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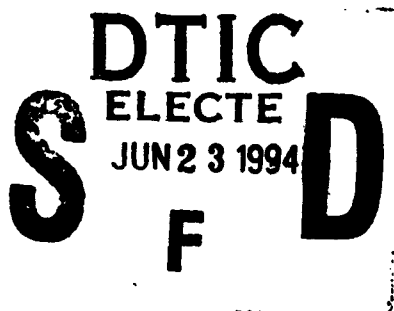
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Tert-butylalumoxanes: synthetic analogs for methylalumoxane (MAO) and new catalytic routes to polyolefins and polyketones

by

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Tert-Butylaluminum Hydroxides and Oxides: Structural Relationship between Alkylalumoxanes and Alumina Gels

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Abstract. The hydrolysis of $Al(^tBu)_3$ in toluene using the hydrated salt.
$Al_2(SO_4)_3 \cdot 14(H_2O)$, results in the formation of the dimeric hydroxide $[(^tBu)_2Al(\mu\text{-}OH)]_2$
(1) and $[Al_4(^tBu)_7(\mu_3\text{-}O)_2(\mu\text{-}OH)]$ (2) as the major and minor products, respectively.
Compound 1 may also be prepared by the addition of water to a refluxing toluene
solution of $Al(^tBu)_3$. Compound 1 is remarkably stable to thermolysis and is converted
slowly to a mixture of alumoxane species. Dissolution of compound 1 in MeCN or THF
yields the hydrogen-bound trimeric complexes $[(^tBu)_2Al(\mu\text{-}OH)]_3.n(MeCN)$ [n = 1(3), 2]
and $[(^tBu)_2Al(\mu\text{-}OH)]_3.2(THF)$. respectively. The large scale synthesis of alumoxanes
from the low temperature thermolysis of the trimeric hydroxide, $[(^tBu)_2Al(\mu\text{-}OH)]_3$,
allows for the isolation of the penta-aluminum compound $[Al_5(^tBu)_7(\mu_3\text{-}O)_2(\mu\text{-}OH)_2]$ (4)
and the heptameric alumoxane $[(^tBu)Al(\mu_3\text{-}O)]_7$ (5). The structure of compound 4 is
consistent with the condensation of $[(^tBu)_2Al(\mu\text{-}OH)]_3$ with $[(^tBu)_2Al(\mu\text{-}OH)]_2$.
Thermolysis of 4 yields an alumina gel. The structural relationship of 4 with respect to
the structures reported for non-alkyl alumoxanes and alumina gels is discussed. Reaction
of $[(^tBu)_2Ga(\mu\text{-}OH)]_3$ with $Al(^tBu)_3$ in toluene yields the octameric alumoxane $Ga(^tBu)_3$
and $[(^tBu)Al(\mu_3\text{-}O)]_8$ (6). as the major isolable products. Mass spectrometry indicates the
incorporation of low levels of gallium (< 8 %) into samples of 6 made by this route. The
molecular structures of compounds 2. 4 and 6 have been determined by X-ray
crystallography. Crystal data for 2: monoclinic. $P2_1/c$, a = 10.012(6). b = 9.426(3), c =
39.14(1) Å. β = 92.53(1) °, Z = 4. R = 0.098. R_w = 0.101. Crystal data for 4: monoclinic.
$P2_1/c$. a = 17.204(3), b = 11.337(2). c = 20.143(4) Å. β = 97.84(3) °. Z = 4. R = 0.054.
R_w = 0.055. Crystal data for 6: monoclinic. C2/c. a = 41.622(3), b = 9.0176(8). c =
21.303(1) Å. β = 99.250(5) °, Z = 8. R = 0.047, R_w = 0.0.053.

Introduction

We have recently reported[2] the first conclusive evidence that alkylalumoxanes, prepared by the hydrolysis of AlR_3, have the general formula of $[(R)Al(\mu_3\text{-}O)]_n$. Based on spectroscopic evidence, and confirmed by the X-ray crystallographic structural determination of $[(^tBu)Al(\mu_3\text{-}O)]_6$ and $[(^tBu)Al(\mu_3\text{-}O)]_9$, we have shown that these compounds have three dimensional cage structures in which the aluminum centers are four-coordinate and the oxygen coordination environment involves the bridging three aluminum atoms. Furthermore, we have proposed that the major species present in methylalumoxane (MAO)[3] are also three dimensional cage structures. This proposal is in direct contrast to the conventional linear or cyclic two dimensional picture expounded by many researchers both in academia and industry,[4] but is clearly consistent with the known chemistry of aluminum,[5,6] and previous spectroscopic studies.[4]

We now report further on the products formed upon the hydrolysis of $Al(^tBu)_3$, and provide evidence for the structural relationship between alkylalumoxanes and siloxy-substituted alumoxanes, alumina gels and the mineral boehmite. In addition, the molecular structure of our previously synthesized $[(^tBu)Al(\mu_3\text{-}O)]_8$ is reported.

Results and Discussion

Hydrated Salt *versus* Direct Hydrolysis of $Al(^tBu)_3$. We have previously reported[2] that the direct reaction of $Al(^tBu)_3$[7] with one molar equivalent of water results in the liberation of *iso*-butane and the formation of the trimeric aluminum hydroxide $[(^tBu)_2Al(\mu\text{-}OH)]_3$; which upon subsequent mild thermolysis yielded $[(^tBu)Al(\mu_3\text{-}O)]_n$ (n = 6, 9 and 12) as the major products. In contrast, the thermolysis of a mixture of $Al(^tBu)_3$ and a suspension of hydrated aluminum sulfate in toluene yielded $[(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$ as the major product.[2] suggesting that only half an equivalent of water had apparently reacted with $Al(^tBu)_3$. While hydrated aluminum sulfate is sold as the octadeca hydrate, $Al_2(SO_4)_3 \cdot 18(H_2O)$,[8] thermogravimetric analysis (TGA) of a

commercially available sample indicated that only 14 ($\pm$ 1) waters of hydration are in fact present. Thus, a less than stoichiometric quantity of water was available for reaction with Al(^{t}Bu)$_3$. This realization has prompted us to reinvestigated the hydrated salt hydrolysis of Al(^{t}Bu)$_3$.

The addition of Al(^{t}Bu)$_3$ to a suspension of Al$_2$(SO$_4$)$_3$·14(H$_2$O) in toluene followed by heating to reflux yields the dimeric aluminum hydroxide [(^{t}Bu)$_2$Al(μ-OH)]$_2$ (1), Eq. 1. Unlike its trimeric analog compound 1 does not decompose in the solid state at room temperature under an inert atmosphere.

$$Al(^tBu)_3 \xrightarrow{\;^1/_{14}\; Al_2(SO_4)_3 \cdot 14(H_2O)\;} {}^1/_2\; [(^tBu)_2Al(\mu\text{-}OH)]_2 \;+\; {}^tBuH \qquad (1)$$
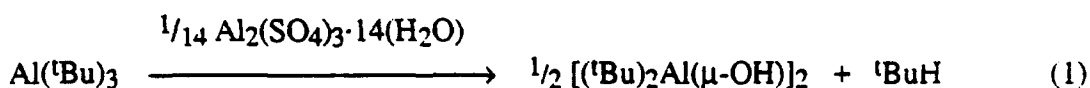
The presence of a hydroxyl group in compound 1 is substantiated by a singlet ^{1}H NMR resonance at 1.12 ppm, and ν(O-H) stretch (3697 cm^{-1}) in the infrared spectrum. The hydroxide resonance in the ^{1}H NMR spectrum is downfield of that observed for the trimeric analog, suggesting a reduction in the acidity of the hydroxide proton (see below). The ^{27}Al NMR spectrum of 1 exhibits a broad resonance at 132 ppm consistent with association of the hydroxide monomers to give a four-coordinate aluminum center. The dimeric nature of 1 (I) in the gas phase is indicated by the presence of a peaks in the mass spectrum due to M$^+$ - H and M$^+$ - ^{t}Bu (see Experimental).

(I)

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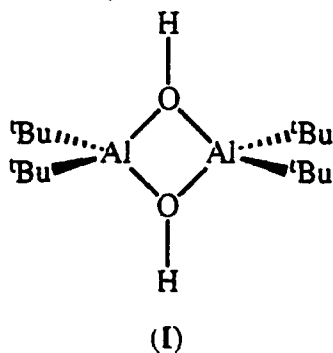
While X-ray crystallographic data was obtained for 1,[9] solvent loss problems preclude analysis of the structure. However, the cell volume, space group and partial solution was sufficient to confirm the dimeric structure of 1.

The reasons for the formation of a dimer from the salt hydrolysis route as opposed to the isolation of a trimer from the direct hydrolysis of $Al(^tBu)_3$ are perhaps unclear. However, it is worth noting that we have recently shown that aluminum alkoxides, $[Me_2Al(\mu\text{-}OR)]_n$, previously reported as dimers actually exist as trimers and dimers in equilibrium,[10] and the relative quantities of dimer and trimer present in a reaction mixture formed from $AlMe_3$ and an alcohol are dependent on the temperature of the $AlMe_3$ solution to which the alcohols were added: decreasing the temperature of reaction increases the relative quantity of trimer produced. From this we concluded that the trimeric alkoxides, $[Me_2Al(\mu\text{-}OR)]_3$, are the thermodynamic products while the dimers, $[Me_2Al(\mu\text{-}OR)]_2$, are the entropically favored products at high temperatures. The same principles appears to apply to the formation of $[(^tBu)_2Al(\mu\text{-}OH)]_n$, since, the direct hydrolysis reaction was, for safety, carried out at -78 °C, while the salt hydrolysis must be carried out in refluxing toluene to enable complete reaction. If the reaction temperature controls the oligomerization of the hydroxide then carrying out the direct hydrolysis at 110 °C should result in the formation of the dimeric hydroxide; this indeed observed. Addition of H_2O to a toluene solution of $Al(^tBu)_3$ heated to reflux [*CAUTION: This reaction is extremely violent*, see Experimental] yields 1 as the major product. Thus, low temperature hydrolysis of $Al(^tBu)_3$ yields the trimer while the high temperature synthesis results in the isolation of the dimer.

