by nonhydrolytic condensation routes. However, their structural diversity and complex reactivity is not completely understood. Here, we report on the synthesis and structural characterization of a series of aluminum chloride alkoxides and aluminum chloride aryloxides $[\text{Cl}_x\text{Al}(\mu\text{-OR})_y]_n$ (R = ⁶nBu, ⁶Hex, Ph, 2,4-⁶Bu₂C₆H₃) with substituents of a different steric demand. Molecular structures and metric parameters of these molecules involving dimeric and trimeric species and the products of their conversion to trinuclear bicyclic molecules are discussed. The Lewis acidity of the Al centers is demonstrated by the coordination of alcohol molecules and an increase of the coordination number of aluminum from 4 to 5 and also from 5 to 6. These alcohol-coordinated species are proposed as precursors to the molecules of high nuclearity. Finally, the solution thermolysis of a mixture of EtAlCl₂ with ⁶HexOH is shown to provide alumina by a nonhydrolytic condensation reaction.

Experimental Section

General. All reactions were carried out under dry N₂ using vacuum line techniques or in an M. Braun drybox with both H₂O and O₂ levels below 1 ppm. EtAlCl₂ was purchased from Aldrich (0.9 M solution in heptane) or from Witco. Cyclohexanol and *n*-butanol were distilled and kept over a molecular sieve. Phenol and 2,4-*t*-Bu₂C₆H₃OH (Fluka) were used as

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received. All hydrocarbon solvents were freshly distilled from Na/benzophenone under N_2 . Tetraglyme was vacuum-distilled (93–105 °C/ 3 Pa) and stored under dry N_2 . Benzene- d_6 was dried over and distilled from Na/K alloy and degassed prior to use. Solution NMR spectra (1H , ^{13}C) were recorded at 300 K on Bruker Avance DRX 300 and DRX 500 MHz spectrometers with deuterated solvents as the internal lock. The 1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual proton signals or carbon resonances of benzene- d_6 (7.15 and 128.0 ppm, respectively). Thermal analyses (thermogravimetric/differential thermal analysis, TG/DTA) were carried out on a MOM Derivatograph-C instrument under static air with a heating rate of 5 °C min $^{-1}$ from 25 to 1100 °C. Samples (10–20 mg) were contained in corundum crucibles. Gas chromatography/mass spectrometry (GC/MS) spectra were obtained on a Shimadzu GCMS-QP2010 mass spectrometer. A DB-XLB column (30 m, diameter 0.25 mm, 150 kPa) was heated at 20 °C min $^{-1}$ to 250 °C. The ionization energy was set to 70 eV, and the spectra were scanned from 35 to 400 m/z . A Stoe-Cie STADI P transmission diffractometer operating with Ge monochromatized Co (λ = 1.788965 Å) radiation (40 kV, 30 mA) and equipped with a position sensitive detector was used for the powder X-ray diffraction (XRD) data acquisition at ambient temperature. IR spectra (4000–400 cm $^{-1}$) were collected on an EQUINOX 55/S/NIR FTIR spectrometer. Samples were prepared as KBr pellets. The FT Raman spectral measurements with FT-RA module FRA 106/S were performed with a resolution of 1.5 cm $^{-1}$. An air-cooled Nd:YAG laser (1064 μ m, max output 500 mW) was used for spectra excitation. The chloride content was determined by potentiometric titrations with $AgNO_3$. A Jobin Yvon 170 Ultrac (lateral observation, generator 40 MHz, output 1.0 kW, plasma gas flow 12 L min $^{-1}$, monochromator 1 m) inductively coupled plasma spectrometer was used for the determination of aluminum content. The measurements were performed at the Al lines at 309.271 and 396.152 nm. A Haake Phoenix P1 Circulator cryostat with controlled cooling at 10 °C day $^{-1}$ was used for growing single crystals suitable for the X-ray diffraction analysis. Scanning electron microscopy (SEM) micrographs were taken on a Jeol 6700 Field emission microscope. Dried powder was suspended in isopropanol and a drop was placed on a cleaned silicon (100) slide. Surface areas and pore volumes were determined by nitrogen adsorption at 77.4 K using a volumetric technique²¹ on a Quantachrome Autosorb-1MP instrument. Prior to the measurements, the samples were degassed at 25 °C for at least 24 h until the outgas rate was less than 0.4 Pa min $^{-1}$. The adsorption–desorption isotherm was measured for each sample at least three times. The specific surface area was determined by the multipoint Brunauer–Emmett–Teller (BET) method with at least five data points with relative pressures between 0.05 and 0.23. Analysis was performed with the instrument software package.

X-Ray Structure Analysis. The intensity data of compounds 1–8 were collected on a KUMA KM-4 CCD κ -axis diffractometer using graphite monochromatized Mo K α radiation (λ = 0.71073 Å) equipped with an Oxford Cryosystem LT device at 120 K and corrected for absorption effects using ψ scan. The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were inserted in calculated positions and isotropically refined assuming a riding model. Where possible, the CH hydrogens were localized from the electron density map and refined isotropically with U_{ij} tied to the parent atom. The disordered "Hex (in the crystal of 4), "Bu (in the crystal of 5), and 'Bu (in the crystal of 8) were refined using geometry and distance restraints (SAME,

SADI) together with the restraints for the U_{ij} values (SIMU, DELU). Compound 4 crystallized as a racemic twin in the space group $P2_12_12_1$ with the Flack parameter refined to 0.50(4). The completeness of the data set for compound 7 is only 88% due to a defect in a low-temperature device during the data collection. Unfortunately, we were not able to grow other crystals of this compound; thus, the incomplete data set is used for the discussion, as the data-to-parameter ratio is 12:9. Compound 6 crystallizes in a monoclinic space group $C2/c$ with half of a molecule in the asymmetric unit (a = 18.491, b = 17.032, c = 16.429 Å, β = 114.44°) and is presented only as a model due to the poor quality of the crystals. The programs included in the SHELXTL, version 5.1 program package have been used to solve²² and refine²³ the structures and to prepare the tables (XCIF). The drawings were rendered using the Gretep and POV-Ray programs.^{24,25}

Synthesis of $[Cl_2Al(\mu-O^iHex)_2AlCl_2]$ (1). A solution of cyclohexanol (140 mg, 1.4 mmol) in heptane (5 cm 3) was added dropwise to a stirred solution of $EtAlCl_2$ (178 mg, 1.4 mmol) in heptane (5 cm 3). A white solid precipitated and was subsequently dissolved to a clear colorless solution by heating to 45 °C in a water bath. A slow cooling to ambient temperature afforded a small crop of colorless crystals of X-ray quality that were used for the X-ray diffraction analysis.