In our previous studies we demonstrated that heating the alkoxide trimer resulted in its conversion to the corresponding dimer (Eq. 2). While, the alkoxide dimer is slowly converted to the trimer (Eq. 2) upon re-equilibration ($t_{1/2} \approx 2$ - 3 months).

$$2 \text{ [Me}_2\text{Al(}\mu\text{-OR)]}_3 \quad \frac{t_{1/2} \text{ } ca. \text{ min., } 110 \text{ °C}}{t_{1/2} \text{ } ca. \text{ weeks @ } 25 \text{ °C}} \quad 3 \text{ [Me}_2\text{Al(}\mu\text{-OR)]}_2 \qquad (2)$$
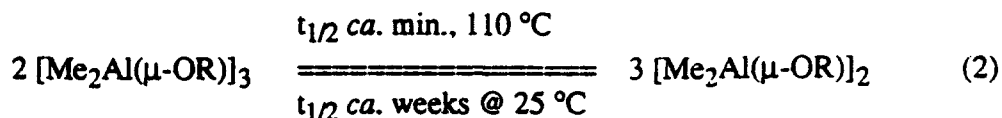
As we have previously reported, heating the hydroxide trimer, $[(^t\text{Bu})_2\text{Al(}\mu\text{-OH)}]_3$, results in its conversion to the alumoxanes, however, if the thermolysis is carried out on a sufficiently large scale (> 50 g) then the ^{1}H NMR of the reaction mixture does show a signal that may be assigned to the dimer, compound 1, see below. At this time we have no evidence for the room temperature conversion of $[(^t\text{Bu})_2\text{Al(}\mu\text{-OH)}]_2$ to $[(^t\text{Bu})_2\text{Al(}\mu\text{-OH)}]_3$.

Unlike $[(^t\text{Bu})_2\text{Al(}\mu\text{-OH)}]_3$ compound 1 is not readily converted to alumoxanes upon thermolysis. Whereas $[(^t\text{Bu})_2\text{Al(}\mu\text{-OH)}]_3$ eliminates alkane even at room temperature, compound 1 shows no reaction until heated in refluxing decane (174 °C) for 15 hours. In this regard compound 1 is similar to $[(^t\text{Bu})_2\text{Ga(}\mu\text{-OH)}]_3$, which requires refluxing in xylene (143 - 145 °C) to enable conversion into $[(^t\text{Bu})\text{Ga(}\mu_3\text{-O)}]_9$.[11] However, unlike $[(^t\text{Bu})_2\text{Ga(}\mu\text{-OH)}]_3$, thermolysis of 1 yields a mixture of alumoxanes, $[(^t\text{Bu})\text{Al(}\mu_3\text{-O)}]_n$ (n = 6 - 12).

The high thermal stability of 1 compared to its trimeric analog may be due to a number of factors. First; if the elimination of *iso*-butane is an intra-molecular reaction then the distance and orientation between the hydroxide proton and the α-carbon of the *tert*-butyl group will control the relative ease of elimination. Second, the higher the acidity of the hydroxide proton, the more facile the elimination. In the present case both factors seem to be significant. It is difficult to estimate the relative acidity of the aluminum hydroxide groups, however, a crude correlation between the hydroxide acidity and the ^{1}H NMR chemical shift has been previously observed:[12] a down field hydroxide proton correlates with an acidic hydroxide. The ^{1}H NMR chemical shift of the hydroxide in 1 (δ 1.12) is upfield of that for $[(^t\text{Bu})_2\text{Al(}\mu\text{-OH)}]_3$ (δ 2.02), and the thermal stability is indeed higher. The uncertainties in determining geometric parameters are significantly

less than estimating hydroxide acidity. However, while the hydroxide proton···*tert*-butyl α-carbon distance in [(^{t}Bu)$_2$Al(μ-OH)]$_3$ can be determined from X-ray crystallography (3.49 Å), the lack of good structural data for [(^{t}Bu)$_2$Al(μ-OH)]$_2$ precludes the corresponding value for the dimeric form from being determined with equal accuracy. An estimate of the hydroxide proton···*tert*-butyl α-carbon distance in [(^{t}Bu)$_2$Al(μ-OH)]$_2$ can be made from the calculated structure of [H$_2$Al(μ-OH)]$_2$ (3.69 Å). The validity of this estimate can be ascertained by comparing the value obtained experimentally for the flat Al$_3$O$_3$ cycle of [(^{t}Bu)$_2$Al(μ-OH)]$_3$ and the values of the axial substituents in [H$_2$Al(μ-OH)]$_3$ (3.51 Å); which is calculated to adopt a chair conformation. The values for [(^{t}Bu)$_2$Al(μ-OH)]$_3$ and [H$_2$Al(μ-OH)]$_3$ are clearly larger than that for [(^{t}Bu)$_2$Al(μ-OH)]$_2$. Furthermore, the orientation between the hydroxide and the *tert*-butyl, as measured by the appropriate torsion angles suggests that the elimination should be more favorable in the trimer, which is indeed observed: ∠(H-O-Al-C) estimated to be approximately 69.5 ° for 1, and determined to be 33 ° for [(^{t}Bu)$_2$Al(μ-OH)]$_3$. Given the similarity in the structure of the aluminum and gallium trimeric hydroxides, and the M-C bond strengths for aluminum and gallium, the stability of [(^{t}Bu)$_2$Al(μ-OH)]$_3$ and [(^{t}Bu)$_2$Ga(μ-OH)]$_3$ would be expected to be similar; which they are.

As noted above compound 1 is the major product isolated from the salt hydrolysis of Al(^{t}Bu)$_3$, while [(^{t}Bu)$_2$Al{μ-OAl(^{t}Bu)$_2$}]$_2$ may be isolated if a less than stoichiometric hydrolysis is employed. However, synthesis of compound 1 on a sufficiently large scale (*ca.* 5 g) allows for the isolation, by fractional recrystallization, of a new tetra-aluminum product, [Al$_4$(^{t}Bu)$_7$(μ$_3$-O)$_2$(μ-OH)] (2). The ^{1}H and ^{13}C NMR spectrum of compound 2 are consistent with the presence of seven *tert*-butyl groups, in a 2:2:2:1 ratio, and a single hydroxide environment. The molecular structure of compound 2 has been confirmed by X-ray crystallography, however, the solution was hampered by significant disorder in the crystal lattice (see Experimental Section).

The molecular structure of compound 2 is shown in Figure 1; selected bond lengths and angles are given in Table I. The tetrameric structure of 2 consists of an Al_3O_3 ladder core, with each of the aluminum atoms being four coordinate; the coordination sphere of Al(1) and Al(3) being that of two *tert*-butyl groups and two oxygen atoms, while that of Al(2) is one *tert*-butyl group and three oxygens. The remaining aluminum, Al(4), is three coordinate and bonded to one of the "end" oxides of the ladder. The formally coordinative unsaturation of Al(4) is undoubtedly due to the steric hindrance of the *tert*-butyl groups attached to Al(3) and Al(2), which preclude further aggregation. All the bond lengths and angles in compound 2 (Table I) are within experimental error of those of other alumoxanes.

The formation and structure of compound 2 may be understood by a comparison with the structure of $[(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$. As can be seen from Scheme 1 hydrolysis of $[(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$ followed by complexation of one of the three coordinate aluminum centers with the hydroxide yields compound 2. Furthermore, as shown in Scheme 1, additional hydrolysis of compound 2 may explain the formation of $[(^tBu)Al(\mu_3\text{-}O)]_8$ which was previously observed to be formed as a side product with $[(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$, but not upon the thermolysis of $[(^tBu)_2Al(\mu\text{-}OH)]_3$.[?] Based upon literature precedent, we have previously assumed that the small quantity of $[(^tBu)Al(\mu_3\text{-}O)]_8$ formed was as a result of the alkyl exchange reaction shown in Eq. 3. A similar ligand redistribution reaction has been suggested to occur during the thermolysis of the proposed (but not isolated) alumoxane $[Me_2Al(\mu\text{-}OAlMe_2)]_2$ to yield $(MeAlO)_n$.[19] However, the isolation of compound 2 would suggest that our previous isolation of $[(^tBu)Al(\mu_3\text{-}O)]_8$ was actually due to the non-stoichiometric hydrolysis conditions employed (see above).

$$\xrightarrow{\Delta} \qquad \xrightarrow{-\,2\,\text{Al}(^t\text{Bu})_3}$$

(3)
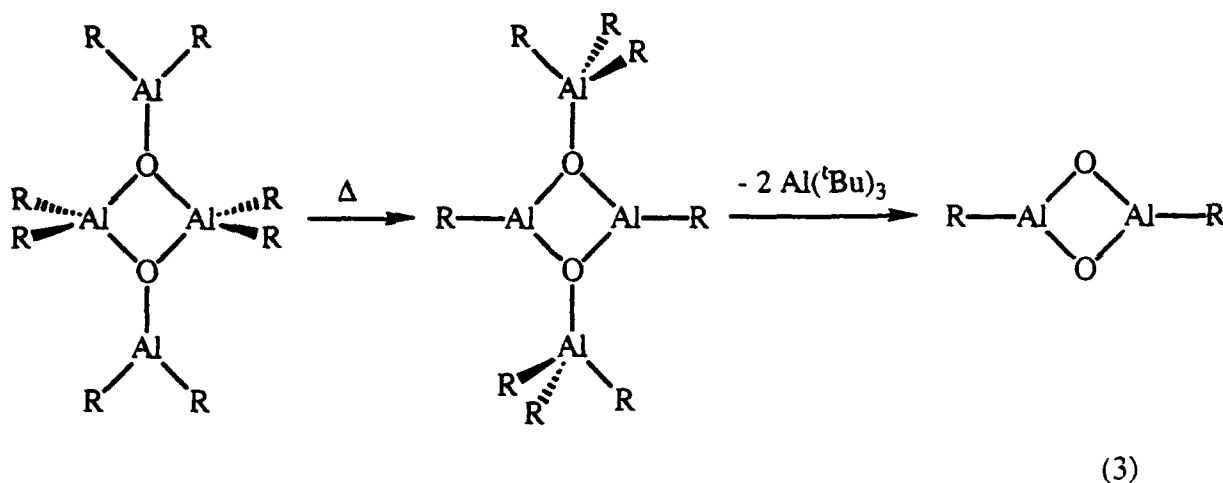
Reaction of [(tBu)₂Al(μ-OH)]₂ with Lewis bases. Recrystallization of

[(tBu)₂Al(μ-OH)]₂ from MeCN yields [(tBu)₂Al(μ-OH)]₃ as the main product; further

cooling of the supernatant yields crystals of [(tBu)₂Al(μ-OH)]₂.(MeCN) (3). In contrast,

pumping of the excess MeCN from a solution of [(tBu)₂Al(μ-OH)]₂ yields [(tBu)₂Al(μ-

OH)]₃.2(MeCN).[2] Compound 3 may also be isolated by stirring equimolar quantities of

[(tBu)₂Al(μ-OH)]₃ and [(tBu)₂Al(μ-OH)]₃.2(MeCN) in hexane. Recrystallization of 1

from THF yields the previously reported solvate, [(tBu)₂Al(μ-OH)]₃.2(THF).[2]

The IR spectra of **3** shows two ν(OH) bands, one due to a free hydroxide (3585

cm⁻¹) and one broad with increased intensity for the hydrogen-bonded hydroxide (3259

cm⁻¹). The ¹H NMR spectra of **3** shows only a single resonance for the hydroxide groups

(δ 3.29). We have previously reported the dependence of the chemical shift of the

hydroxide moiety as a function of the MeCN:Al molar ratio.[2] The shift observed for **3** is

comparable to that we have previously reported for a MeCN:Al ration of 1:3, consistent

with the formulation of compound **3** (II). The solution NMR spectra are therefore

consistent with the rapid and facile exchange of the MeCN molecules with each of the

three hydroxide groups.

(II)
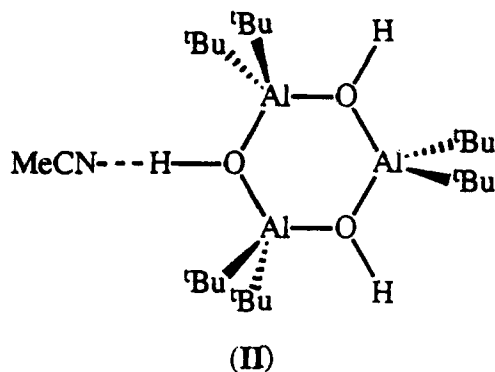
The Lewis-base catalyzed rearrangement of the dimeric to the trimeric hydroxide is not without precedent. It has been previously reported that amines catalyze the dimer to trimer reaction of aluminum amides, $[(R_2)Al(\mu\text{-}NR'_2)]_n$.[13] The only difference in the present case being the solvation of the hydroxide by the Lewis base.

Compound 3 slowly decomposes in the solid state at room temperature to yield $[(^tBu)Al(\mu_3\text{-}O)]_9$ as the major product, along with other alumoxane species. The formation of the nonamer as the major product from the thermolysis of compound 3 is in contrast to the formation of the hexamer, $[(^tBu)Al(\mu_3\text{-}O)]_6$, as the major alumoxane species formed during the thermolysis of $[(^tBu)_2Al(\mu\text{-}OH)]_3$.[2] Similarly, the presence of MeCN during the hexane thermolysis of 1 or $[(^tBu)_2Al(\mu\text{-}OH)]_3$ results in the formation of the nonamer, $[(^tBu)Al(\mu_3\text{-}O)]_9$, in 50 - 60 % yield.

Hydrolysis of Al($^tBu)_2(^iBu)$. Like other workers,[7] we have found that the synthesis of Al($^tBu)_3$ from AlCl$_3$ and *tert*-butyl lithium results in the formation of Al($^tBu)_2(^iBu)$ as a sometimes significant side product. The factors controlling the relative yield of Al($^tBu)_3$ and Al($^tBu)_2(^iBu)$ are unclear, however, we have observed that once Al($^tBu)_3$ is prepared in the absence of Al($^tBu)_2(^iBu)$ then the former does not rearrange to the latter; suggesting that the *tert*-butyl to *iso*-butyl rearrangement is promoted by impurities in the reaction mixture. Since we wish to maximize the yield of the *tert*-butyl alumoxanes, we have investigated the hydrolysis of Al($^tBu)_2(^iBu)$. Direct hydrolysis of

Al(^{t}Bu)$_2$(^{i}Bu), at -78 °C, results in the high yield formation of [(^{t}Bu)$_2$Al(μ-OH)]$_3$. There is no evidence for the formation of the alternative product [(^{t}Bu)(^{i}Bu)Al(μ-OH)]$_n$, suggesting that the hydrolysis occurs with the least sterically hindered alkyl and not the weakest Al-C bond.

Isolation and Structural Characterization of a New Pentameric and Heptameric Alumoxanes. In our original report of the synthesis of *tert*-butyl alumoxanes the thermolysis of [(^{t}Bu)$_2$Al(μ-OH)]$_3$ was carried out on the 3 - 5 mmol scale; allowing for the isolation of three main products [(^{t}Bu)Al(μ_3-O)]$_6$, [(^{t}Bu)Al(μ_3-O)]$_9$, and [(^{t}Bu)Al(μ_3-O)]$_{12}$. If the reaction is carried out on a much larger scale (ca. 90 mmol) then two additional new compound may be isolated in low yield along with a small quantity of the dimeric hydroxide, compound **1**, further suporting the temperature dependence of the hydrolysis reaction.

Thermolysis of a hexane solution of [(^{t}Bu)$_2$Al(μ-OH)]$_3$ yields a mixture of alumoxanes, of which the hexamer [(^{t}Bu)Al(μ_3-O)]$_6$ is the major product, and from which, by repeated fractional crystallization, may also be isolation compound **4**. The ^{1}H and ^{13}C NMR spectra of **4** indicate the presence of seven aluminum-bound *tert*-butyl environments in a 1:2:2:2 ratio, and two non-equivalent hydroxyl groups. The presence of two hydroxide environments is confirmed by IR spectroscopy, ν(O-H) 3681 and 3599 cm^{-1}. The relative shifts of these bands are similar to those observed for **1** and [(^{t}Bu)$_2$Al(μ-OH)]$_3$, suggesting that the hydroxides are positioned within a four-membered Al$_2$O$_2$ and six-membered Al$_3$O$_3$ cycle, respectively (see below). The EI mass spectrum of **4** exhibits a fragment (m/z = 559, 95 %) consistent with the composition Al$_5$^{t}Bu$_6$O$_5$H$_2$ (i.e., M$^+$ - ^{t}Bu). The analytical and spectroscopic characterization of compound **4** is consistent with a penta-aluminum compound, the structure of which has been determined by X-ray crystallography to be [Al$_5$(^{t}Bu)$_7$(μ_3-O)$_3$(μ-OH)$_2$] (**4**).

The molecular structure of compound **4** is shown in Figure 2; selected bond lengths and angles are given in Table II. The pentameric structure of compound **4** is unique, previous aluminum-nitrogen pentamers consisting of either a $[Al_3N_3]$ ring capped by two [AlN] moieties (**III**),[14] or a $[Al_4N_4]$ cube edge sharing an [AlN] unit (**IV**).[15]

(**III**)   (**IV**)
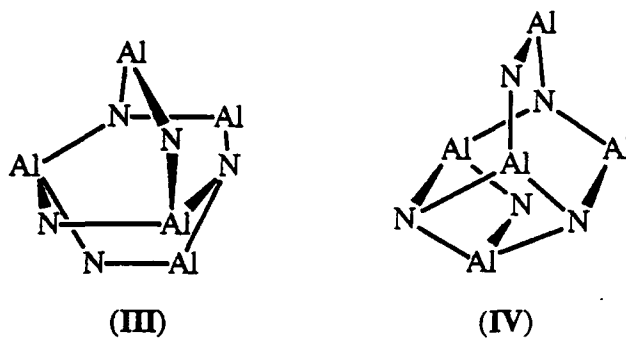
The core structure of compound **4** is best considered to consist of the fusion of a six-membered Al_3O_3 [Al(1), Al(4) and Al(5)] ring with a four-membered Al_2O_2 ring [Al(2) and Al(3)]. However, two alternative views are worth discussion. First, the structure of **4** is clearly related to the unknown Al_4O_4 cubane unit [Al(1), Al(2), Al(3)] edge sharing with an Al_2O unit [Al(4), Al(5)]. Second, as can be seen from Figure 3, the Al_5O_5 core is iso-structural with $^5/_7$ of the Ga_7S_7 heptameric structure we have previously reported for $[(^tBu)Ga(\mu_3\text{-}S)]_7$.[11]

The Al-O and Al-C bond lengths in compound **4** are both within the ranges we have previously reported for alkylalumoxanes. While no difference is discernible in the Al-C bond length between the $[(^tBu)_2AlO_2]$ and $[(^tBu)AlO_3]$ moieties, the Al-O bond lengths associated with the hydroxides are slightly larger (average = 1.862 Å) than those of the oxides (average = 1.816 Å).

One unusual structural feature of compound **4** is geometry around Al(1). While the other aluminum centers are essentially tetrahedral, Al(1) is closer to trigonal bipyramidal: the *tert*-butyl [C(11), O(124) and O(135) occupying the pseudo-equatorial ligand sites (Σ [X-Al-X] = 357.1 °, compared to 360 ° and 328.5 ° for trigonal

bipyramidal and tetrahedral geometries, respectively), while the pseudo-axial sites are occupied by O(123) and a vacant coordination site. A consideration of the space filling diagram of compound 4 (Figure 4) suggests that the unusual geometry of Al(1) is due to steric hindrance between the *tert*-butyl substituent on Al(1) and those on the other aluminum atoms.

Following the separation of the alumoxanes, $[(^tBu)Al(\mu_3-O)]_6$ and $[Al_5(^tBu)_7(\mu_3-O)_3(\mu-OH)_2]$, by fractional crystallization from the large scale hydrolysis of $[(^tBu)_2Al(\mu-OH)]_3$ the isolation of the heptameric alumoxane, $[(^tBu)Al(\mu_3-O)]_7$ (5), in low yield (*ca.* 2 %) is permitted. The EI mass spectrum of 5 exhibits a fragment (m/z = 700, 40 %) consistent with the heptameric structure, while the ^1H and ^{13}C NMR spectra (see Experimental) are analogous to that we have previously observed for the gallium sulfide cage compound, $[(^tBu)Ga(\mu_3-S)]_7$, to which compound 5 is most likely isostructural.