Synthesis of $[Cl_2(HO^iHex)Al(\mu-O^iHex)_2AlCl_2]$ (2) and $[ClAl(\mu-O^iHex)_2AlCl_2]_2$ (3). To a stirred solution of $EtAlCl_2$ (3 mmol) in isohexane (6 cm 3) at 0 °C was added dropwise a solution of cyclohexanol (3 mmol) in hexane (10 cm 3). A white solid was formed, and the suspension was subsequently heated to 50 °C. Upon heating, the solid was observed to dissolve over a 1 h period. The solution was cooled to 0 °C, yielding colorless crystals of 2. The crystals were separated by decantation and washed by a small volume of cold hexane at –50 °C. The solution was further concentrated by solvent evaporation. A batch of single crystals of 3 was obtained after cooling to 0 °C. The crystals were separated by decantation and washed by a small volume of cold hexane at –50 °C. The crystals of 2 and 3 were unstable at room temperature and darkened in a few days on storage in the drybox.

Yield of 2: 0.283 g, 38%. 1H NMR (2, $CDCl_3$, ppm): δ 1.18–1.35 (m), 1.55–1.65 (m), 1.84–1.87 (m), 2.22–2.31 (m), 4.10 (tt, 11.3, 3.8 Hz, OCH), 4.29 (tt, 10.8, 4.0 Hz, OCH), 5.8 (br s, OH). ^{13}C -APT NMR (2, $CDCl_3$, ppm): δ 24.32, 24.50 (C-3/5), 24.76, 25.26 (C-4), 34.59, 35.52 (C-2/6), 78.46, 79.00 (OCH). ^{27}Al NMR: δ 44 ($\nu_{1/2}$ = 470 Hz, $Al^{[5]}$), 93 ($\nu_{1/2}$ = 390 Hz, $Al^{[4]}$). Anal. Calcd for $Al_2Cl_4O_3C_{18}H_{34}$: Al, 10.9; Cl, 28.7. Found: Al, 12.4; Cl, 28.7. For IR and Raman spectra of 2, see the Supporting Information.

Yield of 3: 0.200 g, 30%. 1H NMR (3, C_6D_6 , ppm): δ 0.58–0.85 (m), 0.91–1.07(m), 1.27–1.53 (m), 1.74 (dq, 2 Hz, 11 Hz), 2.07 (d, 10 Hz), 2.40 (d, 10 Hz), 4.01 (tt, 10 Hz, 4 Hz), 4.20 (tt, 11 Hz, 3.5 Hz). ^{13}C -APT NMR (3, C_6D_6 , ppm): δ 24.10, 24.20 (C-3/5), 24.85, 25.35 (C-4), 35.07, 35.95 (C-2/6), 78.86, 79.67 (OCH). ^{27}Al NMR: δ 45 ($\nu_{1/2}$ = 780 Hz, $Al^{[5]}$), 91 ($\nu_{1/2}$ = 900 Hz, $Al^{[4]}$). For IR spectra of 3, see the Supporting Information.

Synthesis of $[Cl(HO^iHex)Al(\mu-O^iHex)_2AlCl_2]_2$ (4). A solution of $EtAlCl_2$ in isohexane (3 mmol, 6 cm 3) was added dropwise to a stirred solution of cyclohexanol (3 mmol) in hexane (20 cm 3) at 25 °C. A small amount of white solid was formed. It was filtered out, and the colorless solution was put into a cryostat. A small crop of crystals was formed at –10 °C.

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Table 1. Crystallographic Data and Refinement Parameters for Compounds **1–5**, **7**, and **8**

compound number	1	2	3	4	5	7	8
empirical formula	C ₁₂ H ₂₂ Al ₂ Cl ₄ O ₂	C ₁₈ H ₃₄ Al ₂ Cl ₄ O ₃	C ₂₄ H ₄₄ Al ₃ Cl ₅ O ₄	C ₃₀ H ₅₆ Al ₃ Cl ₅ O ₅	C ₁₂ H ₂₇ Al ₃ Cl ₆ O ₃	C ₁₂ H ₁₀ Al ₂ Cl ₄ O	C ₂₈ H ₄₂ Al ₂ Cl ₄ O ₂
fw	394.06	494.21	654.78	754.94	512.98	381.96	606.38
cryst syst	triclinic	triclinic	monoclinic	orthorhombic	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
temp, K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
λ , Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
<i>a</i> , Å	6.566(1)	10.349(2)	13.271(3)	10.652(2)	8.345(2)	7.442(2)	12.524(1)
<i>b</i> , Å	8.509(2)	11.416(2)	13.056(3)	15.056(3)	16.094(3)	7.867(2)	16.450(2)
<i>c</i> , Å	8.828(2)	11.892(3)	19.726(4)	24.167(3)	18.646(4)	8.384(3)	15.921(1)
α , deg	97.73(3)	74.84(3)	90	90	101.23(2)	115.09(2)	90
β , deg	111.79(3)	85.43(2)	109.50(3)	90	98.90(3)	113.93(3)	100.26(1)
γ , deg	99.25(2)	67.18(3)	90	90	98.48(3)	94.14(3)	90
<i>V</i> , Å ³	442(1)	1250(1)	3222(1)	3876(1)	2386(1)	388.2(2)	3228(1)
<i>Z</i>	1	2	4	4	4	1	4
μ , mm ^{−1}	0.767	0.560	0.560	0.477	0.840	0.870	0.444
no. of rflns collected	2617	12479	25158	50185	15550	2434	18760
no. of indep. rflns (<i>R</i> _{int})	1505 (0.0364)	4379 (0.0482)	5651 (0.0363)	6812 (0.0479)	8149 (0.0457)	1199 (0.0634)	2838 (0.0239)
no. of data/restraints/params	1505/0/91	4379/0/247	5651/0/325	6812/480/448	8149/95/461	1199/0/91	2838/63/197
GoF on <i>F</i> ²	0.976	0.866	1.045	0.935	0.984	1.004	1.079
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0311, 0.0720	0.0356, 0.0599	0.0287, 0.0681	0.0302, 0.0548	0.0378, 0.0893	0.0425, 0.1021	0.0351, 0.0871
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b (all data)	0.0391, 0.0756	0.0707, 0.0682	0.0385, 0.0727	0.0463, 0.0578	0.0481, 0.0941	0.0553, 0.1113	0.0373, 0.0887