Structural Relationship of $[Al_5(^tBu)_7(\mu_3-O)_3(\mu-OH)_2]$ to Siloxy-substituted Alumoxanes, Alumina Gels and the Mineral Boehmite. We have previously demonstrated that like $[(^tBu)Al(\mu_3-O)]_n$, non-alkyl alumoxanes such as those found in aluminum based sol-gels also have three-dimensional rather that two-dimensional structures. However, the alumoxanes do not have the general formula $[(X)AlO]_n$ (X = OR, OSiR_3, O_2CR) but are of a variable composition best represented by $[Al(O)_x(OH)_y(X)_z]$ (2x + y + z = 3). Furthermore, the core structure of these "sol-gel" type alumoxanes is not that of a closed cage, but related to the mineral boehmite $[Al(O)(OH)]$.[16] The structural characterization of compound 5 provides the missing link between these two structural types.

It can be clearly seen from the highlighted sections in Figure 5 that there exists a definite structural similarity between the core of compound 4 (Figure 5a) and the structure of boehmite (Figure 5b). Further evidence for this relationship is based on the observation that thermolysis of a toluene solution of compound 4 results in gel formation

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from which a white powder may be obtained. The X-ray powder diffraction of which showed broad rings at d-spacing consistent with the two most intense reflections observed for boehmite, and comparable to literature values for gelatinous alumina.[17] Thermal annealing of the solid results in a significant narrowing of the rings.

It is commonly observed that during the reaction of AlR_3 (R $\neq$ ^tBu) with water, soluble alumoxanes are only formed at low water:aluminum ratios. As the relative amount of water is increased, or as the reaction is permitted to proceed at higher temperatures, the reaction mixture often contains gels usually assigned to the formation of hydrated alumina from the reaction of AlR_3 with a local excess of H_2O, Eq. 4.

$$AlR_3 \xrightarrow[-2RH]{+H_2O} RAlO \xrightarrow[-RH]{+H_2O} Al(O)(OH) \qquad (4)$$
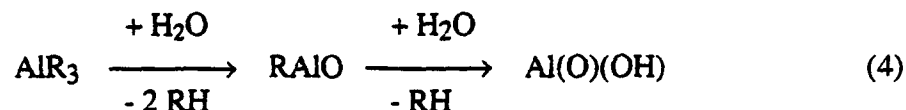
However, during the synthesis of *tert*-butyl alumoxanes, we have previously not observed any gel formation, leading us to question the relationship of our alkylalumoxanes to these alumina gels. Based upon our isolation of compound **4** we now propose that the gel accumulation previously observed during alkylalumoxane synthesis is due to the formation of alkylalumoxanes with structures based not on open cage structures, but on a boehmite core. We propose that during the hydrolysis of AlR_3 the formation of hydroxide trimer is preferred at lower reaction temperatures; thermolysis of the trimer yielding soluble alumoxanes, however, if the temperature of the reaction mixture is sufficiently high, some fraction of the trimeric hydroxide will rearrange to the dimer, and/or the dimer will form directly. Condensation of the trimeric hydroxide will occur to yield soluble cage-like alumoxanes. With significant concentrations of dimer, however, the formation of compounds similar to compound **4** will result. Further condensation will yield the alumina gels containing the boehmite core structure. These reactions are summarized in Scheme 2.

Reaction of $[(^{t}Bu)_{2}Ga(\mu\text{-}OH)]_{3}$ with $Al(^{t}Bu)_{3}$. We have previously reported the tetra-alkyl-dialuminum alumoxane $[(^{t}Bu)_{2}Al\{\mu\text{-}OAl(^{t}Bu)_{2}\}]_{2}$, and suggested that it was formed as a result of the reaction of an aluminum hydroxide with $Al(^{t}Bu)_{3}$. However, at this time attempts to isolate $[(^{t}Bu)_{2}Al\{\mu\text{-}OAl(^{t}Bu)_{2}\}]_{2}$ directly from this route have been unsuccessful. However, since we have previously shown that the gallium hydroxide undergoes self-condensation, we have attempted to synthesis a mixed aluminum-gallium oxide, $[(^{t}Bu)Al_{x}Ga_{1-x}(\mu_{3}\text{-}O)]_{n}$.
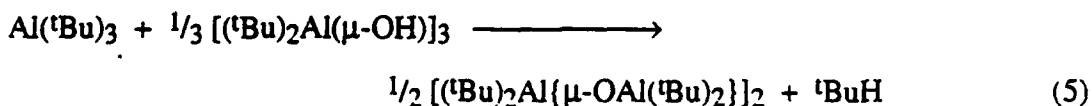
Addition of $Al(^{t}Bu)_{3}$ to a toluene solution of $[(^{t}Bu)_{2}Ga(\mu\text{-}OH)]_{3}$,[18] yields $Ga(^{t}Bu)_{3}$ in near quantitative yield, and a mixture of two aluminum containing species, $[(^{t}Bu)_{2}Al\{\mu\text{-}OAl(^{t}Bu)_{2}\}]_{2}$ and $[(^{t}Bu)Al(\mu_{3}\text{-}O)]_{8}$ (**6**) as the major (> 60 %) and minor (< 5 %) products, respectively. The ^{1}H and ^{13}C NMR spectra of compound **6** is consistent with our previously reported values for $[(^{t}Bu)Al(\mu_{3}\text{-}O)]_{8}$, however, additional peaks are present, even in the samples used for X-ray crystallography. These resonances, whose chemical shifts may be attributed to the presence of a second gallium containing product as an impurity in **6** (see below).

The molecular structure of $[(^{t}Bu)Al(\mu_{3}\text{-}O)]_{8}$ (**6**) is shown in Figure 6; selected bond lengths and angles are given in Table III. The $Al_{8}O_{8}$ core can be described as being derived from the fusing of a hexameric cage and a square, $Al_{2}O_{2}$, ring. A similar structure has been reported for the iminoalanes, $[HAl(\mu_{3}\text{-}N^{n}Pr)]_{8}$ and $[MeAl(\mu_{3}\text{-}NMe)]_{8}$.[19] An alternation of longer [1.905(4) - 1.880(5) Å] and shorter [1.760(6) - 1.795(5) Å] Al-O bonds is observed within the hexagonal rings. However, all are in the region we have reported for aluminum μ_{3}-oxides.[2]

The EI mass spectrum of the crystal of **6** used for X-ray crystallographic determination exhibits a fragment (m/z = 800, 100 %) consistent with $[(^{t}Bu)Al(\mu_{3}\text{-}O)]_{8}$, however, additional low intensity signals due to $(^{t}Bu)_{8}Al_{7}Ga(\mu_{3}\text{-}O)_{8}$ and $[Al_{6}Ga_{2}(^{t}Bu)_{8}(\mu_{3}\text{-}O)_{8}]$, m/z = 842 (5 %) and 884 (2 %), respectively.[20] Based on ^{1}H NMR spectroscopy the total *tert*-butyl gallium content may be estimated as *ca.* 8 %. This

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level of gallium content appears to be constant between crystals. However, attempts to include 8 % total gallium content (1 % per metal center) did not improve the X-ray data refinement, and therefore was not included from the final solution.

The formation of $Ga(^tBu)_3$ as the major gallium containing product indicates that under the reaction condition hydroxide exchange between gallium and aluminum occurs (Eq. 4) preferentially to the condensation elimination reaction between the gallium hydroxide and aluminum alkyl. Subsequent condensation of the aluminum hydroxide yield the alumoxane, $[(^tBu)Al(\mu_3\text{-}O)]_8$. However, we note that thermolysis of $[(^tBu)_2Al(\mu\text{-}OH)]_3$ ordinarily yields $[(^tBu)Al(\mu_3\text{-}O)]_6$ and $[(^tBu)Al(\mu_3\text{-}O)]_9$. We are unable to explain why $[(^tBu)Al(\mu_3\text{-}O)]_8$ should be formed in the presence of $Ga(^tBu)_3$. An alternative explanation for the formation of $[(^tBu)Al(\mu_3\text{-}O)]_8$ could involve the adventitious hydrolysis of $[(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2$ (formed by the reaction given in Eq. 5) via compound 2 (c.f., Scheme 1). The incorporation of a small amount of gallium into the alumoxane suggests that "$(^tBu)_2Ga(OH)$" reacts with the "$(^tBu)_2Al(OH)$" formed (c.f., Eq. 4) to give a *galoalumoxane*; the first to be reported.

$$Al(^tBu)_3 + \tfrac{1}{3}[(^tBu)_2Ga(\mu\text{-}OH)]_3 \longrightarrow$$
$$\tfrac{1}{n}[(^tBu)_2Al(\mu\text{-}OH)]_n + Ga(^tBu)_3 \qquad (4)$$

$$Al(^tBu)_3 + \tfrac{1}{3}[(^tBu)_2Al(\mu\text{-}OH)]_3 \longrightarrow$$
$$\tfrac{1}{2}[(^tBu)_2Al\{\mu\text{-}OAl(^tBu)_2\}]_2 + {}^tBuH \qquad (5)$$
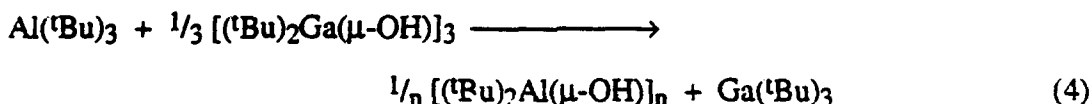
Experimental Section

Melting points were determined in sealed capillaries and are uncorrected. Mass spectra were obtained on a JEOL AX-505 H mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. Infrared spectra (4000 - 400 cm^{-1}) were obtained using a Nicolet 5ZDX-FTIR spectrometer; samples were prepared as mulls

on KBr plates. NMR spectra were obtained on Bruker AM-500, AM-400, AM-300, and AM-250 (^{1}H, ^{13}C) or Bruker WM-300 (^{17}O, ^{27}Al) spectrometers using (unless otherwise stated) d_6-benzene solutions. Chemical shifts are reported relative to external TMS (^{1}H, ^{13}C), H_2O (^{17}O), or aqueous [Al($H_2O)_6$)]$^{3+}$ (^{27}Al).

All procedures were performed under purified nitrogen. Solvents were distilled and degassed prior to use. Al(^{t}Bu)$_3$ and [(^{t}Bu)$_2$Ga(μ-OH)]$_3$ were prepared as previously reported.[7,19]

[(^{t}Bu)$_2$Al(μ-OH)]$_2$ (1), Method 1. Al(^{t}Bu)$_3$ (4.3 g, 47 mmol) was added to a cooled (-78°C) suspension of Al$_2$(SO$_4$)$_3$·14H$_2$O (1.9 g, 43 mmol H$_2$O) in toluene (300 mL). The mixture was stirred at -78°C for one hour and was then allowed to warm to room temperature. Stirring was continued at room temperature for two hours. The mixture was refluxed for fifteen hours, cooled and filtered. The filtrate was concentrated *in vacuo* to approximately one third its original volume and was stored at -20°C for two days. A crude white crystalline product was isolated and recrystallized (2.1 g), isolated crystalline yield: 31 %.

Method 2. *CAUTION: This reaction is very dangerous and should not be attempted as a routine preparation.* To a refluxing toluene (175 mL) solution of Al(^{t}Bu)$_3$ (23.7 g, 120 mmol) was added H$_2$O (2.15 mL, 120 mmol). Mp = 118 °C. Anal. calcd for C$_8$H$_{19}$AlO: C, 60.7; H, 12.1. Found : C, 61.0; H, 12.2. MS (EI, %) *m/z* : 315 (2M$^+$ - H, 5 %), 259 (2M$^+$-^{t}Bu, 100 %). IR (Nujol mull, cm^{-1}): 3697 (s, ν_{OH}), 1760 (m), 1596 (w), 1298 (w), 1248 (w), 1184 (m), 1084 (w), 1048 (m), 991 (m), 935 (m), 874 (m), 813 (m). ^{1}H NMR: δ 1.12 (1H, s, O$\underline{H}$), 1.08 [18H, s, C(C$\underline{H}_3$)$_3$]. ^{13}C NMR: δ 31.40 [C($\underline{C}$H$_3$)$_3$]. ^{27}Al NMR: δ 132 (W$_{1/2}$ = 4090 Hz).

[Al$_4$(^{t}Bu)$_7$(μ_3-O)$_2$(μ-OH)] (2). Fractional crystallization of the supernatant obtained in the synthesis of [(^{t}Bu)$_2$Al(μ-OH)]$_2$ (Method 1) over a period of six weeks

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resulted in the formation of colorless crystals, yield 10 %. Crystals suitable for X-ray crystallography were obtained by recrystallization from hexane. Mp = 138 - 142 °C. MS (EI, %) m/z : 500 (M$^+$-^{t}Bu + H, 100 %), 499 (M$^+$-^{t}Bu, 100 %). IR (Nujol mull, cm^{-1}): 3675 (s, ν_{OH}), 1315 (w), 1266 (w), 1451 (m), 1010 (m), 939 (m), 856 (w), 834 (m), 813 (m). ^{1}H NMR: δ 2.29 (1H, s, O$\underline{H}$), 1.23 [18H, s, C(C$\underline{H}_3$)$_3$], 1.20 [18H, s, C(C$\underline{H}_3$)$_3$], 1.06 [18H, s, C(C$\underline{H}_3$)$_3$], 0.96 [9H, s, C(C$\underline{H}_3$)$_3$]. ^{13}C NMR: δ 31.57 [C($\underline{C}$H$_3$)$_3$], 30.89 [br, C($\underline{C}$H$_3$)$_3$], 30.13 [C($\underline{C}$H$_3$)$_3$].

[(^{t}Bu)$_2$Al(μ-OH)]$_3$·(MeCN) (3). Recrystallization of [(^{t}Bu)$_2$Al(μ-OH)]$_2$ from MeCN yields upon crystallization [(^{t}Bu)$_2$Al(μ-OH)]$_3$. A second batch of solid may be obtained from further reduction of the supernatant. IR (cm^{-1}): IR (cm^{-1}): 3586 (s, ν_{OH}), 3258 (br s, ν_{OH}), 2322 (s, ν_{NC}), 1466 (s), 1392 (m), 1360 (s), 1191 (s), 1039 (s), 999 (m), 950 (m), 815 (m). ^{1}H NMR: δ 3.29 (3H, s, O$\underline{H}$), 1.28 [54H, s, C(C$\underline{H}_3$)$_3$], 0.44 [3H, s, NCC$\underline{H}_3$]. ^{13}C NMR: δ 31.40 [C($\underline{C}$H$_3$)$_3$], 15.71 [$\underline{C}$(CH$_3$)$_3$], -0.32 (NC$\underline{C}$H$_3$).

Synthesis of [Al$_5$(^{t}Bu)$_7$(μ$_3$-O)$_3$(μ-OH)$_2$] (4) and [(^{t}Bu)Al(μ$_3$-O)]$_7$ (5). [(^{t}Bu)$_2$Al(μ-OH)]$_3$ (41 g, 87 mmol) was refluxed in a hexane (350 mL) for 15 h, after which the solution was cooled to room temperature and the solvent removed under vacuum. Fractional crystallization from hexane allowed for removal of [(^{t}Bu)Al(μ$_3$-O)]$_6$ (ca. 4 g), and subsequent isolation of [Al$_5$(^{t}Bu)$_7$(μ$_3$-O)$_3$(μ-OH)$_2$] (ca. 0.7 g, 2.7 %) and [(^{t}Bu)Al(μ$_3$-O)]$_7$ (ca. 0.5 g, 2 %).

[Al$_5$(^{t}Bu)$_7$(μ$_3$-O)$_3$(μ-OH)$_2$] (4). Mp = > 305 °C. MS (EI,%) m/z: 559 (M$^+$ - ^{t}Bu, 90 %), 559 (M$^+$ - 2 ^{t}Bu - H, 100 %). IR (cm^{-1}): 3681 (s, ν_{OH}), 3599 (s, ν_{OH}), 1340 (w), 1182 (m), 1024 (s), 999 (m), 968 (m), 849 (m), 814 (m), 789 (s), 695 (m), 671 (m), 662 (m), 636 (m), 597 (w), 569 (w), 509 (m), 475 (m), 432 (w). ^{1}H NMR: δ 2.56 (1H, s, O$\underline{H}$), 1.72 (1H, s, O$\underline{H}$), 1.27 [9H, s, C(C$\underline{H}_3$)$_3$], 1.18 [18H, s, C(C$\underline{H}_3$)$_3$], 1.11 [18H, s, C(C$\underline{H}_3$)$_3$],

1.10 [18H, s, C(C$\underline{H}_3$)$_3$]. ^{13}C NMR: δ 32.0 [C($\underline{C}H_3$)$_3$], 31.7 [C($\underline{C}H_3$)$_3$], 30.1 [C($\underline{C}H_3$)$_3$], 29.3 [C($\underline{C}H_3$)$_3$].

[(^{t}Bu)Al(μ_3-O)]$_7$ (5). Mp = 285 - 295 °C, MS (EI,%) m/z: 700 (M$^+$, 30 %), 643 (M$^+$ - ^{t}Bu, 100 %). IR (cm^{-1}): 2720 (m), 1198 (m), 1155 (w), 1004 (s), 937 (s). ^{1}H NMR: δ 1.29 [9H, s, C(C$\underline{H}_3$)$_3$], 1.21 [27H, s, C(C$\underline{H}_3$)$_3$], 1.17 [27H, s, C(C$\underline{H}_3$)$_3$]. ^{13}C NMR: δ 29.81 [3C, C($\underline{C}H_3$)$_3$], 29.73 [1C, C($\underline{C}H_3$)$_3$], 27.80 [3C, C($\underline{C}H_3$)$_3$].

Reaction of [(^{t}Bu)$_2$Ga(μ-OH)]$_3$ with Al(^{t}Bu)$_3$. A solution of Al(^{t}Bu)$_3$ (2.8 g, 14.1 mmol) in toluene (10 mL) was added to a cooled (-78 °C) solution of [(^{t}Bu)$_2$Ga(μ-OH)]$_3$ (1.98 g, 3.28 mmol) in toluene (35 mL). The resulting solution was refluxed overnight. The volume of the solution was reduced and cooled to give colorless crystals whose 1H NMR spectrum was consistent with a mixture of Ga(^{t}Bu)$_3$ and [(^{t}Bu)$_2$Al{μ-OAl(^{t}Bu)$_2$}]$_2$. Removal of all the volatiles and recrystallization from toluene yielded further crystals of [(^{t}Bu)$_2$Al{μ-OAl(^{t}Bu)$_2$}]$_2$ and a few large crystals of [(^{t}Bu)Al(μ_3-O)]$_8$. MS (EI, %) m/z: 829 [Al$_6$Ga$_2$(^{t}Bu)$_7$O$_8$, 2 %], 800 [8M$^+$, 5 %], [Al$_7$Ga(^{t}Bu)$_7$O$_8$, 30 %], 743 (8M$^+$-^{t}Bu, 100). ^{1}H NMR: δ 1.23 [36H, s, C(C$\underline{H}_3$)$_3$], 1.18 [36H, s, (C$\underline{H}_3$)$_3$].

Crystallographic Studies. Crystals of compounds 2, 5 and 6 were mounted in glass capillaries attached to the goniometer head. X-ray data were collected on a Nicolet R3m/V four-circle diffractometer. Data collection unit cell and space group determination were all carried out in a manner previously described in detail.[21] The structures were solved using the direct methods program XS[22] which readily revealed the positions of the Al, O, and the some of the C atoms. Subsequent difference Fourier maps revealed the position of all of the non-hydrogen atoms for all structures. After all of the non-hydrogen atoms were located and refined anisotropically, difference map either revealed some of the hydrogen atom positions. However, organic hydrogen atoms were placed in calculated positions [U$_{iso}$ = 0.08; d(C-H) = 0.96 Å] for refinement. Neutral-atom

scattering factors were taken from the usual source.[23] Refinement of positional and anisotropic thermal parameters led to convergence (see Table IV). Final atomic positional parameters are given in Tables V - VII.