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (F_o^2)]^{1/2}.$$

Synthesis of [Cl₂Al(μ-OⁿBu)]₃ (5**).** To a stirred solution of EtAlCl₂ (178 mg, 1.4 mmol) in heptane (5 cm³) was added dropwise a solution of *n*-butanol (104 mg, 1.4 mmol) in heptane (5 cm³). The reaction mixture was stirred for 1 h and then concentrated by solvent evaporation. As no solid precipitated, the solvent was removed completely. The resulting colorless viscous liquid was frozen in liquid N₂ and then left to warm to ambient temperature. This treatment led to the formation of crystals suitable for the X-ray diffraction analysis. ¹H NMR (**5**, CD₂Cl₂, ppm): δ 1.00 (m, CH₃), 1.42 (qn, 7.3 Hz, CH₂), 1.94–1.97 (m, CH₂), 3.86 (m, OCH₂), 4.11 (m, OCH₂), 4.58 (t, 6 Hz, OCH₂). ¹³C-APT NMR (**5**, CD₂Cl₂, ppm): δ 13.84, 13.95 (CH₃), 18.72, 19.34, 33.78, 34.73 (CH₂), 67.05, 73.20 (CH₂O).

Synthesis of [Cl₂Al(μ-OH)(μ-OⁿBu)AlCl(HOⁿBu)₃]₂Cl (6**).** To a solution of EtAlCl₂ (5.6 mmol) in isohexane (10 cm³) at 0 °C was added dropwise a solution of *n*-butanol (5.6 mmol) in hexane (20 cm³). A small amount of a white solid was formed, from which a clear solution was decanted. The solution was concentrated by removing the solvent under reduced pressure. Colorless crystals of **6** were formed after storing the solution for several months at −15 °C.

Synthesis of [Cl₂Al(μ-OPh)₂AlCl]₂ (7**).** To a stirred solution of EtAlCl₂ (178 mg, 1.4 mmol) in heptane (5 cm³) was added dropwise a solution of phenol (132 mg, 1.4 mmol) in heptane (5 cm³). After a short period of stirring, a white solid precipitated. It was dissolved by heating to 65 °C, and a clear colorless solution was left to cool down slowly to room temperature. Colorless crystals of **7** were formed.

Synthesis of [Cl₂Al(μ-O-2,4-^tBu₂C₆H₃)₂AlCl]₂ (8**).** A solution of 2,4-di-*tert*-butylphenol (1.6 mmol) in toluene (10 cm³) was added dropwise to a stirred solution of EtAlCl₂ (1.5 mmol) in toluene (10 cm³) at 0 °C. A light yellow solution was concentrated under reduced pressure and then was cooled to −15 °C. Crystals of **8** were formed.

Reaction of EtAlCl₂ with Cyclohexanol at a High Temperature. To a stirred solution of EtAlCl₂ (3.0 mmol) in tetraglyme (20 cm³) at room temperature was added dropwise a solution of cyclohexanol (4.5 mmol) in tetraglyme (20 cm³). A clear solution was heated to 150 °C for 14 h. A white precipitate was formed. The solid product was isolated by centrifugation and washed twice with toluene and dried under vacuum conditions. IR (KBr, cm^{−1}): ν 591 (s), 682 (s), 809 (s), 851 (s), 1033 (m), 1106 (vs),

1200 (m), 1261 (m), 1302 (w), 1351 (w), 1466 (m), 2893 (s), 2927 (s), 3404 (m). Anal. Found: C, 12.9; H, 5.4%.

Results and Discussion

The syntheses of moisture-sensitive compounds **1–8** were all carried out under anhydrous conditions by employing the reactions between a particular alcohol or phenol and dichloroethylalane in an equimolar ratio in hydrocarbon solvents at a room temperature or with ice-bath cooling. In all cases, the ethyl group of EtAlCl₂ reacted completely with the acidic hydrogen of the alcohol or phenol, and the ethane release served as a driving force in these reactions. Aluminum chloride alkoxides are known to produce mixtures of oligomers and also undergo ligand scrambling and dynamic exchange in solution.^{6,8,9} The distribution of species depends on the reaction conditions, stoichiometry, time, and the nature of substituents. Therefore, it is difficult to relate the solution data, such as NMR spectra or cryoscopic molecular weight, of these reaction mixtures to the solid state structures of isolated products. The resulting stoichiometries of some of the reported products (**3**, **4**, and **6**) differ from the starting 1:1:2 ratio for Al/OR/Cl, which may indicate that other unidentified species were present in the mother liquor. In our case, the X-ray-quality crystals were selected from a small crop of crystalline products, and the molecular structures were established by single-crystal X-ray diffraction experiments. Crystal data and refinement parameters for compounds **1–5**, **7**, and **8** are given in Table 1. A limited stability of the solid products at room temperature even under a drybox atmosphere prevented us from obtaining meaningful CHN elemental analysis data. The content of Al and Cl was established for **2** and agrees with the observed structure.

The reactions provided three products of a general formula [ROAlCl₂]₂ that crystallized from the solution as dimeric cyclic species (Chart 1, **B**) in the case of compounds **1** (^{*c*}Hex), **7** (Ph), and **8** (2,4-^{*t*}Bu₂C₆H₃). A dimer with four-coordinate aluminum and three-coordinate oxygen atoms was previously structurally authenticated only in one aluminum

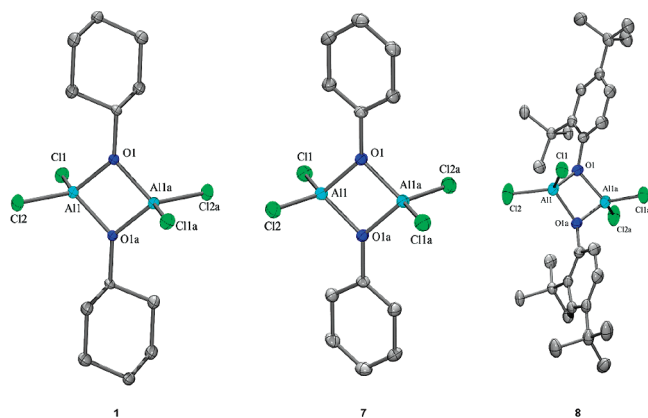


Figure 1. Molecular structures of **1**, **7**, and **8** with numbering schemes. All H atoms were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

dichloride alkoxide with monofunctional bulky $\text{CH}_2\text{C}(\text{CH}_3)_3$ substituents.⁶ Dimeric structures are displayed by a number of aluminum chloride alkoxides with substituents possessing additional oxygen or nitrogen donor atoms, which increase the coordination number of aluminum to five (Chart 1, **G**).²⁶ Molecules **1** and **7** form centrosymmetric dimeric structures with four-membered Al_2O_2 planar cores (Figure 1). In contrast, the molecule of **8** displays a C_2 molecular symmetry with a puckered central Al_2O_2 ring (Figure 1). Selected bond lengths and angles are compared for dimeric molecules in Table 2. Their Al–Cl and Al–O bond lengths are shorter than the corresponding distances in the five-coordinate dimeric aluminum alkoxyalkoxide chlorides.²⁶

A novel compound, **2**, formed in the reaction of EtAlCl_2 with $^i\text{HexOH}$ was obtained by crystallization at 0 °C in contrast to **1**, where the crystals grew at room temperature. The molecule of **2** is derived from **1** by the coordination of cyclohexanol oxygen to one Al center. The presence of excess $^i\text{HexOH}$ over the starting 1:1 stoichiometry may stem from an incomplete reaction. The alcohol coordination reveals that four-coordinate Al atoms in dimeric **1** are still sufficiently Lewis acidic. The molecule of **2** features one tetrahedrally coordinated Al and one trigonal-bipyramidal Al atom (Figure 2). Relevant bond distances and angles are gathered in Table 3. The five-coordinate Al atom displays longer Al–O ^iHex and Al–Cl bonds than the four-coordinate one. In the crystal lattice, two molecules of **2** are connected by pairs of $\text{O} \cdots \text{H} \cdots \text{Cl}$ hydrogen bonds to form supramolecular dimeric aggregates.

To observe the steric influence of the alkoxide α -carbon branching on the structure of ROAlCl_2 , we also carried out the reactions of EtAlCl_2 with $^n\text{BuOH}$. A similar system of MeAlCl_2 and $^n\text{BuOH}$ was previously studied with the aim of preparing $^n\text{BuOAlCl}_2$.⁶ The reported results of ^1H NMR spectroscopy suggested the presence of dimeric and trimeric forms of $^n\text{BuOAlCl}_2$ (Chart 1, **B**, **C**) and a small amount of the tetranuclear Mitsubishi-type molecule (Chart 1, **F**). This tetranuclear species crystallized out on cooling to –15 °C in a

relatively high yield, which implied a partial conversion of $^n\text{BuOAlCl}_2$ to $(^n\text{BuO})_3\text{Al}$.⁶ We then isolated compound **5** by crystallization of an oily product from the reaction mixture of EtAlCl_2 with $^n\text{BuOH}$ and characterized it structurally as a cyclic trimer (Figure 2). A comparison of corresponding bond distances and angles in **5** with two structural data sets⁷ for trimeric $[\text{MeOAlCl}_2]_3$ is given in Table 4. Although the coordination environment around O atoms is nearly planar (Σ° 358.6–359.2), the Al_3O_3 central ring in **5** is highly puckered (skewed boat) due to the packing of the ^nBu and Cl groups.

So far, we have shown that, in the isolated compounds **1**, **2**, **5**, **7**, and **8**, both chlorine atoms remained attached to Al. However, further concentration of the reaction solutions or different crystallization conditions in both $^i\text{HexOH}$ and $^n\text{BuOH}$ systems led to the formation of trinuclear molecules **3**, **4**, and **6**. The RO/Cl group exchange or HCl release must have taken place to replace one Cl by an alkoxide.

The bicyclic trinuclear molecules **3** and **4** were obtained from the $^i\text{HexOH}$ reaction. Compound **4** is derived from **3** by the coordination of one cyclohexanol molecule. Similar derivatives were reported for $^i\text{PrOH}$ (Chart 1, **D**, **E**; $\text{R} = ^i\text{Pr}$).^{10,14} The molecular structures of **3** and **4** are presented in Figure 2, and a comparison of their bond distances and angles with the analogous O ^iPr derivatives is shown in Table 5. Compound **3** was obtained in two polymorphic forms crystallizing in the same monoclinic space group but with different cell parameters. It features a pseudo- C_2 molecular symmetry, implying the presence of two enantiomers. The two four-membered rings are fused at the central Al atom, which is found in a near perfect trigonal-bipyramidal coordination with the value of the geometric parameter $\tau = 98.0\%$.²⁷ The peripheral Al atoms in **3** are four-coordinate with a distorted tetrahedral geometry. The expected differences in the Al–Cl and Al–O bond lengths to four- and five-coordinate Al centers were observed, as well as longer axial Al–O bonds in comparison to the equatorial ones at the trigonal-bipyramidal Al center. The ^{27}Al NMR spectrum of **3** revealed two signals at 45 and 91 ppm that suggest the presence of four- and five-coordinate Al atoms in solution.