After the successful location of the Al, O, and C atoms in the structural refinement of compound 2, a second molecule of $[Al_4(^tBu)_7(\mu_3-O)_2(\mu-OH)]$ could be seen as a minor disorder in the electron difference map. The site occupancy factor for this second molecule was determined by refinement to be *ca.* 5 %. The positional and isotropic thermal parameters for this minor constituent were freely refined, however, they were subsequently fixed in the final refinement. The final R factor of this structure remained high despite the addition of the disordered component. We are at present attempting to further resolve this structural disorder, and the results of this study will be presented elsewhere. Since an examination of the cell packing diagram of 2 indicates that the presence of both orientations of the molecule within the same cell is impossible due to steric hindrance, then the apparent disorder must be due to the presence of crystal twinning. Unfortunately repeated attempts to obtain "single" crystals were unsuccessful.

Supplementary Materials. Full listings of bond length and angles, anisotropic thermal parameters, and hydrogen atom parameters (___ pages); tables of calculated and observed structure factors (___ pages). Ordering information is given on any current masthead page.

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Legends for Figures

Table I. Selected Bond Lengths (Å) and Angles (°) for [Al(^{t}Bu)$_7$(μ_3-O)$_2$(μ-OH)] (2).

Al(1)-O(1)	1.74 (1)	Al(1)-C(11)	1.95 (3)
Al(1)-C(15)	1.89 (2)	Al(2)-O(1)	1.98 (1)
Al(2)-O(2)	1.88 (1)	Al(2)-C(21)	1.93 (4)
Al(2)-C(25)	2.01 (1)	Al(3)-O(1)	1.81 (1)
Al(3)-O(2)	1.77 (1)	Al(3)-O(3)	1.81 (1)
Al(3)-C(31)	2.03 (3)	Al(4)-O(2)	1.79 (1)
Al(4)-O(3)	1.90 (1)	Al(4)-C(41)	1.95 (2)
Al(4)-C(45)	1.95 (2)		

O(1)-Al(1)-C(11)	115.5(8)	O(1)-Al(1)-C(15)	117.4(8)
C(11)-Al(1)-C(15)	127.0(9)	O(1)-Al(2)-O(2)	80.0(6)
O(1)-Al(2)-C(21)	104 (1)	O(2)-Al(2)-C(21)	126(1)
O(1)-Al(2)-C(25)	105(1)	O(2)-Al(2)-C(25)	99(1)
C(21)-Al(2)-C(25)	128(2)	O(1)-Al(3)-O(2)	87.5(5)
O(1)-Al(3)-O(3)	135.1(6)	O(2)-Al(3)-O(3)	82.2(6)
O(1)-Al(3)-C(31)	104(1)	O(2)-Al(3)-C(31)	136(1)
O(3)-Al(3)-C(31)	112(1)	O(2)-Al(4)-O(3)	79.5(5)
O(2)-Al(4)-C(41)	121.6(8)	O(3)-Al(4)-C(41)	108.6(8)
O(2)-Al(4)-C(45)	108.9(8)	O(3)-Al(4)-C(45)	113.4(8)
C(41)-Al(4)-C(45)	118.4(9)	Al(1)-O(1)-Al(2)	137.5(7)
Al(1)-O(1)-Al(3)	128.8(7)	Al(2)-O(1)-Al(3)	93.4(6)
Al(2)-O(2)-Al(3)	98.3(6)	Al(2)-O(2)-Al(4)	150.0(7)
Al(3)-O(2)-Al(4)	100.5(6)	Al(3)-O(3)-Al(4)	95.1(7)

Table II. Selected Bond Lengths (Å) and Angles (°) for [Al$_5$(^{t}Bu)$_7$(μ_3-O)$_3$(μ-OH)$_2$] (**4**).

Al(1)-O(123)	1.823 (5)	Al(1)-O(124)	1.826 (4)
Al(1)-O(135)	1.835 (4)	Al(1)-C(11)	1.963 (7)
Al(2)-O(123)	1.808 (4)	Al(2)-O(124)	1.812 (4)
Al(2)-O(23)	1.845 (4)	Al(2)-C(21)	1.941 (8)
Al(3)-O(123)	1.793 (4)	Al(3)-O(135)	1.818 (4)
Al(3)-O(23)	1.845 (4)	Al(3)-C(31)	1.940 (7)
Al(4)-O(124)	1.813 (4)	Al(4)-O(45)	1.886 (4)
Al(4)-C(41)	1.976 (7)	Al(4)-C(45)	1.990 (7)
Al(5)-O(135)	1.821 (4)	Al(5)-O(45)	1.871 (4)
Al(5)-C(51)	1.981 (8)	Al(5)-C(55)	1.987 (7)

O(123)-Al(1)-O(124)	87.2(2)	O(123)-Al(1)-O(135)	87.3(2)
O(124)-Al(1)-O(135)	100.3(2)	O(123)-Al(1)-C(11)	108.4(3)
O(124)-Al(1)-C(11)	128.6(3)	O(135)-Al(1)-C(11)	128.3(3)
O(123)-Al(2)-O(124)	88.1(2)	O(123)-Al(2)-O(23)	83.4(2)
O(124)-Al(2)-O(23)	107.2(2)	O(123)-Al(2)-C(21)	121.8(3)
O(124)-Al(2)-C(21)	126.0(3)	O(23)-Al(2)-C(21)	119.1(3)
O(123)-Al(3)-O(135)	88.7(2)	O(123)-Al(3)-O(23)	83.8(2)
O(135)-Al(3)-O(23)	107.6(2)	O(123)-Al(3)-C(31)	119.8(3)
O(135)-Al(3)-C(31)	124.5(3)	O(23)-Al(3)-C(31)	121.0(3)
O(124)-Al(4)-O(45)	96.3(2)	O(124)-Al(4)-C(41)	109.5(3)
O(45)-Al(4)-C(41)	108.6(3)	O(124)-Al(4)-C(45)	114.6(3)
O(45)-Al(4)-C(45)	108.4(2)	C(41)-Al(4)-C(45)	117.3(3)

Table II. contd.

O(135)-Al(5)-O(45)	97.1(2)		O(135)-Al(5)-C(51)	112.7(3)
O(45)-Al(5)-C(51)	105.3(2)		O(135)-Al(5)-C(55)	113.0(3)
O(45)-Al(5)-C(55)	110.3(2)		C(51)-Al(5)-C(55)	116.4(3)
Al(1)-O(123)-Al(2)	92.4(2)		Al(1)-O(123)-Al(3)	92.6(2)
Al(2)-O(123)-Al(3)	96.5(2)		Al(1)-O(124)-Al(2)	92.2(2)
Al(1)-O(124)-Al(4)	124.6(2)		Al(2)-O(124)-Al(4)	133.9(2)
Al(1)-O(135)-Al(3)	91.3(2)		Al(1)-O(135)-Al(5)	125.2(2)
Al(3)-O(135)-Al(5)	131.5(2)		Al(2)-O(23)-Al(3)	93.5(2)
Al(4)-O(45)-Al(5)	142.3(2)			

Table III. Selected Bond Lengths (Å) and Angles (°) of [(^{t}Bu)Al(μ_3-O)]$_8$ (**6**).

Al(1)-O(1)	1.905(4)	Al(1)-O(2)	1.795(5)
Al(1)-O(3)	1.782(6)	Al(1)-C(1)	1.913(7)
Al(2)-O(1)	1.791(5)	Al(2)-O(2)	1.880(5)
Al(2)-O(3a)	1.778(5)	Al(2)-C(2)	1.92(1)
Al(3)-O(1)	1.760(6)	Al(3)-O(2a)	1.789(6)
Al(3)-O(3)	1.889(4)	Al(3)-C(3)	1.960(9)
O(1)-Al(1)-O(2)	86.3(2)	O(1)-Al(1)-O(3)	86.3(2)
O(2)-Al(1)-O(3)	112.2(3)	O(1)-Al(1)-C(1)	119.9(3)
O(2)-Al(1)-C(1)	123.1(3)	O(3)-Al(1)-C(1)	118.6(3)
O(1)-Al(2)-O(2)	87.2(2)	O(1)-Al(2)-O(3a)	86.3(2)
O(2)-Al(2)-O(3a)	112.2(2)	O(1)-Al(2)-C(2)	118.1(3)
O(2)-Al(2)-C(2)	124.4(3)	O(3)-Al(2)-C(2)	120.3(3)
O(1)-Al(3)-O(2a)	112.3(2)	O(1)-Al(3)-O(3)	87.4(2)
O(2a)-Al(3)-O(3)	85.2(2)	O(1)-Al(3)-C(3)	119.0(4)
O(2a)-Al(3)-C(3)	122.2(4)	O(3)-Al(3)-C(3)	120.8(3)
Al(1)-O(1)-Al(2)	92.4(2)	Al(1)-O(1)-Al(3)	92.7(3)
Al(2)-O(1)-Al(3)	127.7(3)	Al(1)-O(2)-Al(2)	93.1(2)
Al(1)-O(2)-Al(3a)	127.5(2)	Al(2)-O(2)-Al(3a)	94.1(2)
Al(1)-O(3)-Al(2a)	127.1(3)	Al(1)-O(3)-Al(3)	92.6(3)

Table IV. Summary of X-ray Diffraction Data.

Compound	$[Al_4(^tBu)_7(\mu_3\text{-}O)_2(\mu\text{-}OH)]$ (2)	$[Al_5(^tBu)_7(\mu_3\text{-}O)_3(\mu\text{-}OH)]_2$ (5)
empir. formula	$C_{28}H_{63}Al_4O_3$	$C_{28}H_{65}Al_5O_5$
cryst size, mm	0.40 x 0.35 x 0.30	0.31 x 0.35 x 0.31
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	10.012(6)	17.204(3)
b, Å	9.426(3)	11.337(2)
c, Å	39.14(1)	20.143(4)
β, deg	92.53(1)	97.84(3)
V, Å^3	3690(3)	3892(2)
Z	4	4
D(calcd), g/cm^3	1.002	1.052
μ, mm^{-1}	0.149	0.172
radiation	Mo-Kα (λ = 0.71073 Å) graphite monochromator	
temp, K	298	298
2θ range, deg	4.0 - 40.0	4.0 - 44.0
no. collected	5083	3737
no. ind	4759	3583
no. obsd	1635 ($|F_o| > 4.0\sigma\,|F_o|$)	2311 ($|F_o| > 6.0\sigma\,(|F_o|)$)
weighting scheme	$w^{-1} = \sigma^2\,(|F_o|) + 0.0099\,(|F_o|)^2$	$w^{-1} = \sigma^2(|F_o|) + 0.0004\,(|F_o|)^2$
R	0.098	0.054
R_w	0.101	0.055
largest diff peak. eÅ^{-3}	0.65	0.32

Table IV, contd.

Compound	$[(^tBu)Al(\mu_3\text{-}O)]_8$ (6)
empir. formula	$C_{32}H_{72}Al_8O_8$
cryst size, mm	0.52 x 0.46 x 0.61
cryst system	monoclinic
space group	C2/c
a, Å	41.622(3)
b, Å	9.0176(8)
c, Å	21.303(1)
β, deg	99.250(5)
V, Å^3	7891.7(6)
Z	8
D(calcd), g/cm^3	1.005
μ, mm^{-1}	1.369
radiation	Mo-K$_\alpha$ ($\lambda = 0.71073$ Å) graphite monochromator
temp, K	298
2θ range, deg	2.0 - 44.0
no. collected	5276
no. ind	5202
no. obsd	2680 ($|F_o| > 6.0\sigma$ ($|F_o|$)
weighting scheme	$w^{-1} = \sigma^2(|F_o|) + 0.04 (|F_o|)^2$
R	0.0479
R$_w$	0.0538
largest diff peak. eÅ^{-3}	0.22

Table V. Selected Atomic Coordinates $(x10^4)$ and Equivalent Isotropic Thermal Parameters $(\text{Å} \times 10^3)$ of $Al_4(^tBu)_7(\mu_3\text{-}O)_2(\mu\text{-}OH)$ (2).

Al(1)	2262(5)	119(7)	4206(1)	47(2)
Al(2)	-918(11)	1361(9)	3976(3)	57(2)
Al(3)	837(5)	730(7)	3470(1)	46(2)
Al(4)	-1552(5)	273(7)	3116(1)	55(2)
O(1)	950(11)	699(13)	3935(3)	46(4)
O(2)	-894(10)	1104(12)	3499(3)	45(4)
O(3)	213(11)	-482(16)	3139(3)	66(5)
C(11)	2757(20)	-1877(33)	4157(6)	108(15)
C(12)	2216(23)	-2846(19)	4442(6)	95(579)
C(13)	2240(19)	-2377(32)	3821(4)	85(579)
C(14)	4279(19)	-2097(27)	4178(6)	104(13)
C(15)	3003(23)	1436(21)	4526(6)	68(9)
C(16)	2636(26)	1048(33)	4907(5)	123(14)
C(17)	2809(39)	2870(42)	4543(9)	199(579)
C(18)	4578(20)	1345(30)	4564(7)	117(13)
C(21)	-1672(22)	85(57)	4304(6)	155(579)
C(22)	-1673(23)	-1582(20)	4198(6)	85(10)
C(23)	-730(23)	123(32)	4622(6)	99(11)
C(24)	-3060(22)	381(30)	4388(6)	105(12)
C(25)	-805(35)	3494(14)	3994(9)	55
C(26)	-2555(19)	3687(25)	3873(5)	82(579)
C(27)	-1221(28)	3981(37)	4398(9)	148(336)

Table V. contd.

C(28)	-187(42)	4288(31)	3858(7)	167(336)
C(31)	2496(34)	1806(48)	3333(8)	130(16)
C(32)	2626(24)	3364(32)	3266(9)	73(13)
C(33)	3010(20)	737(35)	2997(6)	114(13)
C(34)	3650(18)	1287(32)	3616(5)	112(13)
C(41)	-2820(21)	-1296(25)	3129(5)	72(9)
C(42)	-3302(35)	-2666(117)	2786(6)	511(86)
C(43)	-4010(24)	-930(36)	3367(8)	147(16)
C(44)	-2196(23)	-2235(18)	3282(6)	101(579)
C(45)	-1828(23)	1716(27)	2762(5)	71(9)
C(46)	-1809(26)	1135(30)	2389(5)	107(13)
C(47)	-3213(20)	2761(28)	2786(5)	83(11)
C(48)	-805(28)	2558(72)	2778(7)	205(26)

Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{Å} \times 10^3$) for $[Al_5(^tBu)_7(\mu_3\text{-O})_3(\mu\text{-OH})_2]$ (5).

Al(1)	7338(1)	1907(2)	7554(1)	39(1)
Al(2)	6653(1)	644(2)	8398(1)	39(1)
Al(3)	6099(1)	679(2)	7085(1)	42(1)
Al(4)	8500(1)	-97(2)	8256(1)	39(1)
Al(5)	7745(1)	-132(2)	6523(1)	38(1)
O(123)	6343(2)	1717(3)	7752(2)	38(2)
O(124)	7650(2)	858(3)	8226(2)	35(2)
O(135)	7074(2)	889(3)	6851(2)	36(2)
O(23)	6181(2)	-411(3)	7771(2)	42(2)
O(45)	8416(2)	-364(3)	7325(2)	43(2)
C(11)	7559(5)	3604(6)	7522(4)	58(3)
C(12)	8306(6)	4134(7)	7340(5)	134(6)
C(13)	7444(5)	4061(7)	8213(4)	89(4)
C(14)	6886(6)	4073(7)	7027(5)	119(5)
C(21)	6303(5)	718(8)	9273(4)	57(3)
C(22)	6716(13)	1724(18)	9657(8)	190(13)
C(23)	5428(9)	1143(18)	9128(7)	139(10)
C(24)	6296(11)	-280(14)	9688(7)	134(9)
C(22a)	5663(20)	-323(33)	9291(18)	112(14)
C(23a)	7013(16)	448(29)	9865(12)	69(8)
C(24a)	5926(22)	1824(27)	9347(16)	70(10)

Table VI. contd.

|				
C(31)	5130(4)	858(7)	6477(4)	55(3)
C(32)	4714(5)	-254(8)	6233(4)	104(5)
C(33)	4583(5)	1551(9)	6851(5)	131(5)
C(34)	5264(5)	1538(9)	5860(4)	126(5)
C(41)	9463(4)	826(7)	8538(3)	55(3)
C(42)	9637(5)	1673(9)	8005(4)	136(5)
C(43)	9361(5)	1559(8)	9153(4)	106(5)
C(44)	10199(4)	106(8)	8728(4)	108(5)
C(45)	8395(4)	-1637(6)	8709(3)	49(3)
C(46)	8682(5)	-1581(7)	9457(3)	90(4)
C(47)	8895(5)	-2561(7)	8406(4)	90(4)
C(48)	7563(4)	-2141(6)	8632(3)	67(3)
C(51)	8399(4)	640(7)	5912(3)	56(3)
C(52)	8573(5)	1908(8)	6116(4)	104(5)
C(53)	8080(7)	634(10)	5196(4)	177(7)
C(54)	9218(6)	81(10)	5955(5)	155(7)
C(55)	7237(4)	-1642(6)	6208(3)	47(3)
C(56)	7878(4)	-2567(7)	6173(4)	83(4)
C(57)	6674(4)	-2198(6)	6639(3)	69(3)
C(58)	6767(5)	-1528(7)	5508(3)	85(4)