The molecule of **4** lacks any symmetry elements and thus has to provide two enantiomers. The central octahedrally coordinated Al atom is bound to one Cl, four alkoxide, and one alcohol O atom. The Cl ligand exerts a strong trans influence that elongates the Al–O bond to the trans alkoxide (Table 5). The preferential cyclohexanol binding to the five-coordinate Al center instead of the four-coordinate one, which would be expected on Lewis acidity grounds, may be caused by additional stabilization by intramolecular hydrogen bonding of the cyclohexanol hydrogen to a bridging alkoxide O atom ($\text{O} \cdots \text{HO} = 2.29 \text{ \AA}$).

A low temperature crystallization of the $\text{EtAlCl}_2/^n\text{BuOH}$ system provided, besides the monocyclic trimer **5**, a novel trinuclear molecule, **6**. Because of the small size of crystals of **6**, only a structural model was obtained from the analysis of X-ray diffraction data. As can be gathered from Figure 3, **6** is an ionic compound with a trinuclear cation and chloride anion. This result corresponds with a low temperature of crystallization, which in the $\text{XAlCl}_2\text{--THF}$ systems ($\text{X} = \text{Me}$, Cl) favored the ionic forms $[\text{Al}(\text{THF})_4][\text{XAlCl}_3]$ over the

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Table 2. Selected Bond Distances (Å) and Angles (deg) of Dimeric [ROAlCl₂]₂

bond	1	CH ₂ ^t Bu ⁶	7	8
Al(1)–Cl(1)	2.089(1)	2.056(2)	2.083(2)	2.094(1)
Al(1)–Cl(2)	2.094(1)	2.049(2)	2.064(2)	2.086(1)
Al(1)–O(1)	1.796(2)	1.772(3)	1.814(2)	1.833(1)
Al(1)–O(1)#1 ^a	1.808(2)	1.776(3)	1.776(2)	1.827(1)
angle	1	CH ₂ ^t Bu ⁶	7	8
O(1)–Al(1)–O(1)#1	81.4(1)	82.5(1)	83.0(1)	80.8(1)
Cl(1)–Al(1)–Cl(2)	114.0(1)	117.0(1)	117.8(1)	114.1(1)
Al(1)–O(1)–Al(1)#1	98.6(1)	97.5(1)	97.0(1)	98.0(1)

^a #1: $x + 1, -y + 1, -z + 1$ (1); $-x, -y + 1, -z$ (7); $-x + 1, y, -z + 1/2$ (8).

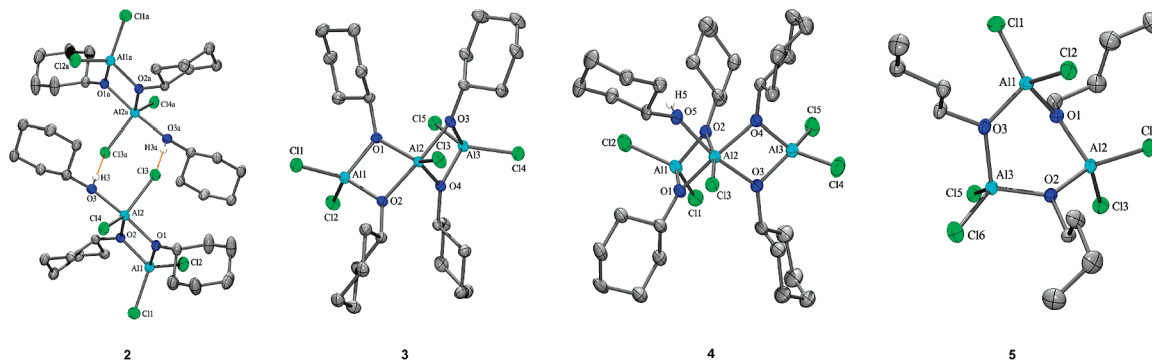


Figure 2. Molecular structure of **2** with C–H hydrogens omitted for clarity and atom the numbering scheme. A pair of **2** molecules is connected by two O–H···Cl bridges to form a dimer. Molecular structures of **3**, **4**, and **5** with all H atoms omitted for clarity are also shown. Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) of **2**

compound 2			
Bond			
Cl(1)–Al(1)	2.097(1)	Al(1)–O(2)	1.811(2)
Cl(2)–Al(1)	2.107(1)	Al(2)–O(1)	1.897(2)
Cl(3)–Al(2)	2.194(1)	Al(2)–O(2)	1.849(2)
Cl(4)–Al(2)	2.142(1)	Al(2)–O(3)	1.931(2)
Al(1)–O(1)	1.764(2)		
Angle			
Al(1)–O(1)–Al(2)	100.2(1)	O(2)–Al(1)–Cl(1)	113.9(1)
Al(1)–O(2)–Al(2)	100.3(1)	O(1)–Al(1)–Cl(2)	115.2(1)
O(1)–Al(1)–O(2)	81.9(1)	O(2)–Al(1)–Cl(2)	115.6(1)
O(1)–Al(2)–O(3)	167.2(1)	O(1)–Al(2)–Cl(3)	93.6(1)
O(1)–Al(2)–O(2)	77.5(1)	O(2)–Al(2)–Cl(3)	118.4(1)
O(2)–Al(2)–O(3)	89.7(1)	O(3)–Al(2)–Cl(3)	91.5(1)
Cl(1)–Al(1)–Cl(2)	111.7(1)	O(1)–Al(2)–Cl(4)	95.1(1)
Cl(3)–Al(2)–Cl(4)	117.4(1)	O(2)–Al(2)–Cl(4)	124.1(1)
O(1)–Al(1)–Cl(1)	115.8(1)	O(3)–Al(2)–Cl(4)	93.1(1)