Table VII. Atomic Coordinates and Equivalent Isotropic Thermal Parameters ($\text{Å} \times 10^2$) for [(^{t}Bu)Al(μ_3-O)]$_8$ (6).
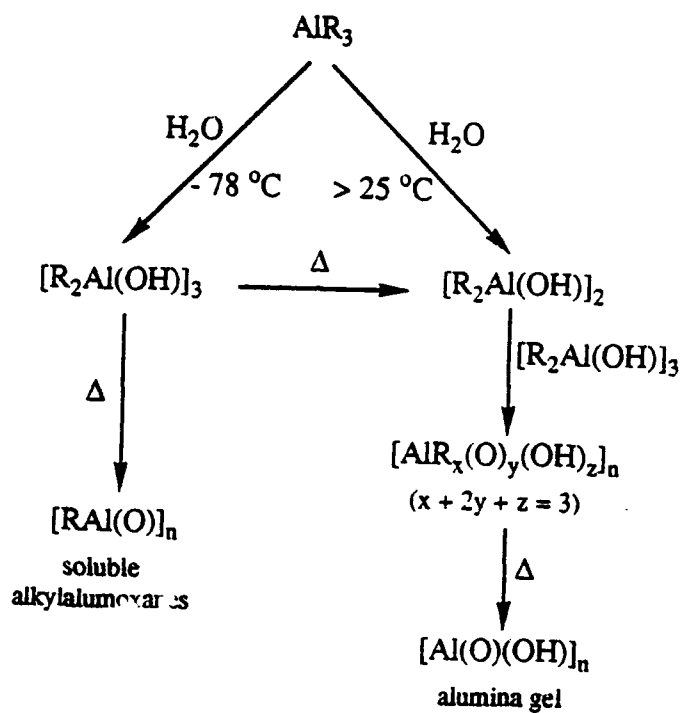
	x	y	z	U(eq)
Al(1)	4446(1)	5247(1)	7762(1)	34(1)
Al(2)	4350(1)	2889(1)	8179(1)	41(1)
Al(3)	4602(1)	1634(1)	6863(1)	37(1)
Al(4)	4153(1)	3993(1)	6672(1)	38(1)
O(1)	4111(1)	3946(2)	7599(1)	40(1)
O(2)	4444(1)	1722(2)	7723(1)	45(1)
O(3)	4690(1)	2940(2)	6564(1)	41(1)
O(4)	4637(1)	5165(2)	6876(1)	40(1)
C(1)	3934(2)	6410(3)	8039(2)	57(2)
C(11)	4324(3)	6809(4)	8746(3)	98(3)
C(12)	3195(3)	6117(4)	8073(4)	95(3)
C(13)	3893(3)	7257(4)	7511(3)	100(3)
C(2)	3873(2)	2819(3)	8932(2)	61(2)
C(21)	3973(4)	1808(5)	9320(4)	140(4)
C(22)	4127(5)	3680(6)	9445(4)	149(4)
C(23)	3092(3)	2950(7)	8674(4)	138(4)
C(3)	4194(2)	480(3)	6266(3)	63(2)
C(31)	4020(4)	746(4)	5506(3)	110(3)
C(32)	3554(3)	98(5)	6469(4)	129(3)
C(33)	4717(3)	-398(4)	6379(4)	118(3)
C(4)	3259(2)	4067(3)	6005(2)	51(2)
C(41)	3362(3)	3892(5)	5267(3)	95(2)
C(42)	2936(3)	5116(5)	6020(3)	117(3)
C(43)	2786(3)	3253(5)	6155(3)	113(3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor
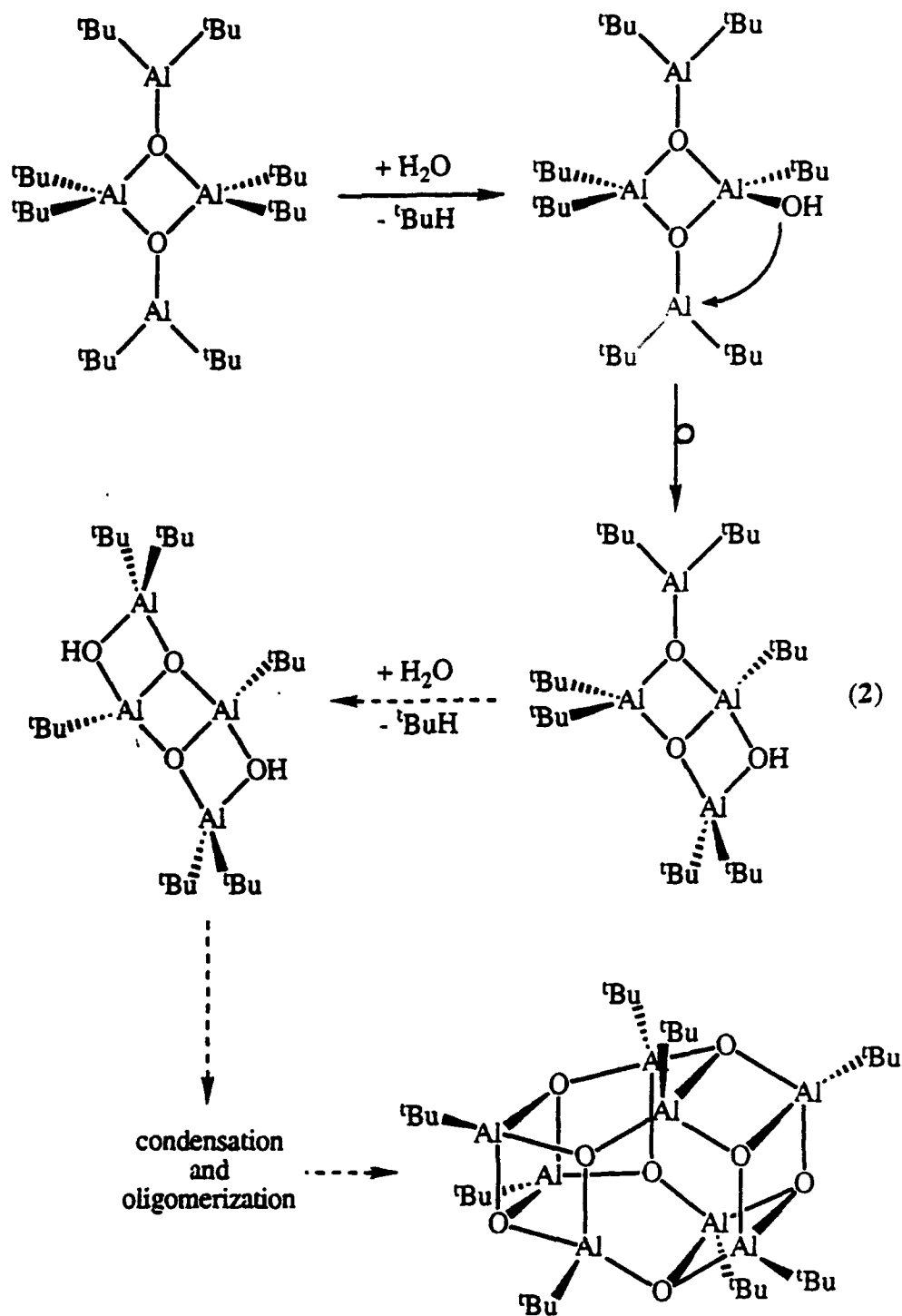
Scheme 1. Proposed reactions responsible for the formation of compound **2** and [(ᵗBu)Al(μ₃-O)]₈ during the salt hydrolysis of aluminum alkyls. Al(ᵗBu)₃.

$$AlR_3$$

$$H_2O \quad\swarrow \qquad \searrow\quad H_2O$$

$$-78\ °C \qquad > 25\ °C$$

$$[R_2Al(OH)]_3 \xrightarrow{\ \Delta\ } [R_2Al(OH)]_2$$

$$\Big\downarrow \Delta \qquad\qquad\qquad \Big\downarrow [R_2Al(OH)]_3$$

$$[RAl(O)]_n \qquad\qquad [AlR_x(O)_y(OH)_z]_n$$

$$(x + 2y + z = 3)$$

soluble
alkylalumoxanes

$$\Big\downarrow \Delta$$

$$[Al(O)(OH)]_n$$

alumina gel

Scheme 2. Proposed reactions responsible for the formation of soluble alkylalumoxanes versus alumina gels during the hydrolysis of aluminum alkyls, AlR_3.

Legends for Figures

Figure 1. Molecular structure of [Al$_4$(^{t}Bu)$_7$(μ_3-O)(μ-OH)$_2$] (2). Thermal ellipsoids are drawn at the 30% level, and the hydrogen atoms of the *tert*-butyl groups are omitted for clarity. Only the major component of the disorder is shown, see Experimental.

Figure 2. Molecular structure of [Al$_5$(^{t}Bu)$_7$(μ_3-O)$_3$(μ-OH)$_2$] (5). Thermal ellipsoids are drawn at the 40% level, and the hydrogen atoms of the *tert*-butyl groups are omitted for clarity.

Figure 3. The core structures of [Al$_5$(^{t}Bu)$_7$(μ_3-O)$_3$(μ-OH)$_2$] (a) and [(^{t}Bu)Ga(μ_3-S)]$_7$ (b). The solid lines represent the common structural fragment present in 4 and 5. Aluminum and gallium atoms are shown in purple and green, respectively.

Figure 4. Space filling representation of [Al$_5$(^{t}Bu)$_7$(μ_3-O)$_3$(μ-OH)$_2$] (4) and its equivalent line drawing (inset), viewed perpendicular to the Al(1)-Al(4)-Al(5) plane, showing the steric hindrance imposed on Al(1) by the *tert*-butyl groups.

Figure 5. Aluminum-oxygen core structure of [Al$_5$(^{t}Bu)$_7$(μ_3-O)$_3$(μ-OH)$_2$] (a). The solid bonds represent the structural fragment present in the mineral boehmite (b). Aluminum atoms shown in purple; oxygen in red.

Figure 6. Molecular structure of [(^{t}Bu)Al(μ_3-O)]$_8$ (6). Thermal ellipsoids are drawn at the 30 % level and all the hydrogen atoms are omitted for clarity.

Fig. 1

Fig 2

Fig 3.1
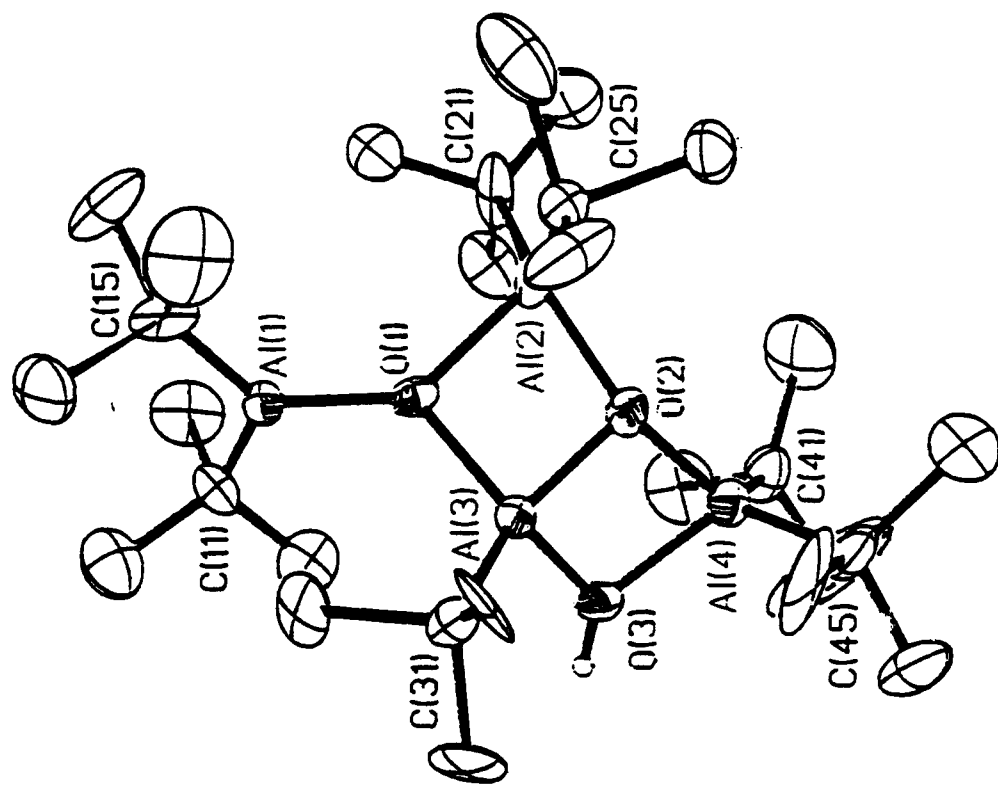
Fig 31

Fig. 2

Fig. 5.

Fig 30