neutral adducts [XAlCl₂(THF)₂].²⁸ The molecule of **6** features a centrosymmetric trinuclear Al(μ-O)₂Al(μ-O)₂Al core with two fused four-membered rings and all three Al atoms octahedrally coordinated. The central aluminum possesses two trans-oriented Cl ligands and four oxygens. Each of the two equivalent outer Al atoms is coordinated to one Cl, bridging OH and alkoxide oxygens, and the octahedron is completed by three *n*-butanol molecules. Their presence may suggest an influence of adventitious moisture during pro-

Table 4. Selected Bond Distances (Å) and Angles (deg) of Trimeric [ROAlCl₂]₃

	5, ⁿ Bu	Me ^{a,7b}	Me ^{7a}
Bond			
Al–Cl	2.094–2.107(1)	2.075–2.117(1)	2.088–2.102(1)
Al–O	1.796–1.815(2)	1.788–1.803(1)	1.801–1.810(2)
Angle			
Cl–Al–Cl	113.6–114.9	113.2–117.7	112.5–116.5
O–Al–O	95.1–101.4	100.6–101.2	95.4–100.4
Al–O–Al	121.1–123.9	124.0–133.3	121.9–122.8

^a Only data for the [MeOAlCl₂]₃ molecule are compared.

longed crystallization. The total charge balance is maintained by one chloride ion equally distributed in two positions and bound by hydrogen bonds to the bridging OH and one alcohol. These Cl ions bind in the same way also to the neighboring molecules, thus forming supramolecular chains (Figure 3). The structure of **6** is related to the previously reported compound [Cl₂Al(μ-OAlCl₃)(μ-OⁱPr)AlCl(PrOH)₃]¹⁴ (Chart 2, **H**) that can be thought of as **6** devoid of one [AlCl(OH)(OR)(ROH)₃] moiety and its bridging oxide atom coordinated by Lewis acid AlCl₃ instead of Brønsted acid HCl.

We also examined the effect of aromatic substituents on the structure of ROAlCl₂. Previous studies on PhOAlCl₂ by cryoscopy and IR spectroscopy^{8a} reported the predominance of a trimer after vacuum distillation and dissolution in benzene. The presence of mixed oxygen–chloride bridges in the trimeric molecule was proposed based on the observed Al–O–C vibrations. In contrast, we found that the

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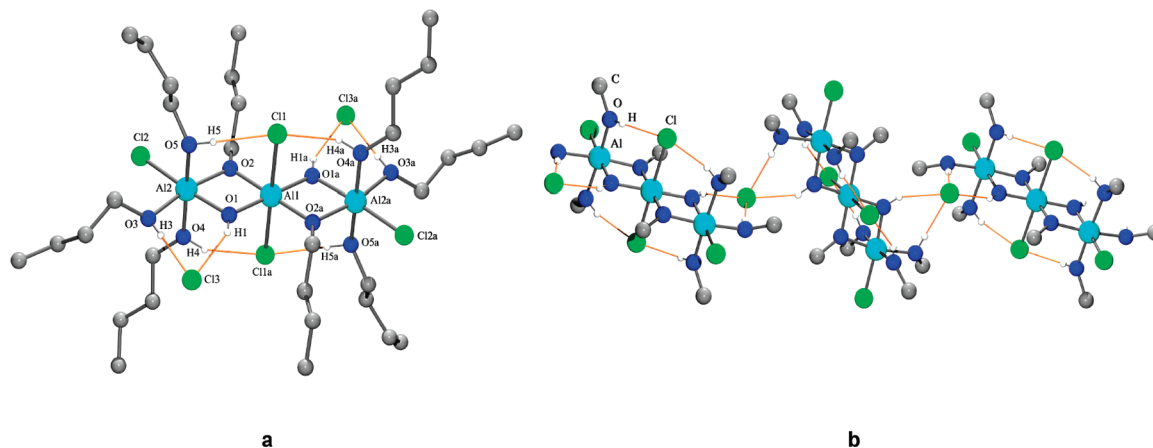


Figure 3. Model of structure **6**. C–H hydrogens were omitted for clarity. (a) Molecule of **6** with intramolecular OH····Cl hydrogen bonds shown. (b) A supramolecular chain connected by intermolecular OH····Cl hydrogen bonds.

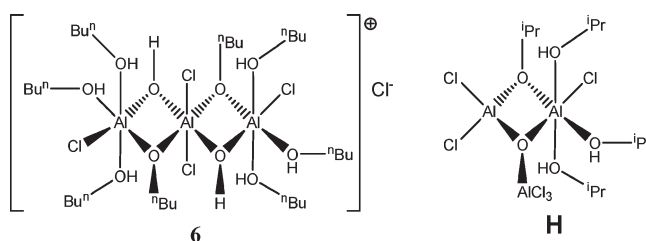
Table 5. Selected Bond Distances (Å) and Angles (deg) of Trinuclear $[\text{ClAl}\{\mu\text{-OR}\}_2\text{AlCl}_2]_2$ (R = ^tHex (**3**), ^tPr (**D**)) and $[\text{Cl}(\text{HOR})\text{Al}\{\mu\text{-OR}\}_2\text{AlCl}_2]_2$ (R = ^tHex (**4**), ^tPr (**E**))

3		D , ^t Pr ¹⁰
Bond		
Al ^V –Cl	2.129(1)	2.141(5)
Al ^{IV} –Cl	2.094–2.108(1)	av. 2.095
Al ^V –O _{axial}	1.898–1.904(1)	1.917(7)
Al ^V –O _{equat}	1.833–1.838(1)	1.840(7)
Al ^{IV} –O	1.772–1.793(1)	av. 1.794
Angle		
O _{axial} –Al ^V –O _{axial}	167.5	170.6
O _{equat} –Al ^V –O _{equat}	108.7	110.8
O–Al ^{IV} –O	av. 82.2	82.8
Cl–Al ^{IV} –Cl	112.9–114.6	112.1
Al–O _{axial} –Al	98.6	98.2
Al–O _{equat} –Al	100.4–100.7	100.6
4		E , ^t Pr ¹⁴
Al ^{VI} –Cl	2.211(1)	2.287(2)
Al ^{IV} –Cl	2.112–2.131(1)	2.101–2.110(2)
Al ^{VI} –O(H)	1.967(2)	1.961(3)
Al ^{VI} –O(trans to Cl)	1.982(2)	1.943(3)
Al ^{VI} –O(trans ROH)	1.936(2)	1.922(3)
Al ^{VI} –O(cis Cl/ROH)	1.929, 1.933(2)	1.906, 1.913(3)
Al ^{IV} –O	1.767–1.783(2)	1.770–1.783(3)

molecular structure of $[\text{Cl}_2\text{Al}(\mu\text{-OPh})_2\text{AlCl}_2]$ (**7**) is dimeric with phenoxide bridges (Figure 1) when **7** is directly crystallized from the reaction mixture. The substitution of the phenyl ring at one of the ortho positions with the ^tBu group did not change the oligomerization degree, and we isolated compound **8**, which is also dimeric (Figure 1) with the aryloxy bridging groups. A similar ortho-disubstituted 2,6-Me₂C₆H₃OAlCl₂^{8b} was proposed to be dimeric with Cl bridges based on molecular weight determination and IR spectra.

The above-discussed series of structurally characterized aluminum cyclohexylalkoxide chlorides **1**–**4** suggests a possible pathway for the transformation reactions that could lead from ROAlCl₂ to trinuclear and to tetranuclear derivatives (Scheme 1). The dimeric **1** is coordinated by an alcohol molecule to form **2**, and this adduct can convert by splitting off HCl through an unidentified intermediate **J** to the tri-

Chart 2



nuclear **3** by the coordination to one-half of dimeric **1**. The second coordination of cyclohexanol provides the hexa-coordinate Al center in **4**. We can speculate that **4** may release HCl and form a putative **K** possessing a terminal alkoxide group, which by reacting with monomeric ROAlCl₂ could finally yield the tetranuclear **F**. In light of the presented structural findings, the previously suggested system of ligand scrambling reactions in ROAlCl₂ with AlCl₃ as one of the products⁶ seems less plausible because the solubility of AlCl₃ in hydrocarbon solvents is low.

To test the effectiveness of the aluminum cyclohexylalkoxide chlorides in nonhydrolytic sol–gel synthesis of alumina, we used the mixture of EtAlCl₂ and cyclohexanol as a precursor for the solution thermolysis, which is expected to induce condensation by alkylhalide elimination. The molar ratio of EtAlCl₂ to cyclohexanol was chosen to be 3:4.5 to ensure a complete elimination of ^tHexCl. A high boiling solvent, tetraglyme (bp 276 °C), was used to heat the mixture to 150 °C for 14 h. During the reaction, a white solid precipitated and was isolated by centrifugation. It consisted of uniform spherical particles with a diameter of about 1 μm (Figure 4). The as-prepared material contained 12.9% C and 5.4% H, which shows an incomplete condensation and partial retention of the ^tHex groups; however, the GC/MS analysis of the volatile components of the reaction solution revealed the presence of ^tHexCl, the expected condensation byproduct. Thermal behavior of the solid powder was studied by TG/DTA, which showed a continuous mass loss (55%) from an ambient temperature to 550 °C. This weight decrease was accompanied by two exothermic effects at 268 and 449 °C that correspond to oxidation of organic groups. The solid residue after the TG/DTA analysis at 1100 °C featured broad lines in the XRD diffractogram that were

assigned to poorly crystalline γ - Al_2O_3 (JCPDS card 10-425). The surface area of the nonhydrolytic alumina powder was measured by the BET method. The as-prepared product had a surface area of $3.9 \text{ m}^2 \text{ g}^{-1}$ when mild degassing conditions (25°C) were applied. However, the surface rose to $150 \text{ m}^2 \text{ g}^{-1}$ after degassing at 350°C under a vacuum for 10 h. This was

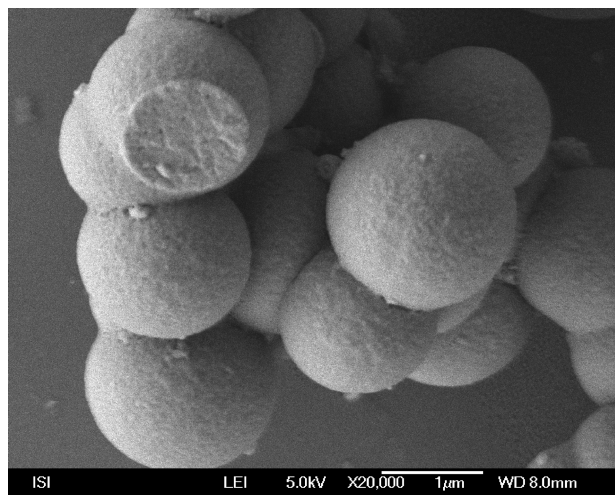


Figure 4. SEM of the alumina particles from a nonhydrolytic condensation of EtAlCl_2 with cyclohexanol.

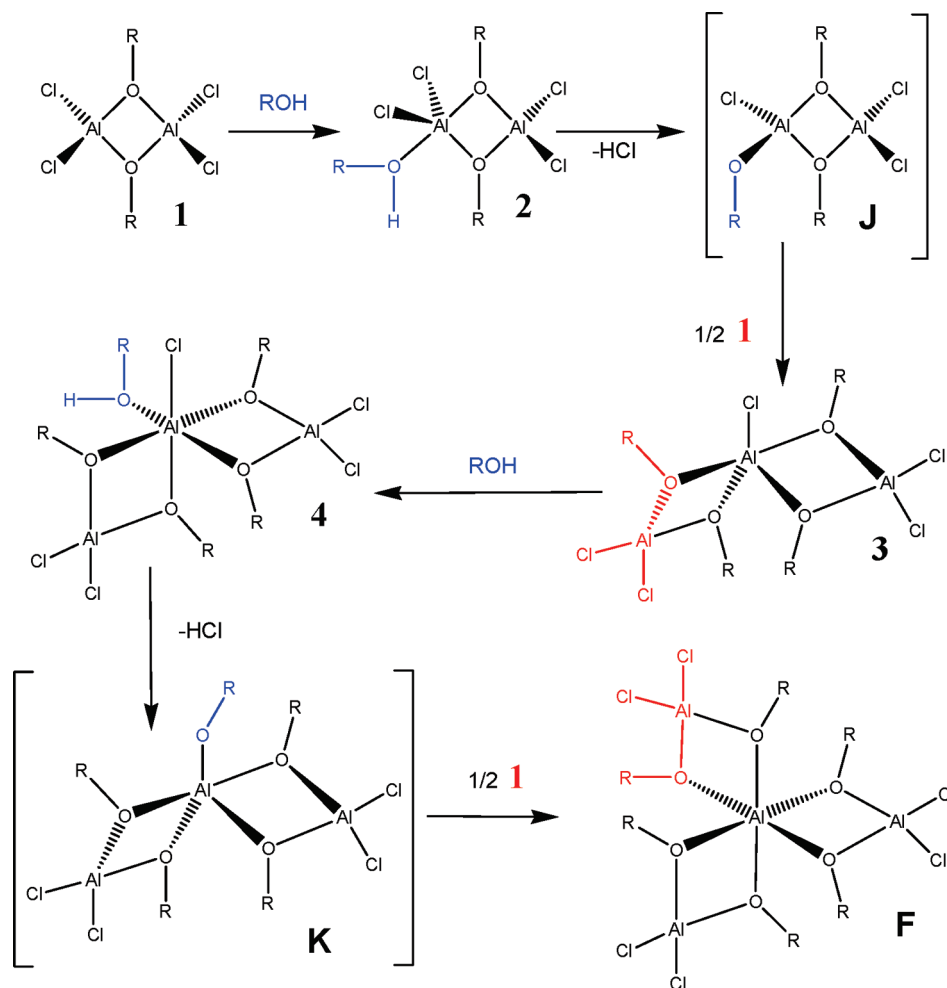
probably caused by the removal of residual organic groups from the surface that decreased the size of alumina particles and consequently increased the surface area.

Conclusions

The reactions of EtAlCl_2 with alcohols yielded a wealth of aluminum alkoxide chloride derivatives. This series shows enormous variability of products that are present in the reaction solution and undergo interconversion reactions upon a slight change of the reaction and crystallization conditions or in correspondence to the character of their substituents.

Three new dimeric $[\text{Cl}_2\text{Al}(\mu\text{-OR})_2\text{AlCl}_2]$ molecules (**1**, **7**, and **8**) were structurally authenticated. The ^iHex , Ph , and $2,4\text{-}^i\text{Bu}_2\text{C}_6\text{H}_3$ groups stabilize these dimers with the alkoxide bridges. Less branched ^iBu substituents allowed the isolation and structural characterization of trimeric $[\text{Cl}_2\text{Al}(\mu\text{-O}^i\text{Bu})_3]$ (**5**) possessing a puckered central six-membered ring. A novel structure of the alcohol-coordinated dimer $[\text{Cl}_2(\text{HO}^i\text{Hex})\text{-Al}(\mu\text{-O}^i\text{Hex})_2\text{AlCl}_2]$ (**2**) was established for the first time. It proves that the AlO_2Cl_2 centers in dimeric $[\text{ROAlCl}_2]_2$ are still sufficiently Lewis acidic to accept the coordination of cyclohexanol oxygen. This species may be an intermediate in the conversion of ROAlCl_2 to trinuclear aluminum alkoxide-chlorides, such as $[\text{ClAl}(\mu\text{-O}^i\text{Hex})_2\text{AlCl}_2]_2$ (**3**), which was obtained in two polymorphic forms. An increase in the coordination

Scheme 1



number of the central Al atom in **3** was effected by the coordination of one alcohol molecule to form **4**, which is only the second example of the hexa-coordinate $[\text{Cl}(\text{HOR})\text{Al}\{\mu\text{-OR}\}_2\text{AlCl}_2]_2$ species. This case shows a coordinatively unsatisfied AlO_4Cl center which is saturated by alcohol bonding. The stability of **4** is augmented by intramolecular hydrogen bonding of cyclohexanol OH to a bridging alkoxide oxygen.

A unique ionic trinuclear molecule, $[\text{Cl}_2\text{Al}\{\mu\text{-OH}\}(\mu\text{-O}^i\text{-Bu})\text{AlCl}(\text{HO}^i\text{Bu})_3]_2\text{Cl}$ (**6**), with a linear $\text{Al}(\mu\text{-O})_2\text{Al}(\mu\text{-O})_2\text{-Al}$ array and all three Al atoms in an octahedral environment represents a novel structural type among aluminum alkoxide chlorides and attests to the known chemical and structural variability in this class of compounds. A low crystallization temperature suggests the entropic preference for its ionic character.

Aluminum chloride alkoxides can serve as precursors to alumina, as was shown by the thermolysis of the mixture of EtAlCl_2 and cyclohexanol in a high boiling solvent tetraglyme that provided 'HexCl and alumina particles by non-hydrolytic condensation reactions.

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Supporting Information Available: Complete X-ray data for compounds **1–5**, **7**, and **8** in CIF format; IR and Raman spectral data of **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.